Anonyme. The Journal of physical chemistry. Published at Cornell university [3puis3 Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1903.

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THE RATE OF OXIDATION OF FERROUS SALTS BY CHROMIC ACID

BY CLARA C. BENSON

In 1858 Schönbein[1] announced that when dilute chromic acid is mixed with a dilute solution of potassium iodide and starch paste, the mixture turns blue very slowly; but that the blue color appears immediately on shaking with platinum moss or with fine iron powder, or on adding a few drops of the dilute solution of a ferrous salt. At the present time the subject of catalysis is attracting a good deal of attention; and as our knowledge of this particular instance — one of the most striking yet met with — is limited to the discoveries of Schönbein, it was suggested by Prof. W. Lash Miller that I should study the reaction between ferrous salts, iodides, and chromic acid, in the light of the prevalent theories of chemical kinetics.

The present paper contains a portion of the results already obtained, *viz*: those of experiments on the reaction between chromic acid and ferrous sulphate in the absence of iodides. In addition to the measurements here published, I have carried out a number of experiments on the rate of liberation of iodine in solutions containing chromic acid, potassium iodide, and ferrous salts, and on the rate of oxidation of the ferrous salt in the same mixtures; when completed, these measurements will form the subject of a second communication. Theoretical discussions have been postponed until all the results are published.

My first experiments showed that the accelerating influence exerted by the ferrous salts is not shared by *ferric* salts.[2] If the chemicals, properly diluted, be mixed in the order — chromic acid, ferrous salt, starch, potassium iodide (with a pause to allow

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[1] Pogg. Ann. 105, 265 (1858). The concentrations are given.

[2] Unpublished experiments by Mr. W. C. Bray show that when chloric acid is used in place of chromic acid, ferrous and ferric salts exert about the same influence on the rate.

of the oxidation of the ferrous salt before the iodide is added) no sudden appearance of the blue color is observed; while if Schönbein's order — chromic acid, potassium iodide, starch, ferrous salt — be adhered to, the blue color appears immediately upon addition of the ferrous salt.

This raises the question whether, after all, the action of the iron can be regarded as truly "catalytic", and not rather as resembling the action of aluminium chloride in Friedel and Craft's synthesis, or that of sodium ethylate in the preparation of acetacetic ether and similar substances; I hope that the results of my experiments may furnish a definite answer to this question.

Method of analysis

I experienced great difficulty in devising a method for determining the amount of ferrous salt present in solutions containing potassium bichromate, sulphuric acid, and ferrous and ferric sulphates.

The first method experimented with consisted in adding to the mixture a known quantity of potassium permanganate, which instantly oxidized the ferrous sulphate. The excess of permanganate — and thus by difference the ferrous sulphate — was determined by adding potassium iodide, and estimating the iodine set free. It soon appeared, however, that in many cases the reduction of the permanganate by the iodide was incomplete; and as the means taken to overcome this difficulty — addition of acid, heating, letting stand — brought about oxidation of the iodide by the chromic acid, I was driven to abandon the method.

An attempt was then made to measure the change in the acidity of the solution caused by the reaction

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O,$$

but without success. Even if a suitable indicator had been discovered, the method would hardly have proved accurate in the presence of a large initial excess of acid. Analysis by electrical conductivity is excluded for the same reason.

Colorimetric analysis was interferred with by the presence of the bichromate and the ferric salts; and the method which promised most, determination of the ferric salt by potassium sulphocyanate, was excluded by the fact that, as will appear later, the rate measurements had to be carried out in presence of a large excess of ferric salt.

In the end I found a means of determining the quantity of ferrous salt present by *measuring its catalytic effect on the rate of oxidation of potassium iodide by chromic acid:* thus the reaction whose study forms the subject of this research furnished the only available method of analysis.

The experiments were carried out in the following manner: (*A*) To 500 cc of a solution containing measured quantities of acid, bichromate, and ferric salt,[1] there was added 100 cc of a solution containing a known amount of ferrous sulphate, and the time was noted. After a suitable interval, 100 cc of a dilute solution of potassium iodide was added and the time noted again. After a further period of four minutes the reaction was stopped, and the free iodine determined. In the earlier experiments the iodine was determined by sodium thiosulphate, the reaction being slowed sufficiently for the purpose by the addition of sodium acetate and tartrate; this method fails however in the presence of large quantities of iron, and ultimately I replaced the thiosulphate by sodium arsenite, and the acetate and tartrate by ammonium bicarbonate.[2]

In order to interpret the results so obtained, and from the amount of iodine liberated in the second part of the experiment to determine the amount of ferrous salt remaining at the end of the first part, a series of experiments were carried out, employing the same chemicals in the same quantities, but mixing them in a different order, as follows: —

(*B*) 500 cc of a solution containing acid, chromate, ferric salt, and part of the ferrous salt (which is promptly oxidized);

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[1] Or oxidation product, see page 5.

[2] Carbon dioxide was passed into a saturated solution of ammonium carbonate until no smell of ammonia was noticeable, the solution was filtered and its own volume of water added. 10 cc of this half saturated solution were used in each titration; the same reading was obtained when 20 cc were used.

100 cc of the dilute solution of potassium iodide (no liberation of iodine takes place), then the remainder of the ferrous salt ("part two") dissolved in 100 cc water. After an interval of four minutes the reaction was stopped by addition of ammonium bicarbonate, starch was added and the iodine determined by sodium arsenite. The results of a set of experiments of series *B* were plotted, using "iodine liberated" and "ferrous salt part two" as coordinates, and by means of the curve so obtained the amount of ferrous sulphate remaining in experiment *A* at the moment of adding the potassium iodide was determined.

This method of determining the ferrous salt involves no assumption as to the laws under which iodine is liberated in the second part of experiment *A*; but the fact that the amount of iodine set free during the four minutes is roughly proportional to the amount of ferrous salt present at the beginning of that time, is of great assistance in the practical application of the method.

Details of the Operations

The solutions were kept in wash-bottles clamped to shelves in a large vessel containing ice and water, well stirred. The requisite quantities were blown out into measuring flasks and mixed in a beaker supported in the bath. The ferrous sulphate and the potassium iodide respectively were poured in quickly from Nessler tubes, the contents of the beaker being stirred meanwhile; the mixing was complete in about 1/5 or 2/5 seconds. Time was taken with a stop-watch.

Owing to the presence of ferric hydrate (as a flocky precipitate, or as a colloidal suspension in the liquid), special precautions had to be taken in determining the iodine by sodium arsenite. Accurate results were obtained only when the arsenite was dropped in very slowly (1 minute for 1 cc 1/100 normal arsenite), the solution being vigorously stirred meanwhile by a small motor. When the blue color of iodide of starch had disappeared, a few drops of an equivalent iodine solution were used to titrate back; with practice the end point could be determined within one or two drops, although the solution was colored by the chromate, its volume was large, and the reading was further interfered with by the presence of the ferric hydrate. Blank experiments showed that when the analysis was carried out in the manner described, the presence of iron had no effect on the result.

Solutions

A solution of potassium bichromate was made by dissolving a weighed quantity of the salt; this formed the standard solution with which the others were compared. The strength of a solution of sulphuric acid was determined by titrating both it and the bichromate against a solution of potash, with phenolphthalein as indicator. A solution of ferrous sulphate free from ferric salt[1] (no color with ammonium sulphocyanate) was prepared and kept under carbon dioxide in a filter bottle; its titre was determined against the standard bichromate. The "product of oxidation" was made by mixing equivalent quantities of bichromate, acid, and ferrous sulphate.

Before using, these solutions were diluted, the compositions of the solutions being as follows:

Bichromate, 0.000827 mol $K_2Cr_2O_7$ per liter.
Acid, 0.00498 mol H_2SO_4 per liter.
Ferrous sulphate, 0.0472 mol $FeSO_4$ per liter.
Oxidation product, 5 cc of the ferrous sulphate were used in making 50 cc.

Thus in the reaction

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O,$$

1 cc of the ferrous solution is equivalent to 9.57 cc of the bichromate, and 11 cc of the acid.

Plan of the experiments

The plan adopted is one which has proved successful in a

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[1] Commercial ferrous sulphate was dissolved in hot water, boiled and filtered. To the filtrate a little barium carbonate was added and the mixture again boiled, cooled in a vacuum, and the flask filled with carbon dioxide, a portion of the solution analyzed, and then the remainder filtered through a siphon into a measuring flask (filled with carbon dioxide) containing the calculated amount of air-free water.

number of investigations recently carried out in this laboratory; the quantity of one of the reagents (here the ferrous salt) being kept much less than those of the others, the concentrations of the latter remained practically unaltered during the reaction, and the "order of the reaction" with respect to the ferrous salt was readily determined.[1] It was however not possible to determine the order of the reaction with respect to the bichromate and to the acid in the same way (*viz.*, by carrying out experiments in which the concentrations of these two substances respectively were kept low); but by simply doubling, trebling, etc., the concentration of the acid or bichromate while still keeping that of the ferrous salt comparatively small, the influence of the former on the rate was easily determined.

Influence of the ferrous salt on the rate

Table I.*a* gives the results of a series of experiments carried out with a mixture of 100 cc of the acid, 200 cc of the bichromate solution, 50 cc of the "oxidation product" and 1 cc of the ferrous sulphate,[2] the volume being made up to 600 cc with water. Under θ is given the time in minutes between the addition of the ferrous salt and that of the potassium iodide, and under *As* the volume of potassium arsenite solution equivalent to the iodine liberated in the second part of the experiment.

Table I.*b* contains the blank experiments by means of which the values of $A-x$ *obs* (amount of ferrous salt remaining at the expiration of θ minutes) in Table I.*a* are calculated. Under k_1, k_2, k_3, finally, are the values of the constants calculated on the assumptions that the rate ($dx/d\theta$) is proportional to the first, second, or third power of $A-x$ respectively.

Tables II.*a* and II.*b* comprise similar measurements in which the initial concentration of the ferrous sulphate was one-half that in Table I. It will be seen that the values of k_2 remain constant throughout the tables, while those of k_1 and k_3 vary. The reaction is thus of the second order with respect to the ferrous

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[1] Ostwald's "Method of Isolation," Lehrbuch, 2 Ed., II. 2; pg. 238

[2] The diluted solutions whose compositions are given on page 5 were used.

TABLE I.*a*

H_2SO_4 100 cc, $K_2Cr_2O_7$ 200 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc,
Vol. 600 cc.[1]

θ	As	$A-x$ obs.	k_1	k_2	k_3	$A-x$ calc.	Diff.
0.0	4.42	1.0	—	—	—	(1.0)	—
0.5	3.35	0.76	0.11	0.63	1.43	0.74	+0.02
1.0	2.60	0.59	0.12	0.69	1.86	0.59	0.0
1.5	2.25	0.51	0.10	0.64	2.34	0.49	+0.02
2.25	1.75	0.39	0.09	0.69	2.48	0.39	0.0

TABLE I.*b*

$FeSO_4$	1.0	0.6	0.5	0.0
As	4.42	2.70	2.15	0.0

TABLE II.*a*

H_2SO_4 100 cc, $K_2Cr_2O_7$ 200 cc, Ox. prod. 50 cc, $FeSO_4$ 0.5 cc,
Vol. 600 cc.[1]

θ	As	$A-x$ obs.	k_1	k_2	k_3	$A-x$ calc.	Diff.
0.0	2.55	0.50	—	—	—	(0.50)	—
1.0	1.93	0.37	0.13	0.70	3.3	0.37	0.0
2.0	1.55	0.29	0.12	0.72	3.9	0.29	0.0
3.0	1.30	0.24	0.11	0.72	4.5	0.24	0.0

TABLE II.*b*

$FeSO_4$	0.5	0.3	0.2	0.0
As	2.55	1.60	1.10	0.0

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[1] In the experiments of Tables I. and II. the acid was slightly stronger than in the others. See Table VI.

salt, a conclusion which is in accordance with my subsequent experiments.

Under the headings "*A–x calc*" in Tables I.*a* and II.*a* are entered the values *A–x* obtained from θ and *A* by means of the equation

$$0.70\theta = 1/(A-x) - 1/A.$$

The difference between *A–x calc* and *A–x obs* ("*Diff*"), is well within the errors of experiment.

Influence of the acid on the rate

In the experiments of Tables III., IV. and V. the amount of potassium bichromate in the solutions was equivalent to ten times the amount of ferrous salt initially present; thus the changes which the concentration of the former underwent during the reaction were not great, while on the other hand it was possible, without unduly increasing the speed of the reaction, to vary the concentration of the acid from five molecules of acid for one of bichromate in Table III. to ten molecules acid for one of bichromate in Table V. By thus keeping the molecular concentration of the acid much greater than that of the bichromate it was hoped that the influence of change of dissociation of the chromic acid on the rate would be eliminated.

Table III.*a*

H_2SO_4 100 cc, $K_2Cr_2O_7$ 100 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc, Vol. 600 cc.

θ	0.0	1.0	2.0	4.0
As	2.25	1.75	1.40	1.15
$A-x$	1.0	0.82	0.68	0.56
k_2	—	0.22	0.24	0.20

Table III.*b*

$FeSO_4$	1.0	0.7	0.5	0.0
As	2.25	1.55	1.00	0.0

TABLE IV.*a*

H_2SO_4 150 cc, $K_2Cr_2O_7$ 100 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc,
Vol. 600 cc.

θ	0.0	1.0	2.0	4.0
As	4.95	3.40	2.75	1.80
$A-x$	1.0	0.66	0.53	0.33
k_2	—	0.50	0.45	0.50

TABLE IV.*b*

$FeSO_4$	1.0	0.7	0.4	0.0
As	4.95	3.55	2.35	0.0

TABLE V.*a*

H_2SO_4 200 cc, $K_2Cr_2O_7$ 100 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc,
Vol. 600 cc.

θ	0.0	0.5	1.0	2.0	4.0
As	7.95	5.65	4.45	3.15	2.10
$A-x$	1.0	0.69	0.54	0.37	0.25
k_2	—	0.90	0.85	0.85	0.75

TABLE V.*b*

$FeSO_4$	1.0	0.7	0.4	0.0
As	7.95	5.75	3.35	0.0

It will be seen that as the concentration of the acid increases in the proportion 1:1.5:2, the value of k_2 increases in the proportion 1:2.4:4, that is, the rate is proportional to the square of the concentration of the acid; in other words, the reaction is of the second order with respect to the acid.

Influence of the bichromate on the rate

Comparing Tables III., VI., VII., it appears that when the concentration of the bichromate increases in the proportion 1:2:3, the rate k_2 increases in the proportion 1:3.2:7, that is, the rate is proportional to the 1.7th or 1.8th power of the concentration of the bichromate.

TABLE VI.*a*

H_2SO_4 100 cc, $K_2Cr_2O_7$ 200 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc, Vol. 600 cc.

θ	0.0	1.0	2.0	4.0
As	4.25	2.55	1.90	1.10
$A-x$	1.0	0.6	0.44	0.26
k_2	—	0.67	0.63	0.71

TABLE VI.*b*

$FeSO_4$	1.0	0.6	0.3	0.0
As	4.25	2.60	1.25	0.0

TABLE VII.*a*

H_2SO_4 100 cc, $K_2Cr_2O_7$ 300 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc, Vol 600 cc.

θ	0.0	1.0	2.0	4.0
As	5.40	2.55	1.80	1.10
$A-x$	1.0	0.42	0.26	0.15
k_2	—	1.38	1.42	1.42

TABLE VII.*b*

$FeSO_4$	1.0	0.4	0.3	0.2	0.0
As	5.40	2.70	2.05	1.45	0.0

One is tempted to ascribe the difference between 1.8 and the round number 2, to "change of dissociation"; in the present case, however, this explanation seems hardly available. The solutions in which the rates were measured contained but 0.000138 gram-mol potassium bichromate per liter (or two and three times that amount, respectively); and as chromic acid has a place among the strongest acids,[1] it must be regarded as com-

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[1] Zeit. phys. Chem. 2, 78 (1888).

pletely dissociated at such dilutions, whereas a simple calculation[1] (based on the assumptions: that the chromic acid dissociates according to the equation $\overset{+}{H} + \overline{Cr_2}\overline{O_7} = H\overline{Cr_2}O_7$; that the sulphuric acid is totally dissociated; and that the reactions between the ions obey the mass law) leads to the conclusion that in a solution of chromic acid containing 0.000138 gram-mol per liter, more than 20 percent of the acid must be in the form $H\overline{Cr_2}O_7$, if the difference between 1.8 and 2.0 is to be ascribed to a difference between the dissociation of the chromic acid in the experiments of Table II. and those of Table VII.

A similar calculation shows that if the discrepancy be due to dissociation, then in the presence of a larger amount of acid the ratio of the rates should more nearly approach the square of the ratios of the amounts of bichromate used. A comparison of Table VIII. with Table IV. shows that the reverse is the case.

TABLE VIII.*a*

H_2SO_4 150 cc, $K_2Cr_2O_7$ 200 cc, Ox. prod. 50 cc, $FeSO_4$ 1 cc,
Vol. 600 cc.

θ	0.0	1.0	2.0	4.0
As	7.25	3.69	2.40	1.55
A−x	1.0	0.46	0.30	0.19
k_2	—	1.17	1.17	1.07

TABLE VIII.*b*

$FeSO_4$	1.0	0.5	0.2	0.0
As	7.25	3.85	1.65	0.0

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[1] $$\overset{+}{H} + \overline{Cr_2}\overline{O_7} = H\overline{Cr_2}O_7$$

From $(11 - 0.2)(1 - 0.2) = 0.2\,k$ $\qquad k = 0.32$

From $(10 - x)(1 - x) = 0.32\,x$ $\qquad x = 0.74$

From $(10 - y)(3 - y) = 0.32\,y$ $\qquad y = 2.14$

$$\frac{k_2 \text{ of Tab. 2}}{k_2 \text{ of Tab. 7}} = \frac{(10 - x)^2(1 - x)^2}{(10 - y)^2(1 - y)^2} = 8.06, \qquad \textit{obs } 7.$$

In order to ascertain whether the potassium sulphate formed by the action of sulphuric acid on the bichromate had any noticeable retarding effect, I carried out a series of experiments in which 20 cc of $F/20$[1] solution of potassium sulphate was added to the reacting mixture. The effect on the rate, if any, fell within the errors of observation.

Further experiments are needed before a satisfactory explanation of these numbers can be arrived at.

Influence of the products of oxidation on the rate

The great retarding influence which the products of oxidation exert on the rate may be seen by comparing the experiments of Table IX. (no oxidation product present initially) with those of Table VI. In the absence of oxidation product (except such as was formed during the course of the measurements) two-thirds of the ferrous salt is oxidized in fifteen seconds; if however the product of oxidation of 5 cc ferrous sulphate be added at the beginning of the experiment, nearly two minutes are required to bring about the same amount of oxidation.

The rapid decrease of the "constant" k_2 of Table IX. is therefore not surprising.

TABLE IX.*a*

H_2SO_4 100 cc, $K_2Cr_2O_7$ 200 cc, Ox. prod. none, $FeSO_4$ 1 cc,
Vol. 600 cc.

θ	0.0	0.25	0.5	1.0	2.0	4.0
As	6.40	3.05	2.30	1.65	1.05	0.60
$A-x$	1.0	0.42	0.3	0.2	0.12	0.07
k_2	—	5.6	4.66	4.0	3.65	3.4
C	—	5.6	3.7	3.3	3.3	3.0
Average x	—	0.29	0.64	0.75	0.84	0.90

TABLE IX.*b*

$FeSO_4$	1.0	0.8	0.6	0.4	0.2	0.0
As	6.40	5.35	4.20	2.95	1.65	0.0

---

[1] One gram-Formula weight in twenty liters.

A number of experiments carried out with addition of potassium sulphate, chrome alum, and iron alum respectively, to the reacting mixture, showed that the retardation was due almost entirely to the ferric salt present in the product of oxidation.

Under *C* in Table IX. are given the values of k_2 calculated from each successive pair of values of θ and $A-x$; these numbers, although very much affected by the errors of observation, show that relatively the most effect is produced by the first addition of ferric salt. From the data collected in Table X. it appears that the same is true for larger additions of the ferric salt as well.

TABLE X.

Ox. prod.	0.29	0.9	5.0	20.0
k_2	5.6	3.0	0.68	0.42
Table	IX.	IX.	VI.	XI.

TABLE XI.

H_2SO_4 100 cc, $K_2Cr_2O_7$ 200 cc, Ox. prod. 200 cc, $FeSO_4$ 1 cc,
Vol. 600 cc.

θ	0.0	0.5	1.0	2.0	3.0	6.0
As	4.10	3.40	3.00	2.15	1.80	1.20
$A-x$	1.00	0.83	0.73	0.52	0.44	0.29
k_2	—	0.40	0.37	0.46	0.42	0.41

These facts might be accounted for — at least qualitatively — by assuming that on addition of ferric salt, part of the ferrous sulphate is converted into a ferroso-ferric compound, thus lowering the concentration of the ferrous salt in the solution, and consequently diminishing the rate. The relatively great effect produced by the first half cc of ferric salt is in harmony with this hypothesis.

Conclusion

(1) An analytical method has been devised for determining ferrous iron in the presence of ferric salts and chromic acid.

(2) The rate of oxidation of ferrous sulphate in solutions containing potassium bichromate and sulphuric acid is proportional to the second power of the concentration of ferrous salt, and to the second power of that of the acid. The order of the reaction with respect to the bichromate is variable. The oxidation is much retarded by the presence of ferric salts.

Further experiments are in progress.

In conclusion I wish to express my thanks to Prof. W. Lash Miller, for the interest he has displayed in this research.

University of Toronto,
July, 1902

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ELECTROMOTIVE FORCE OF ALLOYS OF TIN, LEAD, AND BISMUTH

BY E. S. SHEPHERD

In a previous paper[1] the author showed that tin crystallizes pure from a melt containing either lead or bismuth, while lead and bismuth form two series of solid solutions, the limiting concentration being about ten percent in each of the solid phases. These conclusions were based on quantitative analysis and were in accord with the freezing-point curves, the density relations and the appearance under the microscope. It seemed desirable to find whether measurements of the electromotive force would lead to the same conclusions. To this end measurements were made following the general outlines laid down by Herschkowitsch.[2] The bridge was so adjusted that one millimeter corresponded to 0.14 millivolt. Since relative values only were desired, the electrolyte was of constant but unknown strength.

The potential difference between pure tin and pure lead is so small that nothing was to be gained by measuring the alloys. In Table I. are given the electromotive forces of alloys of bismuth and tin when measured against pure tin in a stannous chloride solution at ordinary temperatures. Tin is anode throughout. The electromotive force is given in millivolts.

TABLE I.

% Bi	E. M. F. in M. V.	% Bi	E. M. F. in M. V.
0	0.02	80	0.07
10	0.07	85	0.07
20	0.07	90	0.05
50	0.07	95	0.12
70	0.07	100	377.4

The addition of a small amount of tin to bismuth makes it be-

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[1] Jour. Phys. Chem. 6, 519 (1902).

[2] Zeit. phys. Chem. 27, 123 (1898).

have electrically like practically pure tin. The agreement of the values at 0.07 millivolt means a difference of only 0.5 mm on the bridge. Since several samples of pure tin gave an average variation of 0.02 millivolt, we are justified in concluding from these measurements that tin and bismuth separate practically pure from the melt.

In Table II. are given the electromotive forces of lead and bismuth alloys when measured against pure lead in saturated lead chloride solution at ordinary temperatures. Lead is anode throughout and the electromotive forces are given in millivolts.

TABLE II.

% Bi	E. M. F. in millivolts		% Bi	E. M. F. in millivolts	
2	1.00	1.23	80	2.57	—
5	1.14	1.56	90	2.57	—
10	2.57	2.56	95	3.43	3.57
30	2.57	—	98	4.68	4.31
50	2.50	—	100	323.10	—
70	2.64	2.57	—	—	—

These results are plotted in Fig. 1. The essential features of

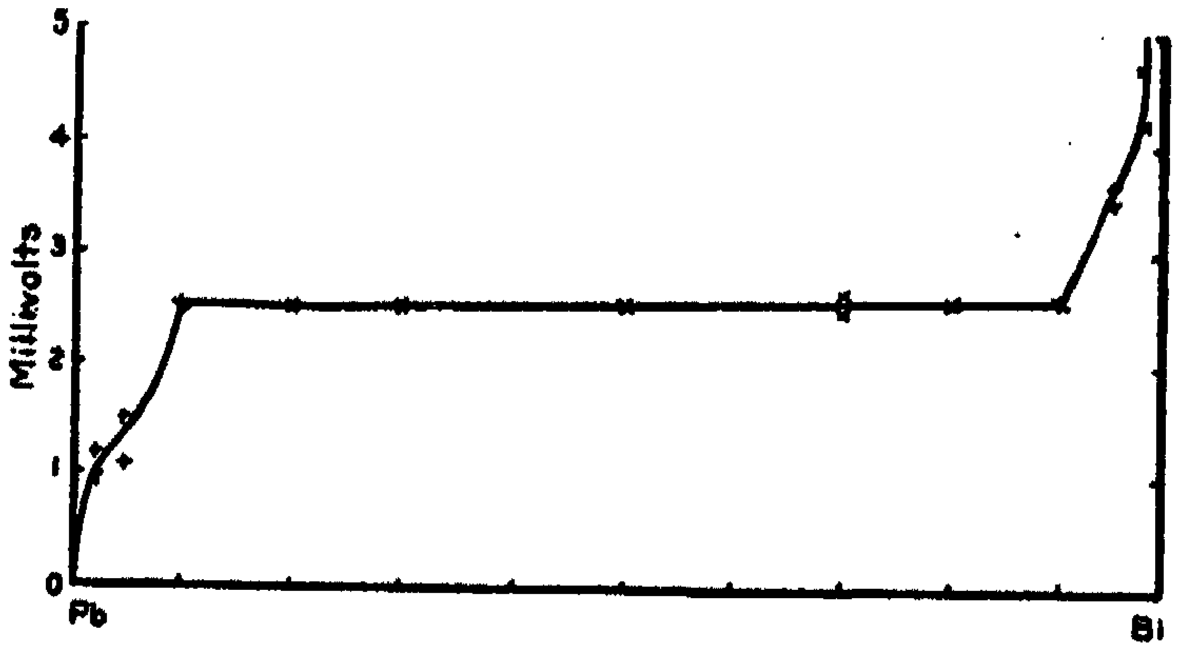

Fig. 1

the curve are a continuously changing voltage as the amount of bismuth in the lead increases from zero to ten percent, a constant voltage while the bismuth content increases from ten to ninety percent, and a continuously changing voltage while the bismuth in the alloy increases from ninety to one hundred percent. This is the form of curve appropriate to a system giving two series of solid solutions. From 0–10 percent bismuth there is a single solid phase of continuously varying composition. From 10–90 percent bismuth there are two solid phases, each of constant composition. From 90–100 percent bismuth there is a single solid phase of continuously varying composition. The electrical measurements therefore confirm the conclusions previously drawn.

It will be noticed that the two series of measurements do not agree very well. This is not surprising. If we start with a melt containing five percent of bismuth, for instance, and let this solidify, the rate of cooling will have a marked effect on the homogeneity of the solid mass. Since the rate of adjustment in solids is often slow, the mass will be apt to vary from the equilibrium condition of nothing but five percent crystals. Any such variation will show itself in the electromotive force, as is the case in these experiments.

Cornell University.

REDUCTION OF INSOLUBLE CATHODES

BY ALFRED T. WEIGHTMAN

The effect of the reducing action of a current at the cathode can show itself in two distinct ways: (1) By the reduction of the ions in the solution, or (2) by the reduction of the electrode itself. The first of these is too well known to dwell upon further here, and it is the latter of these reactions which it is now proposed to discuss. In this case the cathode is usually a compound of a metal and either by the reducing action of the current or by the action of nascent hydrogen, which ever way you are pleased to look at it, the H ions combine with the non-metallic radical forming a new compound. The reduction of AgCl to Ag as in the De la Rue standard cell is a case in point, but probbly the most familiar one is that of the negative plate of a storage cell where, during charge, the insoluble $PbSO_4$ is reduced to the metallic condition.

We have here two possible cathodes, namely, $PbSO_4$, which under the reducing action of the current will yield Pb and H_2SO_4, and the metallic lead, either in the form of a grid or spongy lead from previously reduced sulphate, which will of course evolve H. With two possible cathodes present we have of course two possible reactions, which can take place simultaneously, namely, the reduction of $PbSO_4$ or the evolution of H, and the proportion in which these two reacting substances are present will influence the relative distribution of the current between the two reactions.

The principal conditions, however, which will determine this are or at least should be the heat of formation of those two reactions as in the case of reduction from the solution. The following are the thermo-chemical equations of these reactions:

$$\begin{aligned} PbSO_4 + H_2O = PbO + H_2SO_4\,Aq &= 23400 \text{ cal} \\ PbO = Pb + O &= 50300 \text{ ''} \\ \hline &\ 73700 \text{ ''} \qquad (1) \end{aligned}$$

$$H_2SO_4Aq = H_2SO_4Aq + H_2 + O = 68360 \text{ cal} \qquad (2)$$

It will be seen that the reduction of $PbSO_4$ requires a slightly higher voltage than the liberation of hydrogen. It is an astonishing thing therefore that more hydrogen is not evolved from a negative plate during charge than is actually found to be the case. As a matter of fact very little hydrogen is evolved until the extreme end of the charge is reached, when practically all the $PbSO_4$ has been reduced. This is still more extraordinary when higher current densities are used. In the case of a storage battery on raising the current density the liberation of hydrogen increases, although this is the reaction which requires the least energy absorption. From the consideration of reduction from solution on raising the current density the reaction requiring the greater energy absorption increases. Of course, I quite realize in the latter case, as the ions undergoing reduction are in solution, that diffusion comes into account, while in the former case it does not, but it is still rather unlooked for that the amount of hydrogen should actually increase.

In the Salom process for the production of lead sponge and at present worked by the Electrical Lead Reduction Company, at Niagara Falls, the reactions are similar to those described for the negative plate of a storage cell with this difference: PbS (in the form of native galena) is used instead of $PbSO_4$ with the production of H_2S instead of H_2SO_4. But on considering the heat of formation of the two possible reactions they are found to lie even farther apart than in the case of the reduction of the sulphate just considered, still more favoring the reduction of hydrogen in preference to the reduction of the lead compound. The following thermo-chemical equations clearly show this:

$$\begin{aligned}
PbS &= Pb + S = -\ 20400 \text{ cal} \\
S + H_2 &= H_2S = +\ \ 4510 \text{ ''} \\
H_2O &= H_2 + O = -\ 68360 \text{ ''} \\
&\qquad\qquad \overline{-\ 84250} \text{ ''} \qquad (1)
\end{aligned}$$

$$H_2SO_4Aq = H_2 + O + H_2SO_4Aq = 68360 \text{ cal.} \qquad (2)$$

The heat of solution of H_2S does not come into account excepting right at the start, as the solution is quickly saturated. In fact, in most of the experiments to be hereafter described, the solution was saturated with H_2S from an outside source beforehand so as to eliminate any variations this might bring about.

The difference is so great that at first sight it appears to be an almost impossible problem to reduce the sulphide without having an enormous waste of current spent in the liberation of hydrogen which is of course, from the point of view of the manufacturer, an undesirable reaction and merely represents so much waste of current. I have conducted a very large number of experiments at the works of the Electrical Lead Reduction Company, with a view of producing as small an evolution of hydrogen as possible, or in other words, raising the current efficiency as high as possible so as to reduce the largest quantity of PbS for a given current. The efficiency is extremely sensitive to (1) Degree of purity of ore and the nature of those impurities; (2) Conductivity of ore; (3) Fineness of grinding; (4) Strength and purity of the electrolyte; (5) Thickness of layers of ore; (6) Temperature of solution, and the various other causes; but strange to say, is almost unaffected by current density. Of course the first essential point for the reduction of an electrode is that it should be an electrical conductor. When the electrical resistance of the ore is spoken of it must not be inferred that pure PbS in the mass is of variable conductivity, but impurities present, influence it very considerably. The grinding also affects it, the principal source of resistance not being so much in the ore itself as in the resistance at the points of contact between each particle of ore, which is an extremely variable quantity. By finer grinding the number of points of contact is increased and the resistance is correspondingly raised. The electrical resistance of pure PbS is given by J. Guinchant as 0.000298 at 0° C, increasing almost proportionately to 0.01294 at 920° C.

Ores as obtained direct from the mine differ considerably in their electrical conductivity, and this is a property of lead ore which miners are not usually called upon to consider.

All sorts of variations were at first obtained, due to neglect of these conditions, and it would be tedious to go through the influence all these various properties have upon the efficiency of the reduction, but a few results given under the most favorable conditions and in the most perfect form of the process may be of interest.

By analyzing the gases evolved from a reduction it is possible to tell what proportion of the current is being used in depriving the ore of sulphur and what proportion is being used in liberating hydrogen.

For the purpose of ascertaining the progress satisfactorily, it was found to be important to keep the gases from the anode and cathode separate for reasons to be explained later. The gases from the cathode were collected at intervals during reduction, and a sample of the more or less reduced ore removed. These were then analyzed, the gases for their percentages of H and H_2S and the ore for Pb and PbS. Plotting time as abscissæ and the percentages of H_2S as ordinates, we obtain a curve showing the composition of the liberated gases at any moment. Again plotting time as abscissæ and the percentage of PbS as ordinates, we obtain a curve showing the composition of the ore at any moment. Some interesting comparisons can then be made showing how the composition of the ore will influence the composition of the gases. The following tables and curves give the results obtained for various current densities.

The current density is not given as, owing to the porosity of the PbS constituting the cathode, it is not possible to measure the surface. The relative values of the current densities will however be proportional to the different currents as it can be safely assumed that the surface remains the same at various rates.

The similarity in the shape of the curves under different current densities is remarkable, in fact, the number of ampere hours necessary for a given percentage of sponge in the ore agree within the limits of experimental error. This was further corroborated by stopping experiments at various points in the curve and then raising and lowering the current. The composition of the evolved gases was scarcely altered by doing this. Perhaps this might be accounted for by the fact that diffusion does not come into account as in the case of reduction from solution.

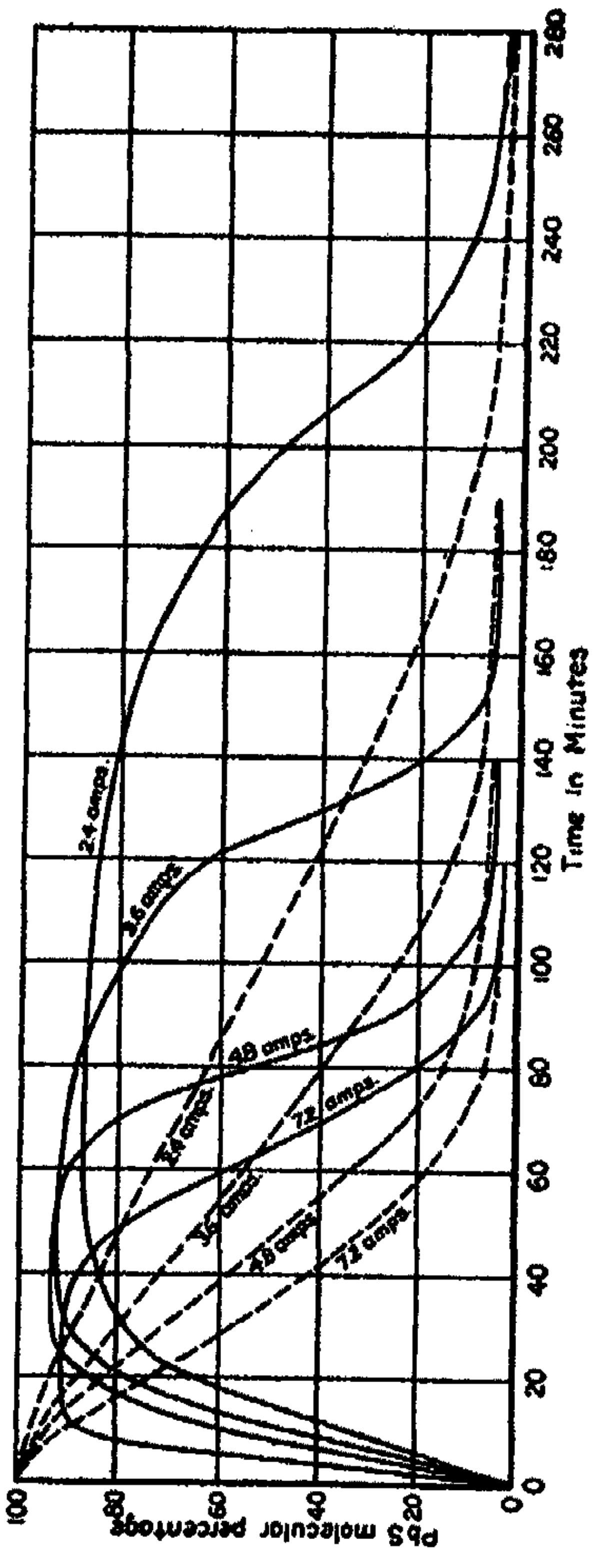

Fig. 1

But probably a more remarkable thing is that the yield of H_2S should be so high when we refer back to the thermochemical equations previously given. It was here shown that the reaction $PbS + H_2 = Pb + H_2S$ requires a very much higher absorption of energy than the mere liberation of hydrogen. And yet under proper conditions this reaction can be kept up to an efficiency yield of 80 percent or over for two-thirds of the reduction even when the compound undergoing reduction, namely, PbS, is present to the extent of only 25 percent. It is natural to expect that H_2S would only be evolved when the percentage of Pb was small and would not be evolved at all when the percentage of Pb had reached 20 or 30 percent. Yet in the case under discussion with a difference of 15890 cals between the two possible reactions, precisely the opposite effect is produced and the reaction requiring the greater absorption of energy gives as large as an 80 percent yield when only 25 percent of the reacting substance is present, in spite of the fact too that the reduced lead sponge is even a better electrical conductor than the PbS. If it had been the other way about, namely, that the lead sponge was of higher electrical resistance than the PbS, some explanation might be forthcoming as more current would be carried by the latter in proportion to its superior conductivity.

The voltage curve does not tell us much and only in one case is it given in the above experiments, as it possesses little interest, keeping quite steady after once the contact resistance of the particles has been overcome. The actual volts given are not the actual volts required in practical work. It has been previously mentioned that it was necessary for experimental purposes to keep the gases from the anode and cathode separate, and the method adopted for doing this introduced considerable resistance in the circuit which accounts for the volts per cell being so high. This, however, does not affect the relative value of the readings, that is to say, any rise or fall of volts would be noticeable as the resistance remains constant.

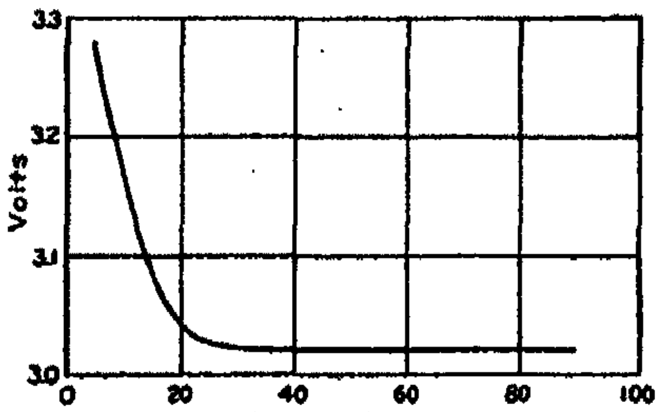

Fig. 2

The first sudden rise of the gas curve from zero to about 90 percent is a little mysterious, but is probably due to a comparatively high resistance of the ore at the start, as indicated by the voltage curve. The gases would then tend to be evolved from the supporting grid, which being of sheet lead would, of course, account for the larger percentage of H in the evolved gases.

The measurement of the cell Zn | H_2SO_4 | PbS does not throw much light on the matter. Actual measurements gave 0.19 volt, the calculated voltage being 0.18 volt, taking the heat of solution of H_2S into account.

Great care is necessary in making this measurement or a wrong conclusion may be arrived at, because the resultant substance of the reaction is the very one we wish to avoid in the measurement. That is to say, that if the cell is allowed to send a current a film of spongy lead is produced over the complete surface of the PbS, and it then behaves to all intents and purposes like a mass of pure spongy lead. To take the first deflection before it has sent any current is also misleading, as there is apparently a film on the surface of some other lead compound which gives a voltage of 0.68 volt.

To get consistent results, therefore, it is necessary to allow the cell to send a current to reduce this film and then amalgamate the film away with mercury. A surface of pure PbS is then produced which gives the above measurement.

From the manufacturers' point of view it is a disappointment that the reaction can not be brought to completion, as on reference to the curves it will be seen that they fall off in an aggravating way when 5 percent of PbS still remains. The probable explanation of this is that a few particles of PbS become encased in lead sponge which then behaves to all intents and purposes like pieces of pure lead sponge, the reducing action of the current being unable to penetrate the casing.

It has been previously mentioned that for experimental purposes it was necessary to keep the gases from the anode and cathode separate, and if it is not wandering too far away from the subject, it might be interesting to refer briefly to the reasons for this. In the earlier experiments before this was done, some rather curious analyses of the gases were obtained, a few of which are given below:

H_2S Percent	H Percent	O Percent
9.6	82.0	8.4
64.0	35.8	0.2

It will be noticed that there is a curious absence of O, as, of course, it was expected that the volume of the gases would be in the ratio of two volumes of H and H_2S to one of O, and even if the H_2S should act as a depolarizer at the anode to some extent, thus: $H_2S + O = H_2O + S$; this would not alter the relative volumes of the gases evolved and they should still remain in the proportion of 2 to 1. The absence of O, as shown in the above analyses, came therefore as rather a surprise. On investigation, however, it was found that under proper conditions H_2S could be oxidized to various oxy-sulphur compounds without passing through the stage $H_2S + O = H_2O + S$, as the liberation of free S would have been a necessary conclusion to the reaction. This depolarizing effect of the H_2S acts advantageously as, of course, it reduces the polarization of the cell. It is not, however, the object of this paper to go further into this, but it must be left over for another occasion.

Referring back to the singularity of the high efficiency of the reduction when compared with the difference in the thermochemical equations of the two reactions, I thought it would be interesting to see how far this applied to the sulphides of other metals. But the conditions are somewhat restricted, as it is necessary that (1) the sulphide should be a conductor; (2) that it must not be a sulphide precipitated from solution, as these are usually poor conductors due, no doubt, to their fine state of divisions; (3) that it should be capable of being prepared of reasonable purity; (4) that for the purpose of comparison its heat of formation should not be greatly higher or lower than PbS. Cu_2S seemed to come well within these confined limits, as it is an excellent conductor, it is easily prepared in the mass by fusion, it can be prepared perfectly pure and its heat of formation is almost exactly the same as PbS, namely, 20240 cal. The thermo-chemical equation then becomes:

$$\begin{aligned} Cu_2S = 2Cu + S &= -\ 20240 \text{ cal.} \\ S + H_2 = H_2S &= +\ \ 4510 \text{ ''} \\ H_2O = H_2 + O &= -\ 68360 \text{ ''} \\ \hline &\ \ -84090 \text{ ''} \qquad (1) \\ H_2SO_4Aq = H_2 + O + H_2SO_4Aq &= 68360 \text{ ''} \qquad (2) \end{aligned}$$

The Cu_2S was reduced under precisely similar conditions in every respect as the PbS, but vastly different results were obtained, as is shown by the following table and curve:

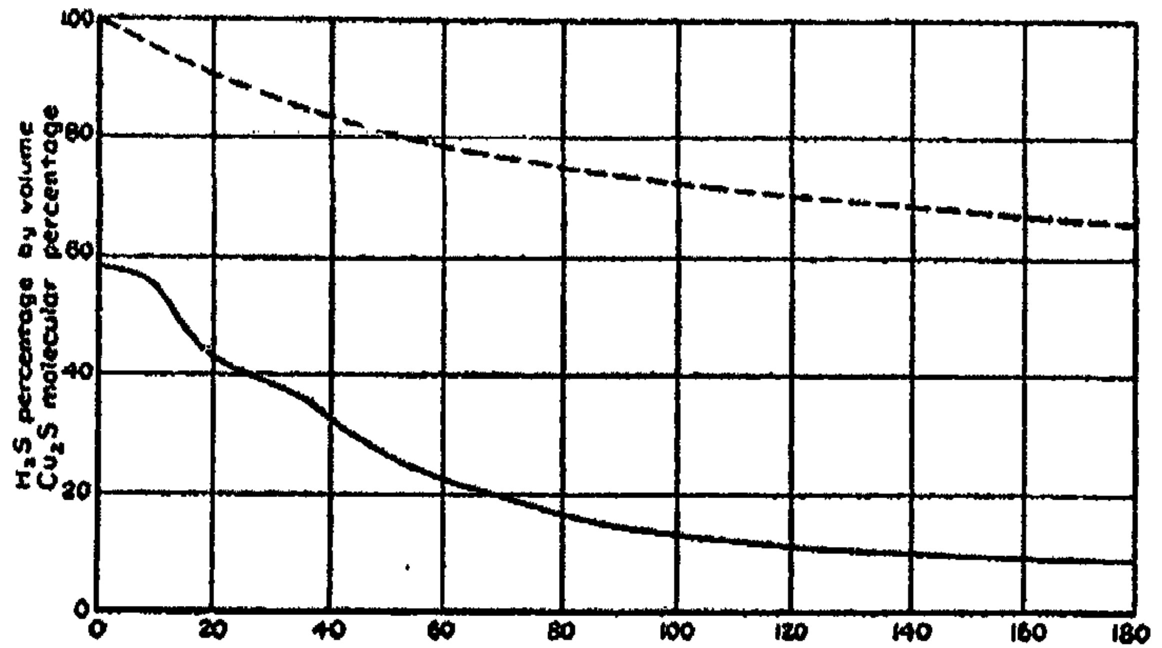

Fig. 3

The percentage of hydrogen is always higher than the H_2S in proportion to the percentages of reacting substances (Cu_2S and Cu) present, which is just what would be expected from a study of the thermo-chemical equations. I am not prepared to admit, however, that the physical condition of the Cu_2S undergoing reduction is entirely irresponsible for this. After about the first hour it assumed a very bulky condition, which would offer poor facilities for conducting the current and quite different from the spongy form which reduced PbS assumes. But this would not account for the shape of the curve during say, the first hour.

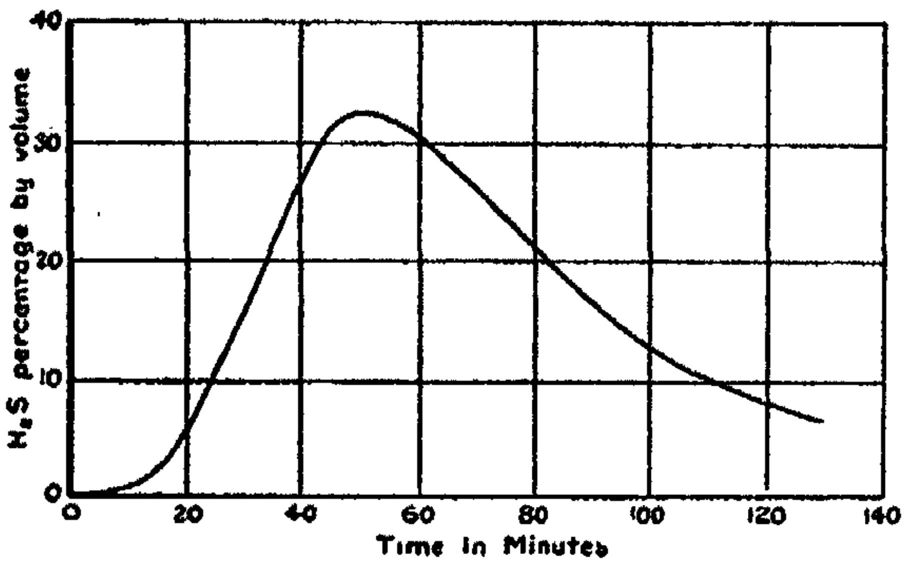

Fig. 4

NiS also offers a suitable sulphide for reduction as it comes reasonably well within the above prescribed limits, the heat of formation being near that of Cu_2S. The gas curve, however, gives results differing largely from those previously considered, keeping at almost zero for some distance, rising to a maximum after about fifty minutes, and then gradually falling.

The percentage composition of Ni and NiS was not taken as some of the reduced Ni being in a very fine state of division, went into solution. The results are given in Fig. 4.

Ag_2S has a very low heat of formation and is in fact an ideal substance for efficient reduction.

$$\begin{aligned} Ag_2S &= 2Ag + S = -\ 5310 \text{ cal.} \\ S + H_2 &= H_2S = +\ 4510 \text{ ''} \\ H_2O &= H_2 + O = -\ 68360 \text{ ''} \\ & \overline{\quad -\ 69160 \text{ ''}} \qquad (1) \end{aligned}$$

$$H_2SO_4Aq = H_2 + O + H_2SO_4Aq = 68360 \text{ ''} \qquad (2)$$

It will be seen that the heats of formation in equations (1) and (2) are very nearly equal. It is necessary however to prepare the Ag_2S by precipitation which, as a rule, is of high electrical resistance, but in the case of Ag_2S seems to conduct fairly well.

The curve is very similar to that obtained for lead, but shows a much sharper drop. The following results were obtained.

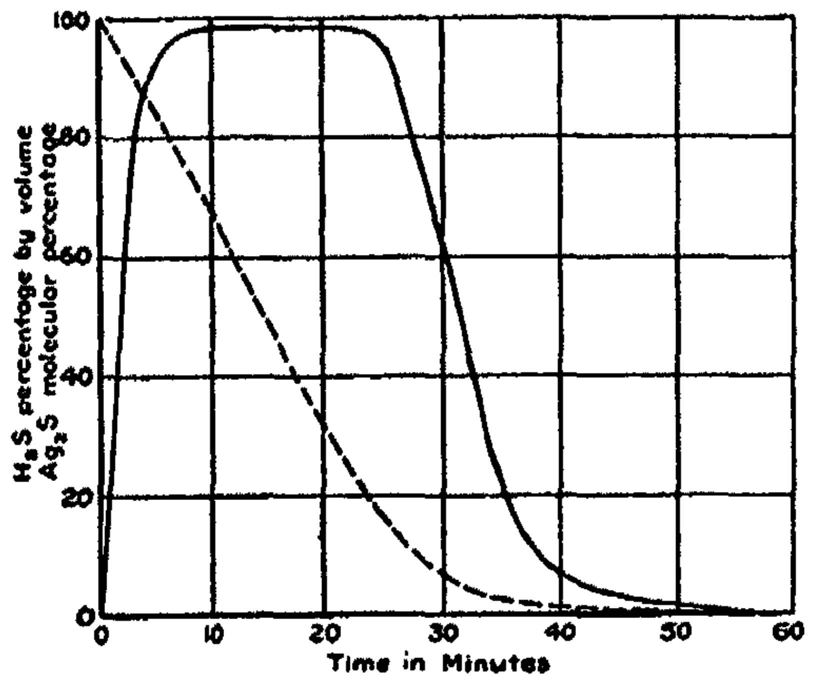

Fig. 5

Very few other sulphides are available, being either non-conductors difficult of preparation in suitable form, or having too high heat of formation.

A sulphide which has a high heat of formation as for instance FeS, is not reduced at all, nothing but pure H being evolved from the start excepting in so far as it is acted on by the solution chemically. A possible explanation of some of the above experiments and the disconformity of actual results with the thermo-chemical equations is as follows:

It has been assumed that the number of cal necessary for the decomposition of H_2O is 68360, or, expressed in volts, $\frac{68360}{2 \times 23040} = 1.48$ volts. It has been shown by Caspari and others that the voltage necessary to liberate H is constant, but is dependent on the metal which constitutes the cathode.

This is what he calls the "overvoltage" (Ueber-Spannung) and differs for different metals. There would have to be added therefore on to each of the above equations a certain overvoltage which might be sufficiently high to bring the voltage necessary for the liberation of H above that for the liberation of H_2S, which would account for some of the above unexpected results. This must not be relied on too completely, however, as there is probably also an overvoltage for H_2S with different metals which as far as I am aware has not yet been determined.

ELECTROLYTIC PREPARATION OF SODIUM AMALGAM

BY E. S. SHEPHERD

The ordinary electrolytic methods for making sodium amalgam[1] give a dilute amalgam and require a high voltage — fourteen volts in one case. As the electrolytic preparation of a solid sodium amalgam makes a very satisfactory lecture experiment, it seemed desirable to devise a method which would eliminate some of the difficulties. The chief reason why a solid amalgam is hard to obtain is that it has a lower density than mercury and rises to the surface. When the electrolyte is above the mercury, the solid or pasty amalgam separates the electrolyte from the mercury, cutting the current efficiency down very nearly to zero. To obviate this, the mercury was placed in a porous cup, the bottom of which dipped into the electrolyte. The amalgam then rises to the free surface, leaving fresh mercury in contact with the electrolyte. As soon as the whole mass becomes solid the sodium is no more readily absorbed, and the current efficiency drops off. Since a 1.5 percent amalgam is solid at 25° and a 2 percent amalgam is quite stiff at 100°, we should hardly expect to prepare a richer amalgam even though the 10 percent amalgam[2] only melts at 100°. A saturated sodium chloride solution was used with a platinum anode. The mercury was placed in a porous cup, the bottom of which dipped just below the surface of the solution. By this arrangement, electrical endosmose was decreased though not eliminated. Drops of water will pass through the diaphragm and these were removed, so far as possible, by means of filter paper. In one run melted naphthalene was placed on the surface of the mercury. This decreases oxidation and prevents sparking between

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[1] Nernst. Zeit. Elektrochemie, 3, 308 (1897); Kerp. Zeit. anorg. Chem. 17, 300 (1898); Cf. Reuter. Zeit. Elektrochemie, 8, 801 (1902).

[2] Kurnakow. Zeit. anorg. Chem. 23, 439 (1900).

the surface of the amalgam and the moist walls of the cup. If the porous cup is boiled in the solution so as to get the walls thoroughly saturated, a run can be made with a mean potential difference of about seven volts. If this precaution is not taken, the voltage may rise to fourteen volts and there will be occasional sparking between the mercury and the walls of the cup. The following runs were made. The second column gives the temperature, the third the voltage, the fourth the current density in amperes per square decimeter, the fifth the concentration of the amalgam, and the sixth the current efficiency. The absolute current was 1–4 amperes and was held practically constant in each run.

No.	Temp.	Volts	$N.D._{100}$	Pct. Na	Efficiency
1	30°	5–8	10.5	0.5	28 pct
2	35°	6–8	18.3	1.5	37 pct
3	90°	5–7	19.0	1.3	29 pct
4	90°	—	4.0	0.3	65 pct
5	95°	6	7.8	1.6	60 pct

Run 5 was made with a covering of molten naphthalene above the amalgam. In all cases the porous cup is attacked by the caustic, especially after the amalgam grows pasty. The experiments show that a solid amalgam can readily be prepared electrolytically and that the yield is better at a higher temperature than at a lower. It seems probable that a better yield could be obtained at a lower voltage if a more satisfactory diaphragm were available.

Cornell University.

NEW BOOKS

Lehrbuch der allgemeinen Chemie. *By W. Ostwald. In zwei Bänden. Zweite, umgearbeitete Auflage. Zweiten Bandes, zweiter Teil: Verwandtschaftslehre. Erster Teil. 16 × 23 cm; pp. xi + 829 to 1188. Leipzig: Wilhelm Engelmann, 1896-1902. Price: paper, 9 marks.* — With this number the second part of the second volume is at last completed. It is interesting to note the general development in the course of time. In 1896 Ostwald was but slightly interested in the phase rule. In this number, everything is arranged according to the phase rule classification, and such experiments as those of Zaitschek on the equilibrium between sulphuric acid, ethyl alcohol and water are treated where they belong, under three components with one liquid phase. It seems reasonable to assume that when Ostwald starts a third edition, we shall find all the quantitative relations brought in where they belong under the number of components and the degree of variance. We shall then have a really systematic presentation of physical chemistry.

This number begins with two-component systems and discusses the quadruple points. Next comes a brief recapitulation of two-component systems which have been actually studied experimentally: sulphur dioxide and water; chlorine or bromine and water; ammonium bromide and ammonia; chlorine and iodine; calcium chloride and water; ferric chloride and water; systems with organic compounds; alloys.

The rest of the number is given up to three-component systems and the material is arranged under the following captions: mixtures of several gases; a solid and a gaseous phase; two solids and vapor; three solids and vapor; liquid and vapor; several liquid phases; liquids and solid. Under liquid and vapor and two liquid phases and vapor, there is a very extended discussion of vapor pressure curves in ternary systems. This is necessarily largely theoretical because the experimental data are extremely few in number.

As Ostwald himself says in the preface, each reader will probably note the omission of something which he thinks should have been included. That is inevitable even in a work of this size. There are paragraphs also which might well have been worded otherwise. That is also inevitable in a book which is so markedly subjective. Speaking for himself, the reviewer feels that the subjective feature of the book is one of its most excellent points and he does not feel called upon at this time to point out the places in which he differs radically from the author. There is so much that is excellent and lasting that differences of opinion can be left to time to settle.

In the second part of the second volume "there have not been included the special cases of chemical equilibrium occurring in solid solutions, isomorphous mixtures, and enantiomorphous crystals; nor the extensive field of electrochemical equilibria. These will be considered in a third part of the second volume which will include an outline of our knowledge of catalysis and a compilation of special data bearing on chemical mechanics (dissociation and equilibrium constants, special kinetic studies, etc.). A supplement will give a systematic analysis of the investigations which have been published too late to be included in the second edition. This will complete the work.

Wilder D. Bancroft

Acht Vorträge über physikalische Chemie. *By J. H. van't Hoff. 15 × 23 cm; 81 pp. Braunschweig: F. Vieweg und Sohn, 1902.* — These are the lectures delivered at Chicago University in June, 1901. The subject is divided into four parts with two lectures to each subdivision. The four points brought out are the relations of physical chemistry to chemistry, industry, physiology, and geology.

In the lectures on physical chemistry and chemistry, the author takes the osmotic theory of solutions, the second law of thermodynamics and the electrolytic dissociation theory as his three fundaments and points out that these represent three steps forward in inorganic chemistry. "As a first step one can say that physical chemistry has introduced an entirely new and comprehensive method for attacking inorganic problems. Secondly, we have a principle which tells in which sense and how far a chemical reaction will run. Thirdly, physical chemistry introduces new conceptions of the nature of solutions of so-called electrolytes, i. e., of bases, acids and salts." The illustrations of these points are the application of the phase rule to carnallite, the inversion points for carnallite and the heats of reaction, the behavior of salts in dilute aqueous solutions.

In the lectures on physical chemistry and technical chemistry, van 't Hoff speaks a truth which is often not recognized in this country. "There is of course a difference between a laboratory experiment and a technical test. In the laboratory experiment, the question of cost is immaterial, while it is the vital point in an industrial process. But, apart from this, one can say that whatever can be made in a test-tube can be made by the hundred weight; only the conditions, temperature, etc., must be reproduced exactly." As an illustration of an application of physical chemistry to technical chemistry, the author cites the extraction of potassium chloride and of hydrated magnesium chloride from carnallite by heating to 168° and then cooling to 115°. Cohen's investigations on tin are also cited as illustrating the way in which the peculiar behavior of tin in cold weather has been traced to its true cause. The second lecture on this subject is devoted to Roozeboom's work on carbon and iron, work of the highest technical as well as scientific importance.

Under physical chemistry and physiology, the author takes up the experiments of de Vries on plant cells, of Donder and Hamburger on the red blood corpuscles, of Massart on the eye, of Wladimiroff on bacilli, of Loeb on the development of sea urchin's eggs. The toxic action of salts and the catalytic action of enzymes are also considered.

With physical chemistry and geology we come back to carnallite and the phase rule, and the author shows how a laboratory study of the equilibrium between the sulphates and chlorides of magnesium, potassium, sodium and calcium in aqueous solution enables us to reconstruct the history of the vanished seas even to the point of telling the approximate temperature at which the water evaporated.

This is a most interesting course of lectures and fortunate indeed were the students of Chicago University who were privileged to hear it. It is to be hoped, however, that the authorities of Chicago University do not intend to rely indefinitely on such necessarily sporadic teaching of physical chemistry.

Wilder D. Bancroft

Electro-Chemical Analysis. *By Edgar F. Smith. Third edition, revised and enlarged. 13 × 20 cm; pp. vi + 199. Philadelphia: P. Blakiston's Sons and Co., 1902. Price: $1.50, net.*—The author has been recognized for years as one of the leading authorities in the subject of electrochemical analysis and a new edition of his book will be very welcome to the student. The metals are taken up in the following order: copper, cadmium, mercury, bismuth, lead, silver, zinc, nickel and cobalt, manganese, iron, uranium, thallium, platinum, palladium, rhodium, molybdenum, gold, tin, antimony, arsenic. After this comes the separation of one metal from another. Under the heading copper, the author discusses the separation of copper from aluminum, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, gold, iron, magnesium, manganese, mercury, molybdenum, nickel, palladium, platinum, potassium, selenium, sodium, strontium, silver, tellurium, thallium, tin, tungsten, uranium, vanadium, zinc. The other metals are discussed with the same fullness, so that we really have a systematic treatment of the subject. In the last half a dozen pages, we find the electrolytic determination of the halogens, the electrolytic determination of nitric acid and the electrolytic oxidation of natural sulphides. The work has been admirably done. Full literature references are given. In each case the author points out which method he himself prefers and then describes other methods which have been employed by himself and others. This is exactly as it should be, and the book is both the best and the smallest of the standard works on the subject.

It was inevitable that there should be an introductory part, and the author is to be congratulated in keeping it down as much as he has. Many of us would have rejoiced if the blue pencil had been used even more vigorously. We are all glad to read the details in regard to the author's laboratory; but when we find both the volt and the ampere defined with reference to Ohm's law, we cannot help wondering who is expected to profit by this and other paragraphs

Wilder D. Bancroft

Die Elektrolyse wässriger Metallsalzlösungen. *By E. Jordis. 17 × 24 cm; pp. 137. Halle: Wilhelm Knapp, 1901.*—What the author wished to do was to discuss the processes in electroplating from a scientific point of view, showing why each particular bath should or should not have the composition it does. As the author admits from the start, it is not possible to carry out such a plan in the present state of our knowledge. The book is therefore largely a compilation of empirical statements, attention being drawn to various points which call for investigation. The last thirty pages contain measurements by the author, and it seems fair to take these as showing on a small scale how he thinks some of the problems should be attacked. There is nothing in the text, however, to show what point the author has cleared up. He has made a number of measurements and we now have some facts which we did not have before;

but they do not seem to be facts which bear on anything. If an investigation of this sort is really the necessary result of a study of physical chemistry, it may well be asked what is the use of such a study? *Wilder D. Bancroft*

Die Gewinnung des Aluminiums. *By A. Minet. In Deutsche übertragen von Dr. Emil Abel. (Monographien über angewandte Elektrochemie, Band II.). 16 × 24 cm; pp. vii + 129. Halle: Wilhelm Knapp, 1902. Price: 5 marks.*—We have recently (6, 270) had occasion to refer with pleasure to the appearance of the monographs on applied electrochemistry, and to one on the electrolysis of water. The second, on the electrolytic preparation of aluminum, has made its appearance with commendable promptness. The first ten pages deal with the chemical methods of preparing aluminum, then come thirty pages on purely electrothermal processes and forty-seven pages on the electrolytic preparation of aluminum. In the second part there are chapters on the aluminum industry, on the properties of aluminum and its alloys, on the working of aluminum, and on the applications of aluminum.

Nothing could read better than this; but unfortunately the text is not so good as the headings. Only two pages are given to Hall's process, and these two contain no information of very much later date than 1887. The furnaces described bear no resemblance whatsoever to those actually in use. According to Minet, aluminum is now made at Pittsburgh by Hall's process. The works at Niagara are much too recent to be mentioned in a book published in 1902. The impression is given by the author that his own process is much the best and no one would gather that it is now being superseded in the few places in which it has been in use. It must be admitted regretfully that this volume is not up to the standard of the first of the series. *Wilder D. Bancroft*

Die Darstellung des Chroms und seiner Verbindungen mit Hilfe des elektrischen Stromes. *By Max Le Blanc. 16 × 24 cm; pp. 108. Halle: Wilhelm Knapp, 1902. Price: paper, 6 marks.*—The monograph deals with the literature down to the end of 1901. The work has been well done; the book is a credit to the series; and will be of great use to all who are struggling with electrochemical problems. The first chapter deals with the preparation of metallic chromium by electrolysis of aqueous solutions, and at high temperatures. In the second chapter, the preparation of chromium alloys is discussed from the same two standpoints. In the third chapter, we have the compounds of chromium: the carbon, silicon, phosphorus, sulphur, and oxygen compounds. Under oxygen compounds come the chromous and chromic salts, and all the chromates. It has been the object of the author to make the monograph complete in itself, so that it should not be necessary to look up the original papers. This has necessitated publishing much from patent literature which may seem superfluous to many. In this particular case, the best answer to this objection is that the monograph only runs a little over 100 pages and that an amount of detail is therefore permissible which would otherwise be out of place.

Wilder D. Bancroft

Galvanoplastie et Galvanostégie. *By A. Minet. (Encyclopédie des Aide-Mémoir). 11 × 18 cm; pp. 182. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs.*—These little volumes of the Aide-Mémoire series are always welcome. This one is based chiefly on Fontaine's book and has both the merits and defects of that work. *Wilder D. Bancroft*

Elementary Principles in Statistical Mechanics. *Developed with especial reference to the rational foundation of thermodynamics. By J. Willard Gibbs. 14 × 22 cm; pp. xviii + 207. New York: Charles Scribner's Sons, 1902. Price: $4.00, net.* — The study of statistical mechanics has arisen from the development of the kinetic theory of gases. In the application of the theory of probability to gas theory it was found that to some extent the results were independent of the special assumptions made regarding molecular force. It accordingly became desirable to investigate the general consequences of the principles of mechanics and statistics, i. e., the consequences to be obtained without the introduction of hypotheses concerning the nature of the elements of the systems considered. Gibbs presents such an inquiry in the present book, which is one of the volumes of the Yale Bicentennial Publications. Gibbs's preface so admirably states the point of view in the study of the subject, and gives so clear an analysis of the development of his argument, that we reproduce it below.

"The usual point of view in the study of mechanics is that where the attention is mainly directed to the changes which take place in the course of time in a given system. The principal problem is the determination of the condition of the system with respect to configuration and velocities at any required time, when its condition in these respects has been given for some one time, and the fundamental equations are those which express the changes continually taking place in the system. Inquiries of this kind are often simplified by taking into consideration conditions of the system other than those through which it actually passes or is supposed to pass, but our attention is not usually carried beyond conditions differing infinitesimally from those which are regarded as actual.

"For some purposes, however, it is desirable to take a broader view of the subject. We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time. The fundamental equation for this inquiry is that which gives the rate of change of the number of systems which fall within any infinitesimal limits of configuration and velocity.

"Such inquiries have been called by Maxwell *statistical*. They belong to a branch of mechanics which owes its origin to the desire to explain the laws of thermodynamics on mechanical principles, and of which Clausius, Maxwell, and Boltzmann are to be regarded as the principal founders. The first inquiries in this field were indeed somewhat narrower in their scope than that which has been mentioned, being applied to the particles of a system, rather than to independent systems. Statistical inquiries were next directed to the phases (or conditions with respect to configuration and velocity) which succeed one another in a given system in the course of time. The explicit consideration of a great number of systems and their distribution in phase, and of the permanence or alteration of this distribution in the course of time is perhaps first found in Boltzmann's paper on the *Zusammenhang zwischen den Sätzen über das verhalten mehratomiger Gasmoleküle mit Jacobi's Princip des letzen Multiplicators* (1871).

"But, although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics. Moreover, the separate study of this branch of mechanics seems to afford the best foundation for the study of rational thermodynamics and molecular mechanics.

"The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results. The laws of statistical mechanics apply to conservative systems of any numbers of degree of freedom, and are exact. This does not make them more difficult to establish than the approximate laws for systems of a great many degrees of freedom, or for limited classes of such systems. The reverse is rather the case, for our attention is not diverted from what is essential by the peculiarities of the system considered, and we are not obliged to satisfy ourselves that the effect of the quantities and circumstances neglected will be negligible in the result. The laws of thermodynamics may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression, but they make a somewhat blind guide in our search for those laws. This is perhaps the principal cause of the slow progress of rational thermodynamics, as contrasted with the rapid deduction of the consequences of its laws as empirically established. To this must be added that the rational foundation of thermodynamics lay in a branch of mechanics of which the fundamental notions and principles, and the characteristic operations, were alike unfamiliar to students of mechanics.

"We may therefore confidently believe that nothing will more conduce to the clear apprehension of the relation of thermodynamics to rational mechanics, and to the interpretation of observed phenomena with reference to their evidence respecting the molecular constitution of bodies, than the study of the fundamental notions and principles of that department of mechanics to which thermodynamics is especially related.

"Moreover, we avoid the gravest difficulties when, giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms. Yet any theory is obviously inadequate which does not take account of all these phenomena. Even if we confine our attention to the phenomena distinctively thermodynamic, we do not escape difficulties in as simple a matter as the number of degrees of freedom of a diatomic gas. It is well known that while theory would assign to the gas six degrees of freedom per molecule, in our experiments on specific heat we cannot account for more than five. Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.

"Difficulties of this kind have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics. Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid.

"The matter of the present volume consists in large measure of results which have been obtained by the investigators mentioned above, although the point of view and the arrangement may be different. These results, given to the public one by one in the order of their discovery, have necessarily, in their original presentation, not been arranged in the most logical manner.

"In the first chapter we consider the general problem which has been mentioned, and find what may be called the fundamental equation of statistical mechanics. A particular case of this equation will give the condition of statistical equilibrium, i. e., the condition which the distribution of the systems in phase must satisfy in order that the distribution shall be permanent. In the general case, the fundamental equation admits an integration, which gives a principle which may be variously expressed, according to the point of view from which it is regarded, as the conservation of density-in-phase, or of extension-in-phase, or of probability of phase.

"In the second chapter, we apply this principle of conservation of probability of phase to the theory of errors in the calculated phases of a system, when the determination of the arbitrary constants of the integral equations are subject to error. In this application, we do not go beyond the usual approximations. In other words, we combine the principle of conservation of probability of phase, which is exact, with those approximate relations, which it is customary to assume in the 'theory of errors.'

"In the third chapter we apply the principle of conservation of extension-in-phase to the integration of the differential equations of motion. This gives Jacobi's 'last multiplier,' as has been shown by Boltzmann.

"In the fourth and following chapters we return to the consideration of statistical equilibrium, and confine our attention to conservative systems. We consider especially ensembles of systems in which the index (or logarithm) of probability of phase is a linear function of the energy. This distribution, on account of its unique importance in the theory of statistical equilibrium, I have ventured to call *canonical*, and the divisor of the energy, the *modulus* of distribution. The moduli of ensembles have properties analogous to temperature, in that equality of the moduli is a condition of equilibrium with respect to exchange of energy, when such exchange is made possible.

"We find a differential equation relating to average values in the ensemble which is identical in form with the fundamental differential equation of thermodynamics, the average index of probability of phase, with change of sign, corresponding to entropy, and the modulus to temperature.

"For the average square of the anomalies of the energy, we find an expression which vanishes in comparison with the square of the average energy, when the number of degrees of freedom is indefinitely increased. An ensemble of systems in which the number of degrees of freedom is of the same order of magnitude as the number of molecules in the bodies with which we experiment, if distributed canonically, would therefore appear to human observation as an ensemble of systems in which all have the same energy.

"We meet with other quantities, in the development of the subject, which, when the number of degrees of freedom is very great, coincide sensibly with the modulus, and with the average index of probability, taken negatively, in a canonical ensemble, and which, therefore, may also be regarded as corresponding to temperature and entropy. The correspondence is, however, imperfect when the number of degrees of freedom is not very great, and there is nothing to recommend these quantities except that in definition they may be regarded as more simple than those which have been mentioned. In Chapter XIV, this subject of thermodynamic analogies is discussed somewhat at length.

"Finally, in Chapter XV, we consider the modification of the preceding results which is necessary when we consider systems composed of a number of entirely similar particles, or, it may be, of a number of particles of several kinds, all of each kind being entirely similar to each other, and when one of the variations to be considered is that of the numbers of the particles of the various kinds which are contained in a system. This supposition would naturally have been introduced earlier, if our object had been simply the expression of the laws of nature. It seemed desirable, however, to separate sharply the purely thermodynamic laws from those special modifications which belong rather to the theory of the properties of matter."

J. E Trevor

Higher Mathematics for Students of Chemistry and Physics. *With special reference to practical work. By J. W. Mellor. New York: Longmans, Green, and Co., 1902. Price: bound, $4.00.* — In recent years a number of textbooks have been provided for the purpose of furnishing students of chemistry and physics with the mathematical equipment necessary for their work. Among the more conspicuous of these may be recalled the treatises of Fuhrmann, of Nernst and Schoenflies, the adaptation of the latter by Young and Linebarger, and the more recent volumes of Vogt (in French), and of Lorenz (in Dutch and in German). This series is now extended by the appearance of Dr. Mellor's admirable book. Dr. Mellor points out that it is almost impossible to follow the later developments of physical or general chemistry without a working knowledge of higher mathematics, and he states that he has found that the regular textbooks of mathematics rather perplex than aid the chemical student who seeks a direct road to this knowledge. During the last five years he has accumulated notes on the chief difficulties met in the use of mathematics in physical chemistry, and he has utilized these notes in the task of interesting students of chemistry in such applications. His success in this has led him to work these notes up into the form of a book.

The matter treated is much more extensive than in the earlier works. It is divided into three parts, under the successive captions: Elementary, Advanced, and Useful Results from Algebra and Trigonometry. The Elementary Part includes the differential calculus, analytical geometry (wherein trilinear coordinates are introduced), functions with singular properties, the integral calculus, and infinite series. The Advanced Part deals with hyperbolic functions, the solution of differential equations, and Fourier's theorem. The concluding part treats the solution of numerical equations, determinants, and probability and the theory of errors; and finishes with a collection of formulas for reference, and extensive tables of integrals, numerical values of functions, etc.

The arrangement of the matter is admirable; every topic considered is clearly and carefully explained and commented upon; and a great number of interesting and well distributed applications to problems in physical chemistry is incorporated into the text. The book should prove of great service to every earnest student of physical chemistry, and its extent will render it of permanent value as a book of reference. It might be used to marked advantage as the basis of a regular course of instruction in mathematics as applied to physical chemistry. The typography and diagrammatic illustrations are clear, and a good index has been provided. *J. E. Trevor*

Anwendung der Differential- und Integralrechnung auf Geometrie; *eine Revision der Principien. Vorlesung, gehalten während des Sommersemesters 1901. Von F. Klein. Ausgearbeitet von Conrad Müller. 17 × 22 cm; pp. 468. Leipzig: B. G. Teubner, 1902. Price: bound, 10 marks.* — This very interesting course of lectures is designed to aid in the establishment of a better understanding than now exists between the representatives of abstract and of applied mathematics. It is concerned with the reciprocal relations of what Klein terms precision mathematics and approximation mathematics. The former is abstract and exact, and is based upon the number concept; the latter is the study of the approximative relations with which solely the applications of mathematics are concerned. The relationship between the two is here discussed with reference to geometry alone; but this is sufficient for all purposes, since the analytical treatment of physical phenomena is customarily considered in connection with graphic representation.

The first part of the book, On Functions of Real Variables and their Representation in Rectangular Coordinates, considers successively the single independent variable x, approximative representations of functions, and functions of two variables; the second part, entitled Free Geometry, enters into precision-theoretical considerations regarding plane geometry, and concludes with a discussion of the transition to practical geometry. An appendix is devoted to the representation of ideal figures by drawings and models.

The point of departure is the idea that an empirical curve is always a "function-strip"

$$y = f(x) \pm \epsilon,$$

where ϵ is an undetermined quantity smaller than the uncertainty of the observations. This strip is given by experience; and when we assign direction, curvature, etc., to it, what we do is to replace it by the curve

$$y=f(x),$$

which is defined with unlimited accuracy by the aid of the number concept. What we further do is to assume f to be a "reasonable function," i. e., to be continuous, to possess a finite number of maxima and minima in a finite interval, to possess first and higher derivatives, etc. Things like the famous Weierstrass function are expressly excluded, although they may equally well represent the empirical data. Klein refers to the practical standpoint taken by John Perry in his well known Calculus for Engineers. Perry leaves the general curve concept alone, and begins with the statement that in practice only three fundamental functions,

$$y=x^n, \qquad y=e^x, \qquad y=\sin x,$$

come into consideration, and that all problems of ordinary practice can be treated with sufficient accuracy when one admits only functions that can be obtained from these three by a finite number of applications of the four fundamental operations, as for example in

$$y=\frac{a+bx+cx^2}{d+ex+fx^2}.$$

This view has often been characterized as unscientific; but Klein insists that such is not the case. He adds that the purpose of his course of lectures is to choose the standpoint in such wise that Perry's ideas shall find their place in a system of mathematics including simultaneously both the ideal and the empiric fields.

With great clearness Klein introduces a large number of special considerations regarding reasonable functions. These must be studied in the original. But certain philosophical digressions deserve mention. It is maintained that, like a drawn curve, the representation of a curve in the imagination lacks absolute sharpness: we can represent to ourselves only function-strips. Further, this distinction between absolute and limited accuracy has a metaphysical as well as a practical aspect. All measurements being inaccurate, one can at will either refer natural processes to continuous functions of continuous variables, or regard changes in space and time as discontinuous, like kinetoscope pictures. Both views go beyond experience — are metaphysical. For Klein it remains questionable whether in the representation of natural phenomena we *can* proceed beyond an application of approximation mathematics. Our expression of natural laws by simple formulas results from our tendency to represent the phenomena by the simplest means.

The volume is a facsimile reproduction of the manuscript of Klein's collaborator, Conrad Müller. Its pages are clear and readable, and are illustrated by many very interesting and well made drawings. The title page and table of contents have been set in type.

J. E. Trevor

Die Analyse der Empfindungen, und das Verhältniss des Physischen zum Psychischen. *E. Mach. Dritte, vermehrte, Auflage. 16 × 23 cm; pp. viii +*

286. *Jena: Gustav Fischer, 1902. Price: paper, 5; bound, 6 marks.*— Every one interested in the philosophy of science should know Mach's Analysis of the Sensations, which now appears in a revised and somewhat enlarged edition. The book was first published in 1885; the Open Court Company's English version appeared in 1897; and the second German edition, revised, in 1900. The present edition, which is dedicated to Karl Pearson, is the third. The extent to which Mach has succeeded in arousing interest in his views is apparent from the fact that the second edition was exhausted within a few months. Considerable matter has been added since the Chicago edition; and two of the chapters, the ninth, A Biologic-Teleological Consideration Concerning Space, and the fifteenth, on the Reception of the Views here Presented, are entirely new.

The chapters as they now stand are: Antimetaphysical Introductory Remarks; On Preconceived Opinions; My Relation to R. Avenarius; The Chief Points of View for the Investigation of the Senses; Physics and Biology — Causality and Teleology; The Space Sensations of the Eye; Further Study of Space Sensations; The Will; A Biologic-Teleological Consideration Concerning Space; Relations of the Sensations of Sight to one another and to other Psychic Elements; Sensation, Memory, and Association; The Sensation of Time; The Sensations of Tone; Physics — Influence of the foregoing Investigations on the Mode of its Conception; The Reception of the Views here presented.

As characteristic, we quote from the Antimetaphysical Introduction. "Bodies do not produce sensations, but complexes of elements (complexes of sensations) make up bodies. If, to the physicist, bodies appear the real, abiding existences, while the 'elements' are regarded merely as their evanescent, transitory show, the physicist forgets, in the assumption of such a view, that all bodies are but thought-symbols for complexes of elements (complexes of sensations). Here, too, the *elements* form the real, immediate, and ultimate foundation, which it is the task of physiologic-physical research to investigate. Through the recognition of this fact, many points of psychology and physics assume far more distinct and economical forms, and many spurious problems are disposed of.

"For us, therefore, the world does not consist of unintelligible entities, which by their interaction with another, equally unintelligible, entity, the ego, produce the sensations that alone are accessible. For us, colors, tones, spaces, time, etc., are the ultimate elements, whose given connection it is our task to investigate."

Mach adds, in another place, that although matter [a body] is to be regarded as a thought-symbol for a relatively stable complex of sense-elements, this by no means involves viewing the world as a mere sum of sensations; emphasis is to be laid upon the functional relationships of the elements. "All that we can know of the world is necessarily expressed in sensations, which in definitely assignable wise can be freed from the individual influences of the observer. All that we can wish to know is offered in the solution of a problem of mathematical form, in the determination of the functional dependence of the sense-elements upon one another. With this knowledge, the knowledge of 'actuality' is exhausted."

A more thoughtful, more illuminating, and more fundamentally important book might be hard to find. It is one of the notable books of the present time.

J. E. Trevor

An Elementary Book on Electricity and Magnetism and their Applications. *A text-book for manual training schools and high schools, and a manual for artisans, apprentices, and home readers. By Dugald C. Jackson and John Price Jackson. 13 × 18 cm; pp. xi + 482. New York: The Macmillan Company, 1902. Price: $1.40.* — "While this book is more especially intended for an elementary text-book, it is believed that it will be interesting to all readers who have a taste for science and that it will prove a useful manual for apprentices and artisans. Every effort has been exerted to make it clear, forceful, and of strict scientific accuracy, though it is written in reasonably colloquial language.

"The book is essentially the outcome of the authors' belief that elementary physical science may properly be — nay, should only be — taught in an atmosphere filled with the inspiration gathered from an interest in every-day occurrences. (Physics is a science of our daily life and experiences.) If this is a very ordinary belief, it surely is one much honored in the breach."

These paragraphs from the authors' breezy introduction give a foretaste of the book. It is a clear and well arranged account of the phenomena of electricity and magnetism, with extended comment on their industrial applications. That the reader is expected to *learn* something from it is indicated by the numerous problems and insistent questions scattered throughout the text. The book is profusely illustrated with all sorts of relevant things, from a load curve or a thermopile to an electric locomotive and the interior of the Niagara power station. It makes a lot of interesting information very easily accessible.

J. E. Trevor

Die Entwickelungsgeschichte der künstlichen organischen Farbstoffe. *By R Nietzki. (Sammlung Chemischer und chemisch-technischer Vorträge.) VII Band, 6 Heft. 16 × 24 cm; pp. 159–188. Stuttgart: Ferdinand Enke, 1902. Price: 1.20 marks.* — The general historical development of the organic dye-stuffs, as outlined by the author is something as follows: general study of benzene, phenol, aniline, benzoic acid and benzaldehyde; rosaniline colors in 1856; alizarine and also the naphthol colors in 1868; the phthaleine colors in 1874 and the rhodamines in 1880; malachite green and methylene blue in 1877, the azo-compounds 1876–1900; indigo. The author closes with the remark that an organic chemist who does not interest himself in the organic dye-stuffs because they are purely technical is quite as bad as the manufacturing chemist who thinks it a waste of time to keep track of the developments in pure science.

Wilder D. Bancroft

Annuaire pour l'An 1902. *Publié par le Bureau des Longitudes. 10 × 15 cm. Paris: Gauthier-Villars. Price: paper, 1.50 francs.* — The current *Annuaire* of the Bureau of Longitudes contains the usual admirable tables and appended scientific papers. The latter are four in number. Poincaré writes on wireless telegraphy, giving perhaps the best brief exposition of this subject yet published. The other articles are by Cornu, Guyou, and Janssen, on polyphase currents, the decimal division of the circle, and the foundation and work of the Mont Blanc observatory.

J. E. Trevor

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

One-Component Systems

Non-existence of the so-called sub-oxide of phosphorus, II. *C. H. Burgess and D. L. Chapman. Jour. Chem. Soc.* 79, *1235* (*1901*). — The authors conclude: —

1. That no sub-oxide of phosphorus having the formula P_4O has ever been prepared, because the percentage of phosphorus is variable, and because the latest substance, described as having the composition P_4O, contains other elements in addition to phosphorus and oxygen, hydrogen being present in considerable quantity.

2. That the substance described as a sub-oxide of phosphorus is impure red phosphorus, because the properties of both are the same and because direct analyses have shown that the impurities in the alleged sub-oxide (regarding it as red phosphorus) are such as might be expected from the methods of preparation. *W. D. B.*

Investigations on the viscosity of sulphur. *C. Malus. Ann. Chim. Phys.* (*7*) 24, *491* (*1901*). — The author has studied the way in which the rate of crystallization of sulphur varies with the previous thermal treatment. It appears that the unexpected viscosity of melted sulphur at about 180° is due to the absorption of sulphur dioxide, which is not set free when the sulphur solidifies. When sulphur has been carefully freed from sulphur dioxide, it does not become viscous at any temperature.

Owing to the death of the author, a number of questions have necessarily been left unanswered; but the investigation, as it stands, is a model of careful, well-planned and convincing work, while the final results are of great value and show how much we have yet to learn in regard to the chemical elements. *W. D. B.*

On the periodic system and the properties of inorganic compounds, II., III. *J. Locke. Am. Chem. Jour.* 26, *166*, *332* (*1901*). — The author believes that in order to criticize an element in a given degree of oxidation, the first step would be not to ascertain how stable or instable its compounds are, but how nearly they approach in their physical properties, solubility, etc., the corresponding salts of other elements of the same valence. He has therefore studied the solubility of a large number of alums. When these solubilities are plotted against atomic weights, the chromium alums appear to be absolutely abnormal. From this the author draws the conclusion that the solubilities are not a function of the atomic weight of the elements and the further conclusion that "the properties of the compounds are not a function of the atomic weight of the element." On plotting the melting-points of these alums against the atomic weights, it is found that the chromium alums again behave abnormally. Consequently, the author concludes that the values of the melting-points do not depend upon the atomic weights. It is worth noting that the melting-points of the caesium and rubidium alum of aluminum, vanadium, iron and cobalt, are represented by nearly parallel straight lines, the discrepancies occurring solely with the chromium alums.

In the third paper, the author points out that "the lines joining the solubility points of the successive univalent metals with two active trivalent metals have approximately a common point of intersection", and that this is true for other temperatures besides that of 25°. He also shows that "the ratio between increments of solubility and the corresponding alums of two trivalent metals for any two alkali metals is constant." *W. D. B.*

Notes on gas thermometry. *P. Chappuis. Phil. Mag.* [*6*] 3, *243* (*1902*). — The author points out that the direct measurements of Holborn and Day (6, 277) on the expansion of Berlin porcelain modify slightly his results. The new formula for the expansion of porcelain brings the boiling-point of sulphur which he previous placed at 445.2° C to 444.7°, a value agreeing closely with the result of Callendar and Griffiths. *H. T. B.*

The thermal expansion of porcelain. *A. E. Tutton. Phil. Mag.* [*6*] 3, *631* (*1902*). — The author redetermines the coefficient of expansion of Bayeux porcelain by his interference-dilatometer method. The advantages claimed over the Fizeau apparatus are: (1) The employment of a micrometric method of measuring the position and width of the interference bands; (2) the use of autocollimation; (3) the employment of the *c* hydrogen light instead of sodium, as being more truly monochromatic; and (4) an arrangement of the thermal chamber which readily permits an extension of the range to an upper limit of 120° C. The conclusions agree with the recent work of Holborn and Day on the expansion of Berlin porcelain and support the suggestion made earlier by Callendar that an anomaly exists in the expansion of porcelain between 0° and 100°. The anomaly consists of a much larger increment for this interval than for the higher interval between 200° and 600°. *H. T. B.*

Two-Component Systems

A method for the determination of the freezing-point of a solution at constant temperatures. *K. Prytz. Drude's Ann.* 7, *882* (*1902*). — The solution contained in a reservoir is made to flow through a spiral contained in a vessel of ice so as to cool it nearly to the freezing-point. It then passes to a second vessel and through a spiral wound around a sensitive Beckmann thermometer. It emerges from this second spiral which ends at the bottom of the vessel and rises through a quantity of ice. The thermometer which is protected from actual contact with the ice by the spiral assumes the freezing-point in from 25 to 30 minutes. Special precautions are taken to guard against errors due to heat from the surroundings and the true freezing-point is defined as that at which neither melting nor freezing occurs. The freezing-points of potassium chloride and cane-sugar are determined. The method appears to yield very consistent results and should prove useful where large quantities of solution are available. *H. T. B.*

Vapor pressure of carbon dioxide and of ethane at temperatures below 0° C. *J. P. Kuenen and W. G. Robson. Phil. Mag.* [6] 3, *149* (*1902*).—On account of not having the data on the vapor pressure of CO_2 and ethane at temperatures below 0° C available for an investigation, the authors are obliged to make special determinations. They use platinum resistance thermometers for obtaining the low temperatures and describe a number of difficulties they had with them. The triple point temperature was found to be −56.2° at a pressure of 5.10 atms. *H. T. B.*

On the thermal properties of carbon dioxide and ethane. *J. P. Kuenen and W. G. Robson. Phil. Mag.* [6] 3, *622* (*1902*).—The measurements obtained by the authors on the vapor pressures of CO_2 and ethane given in their previous paper (preceding review) enable them to continue the work on the thermal properties of these substances over wider ranges of temperature. The present paper contains their determinations of the latent heats of evaporation. They find that the latent heat of sublimation of CO_2 increases as the temperature rises. *H. T. B.*

On the physical peculiarities of solutions of gases in liquids, I. *J. A. Wanklyn. Phil. Mag.* [6] 3, *346* (*1902*).—Tests were made to see whether a gas in contact with a quiet liquid surface will dissolve beyond the surface layer. The simple process of diffusion would be too slow to allow of any large quantity of gas being dissolved unless the process was aided by the dissolved gas forming a heavier compound with the liquid and being continually removed by gravity from the surface. The experiments described appear to indicate this. CO_2 and water are used. *H. T. B.*

On the physical peculiarities of the solution of gases in liquids, II. *J. A. Wanklyn. Phil. Mag.* [6] 3, *498* (*1902*).—Experiments for ammonia in water are tried in a similar way to the author's previous experiments on CO_2 in water (preceding review). It is found that his previous conclusions in regard to the solution of a gas in a quiet liquid surface are confirmed. *H. T. B.*

On the determination of the density of dilute solutions with a special form of dilatometer. *F. Moller. Drude's Ann.* 7, *256* (*1902*).—The author designs a special form of dilatometer to determine small changes in volume when a solution is diluted or when a small quantity of salt is dissolved. Various corrections and possible sources of error are carefully discussed. The results are expressed to the seventh decimal place, although it is probable that this order of accuracy has very little meaning. *H. T. B.*

The union of hydrogen and chlorine, IV. *J. W. Mellor and W. P. Anderson. Jour. Chem. Soc.* 81, *414* (*1902*).—

1. Hydrogen chloride is produced during the phenomenon called the Draper effect.
2. The Draper effect is only produced by the luminous rays of light.
3. The Draper effect occurs with mixtures of approximately equal volumes of hydrogen and chlorine, but not with chlorine alone or mixed with steam, air, nitrogen, carbon dioxide, carbon monoxide, or methane.

4. The amount of combination depends not only upon the number, but also upon the intensity of the sparks. When the effect reaches a certain magnitude, depending on the "sensibility" of the gas, explosion occurs. An explosion appears to be a large Draper effect.

Thus the amount of the index fluid which occurs when the insulation vessel, Bunsen and Roscoe actinometer, is exposed to a flash of light appears to be brought about by some disturbance in the gas attending chemical combination.

W. D. B.

On the direct union of chlorine with carbon. *R. Lorenz. Zeit. Electrochemie*, 8, *203* (*1902*). — The author objects to the statement of Bolton (6, 282) that a direct union of chlorine with carbon had not been hitherto observed and points out that he himself had obtained such a union in 1888 being passing chlorine over steel or over a mixture of carbon and boric anhydride.

W. D. B.

Multi-Component Systems

The influence of salts or other substances on the vapor pressure of aqueous ammonia solutions. *E. P. Perman. Jour. Chem. Soc.* 81, *480* (*1902*). — When urea is added to an ammoniacal solution, there is no change in vapor pressure when compared with a solution containing the same ratio of ammonia to water, but there is an increase in vapor pressure when compared with a solution containing the same mass of ammonia in unit volume of the solution. When mannitol is added to an ammoniacal solution, the reverse is the case. When ammonium chloride is added, the observed vapor pressures lie between those for solutions calculated in these two ways. *W. D. B.*

The existence of poly-iodides in nitrobenzene solution, I. *H. M. Dawson and R. Gawler. Jour. Chem. Soc.* 81, *524* (*1902*). — It was found that when iodine was added to nitrobenzene and an aqueous solution of potassium iodide, some iodide passes into the nitrobenzene layer. This peculiarity has been studied and the authors come out with the usual constant ratio after making the usual assumptions and therefore conclude that complex iodides exist in nitrobenzene. *W. D. B.*

A method of determining the ratio of distribution of a base between two acids. *H. M. Dawson and F. E. Grant. Jour. Chem. Soc.* 81, *512* (*1902*). — The authors determine the distribution of acetic acid between water and chloroform, ignoring the increase of miscibility due to the presence of acetic acid. They then add salts to the aqueous layer, and determine the change in concentration of the acid in the chloroform. They are very much pleased with the results of this method, although it is obvious that it cannot be right.

W. D. B.

The molecular complexity of acetic acid in chloroform solutions. *H. M. Dawson. Jour. Chem. Soc.* 81, *521* (*1902*). — Having found that the distribution ratio for acetic acid in water and chloroform is not a constant, the author proceeds to calculate the degree of polymerization of acetic acid in chloroform. By making the necessary assumptions, he comes out with a phenomenally satisfactory constant for the distribution. This is a beautiful illustration of the utter unreliability of the conclusions based on a hypothetical constant. In this particular case we know that acetic acid makes chloroform and water more miscible and that therefore the preliminary assumptions of the author are unjustifiable. In spite of starting from inaccurate premises, he comes out with a result which is an apparent confirmation of an avowedly incorrect theory. If figures can be and are juggled in this way so as to lead to false results in a case where they can be detected, what reason we have to suppose that false results have not been so reached in many other similar cases? *W. D. B.*

The reduction of copper by solutions of ferrous salts. *H. C. Biddle. Am. Chem. Jour.* 26, *377* (*1901*). — The author starts with the assumption that: — "the precipitation of metallic copper by solutions of ferrous salts is a reversible action, whose direction in any case is determined by the relative concentration of the ferrous, ferric, and copper (cuprous and cupric) ions." This assumption is confirmed by the experiments. The best results were obtained by mixing a solution of ferrous and cupric chlorides with a saturated solution of potassium bicarbonate and an excess of carbon dioxide. *W. D. B.*

The action of ammonia on metals at high temperatures. *G. T. Beilby and G. G. Henderson. Jour. Chem. Soc.* 79, *1245* (*1901*). — The authors find that all metals are attacked by ammonia at a temperature of about 800°, becoming spongy and disintegrated. Special experiments showed that this was due to the formation of nitrides. *W. D. B.*

The decomposition of sodium nitrate by sulphuric acid, III. *C. W. Volney. Jour. Am. Chem. Soc.* 24, *222* (*1902*). — In order to confirm the author's previous conclusions that the action of sulphuric acid on sodium nitrate takes place in two distinct stages, and that these two stages of the process are marked by distinctly different temperatures, he has made a special study of the distillation of nitric acid. The conclusions drawn from the experimental work are expressed by him as follows:

1. At room temperature, or below 20°, neither concentrated sulphuric acid nor the polysulphate acts on sodium or nitrate. The reaction is, at least, so very slow that during the contact of three or four days only traces of free nitric acid can be observed.

2. At a high temperature, the nitrate is decomposed by sulphuric acid and the reaction is finished at a temperature below 100°, free nitric acid and $NaH_3(SO_4)_2$ resulting.

3. The dry sulphate acts on the nitrate at *temperatures over 165°*, products of the reaction being active free nitric acid and sodium bisulphate.

4. The nitric acid resulting during this stage at the corresponding high temperature is always decomposed; its vapors in distilling over showing a temperature of 120°-123°, and this acid was formerly considered the second hydrate of nitric acid $(HNO_3)_2H_2O$. *W. D. B.*

On an article by Mr. Schükarew. *J. J. van Laar. Zeit. phys. Chem.* 39, *342* (*1901*). — The author points out some of the mistakes in a recent article by Schükarew (6, 152). *W. D. B.*

On the question of hydrogen in the atmosphere. *Lord Rayleigh. Phil.*

Mag. [*6*] 3, *416* (*1902*).—The present paper contains further experiments which confirm the author's previous conclusions that the amount of hydrogen in the air is much less than that found by M. Gautier. This amount in country air does not exceed one part in 30000. *H. T. B.*

On the clearing of turbid solutions. *G. Quincke. Drude's Ann.* 7, *57* (*1902*).—The first part of the paper is a historical sketch taking up the work of previous observers since 1851. Turbidity or turbid solutions consist of water in which are suspended small particles of mastic, alumina, kaolin, shellac, gamboge, albumen, soap, oleic acid, black ink, or silver. Small quantities of acids or salt solutions produce a clearing. The flocculent masses formed consist of small bubbles of liquid, drops or solidified liquid and generally hold a small quantity of air. Substances may be arranged in the order of their clearing power. Illustrations are given of the flocks as they are produced in the different media, which convey a good idea of what actually takes place. The action of light is also studied. *H. T. B.*

Velocities

The chemical dynamics of bromine substitution. *L. Bruner. Zeit. phys. Chem.* 41, *513* (*1902*).—

(*i*) *Bromine and benzene:* In dilute solutions of bromine in benzene the reaction is too slow for measurement, except in the presence of a catalyzer. Iodine accelerates the bromination, which proceeds until the residual bromine is just sufficient to form IBr with the iodine added. The author has carried out a number of rate measurements with dilute solutions of bromine and iodine in benzene, and gives his results in tables and in curves.

The mathematical discussion is however not worthy of the experiments. In calculating the "constants" in the various tables, the weight, not the concentration, of the bromine is introduced; in deducing the order of the reaction from the times of equal relative disappearance of the bromine, Table VII., solutions are compared in which the concentration of the iodine as well as that of the bromine varies [recalculation of Table V. shows that the author's constant K_2 is proportional to the square of the iodine concentration]; and finally no account is taken of the effect on the rate caused by the products of the reaction, though a comparison of Tables I.C and III.B shows an acceleration, due, no doubt, to the hydrobromic acid formed. The author's conclusions as to the mechanism of the reaction are therefore subject to revision.

(*ii*) *Comparison of various bromine carriers:* Experiments with concentrated solutions of bromine in benzene, alone and in the presence of I_2, $FeBr_3$. $FeCl_3$, $AlBr_3$. TlCl, Tl metal, $CrCl_3$, Cr metal, PCl_3, PBr_3, $SbCl_3$ and $SbBr_3$; also with solutions of bromine in brombenzene, alone, and in presence of iodine. Iodine accelerates the bromination of benzene much more than that of brombenzene; with $AlBr_3$ the reverse appears to be the case. The rate of bromination of nitrobenzene is totally unaffected by $AlBr_3$, which is the most vigorous accelerator of the reactions between benzene and bromine; and the author directs special attention to his isolation of the compound $AlBr_3.2C_6H_6$, which shows that the formation of molecular compounds is not in itself sufficient to cause acceleration.

(*iii*) *The relative velocities of instantaneous reactions:* Bromine water was poured into a mixture of phenol and potassium iodide dissolved in water, and from the amounts of iodine and of bromphenol formed, the relation between the velocities of the two reactions was calculated. The formulas employed were deduced under the assumption that both reactions are bimolecular. Similar experiments were carried out with bromine water, aniline, and potassium iodide, and with bromine water, aniline, and phenol. The ratio in the last case is exactly *equal to the quotient of these in the other two.*

Experiments with bromine, phenol, and iodide at 4°, 25°, 40°, 60°, and 80° show that the velocity of bromination increases with rise in temperature more rapidly than that of the liberation of iodine, and the same is true of the reaction of bromine with aniline, and with ortho- and para-bromphenol. Addition of water likewise increases the proportion of bromphenol formed. *W. L. M.*

The velocity and the nature of the reaction between bromine and oxalic acid. *T. W. Richards and W. N. Stull. Zeit. phys. Chem.* 41, *544* (*1902*).—After satisfying themselves that oxalic acid is oxidized by bromine in aqueous solution, the authors have subjected this reaction to a quantitative investigation. They find that the rate is roughly proportional to the first power of the bromine concentration, though only slightly dependent on the concentration of the oxalic acid, a maximum velocity being observed for about 3.5 percent oxalic acid. Sodium hydroxide and sodium acetate increase the rate, while strong acids diminish it. The retarding influence of hydrobromic acid is about ten times as great as that of hydrochloric acid, and increases more rapidly than the *first power of its concentration. Most of the experiments were carried out at* 23°, a few at 50°.

The authors attempt to explain these effects by assuming that it is the C_2O_4'' ions which take part in the reaction, and that Br_2 unites with HBr to form HBr_3. The latter fact, it is true, is amply supported by experiment, but it is not clear to the reviewer that on diluting oxalic acid the concentration of the C_2O_4'' ion should pass through a maximum, as stated by the authors.

F. B. K.

The reaction between potassium persulphate, hydrogen iodide, and phosphorous acid. *W. Federlin. Zeit. phys. Chem.* 41, *565* (*1902*).—The rate of oxidation of phosphorous acid by persulphate is extremely slow; but as the oxidation of phosphorous acid by iodine and the oxidation of hydrogen iodide by persulphate occur with measurable velocity, it follows that addition of an iodide to a mixture of phosphorous acid and persulphate will accelerate the oxidation of the former.

The author has studied the kinetics of the three reactions at 25°.

(*i*) *Persulphate and iodide:* Price's experiments (3, 425) were extended to higher concentrations; the reaction is bimolecular, is retarded by iodine, and (in contradiction to Price) is accelerated by acids.

(*ii*) *Phosphorous acid and iodine:* "The reaction proceeds according to the law of the second order"; publication of the measurements is reserved for a future paper.

(*iii*) *Persulphate, phosphorous acid, and iodide:* The presence of phosphorous acid accelerates the action of the persulphate on the iodide, otherwise the observed total velocity is fairly in accord with that calculated from those of reactions (*i*) and (*ii*). *W. L. M.*

The rate of decomposition of bromsuccinic acid in aqueous solution, I. *W. Müller. Zeit. phys. Chem.* 41, *483* (*1902*). — The products of this reaction are hydrobromic acid and a mixture of malic and fumaric acids, the relative amounts of which depend on the concentration of the bromsuccinic acid. The author finds that between 0.01 and 0.25 normal acid the reaction is practically non-reversible, and that the velocity conforms to the expression for a monomolecular process, subject to a retardation proportional to the concentration of the hydrogen ions. He explains the effect of the latter by assuming that only the anion of the bromsuccinic acid takes part in the reaction.

The measurements were carried out at 50°; experiments at other temperatures are reserved for future communication. *F. B. K.*

The decomposition of ammonium nitrite. *A. A. Blanchard. Zeit. phys. Chem.* 41, *681* (*1902*). — The formation of nitrogen and water from ammonium nitrite in acid solution is accompanied by the evolution of nitric oxide, due to the decomposition of the nitrous acid; these two reactions are independent of one another.

The rate of formation of nitrogen is proportional to the concentrations of the ions $NH_4^{\cdot}$ and NO_2', and is accelerated by $H^{\cdot}$ and by HNO_2. The author assumes two independent reactions leading to the evolution of nitrogen, whose rates are proportional to the concentrations of $H^{\cdot}$, NO_2', $NH_4^{\cdot}$, and of HNO_2, NO_2', $NH_4^{\cdot}$, respectively.

Iron salts, colloidal platinum solution, and a number of other substances are found to have no effect on the rate, except in cases where the concentration of the $H^{\cdot}$ was affected by the precipitation of a basic salt.

The experiments lead to a determination of the dissociation constant of nitrous acid, which is in agreement with the results of conductivity measurements. The method of calculation employed by Arndt, who has carried out experiments on the same reaction (5, 154), is criticized. *W. L. M.*

The simultaneous equilibria of the relations between thermodynamics and kinetics of homogeneous systems. *R. Wegscheider. Zeit. phys. Chem.* 39, *257* (*1901*). — The author criticizes Euler's hypothesis in regard to reaction velocities (5, 325) on the ground that Euler's equation as written is really an identity which therefore cannot lead to a reaction velocity equation.

The author next considers a system in which three separate reversible reactions can take place between four constituents, and shows that the equilibrium equations and reaction velocity equations do not agree if we postulate that all three sets of reaction velocity constants are independent. The author dwells upon this point at some length and appears to consider it most remarkable that these reaction velocity constants should not be independent. To most people this will not seem in the least surprising. *W. D. B.*

On the theory of chemical reaction velocities. *H. Euler. Zeit. phys. Chem.* 40, *498* (*1902*). — A reply to Wegscheider (preceding review).
W. D. B.

On the theory of chemical reaction velocities. *R. Wegscheider. Zeit. phys. Chem.* 41, *62* (*1902*). — This is a reply to the paper of Euler (preceding review). *W. D. B.*

On the inhibition of chemical reactions by foreign substances, I. *S. W. Young. Jour. Am. Chem. Soc.* 24, *297* (*1902*). — The author finds that the rate of oxidation of sodium bisulphite is reduced by the presence of practically any organic substance and also by potassium cyanide, hydroxylamine, and ammonium salts. The inhibitive effect is in no case instantaneous, but develops somewhat slowly with the oxidation of the solution, in many cases initial acceleration being found. The limit of the dilution at which substances still show inhibitive effect differ for different substances, being in some cases still noticeable at a dilution of 1/2,600,000 molar. *W. D. B.*

Lecture experiments illustrating various types of catalytic action. *A. A. Noyes and G. V. Sammet. Jour. Am. Chem. Soc.* 24, *498*; *Zeit. phys. Chem.* 41, *11* (*1902*). — The reactions described are: the change of sulphur dioxide to sulphur trioxide in presence of nitric oxide; the formation of ether from alcohol in presence of sulphuric acid; the formation of brombenzene from benzene and bromine in presence of ferric bromide; the action of acetyl chloride on benzene in presence of aluminum chloride; the oxidation of methyl alcohol in presence of platinum foil; the oxidation of ammonia in presence of platinum; the formation of silver trioxide in presence of platinum; the decomposition of hydrogen peroxide in presence of platinum black and bone black; the action of hydrochloric acid on tin in presence of platinum; the action of zinc on ethylene bromide in presence of copper; the action of hydrogen sulphide on sulphur dioxide in presence of water; the action of iodine and hydrogen sulphide in presence of water; the action of zinc on iodine in presence of water; the action of chlorine on sodium in presence of water; the hydrolysis of starch in presence of sulphuric acid; the coagulation of colloidal arsenious sulphide in presence of barium chloride and sodium chloride; hydrolysis of starch by ptyalin; the hydrolysis of salicine by emulsin; the decomposition of hydrogen peroxide by blood; the precipitation of colloidal casein by rennet; decomposition of hydrogen peroxide by colloidal platinum. *W. D. B.*

The cause of the catalytic action of hydrogen ions on hydrolytic reactions. *P. Rohland. Zeit. phys. Chem.* 41, *739* (*1902*). — "The acceleration may perhaps be due to the formation of water *in statu nascendi*, not dissociated, but very reactive, from the OH ions of the water and the H of the acid, or from the H of the water and the OH of a base." The author considers this view to be identical with that of Noyes and Sammet (preceding review) who suggest that the H· ions may form a hydrate with water and thus act as "water carriers." *W. L. M.*

Enzyme action. *A. J. Brown. Jour. Chem. Soc.* 81, *373* (*1902*). — From the experiments of O'Sullivan and Tompson on the action of invertase on cane-sugar, it has been believed that the velocity of enzyme action indicates the operation of a simple mass action. The author has repeated these experiments, using an extract of invertase prepared from dried yeast by digestion with water. It was found that the velocity constant increases with the time, while a very satisfactory constant could be obtained by using Henri's empirical formula (6, 153). Further experiments showed that the presence of invert sugar decreases the activity of invertase.

In sugar solutions varying in concentration from 5–40 percent, approximately constant quantities of cane-sugar are inverted in unit time. The author believes that this is due to a preliminary formation of a compound between sugar and the enzyme. He further concludes that if the sugar solution were sufficiently dilute, the reaction would be monomolecular. He finds this to be the case with solutions containing less than one gram of sugar per 100 cc.

W. D. B.

The velocity of hydrolysis of starch by diastase, with some remarks on enzyme action. *H. T. Brown and T. A. Glendinning. Jour. Chem. Soc.* 81, *389* (*1902*). — The authors find that it is possible to divide their time curves into two parts: an upper one which is linear, and a lower one which is approximately logarithmic, the change from one expression to another being gradual and not abrupt. The authors believe that this is to be accounted for in the same way as the action of enzymes on cane-sugar (preceding review), namely by the assumption of the formation of a compound between the starch and the enzyme. *W. D. B.*

The change of trimethylene into propylene. *S. Tanatar. Zeit. phys. Chem.* 41, *735* (*1902*). — At 600° trimethylene is converted into propylene, while at room temperature no appreciable change could be detected after an interval of several years. The author holds that the difference is one of rate merely, and shows that in presence of platinum black the reaction takes place with measurable velocity at 100°, and that at room temperature 20 percent of the trimethylene is isomerized in three months. Light does not appreciably accelerate the reaction. *W. L. M.*

The slow oxidation of methane at low temperatures. *W. A. Bone and R. E. Wheeler. Jour. Chem. Soc.* 81, *535* (*1902*). — The authors find that methane and oxygen react in glass vessels at temperatures just above 300°. In no case is there liberation of free hydrogen or of free carbon at any stage, even though methane was always present in excess. The first stage in the "partial" combustion of methane at low temperatures is a simultaneous oxidation of carbon and hydrogen to carbon monoxide and steam. *W. D. B.*

Electromotive Forces

On the variation with temperature of the thermoelectromotive force and of the electrical resistance of nickel, iron and copper between the temperatures of − 200° and + 1050° C. *E. P. Harrison. Phil. Mag.* [6] 3, *177* (*1902*). — The present work was undertaken to trace over as wide a range of temperature as possible the thermoelectromotive force and the resistance of nickel and iron. The occurrence of peculiarities in the two curves at the same temperatures was looked for, and the result of the work shows a coincidence for the nickel-copper couple and the resistance change, but no thermoelectric peculiarity for the iron-copper couple at the temperature where a change occurs in the iron resistance curve. *H. T. B.*

Investigation into the magnetic properties of nickel amalgam. *H. Wunsche. Drude's Ann.* 7, *116* (*1902*). — Iron and cobalt amalgam have both been shown to be strongly magnetic, but from the result of the author's work nickel amalgam is only weakly so. He shows that the amalgam is a chemical compound which is best produced by electrolysis and is acted on rapidly by the air. A low temperature of —78° C does not appear to alter the magnetic properties. It is interesting to compare this result with previous results for a cobalt-copper alloy. Cobalt appears to differ from nickel-copper alloys in its magnetic properties. Thus a cobalt-copper alloy is magnetic while a nickel-copper alloy is not so. *H. T. B.*

On a thermodynamic theory of the potential difference between metals and completely dissociated solutions of their salts, and on an electrical method to determine the molecular forces. *A. Einstein. Drude's Ann.* 8, *798* (*1902*). — The author develops his theory by making certain hypothetical extensions of the second law of thermodynamics in its application to physical mixtures. The paper is almost entirely mathematical in nature. *H. T. B.*

On the inversion temperature of the Kelvin effect in hydrogen. *K. Olszewski. Drude's Ann.* 7, *818*; *Phil. Mag.* [*6*] 3, *535* (*1902*). — From an empirical formula deduced by Rose-Innes (6, 148) the Kelvin effect was shown to change sign at —79.3° C by Witkowski. In the present paper the author describes some experiments made to determine this point. The temperatures of liquid air, liquid ethylene and solid CO_2 and ether were taken for the measurements and determined by means of an electrical thermometer. The inversion point was found by the reversal of the deflection of a galvanometer. This took place between the limits of temperature of —78° and —85°. At —80.5° the gas apparently did not change on expanding. This point is in good agreement with the one calculated by Witkowski. The critical temperature of hydrogen is calculated to be —232.6° C, very near the author's experimental value. It is pointed out that a temperature of —100° should be sufficient to liquefy hydrogen by its own expansion, although the temperature of liquid air will greatly accelerate the liquefaction. *H. T. B.*

Electrolytic cell with liquid solvent. *A. Hagenbach. Drude's Ann.* 8, *568* (*1902*). — Above the critical temperature SO_2 exhibits dissociating power as was shown in a previous paper by the author. In the present paper measurements of the resistance of a solution of rubidium iodide in SO_2 were taken about the critical temperature in order to verify the previous results. Determinations of the E. M. F. of the cell, which was constructed with two platinum electrodes of which one was copper-plated, showed that above the critical temperature with SO_2 in the gaseous state the cell maintained a current. The E. M. F. of the cell remained the same over the critical temperature. *H. T. B.*

On the validity of Ohm's law. *J. Stark. Drude's Ann.* 7, *932* (*1902*). — In a previous paper certain relations between the impressed E. M. F. and ionic velocity in gases and Ohm's law are deduced. In the present paper the author points out an inaccuracy in his first formula. *H. T. B.*

Unipolar electric currents in electrolytes. *C. Christiansen. Drude's Ann.*

8, *787* (*1902*). — The author communicates some preliminary results on polarization effects in which a variation from Ohm's law is observed. An electrolytic cell of $HgNO_3$ in a normal solution of HNO_3 is set up with mercury electrodes. It is found, on applying a weak E. M. F., that the current rapidly sinks to a small constant value. This current which he calls the unipolar current is found to be the same irrespective of the E. M. F. between the limits 0 and 1.7 volts. Calling the hydrogen polarization E. M. F. p, that of the cell V, then $V - p = ru$, where u is the unipolar current. The result of the work shows that the unipolar current is independent of the E. M. F., of the resistance, of the concentration of the HNO_3, while it is proportional to the amount of surface of the cathode and the concentration of the $HgNO_3$. *H. T. B.*

On the electricity of the human body. *A. Heydweiller. Drude's Ann.* 8, *227* (*1902*). — The author experiments on the electricity developed in the human body by muscular action. The hand or knee is placed near a plate connected with a charged electrometer with one pair of quadrants earthed. It is found that a positive or negative charge accompanies a movement, and that the charge is in accord with du Bois-Reymond's theory in regard to the electromotive force set up by muscular action. The experiments of du Bois-Reymond were repeated and the size of the current determined. This amounted to between 2 and 5×10^{-8} coulomb for a contraction or extension of the arm or leg muscle.
H. T. B.

The production of a magnetic field by a flight of charged particles. *R. W. Wood. Phil. Mag.* [*6*] 3, *659* (*1902*). — To produce higher velocities and thus to measure the electrical effect due to electrical convection more accurately, the author drives a cloud of charged particles of solid carbon dioxide through a long glass tube placed under a magnetic needle. Definite deflections were obtained which were reversed on reversing the direction of flow. Further results are promised. *H. T. B.*

Electrolysis and Electrolytic Dissociation

Determinations of the conductivity and dielectric constant of solvents and solutions and the dependence on temperature up to the critical point. *P. Eversheim. Drude's Ann.* 8, *539* (*1902*). — The author studies SO_2 and the solutions of KCl, KBr and RbI in SO_2. It is found that an amount of the latter salt of only 1.2 parts in 1000 lowers the resistance of the pure SO_2 by 30 times. For pure SO_2 the conductivity is found to decrease with rising temperature, the same being the case for the dielectric constant. In both cases a characteristic change occurs in the curves at the critical temperature. Determinations of the dielectric constant of solutions in SO_2 could not be accurately made on account of the great increase in conductivity. Experiments were also carried out with ether and monochlorethane. *H. T. B.*

On electrolytic phenomena at the boundary of two liquid solvents. *W. Nernst and E. H. Riesenfeld. Drude's Ann.* 8, *600* (*1902*). — The authors work out a mathematical theory for the diffusion of two solvents at their boundary, resulting from the movement of the ions. Water and phenol are the solvents employed. As an example of the method the transport number of KI in phenol is determined, which leads to a simple method of determining the transport number for one solvent when that of the other is known. *H. T. B.*

The temperature variations of the specific molecular conductivity and of the fluidity of sodium chloride solutions. *T. R. Lyle and R. Hosking. Phil. Mag.* [*6*] 3, *487* (*1902*). — The experiments described in the present paper were carried out to obtain a set of accurate values and at the same time to test the identity of the temperature variation of the electrical conductivity and fluidity of any given electrolytic solution. Sodium chloride solutions were taken, but although considerable similarity was found between the two sets of curves, the temperature coefficients of the fluidity and specific molecular conductivity were not found to be the same. *H. T. B.*

The ionic and thermal coefficients of nitric acid. *V. H. Veley and J. J. Manley. Phil. Mag.* [*6*] 3, *118* (*1902*). — The authors calculate the amount of the ionization μ/μ_∞ for different concentrations and show that for strong solutions between 98 and 100 percent an irregularity occurs. From the fact that other irregularities occur in the physical properties for these concentrations, the authors are led to the conclusion that the result is due to the incipient formation of a compound $2HNO_3.N_2O_5$. It is shown from density determinations at 4°, 14.2°, and 24.2° that, as regards the mere coefficient of expansion, nitric acid does not behave as though it were a simple mixture of the acid and water. *H. T. B.*

Conductivity and atomic heat of metals. *F. Streintz. Drude's Ann.* 8, *847* (*1902*). — In the light of the recent work by Dewar and Fleming, and Jaeger and Diesselhorst, the author deduces a number of conclusions based on considerations of the temperature coefficent of the metals in relation to the kinetic condition. In regard to the theory of Clausius that the temperature coefficient is linear and proportional to the absolute temperature, it is pointed out that palladium is the only metal with a coefficient slightly under 1/273 while all the others are above this value. A summary of values of the coefficient shows that this increases with the atomic weight for the different groups in the periodic table. For each group it is found that the metals with high atomic weights show a decrease in temperature coefficient with temperature, while the reverse is the case for the lower. Lorenz's law appears to hold only for metals with an atomic weight intermediate in the periodic table. The temperature coefficient for metals with low melting-points is greater than for metals with high melting-points. A table is given of the atomic heats of a number of metals for the temperatures between $-79°$ and $-180°$ and $+18°$ and $-79°$. It is seen that only metals with no temperature change in atomic heat follow accurately Dulong and Petit's law. It appears that the smaller the displacement of the atom in relation to the distance from a neighboring atom the greater is the value of the temperature coefficient of the electrical resistance. *H. T. B.*

On the temperature variation of the electrical resistance of pure metals and allied matters. *W. Williams. Phil. Mag.* [*6*] 3, *575* (*1902*). — The author has collected a number of interesting data showing the relation between many of the physical properties of the metals and their periodic arrangement. *H. T. B.*

Variation of the electrical conductivity of a metal powder by induction. *H. Muraoka and T. Tamaru. Drude's Ann. 7, 554 (1902).* — The metal powder is placed between two plates connected to a battery. By short-circuiting the two plates for an instant a coherer action results in the powder, and its resistance immediately falls. Sundorph's experiments on iron and nickel powder are extended in the present paper to a non-magnetic substance, i. e., brass powder, and it is found that the same results are obtained as for the magnetic substances. An extended study of the effect of induced currents on the conductivity of the powder is made, but no new ideas are advanced as to the cause of this particular coherer action. It is described as a very irregular phenomenon. *H. T. B.*

On the change of the electrical resistance of metals when placed in a magnetic field. *J. Patterson. Phil. Mag. [6] 3, 643 (1902).* — The author investigates certain non-magnetic metals to detect and measure any change in electrical resistance when placed in a magnetic field. Copper, German silver, mercury, cadmium, zinc, gold, platinum tin, silver and carbon were all found to change in resistance slightly, the amount varying from 0.03 to 0.007 percent for the different materials. The results are interpreted in the light of the recent theory of J. J. Thompson in regard to the existence of corpuscles in the metal, the effect of the magnetic field being to alter the path of the moving electron and thus alter the resistance. The pressure exerted by the corpuscles in the case of platinum is found to be 700 atms. The number of corpuscles per unit volume is found to be 1.4×10^{22}, and the number produced in the steady state 1.8×10^{23}. The mean free path comes to 5.9×10^{-7}. *H. T. B.*

Comparison of the methods for the determination of the ratio of charge to mass for cathode rays. *W. Seitz. Drude's Ann. 8, 233 (1902).* — The author compares experimentally in the same tube the three methods for determining the value of $\frac{mv^2}{2e}$; the methods due to J. J. Thomson, Kaufmann-Simon, and Wien-Lenard. The measurements show good agreement for potentials over 8500 volts. The value of $\frac{e}{m}$ deduced from the magnetic deflection of the rays comes 1.87×10^{-7}, which is in good agreement with the measurements of Simon. *H. T. B.*

Research on the electric discharge of rarefied gases. *W. Wien. Drude's Ann. 8, 244 (1902).* — This is a third of a series of papers by the author on the canal rays. Experiments in very high vacuum show that canal rays are not present although cathode rays still remain. The fluorescence resulting from the canal rays appears to be very variable for the same gas under similar conditions. The electrostatic deflection of the rays in conjunction with the discharge potential is studied in order to see whether the variable results obtained for the measurements of the ratio of charge to mass is accounted for by a splitting off of a number of negative ions from the positive ions while on their way through the gas, and a recombination again further on. No very definite conclusions are arrived at.

It is found that the canal rays may be accelerated or retarded in their passage by a negative or positive charge in a similar way to cathode rays.

A careful study of the magnetic and electrostatic deflection of the rays gives for the ratio of $\frac{e}{m}$ very different values, but in round numbers the author places it at 10^4, the same as for the electrolytic ion.

The author studies the discharge from a glowing electrode in high vacuum.
H. T. B.

The decomposition of hydrogen peroxide by light and the electrical discharging action of this decomposition. *R. F. D'Arcy. Phil. Mag.* [*6*] 3, *42* (*1902*). — The author tries to discover a chemical action in the decomposition of H_2O_2 by light to account for the existence of charged particles, or nuclei of condensation, which have been shown to be present in air. The water and oxygen formed during the composition are oppositely charged, the latter negatively. Further experiments were tried to show that a surface of H_2O_2, undergoing decomposition, is capable of discharging electrification as compared with a water surface. Definite results were obtained with the surface negatively charged.
H. T. B.

The rôle of water vapor in gaseous conduction. *P. Lewis. Phil. Mag.* [*6*] 3, *512* (*1902*). — The author criticizes the conclusions made by J. Trowbridge (6, 284) that water vapor is essential to gaseous conduction. A number of experiments are cited which indicate the contrary. *H. T. B.*

Condensation of vapors of organic liquids in the presence of dust-free air. *F. G. Donnan. Phil. Mag.* [*6*] 3, *305* (*1902*). — The author repeats the experiments of C. T. R. Wilson of the condensation of water vapor on nuclei in dust-free air (4, 334). In addition to water vapor of high ionizing power he uses several other organic liquids of smaller power. The result of the work indicates that with these liquids ionization takes place with greater difficulty, with a marked exception in the case of CS_2. The expansion ratio required to produce rain drops varied from 1.29 in the case of water to 1.89 in the case of carbon tetrachloride. *H. T. B.*

Dielectricity and Optics

Determination of the dielectric constant of crystals in a homogeneous electric field. *R. Fellinger. Drude's Ann.* *7*, *333* (*1902*). — The author extends the work of Graetz and Fomm and gives at some length the theory of the method proposed by Graetz. This method consists in suspending the crystal in an electric field set up between condenser plates connected to an oscillator. It is found that the crystals exert a turning moment, the direction of greatest expansion following the direction of the lines of force. Formulas for uni- and biaxial crystals are studied; as amorphous bodies, sulphur and paraffin are used.
H. T. B.

Measurement of the dielectric constant by means of electric waves. *P. Drude. Drude's Ann.* 8, *336* (*1902*). — After many years of experience with his now famous method, the author points out in the present paper several improvements in the apparatus and arrangements. *H. T. B.*

Dielectric constant of paraffin. *W. G. Hormell. Phil. Mag.* [*6*] 3, *52* (*1902*). — Reviewed (6, 445) from Am. Jour. Sci. (4) 12, 433 (1901).

On the absorption of electric oscillations in liquids. *K. Wildermuth. Drude's Ann.* 8, *212* (*1902*). — The author uses short waves from 63 to 22 cm in length with the general arrangement adopted by Zeeman and Eichenwald. The absorption coefficients for water, sodium chloride and copper sulphate solutions and alcohol are determined. A number of experiments are given showing the effect of dilution and of waves of different periods. *H. T. B.*

Note on the band spectrum of nitrogen. *G. Berndt. Drude's Ann.* 7, *946* (*1902*). — The work described in the present paper is a reply to a paper by Hemsalech in which a doubt was expressed as to the possibility of distinguishing the nitrogen spectrum produced by a spark gap and self-induction, since the author's measurements of the wave-length differ from his. The work shows that the band spectrum of nitrogen produced either from the negative pole of a Geissler tube or from the oscillating spark is the same. This intensity of the bands is entirely unlike, since the wide difference in the pressure of the air in the two arrangements make the conditions dissimilar. *H. T. B.*

The refractive index of solutions in carbon bisulphide. *C. Forch. Drude's Ann.* 8, *675* (*1902*). — Solutions of sulphur, naphthalene, ethyl ether, chloroform, paraffin oil and castor oil in CS_2 are taken for the measurements. A differential method is used by which the solution and pure solvent are compared at the same time. This obviates a large error due to the effect of temperature on the refractive index, but not the small difference between the solution and pure solvent. Curves are drawn showing the relation to the concentration. *H. T. B.*

Refractive index of salt solutions. *C. Bender. Drude's Ann.* 8, *109* (*1902*). — In this, a fourth of a series of papers, a sodium chloride solution is studied for the three hydrogen lines, and the sodium line. The method is the same as was used previously by the author (4, 14). Limits of temperature are taken between 10° and 70° C. The molecular refraction of the salt is calculated, and, from data on the atomic refraction of chlorine, the refractive index of metallic sodium for the sodium lime is found to be 1.23601 at 15° C.

H. T. B.

The influence of solvents on the rotatory powers of ethereal dimethoxy succinates and tartrates. *T. Purdie and W. Barbour. Jour. Chem. Soc.* 79, *971* (*1901*). — The authors have studied the behavior of methyl and ethyl dimethoxy succinates in water, methyl alcohol, and benzene; of propyl dimethoxy succinate in methyl alcohol and benzene; of methyl tartrate in water; of ethyl tartrate in benzene; and of propyl tartrate in water and benzene. The three dimethoxy succinates indicated a considerable rise of rotation when dissolved in benzene, the rotations increasing with dilution. Water and methyl alcohol decrease the rotations of the three esters, but the rotation in water is scarcely affected by change of concentration.

The authors confirm Freundler's results, that benzene lowers the rotation of methyl tartrate and raises that of the propyl compound. They find, further, that the rotation of ethyl tartrate is scarcely affected by benzene.

From molecular weight determinations, the authors conclude that there is no definite relation between molecular association and the change of rotation produced by the solvent. *W. D. B.*

The absorption spectra of cyanogen compounds. *W. N. Hartley, J. J. Dobbie, and A. Lauder. Jour. Chem. Soc.* **79**, *848 (1901)*. — The derivatives of cyanic acid which were examined are highly diactinic and show only general absorption. All the cyanuric compounds which have been examined show only general absorption and give no indication of the presence of absorption compounds. While this was to be expected in the case of isocyanuric compounds the absence of selective absorption is not in harmony with the constitution of cyanuric acid, and the author therefore considers it doubtful whether the constitution of cyanuric acid is rightly understood. *W. D. B.*

The absorption spectra of metallic nitrates. *W. N. Hartley. Jour. Chem. Soc.* **81**, *556 (1902)*. — The author has determined the absorption spectra of nitric acid and the nitrates of potassium, sodium, silver, and thallium. All show an absorption band in the ultra-violet, and the absorption curves for nitric acid and potassium nitrate are identical in every particular, while that of silver and thallium nitrates are somewhat different, not only from that of nitric acid but from each other. *W. D. B.*

The colloidal form of piperidine with especial reference to its refractive and dispersive powers. *H. G. Madan. Jour. Chem. Soc.* **79**, *922 (1901)*. — At a temperature only slightly, if at all, above its melting-point, crystalloid piperidine is converted, for the most part at any rate, into the colloidal condition. This latter condition is not permanent, but reverts spontaneously after a lapse of a moderate time and quickly when exposed to a temperature of 100°, to the crystalloid form. It was found that colloid piperidine possesses a higher refractivity than most, perhaps all other, resins or resin-like substances. The dispersive power of piperidine is still more remarkable, being probably as great as, if not greater than, that of any other known substance. *W. D. B.*

Photographs of the ultra-red spectrum of the alkaline earths. *H. Lehmann. Drude's Ann.* **8**, *643 (1902)*. — By the photographic method described in another paper the author studies the extreme red and ultra-red end of the spectrum. He finds 13 new calcium lines, 12 new strontium lines, and 85 new barium lines. *H. T. B.*

Metallic reflection for ultra-violet and ultra-red rays. *E. Hagan and H. Rubens. Drude's Ann.* **8**, *1 (1902)*. — The authors extend their work on metallic reflection from the visible spectrum to the two extremes. Surfaces from various silvering solutions are compared in reflecting power over the entire spectrum. *H. T. B.*

On the influence of temperature on the dispersion of ultra-violet rays in fluorspar, rock salt, quartz and calcspar. *F. J. Micheli. Drude's Ann.* **7**, *772 (1902)*. — The effect of temperature on the refractive index for visible rays through the various substances studied has already been made. The present experiments were carried out with ultra-violet rays in a similar way. The method employed is a photographic one due to Martens. The result of a great many observations shows that the change in refractive index is dependent on the wave length and the relation is found to hold for all substances investigated. A relation between change in refractive index and wave lengths was originally deduced by Martens. *H. T. P.*

The radio-activity of thorium compounds, I. *E. Rutherford and F. Soddy. Jour. Chem. Soc.* 81, *321; Zeit. phys. Chem.* 42, *81* (*1902*). — The paper contains a preliminary account of an investigation into the property possessed by the compounds of thorium of giving a radio-active emanation, also into the nature of the emanation itself. The authors come to the conclusion that there is a radio-active constituent which is a substance distinct from thorium and therefore capable of separation therefrom. They believe, however, that the active constituent has only been obtained in relatively minute quantity and therefore does not answer to any definite analytical reactions. *W. D. B.*

Absorption of Roentgen rays by aqueous solutions. *R. K. McClung and D. McIntosh. Phil. Mag.* [*6*] 3, *68* (*1902*). — The authors investigate the subject by an electrical method instead of a photographic one. Two parallel plates are charged and arranged so that the rays pass between them. The rate of leak on an electrometer determines the current between the plates, which current is proportional to the rays. The absorption of the rays in a cell containing the solution was compared with the absorption in a standard cell containing water. It is found that with but one or two exceptions an increase of atomic weight is accompanied by an increase in the absorption. Colloidal solutions of finely divided metals were tried but found to differ only slightly from water. Further experiments are promised. *H. T. B.*

On the chemical action of cathode rays. *G. C. Schmidt. Drude's Ann.* 7, *321* (*1902*). — The author shows that the negative electron has the power of reducing compounds with lightly held acid radicals. According to his views which he has endeavored to prove experimentally in the present paper the negative electron is capable of satisfying a positive metal valency charge. In the case of Ag_2Cl_2 it is reduced to Ag_2Cl, one Ag valency being satisfied by an electron. The chlorine set free is supposed to pass either to a positive electron or to attach itself to a neutral silver chloride molecule. A number of chemical tests have been made on salts subjected to cathode rays. The superficial layer only is affected by the rays, and hence very delicate tests had to be made. The salts tested were the chlorides of iron, mercury and silver, the haloid salts of the alkali metals and barium, strontium and mercuric sulphate. *H. T. B.*

On spectrum lamps, IV. *E. Beckmann. Zeit. phys. Chem.* 40, *465* (*1902*). —The author purifies the gases from a spectrum lamp by washing them and passing them through antiseptic cotton. He also describes a method for spraying the flame of a spectrum lamp by blowing air under pressure through the solution. Where one has plenty of material and gas under high pressure, the author recommends spraying by means of porous substances, although electrolytic spraying may be more advantageous where one has the current. If one has only a small amount of substance and an air current under low pressure, the method of spraying described in this paper is the most suitable.

W. D. B.

THE COMPENSATION METHOD OF DETERMINING THE RATE OF OXIDATION OF HYDROGEN IODIDE

BY JAMES M. BELL

Among the earliest researches on the rate of progress of a chemical reaction is that of Messrs. Harcourt and Esson, "On the Oxidation of Hydrogen Iodide by Hydrogen Peroxide."[1] This paper is important, not only because it is one of the very first successful attempts to formulate the relation between the rate of a chemical reaction and the concentration of the reacting substances, but because the method of measurement introduced by the authors has since been employed in many similar researches. The method in question, which, borrowing a word from Schükarew, I propose to call the "Compensation Method," is described in the section following.

Owing to discrepancies between the results of certain rate measurements carried out by means of the Compensation Method, and others in which more direct methods were employed, I was led to enquire into the conditions under which the former method is applicable. The present paper contains the results of this examination, a résumé of the various cases in which the Compensation Method has been employed heretofore, and three series of experiments to test its applicability when hydrogen peroxide, chloric acid, and chromic acid, respectively, are the oxidizing agents.

The Compensation Method

Harcourt and Esson's method of working "consisted in the addition to a solution containing hydrogen dioxide, hydrogen iodide, and a little starch, of successive portions of sodium hyposulphite. Not only is the iodine which may have been formed in the solution instantly converted into iodide by this reagent, but the iodine which is continually being liberated is at once

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[1] Jour. Chem. Soc. 20, 476 (1867).

combined, so that the liquid, though it contain starch, and though iodine is being formed in it, rests quite colourless, as long as any hyposulphite remains. But when the last trace of hyposulphite has been changed into tetrathionate by the action of the iodine, the portion of iodine next formed remains free, and the liquid suddenly becomes blue. The addition of another small portion of hyposulphite again removes the colour; till all the hyposulphite has been destroyed, it remains colourless, and then the blue color reappears."[1]

The ratio between the amount of each "small portion" of thiosulphate of soda and the time which elapsed before the blue colour appeared was regarded as measuring the rate of oxidation of the hydriodic acid by hydrogen peroxide; and the thiosulphate was supposed to act only as a "compensator", by means of which the passage of the reaction through a given point — adjusted by altering the amount of thiosulphate — could be detected.

Conditions of applicability

It is obvious that the intervals between the reappearances of the blue color in Harcourt and Esson's experiments only measured the time necessary for the destruction of the thiosulphate in the reacting mixture; the authors' interpretation is based on the assumptions, (1) that the thiosulphate reacts only with the iodine liberated by the action of the oxidizing agent on the hydriodic acid, and (2) that its presence in no way influences the course of that action. The truth of these assumptions can be proved only by a special investigation, *which must be repeated with each oxidizing agent.* This point, which was apparently quite clear to Harcourt and Esson, seems to have been overlooked by the chemists who subsequently employed the Compensation Method.

In a solution containing acid, an oxidizing agent, and an iodide, sodium thiosulphate may enter into reaction in one or more of the following ways: —

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[1] Loc. cit. page 476.

(I) It may be converted into tetrathionate by the iodine liberated from the iodide by the oxidizing agent.

(II) It may be converted into sulphite, etc., by the action of the acid.

(III) It may be oxidized by the direct action of the oxidizing agent.

Moreover,

(IV) The rate of oxidation of the iodide may be affected by the presence of the thiosulphate or of its oxidation products; and similarly,

(V) The rates at which reactions (II) and (III) take place may be modified (catalyzed) by the presence of the oxidizing agent, the iodide, or the products of the reactions themselves.

The rate of the reaction between thiosulphate and acid has been studied by v. Oettingen.[1] It depends upon the concentration of the acid and may be reduced by diminishing the latter. With acids of the concentrations employed by the authors enumerated in the succeeding paragraph, the rate of this reaction is very slow. This is doubly fortunate, for not only would the sulphite react with the iodine, but as will be shown in the experimental part, it may cause a remarkable acceleration of the reaction between the thiosulphate and the oxidizing agent. The rate of oxidation of the thiosulphate, on the other hand, has been very little studied (a few measurements are contained in the present paper), and nothing has been published as to the magnitude or sign of the catalytic actions enumerated under (IV) and (V).

The Compensation Method is applicable only to cases where the amounts of thiosulphate entering into reactions (II) and (III) are negligible in comparison with that entering into reaction (I), and where the catalytic influences enumerated in (IV) are non-existent. If these conditions are fulfilled, the results of the experiments will be unaffected by the concentration of the thiosulphate in the reacting mixture, i. e., by the amount

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[1] Zeit. phys. Chem. 33, 1 (1900).

of each "small portion" added: whereas it is obvious that if the thiosulphate enters into direct reaction with any of the constituents of the solution (the acid, or the oxidizing agent, for instance), or if it accelerates the reaction whose rate is supposed to be measured, an increase in the amount of each small portion will increase the apparent rate.

The last consideration suggests an easy test of the *inapplicability* of the compensation method to any particular case; but it is only by comparison of the results of the method in question with those obtained in the absence of thiosulphate, that evidence of its applicability can be obtained. In making the comparison, allowance must obviously be made for the possible effect of iodine accumulated in the solution.

Cases in which the Compensation Method has been employed

Harcourt and Esson. — "*On the Oxidation of Hydrogen Iodide by Hydrogen Peroxide.*"[1] The authors assured themselves that "in a dilute solution containing iodide, hyposulphite is neither decomposed into sulphur and sulphite by the action of hydrogen sulphate or chloride, nor is it oxidized, or in any way acted on directly by hydrogen dioxide."

Pendlebury and Seward. — "*An Investigation on the Interaction of Hydrogen Chloride and Chlorate in the Presence of Potassium Iodide.*"[2] Apparently no endeavor was made to check the results by the use of different amounts of thiosulphate, or by comparison with those furnished by other methods of analysis. The whole matter is dismissed with the words, "the intervals date from one appearance of the color to the next appearance, and as the rate is not affected by the presence of a small amount of iodine or a small diminution in the amount of iodide, it is clear that the fact of the addition and admixture of the thiosulphate, not following immediately on the appearance of the blue color, does not disturb the uniformity of the rate change."

Judson and Walker. — "*Reduction of Bromic Acid; and*

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[1] Jour. Chem. Soc. 20, 476 (1867).

[2] Proc. Roy. Soc. 45, 396 (1889).

the Law of Mass Action."[1] In their first series of experiments, the authors added thiosulphate to the reacting mixture, and noted the time at which the yellow color of free bromine appeared in the solution. Finding, however, that the time which elapsed before the yellow color appeared was much shorter when the thiosulphate was added *in toto* at the beginning of the experiment, than when the same quantity was added in small portions as the reaction proceeded, they abandoned the Compensation Method and adopted the "more tedious and less accurate method" of titration at measured intervals of time.

Schükarew.—"*Über polymolekulare Umwandlungen.*"[2] The author employed the Compensation Method to measure the rates of oxidation of various iodides by ferric salts, chromic acid, and nitrous acid. The results are not checked by the use of an independent method, but the author assured himself that under the conditions of his experiments "the time was proportional to the quantity of thiosulphate employed", that is, that changing the concentration of the thiosulphate did not affect the rate.

With regard to direct action between the oxidizing agent and thiosulphate, Schükarew says—"One might think that the thiosulphate would react directly with the ferric chloride. This is possible;[3] it is still more probable that the thiosulphate acts merely as an accelerator. * * * In the first case we have a simple method of calculation by means of which this secondary reaction is eliminated, while for the purposes of this paper the acceleration is of no moment."

The "simple method of calculation" is based upon the assumption that the two reactions (viz., oxidation of the thiosulphate, and oxidation of the iodide) take place independently in the solution, so that the rate of the former is not affected by the concentration of the iodide. In the next section I have de-

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[1] Jour. Chem. Soc. 73, 410 (1898).

[2] Zeit. phys. Chem. 38, 353 (1901).

[3] Sodium thiosulphate is oxidized by ferric chloride so rapidly that it has been proposed (by Scheerer, in 1859) to employ a solution of sodium thiosulphate for the volumetric determination of iron. F. Mohr's Titrirmethode, 7th ed., p. 355.

veloped the mathematical consequences of this assumption; as will be shown in the experimental part, they are not in accordance with the observations.

To recapitulate: the Compensation Method has been employed in measuring the rate of oxidation of hydriodic acid by hydrogen peroxide, chloric acid, ferric salts, chromic acid, and nitrous acid. In no case have the results been checked by the use of an independent method. Except in the case of hydrogen peroxide, the direct action of the oxidizing agent on the thiosulphate has not been studied; and the attempt which one author has made to eliminate the effect of this direct action by calculation, is based on erroneous assumptions.

Development of the theory of the Compensation Method, allowing for direct oxidation

The equations of this section are obtained by assuming that in a solution containing a thiosulphate, an iodide, and an oxidizing agent, the thiosulphate is simultaneously acted on by the oxidizing agent, and by the iodine set free by the oxidation of the iodide. The action of the acid on the thiosulphate is neglected, and no account is taken of catalytic actions. In other words, of the five possibilities enumerated on page 63, the first and second are admitted, and the other three rejected. It is further assumed, that the oxidizing agent is present in a large quantity as compared with the thiosulphate; so that the concentration of the former remains sensibly constant during the reaction; the concentration of the iodide remains, of course, absolutely so. Lastly, in accordance with experiments described later, the rate of oxidation of the thiosulphate is set proportional to the first power of its own concentration. It would be an easy matter to introduce the second or a higher power if occasion should arise.

As the reaction between iodine and thiosulphate is instantaneous, and as (under the assumptions enumerated above) the rate of oxidation of the iodide is constant, the rate of loss of thiosulphate due to reaction (I) p. 63 must be constant also, or

$$\partial x/\partial t = k_0,$$

where the value of k_0 depends on the temperature, and on the concentration of the iodide and of the oxidizing agent.

Integrating, with the condition that $x = 0$ when $t = 0$ and setting $x = A$ (the initial concentration of the thiosulphate) we obtain

$$T_0 = k_0, A \qquad (1)$$

the time in which the thiosulphate would be totally destroyed by the operation of reaction (I) alone.

The rate of loss of thiosulphate due to direct oxidation is represented by the equation

$$x/t = k_1(A - x),$$

(A being the initial concentration of the thiosulphate, as before) and the total loss due to both causes combined, by

$$dx/dt = k_0 + k_1(A - x).$$

Integrating, under the same condition as before, and introducing the abbreviation $k = k_0/k_1$, this becomes

$$k_1 t = log.\ nat. \{ (A + k)/(A + k - x) \}, \qquad (2)$$

whence the time T, at which the solution turns blue, viz: when $x = A$.

$$T = (1/k_1)\ log.\ nat.\ (1 + A/k). \qquad (3)$$

The following table gives the values of T_0 in seconds calculated from equations (1) and (3) for three values of T and five of k_1; under E are entered the percentage errors introduced by confounding T with T_0, that is, by neglecting the effect of the direct action of the oxidizing agent on the thiosulphate. Other circumstances equal, the error decreases with decrease in T; in practice, however, it is not possible to obtain accurate results when T is less than 20 seconds.

TABLE I.

	T = 20		T = 40		T = 60	
k_1	T_0	E Percent	T_0	E Percent	T_0	E Percent
0.001	20.2	1	40.7	2	61.8	3
0.005	21.04	5	44.3	11	70.0	17
0.010	22.15	11	49.2	23	82.2	37
0.020	24.59	23	61.3	53	116.0	93
0.050	34.36	72	127.8	219	382.0	536

For values of A/k not greater than 1.3, equation (2) may be replaced by the following with an error of less than three percent :

$$k_1 T = A/k - (1/2)(A/k)^2,$$

whence

$$T/A = 1/k_0 - (1/2)Ak_1/k_0^2. \tag{4}$$

That is to say, if T be determined for different values of A, and the results be plotted with A and T/A as coordinates, the points should lie on a straight line, which is parallel to the A axis if $k_1 = 0$, and whose inclination increases with increase in the ratio k_1/k_0.

I. HYDROGEN PEROXIDE AS OXIDIZING AGENT

The following experiment were carried out (under the same conditions of concentration and temperature as those of Messrs. Harcourt and Esson) to ascertain whether the ratio T/A is independent of A, whether sodium thiosulphate is oxidized by hydrogen peroxide, and whether the results of the Compensation Method are identical with those obtained in the absence of thiosulphate.

Solutions

As comparative results, only, were wanted, the compositions of the solutions were not determined with any great accuracy. The stock solutions were: —

Acid: sulphuric, approximately 8 times normal.

Iodide : 30 grammes potassium iodide per liter.

Thiosulphate : 4 grammes cryst. sodium thiosulphate per liter.

Iodine: one volume of the thiosulphate solution was equivalent to approximately five volumes of the iodine solution.

Peroxide : 0.75 gramme sodium peroxide per liter. A direct experiment showed that the amount of iodine liberated by the action of hydriodic acid in excess on 10 cc of the peroxide solution, was equivalent to 7.35 cc of the thiosulphate solution.

Results of the measurements — Series A

In each of the following five experiments, one liter of an "oxidizing mixture" was used, containing water, 100 cc acid, 10 cc peroxide, and 5 cc of a dilute starch solution. The experiments were carried out at 17° C in a glass cylinder standing in a battery jar full of water by means of which its temperature could be regulated; the contents of the cylinder were stirred from time to time by bubbles of carbon dioxide.

Experiment 1. — 20 cc iodide were added to the oxidizing mixture, and then, immediately, 3.85 cc thiosulphate, in one portion; the blue color appeared 932 seconds after adding the iodide.

Experiment 2. — 20 cc iodide were added to the oxidizing mixture, and then 3.85 cc thiosulphate in seven portions, each new portion being added as the blue color reappeared. (See Table II.) The final appearance of the blue color occurred 935 seconds after the addition of the iodide. Thus the rate is not measurably affected by changes in the concentration of the thiosulphate.

Experiment 3. — 20 cc iodide were added to the oxidizing mixture; the amount of iodine liberated in 935 seconds was equivalent to 3.55 cc thiosulphate (instead of 3.85).

Experiment 4. — 3.85 cc thiosulphate were added to the oxidizing mixture and immediately titrated with iodine; 20.35 cc iodine were required.

Experiment 5. — 3.85 cc thiosulphate were added to the oxidizing mixture and an interval of 935 seconds allowed to elapse before titration; 22.33 cc iodine were required. The excess of 10 percent over the reading of Experiment 4 may be referred to formation of sulphite from the thiosulphate under the influence of the acid. The retardation in Experiment 3 is thus most probably due to free iodine.

From these experiments no conclusions can be drawn adverse to the use of the Compensation Method when hydrogen peroxide is the oxidizing agent.

TABLE II.

Under *t* is entered the time (in seconds from adding the iodide) at which the blue color appeared in the solution; under *x* the total number of cc thiosulphate that had been added up to that moment; under *A-x* the residual peroxide; and under k_1 the value of *log*. *A*/(*A-x*).

t	*x*	A - *x*	k_1
0	0.0	7.35 **	—
*	0.55	6.8	—
185	1.10	6.25	0.00042
*	1.65	5.7	—
440	2.15	5.2	0.00034
590	4.68	4.67	0.00033
770	3.35	4.0	0.00034
938	3.85	3.5	0.00034

* The watch not read. ** See page 68.

II. CHLORIC ACID AS OXIDIZING AGENT

The experiments of Series B were carried out under the same conditions of temperature and concentration as those of Pendlebury and Seward (see p. 64). The "oxidizing mixture" contained 37.5 grammes of potassium chlorate, 10 cc of a dilute starch solution, and 250 cc of hydrochloric acid (approximately 5 times normal) in a total volume of 900 cc. The temperature was 20° C.

Results of the measurements — Series B

To 900 cc of the oxidizing mixture were added 100 cc one percent potassium iodide solution, and a few drops of a solution of sodium thiosulphate (60 grammes cryst. salt per liter). When the blue color reappeared, the time was noted and 0.5 cc thiosulphate run in from a burette; 215 seconds later the solution again turned blue and another 0.5 cc thiosulphate was added, and so on, as in Table III. The apparatus described on p. 69 was used; a smell of chlorine was perceptible at the mouth of the jar.

TABLE III.

A	T	T/A	A	T	T/A
0.5	215	430	0.5	237	475
0.5	215	430	1.5	638	425
0.55	235	428	0.52	233	452
0.52	235	452	0.52	235	452
0.48	222	462	5.0	1567	313
3.0	1120	373	0.5	233	466
0.65	295	347	0.58	267	460
0.5	223	446			

A glance at Table III shows that, with the exception of the first three portions, the time required to destroy 0.5 cc thiosulphate is constant within the rather large errors of experiment. No correction has therefore been applied to the figures of Table IV for the effect on the rate produced by the addition of sodium salts, or by increase of the volume of the reacting mixture during the experiment.

TABLE IV.

A	T	T/A *obs.*	T/A *calc.*
0	—	—	476
0.5	230	460	(460)
1.5	638	425	427
3.0	1120	373	378
5.0	1567	313	(313)

It is apparent that quotient T/A is not independent of A. In Table IV in which the experimental numbers are compared with those calculated from the formula $T/A = 476 - 32.7\ A$ shows that, in accordance with equation (4) p. 68, the relation between T/A and A is linear. The amount of thiosulphate in each "small portion" of Pendlebury and Seward's measurements was equal to about 0.5 cc of my solution; hence, by extrapolation, their rates are about 3 percent too high.

As calculated by equation (4) from the data of Table IV, the value of the rate constant for the direct oxidation of sodium thiosulphate by chloric acid is $k_1 = 0.0003$. An attempt was made to determine its value directly. To 900 cc of the oxidizing mixture were added 100 cc of water, and then 5 cc thiosulphate. After an interval of one minute, a titration with iodine showed that over 97 percent of the thiosulphate had been oxidized; and after four minutes over 99 percent. The first value corresponds to $k_1 = 3.50$ (instead of 0.0003). Thus the oxidation of thiosulphate by chloric acid is greatly retarded by addition of potassium iodide, and the assumption on which the calculations p. 66 and those of Schükarew are based, viz., that the two reactions, oxidation of iodide, and oxidation of thiosulphate, proceed independently of one another in the same solution, is radically false. It is, in fact, this very retardation that renders the Compensation Method in its original form even approximately applicable with chloric acid as oxidizing agent.

Series C

When discussing Table IV it was pointed out that the rates obtained by the use of the Compensation Method were probably 3 percent too high. This conclusion, based on an extrapolation of a formula which in the light of the experiments of Series B, can only be regarded as purely empirical, is much too favorable to the method in question. Table V, for which I am indebted to Mr. W. C. Bray, shows how widely the results obtained by the Compensation Method may vary from the truth.

TABLE V.

p	$500\,k_1$ (*Til'n.*)	$500\,k_1$ (*Comp.*)
$^1/_{16}$	0.172	0.085
$^1/_4$	0.125	0.10
1	0.12	0.112
3	0.25	0.285
5	0.375	0.43

The experiments were carried out at 30.5° with solutions containing 1/12 × 122.5 gm $KClO_3$, 1.023 × 36.4 gm HCl, and 0.0965 p gm KI per liter. The numbers entered under

"k_1 *(tit'n)*" were obtained as described below, those under "k_1 *(comp)*" by the Compensation Method.

Not only do the two series differ (in one case by 100 percent), but while the titration method shows the existence of a minimum rate when $p = 1$, according to the Compensation Method the rate increases continuously with increase in the concentration of the potassium iodide.

Series D — Rate of oxidation of the thiosulphate

A number of experiments were carried out with the object of determining how the rate of oxidation of sodium thiosulphate by chloric acid is affected by changing the concentrations of the reagents involved. As these measurements have only an indirect bearing on the subject of this paper, the results are communicated in as brief a form as possible.

Stock solutions were made up as follows: —

Chlorate: 40.5 grammes $KClO_3$ in one liter.

Acid: Hydrochloric acid, approximately 4 times normal.

Thiosulphate: 24.8 grammes $Na_2S_2O_3.5H_2O$ in one liter.

Iodine: 1.28 grammes iodine dissolved (with potassium iodide) in one liter.

In carrying out the measurements, the thiosulphate, chlorate and water, previously brought to the proper temperature, were mixed in a beaker supported in the thermostat; the acid was then added from a pipette, and the time noted. At intervals a portion was removed in a pipette, run into a measured quantity of the "restrainer", and titrated with solutions of iodine and thiosulphate. The "restrainer" consisted of a solution of sodium acetate to which enough sodium bicarbonate had been added to almost neutralize the acid in the portion taken for analysis. Blank experiments showed that the reaction was brought to a standstill without the titer being affected.

Influence of the Thiosulphate. — In the experiments of Table VI where the concentration of the thiosulphate is much less than those of the other reagents, the "constant of the first order", $k_1 = (1/t) \log \{ A/(A-x) \}$, is fairly constant when the thiosulphate is present in concentration of F/400 or less,[1] while above F/200 the "constant of the second order" is less changeable.

Chlorate; Acid. — On doubling the concentration of the chlorate in experiment *c* of Table VI, the rate is multiplied by less than 1.5; and on doubling the concentration of the acid, the rate is slightly more than doubled.

TABLE VI.

Chlorate, 5 cc; Acid, 5 cc; Total volume, 20 cc; Temperature, 20° C.

Ex.	Thio.	t	$A-x$	k_1	k_2
a	3 cc	0	28.85	—	—
		4	11.83	0.0967	0.0129
b	2 cc	0	19.20	—	—
		4	10.24	0.0883	0.0114
c	1 cc	0	9.65	—	—
		2	7.93	0.0426	0.0117
		4	6.75	0.0421	0.0110
		6	5.46	0.0413	0.0113
d	0.5 cc	0	4.85	—	—
		2	4.20	0.0312	0.0159
		4	3.70	0.0294	0.0160
		6	3.25	0.0289	0.0169
e	0.25 cc	0	2.45	—	—
		2	2.10	0.0335	0.0390
		4	1.80	0.0335	0.0368
		6	1.68	0.0273	0.0312

TABLE VII.

Temperature, 30° C; Total volume, 20 cc; Time, 2 minutes.

Chlorate	Thio.	Sulphite	Acid	Iodine
5 cc	1 cc	0 cc	5 cc	0.84 cc
5	1	1	5	0.06
5	0	1	5	0.00

Sulphite. — A solution of sodium sulphite was prepared containing 31.5 grammes of the crystallized salt per liter. In Table VII the first four columns give the initial composition of the solu-

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[1] One four-hundredth of a Formula weight in grammes per liter.

tions, and under "Iodine" is entered the volume of an iodine solution required to produce a blue color with starch at the expiration of two minutes after adding the thiosulphate. (1 cc. Iodine = 1 cc stock thio. = 0.5 cc sulphite.) The acceleration produced by the sulphite is very marked.

III. CHROMIC ACID AS OXIDIZING AGENT

Series E

The experiments of Series E are analogous to those of Series B; and the results are presented in Table VIII, the arrangement being the same as that of Table III.

The oxidizing mixture was made up as follows: — Potassium iodide, 2 grams; potassium bichromate, 0.5 gram; sulphuric acid, 25 cc of 0.975 normal acid; water to make one liter; temperature, 20° C. The solution of sodium thiosulphate in the burette was approximately decinormal.

TABLE VIII.

Ex.	A	T	T/A	Ex.	A	T	T/A
a	0.5	135	270	*h*	0.48	172	358
b	0.48	145	302	*j*	0.47[1]	198	421
c	0.52	148	285	*k*	0.83[1]	372	447
d	1.0	280	280	*l*	0.52	192	369
e	0.5	146	292	*m*	1.60[1]	698	436
f	0.5	154	308	*n*	0.52	201	386
g	3.0	630	210	*p*	0.46	204	443

Although the time required to oxidize 0.5 cc thiosulphate increases steadily from the beginning to the end of the experiment, it is nevertheless quite obvious that the "oxidation of hydriodic acid" takes place more quickly in the presence than in the absence of thiosulphate (cf. Ex. *j*, *k*, *m*, with Ex. *h*, *l*, and *n*). That the difference is not due to retardation by free iodine, is shown by the similarity of the rates in Ex. *j*, *k*, and *m*, where thiosulphate is absent; it must therefore be ascribed to accelera-

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[1] In these three cases the thiosulphate was added *after* the expiration of the *T* seconds.

tion by the thiosulphate, or, more probably, to direct oxidation of the latter. This view is confirmed by a comparison of Ex. *d* and *g* with Ex. *c*, *e*, *f*, and *h*, which shows that increase in the concentration of the thiosulphate increases the rate.

The rate of oxidation of hydrogen iodide by chromic acid, as measured by the Compensation Method, is therefore not unaffected by the presence of the "compensator."

Series F — Influence of potassium iodide on the rate of oxidation of sodium thiosulphate by chromic acid

On p. 72 it has been shown that addition of potassium iodide retards the rate of oxidation of sodium thiosulphate by chloric acid, the experiments of the present series prove that the same effect is produced when chromic acid is the oxidizing agent.[1] The measurements were carried out as described on p. 73; in the presence of much chromate, it was difficult to be sure of the end point of the titration. When the liquid to be analyzed contained free iodine, the restrainer was made up without bicarbonate.

The stock solutions were: Sodium thiosulphate, F/100; potassium bichromate, F/50; sulphuric acid, F/100; potassium iodide, F/10. In Tables X–XIII, A − *x* gives the number of cc of 0.012 − *n* iodine equivalent to the thiosulphate remaining at time θ; in the other tables of this series, *x* represents the number of cc *n*/100 thiosulphate that have been converted into tetrathionate.

TABLE IX.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 3 minutes.

Iodide	0	1	2	3	4	6	8	10	15	30 cc
x	4.65	3.05	2.10	1.25	1.10	0.70	0.85	0.65	0.85	1.55

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[1] Likewise with bromic acid. In a mixture containing 10 cc F/100 thiosulphate and 20 cc bromic acid (F/100 $KBrO_3$ and F/200 H_2SO_4) in 60 cc, 8.4 cc of the thiosulphate were oxidized in 5 minutes at 30° C. If 10 cc of the water were replaced by 10 cc F/10 KI, 7.25 cc were oxidized. When 10 cc iodide and 20 cc bromic acid were diluted to 60 cc, the iodine liberated in 5 minutes was equivalent to 0.2 cc thiosulphate.

Table IX gives the amount of thiosulphate oxidized in three minutes in solutions containing various amounts of potassium iodide; as the quantity of the iodide increases, x first falls, then remains stationary, and finally rises again.

TABLE X.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C.

θ	0	1	2.5	4.5	6.5	9.0	11.5	14.25	16.25	21.0
$A-x$	8.35	6.6	4.95	4.0	3.5	3.0	2.6	2.4	2.3	2.25

TABLE XI.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Iodide, 4 cc; Vol., 60 cc; Temp., 30° C.

θ	0	1.5	3.5	8	14	20.5	28	35	42.5	68
$A-x$	8.35	7.9	6.6	5.75	4.6	4.0	3.05	2.55	2.25	1.5

TABLE XII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Iodide, 8 cc; Vol., 60 cc; Temp., 30° C.

θ	0	2	5	10.5	18	27	34.5	44.5	56
$A-x$	8.35	7.85	7.05	6.0	5.1	4.35	3.7	2.9	2.75

TABLE XIII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Iodide, 12 cc; Vol., 60 cc; Temp., 30° C.

θ	0	1.5	5.5	10	18	28	38	48	58
$A-x$	8.35	7.9	6.65	5.8	4.45	3.55	3.1	2.65	2.2

Tables X, XI, XII and XIII, in which the progress of the reaction in presence of various amounts of iodide is detailed, establish the existence of a minimum rate when about eight molecules of iodide are added for one of thiosulphate. See Fig. 1.

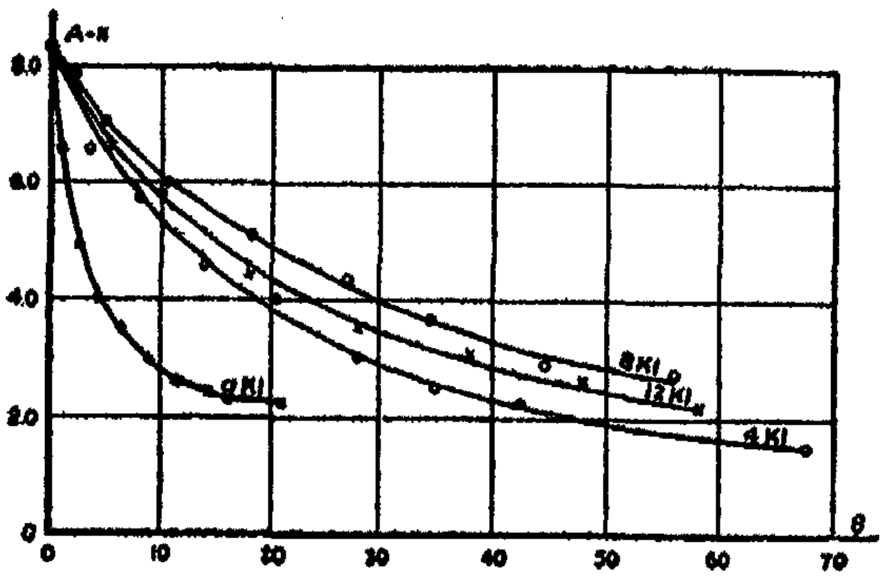

Fig. 1

TABLE XIV.

Thio., 10 cc; Bichr., 5 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 5 min.

Iodide	0	2	4	6	8	10	15	20	(40)[1]	(80) cc
x	5.5	3.55	2.05	1.75	1.5	1.45	1.45	1.65	2.35	4.6

TABLE XV.

Thio., 10 cc; Bichr., 2.5 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 5 min.

Iodide	0	2	4	8	10	15	(40) cc
x	5.97	4.3	3.21	3.1	3.05	3.1	4.15

Tables XIV and XV show that the amount of iodide present at the minimum is not sensibly changed when the concentration of the bichromate or the duration of the oxidation is

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[1] In order to keep the total volume down to 60 cc, an equivalent amount of a more concentrated iodide solution was employed.

varied; while if the concentration of the thiosulphate be halved, the amount of iodide changes from 8 or 10 cc to 2 cc. (Table XVI). The results are represented graphically in Fig. 2.

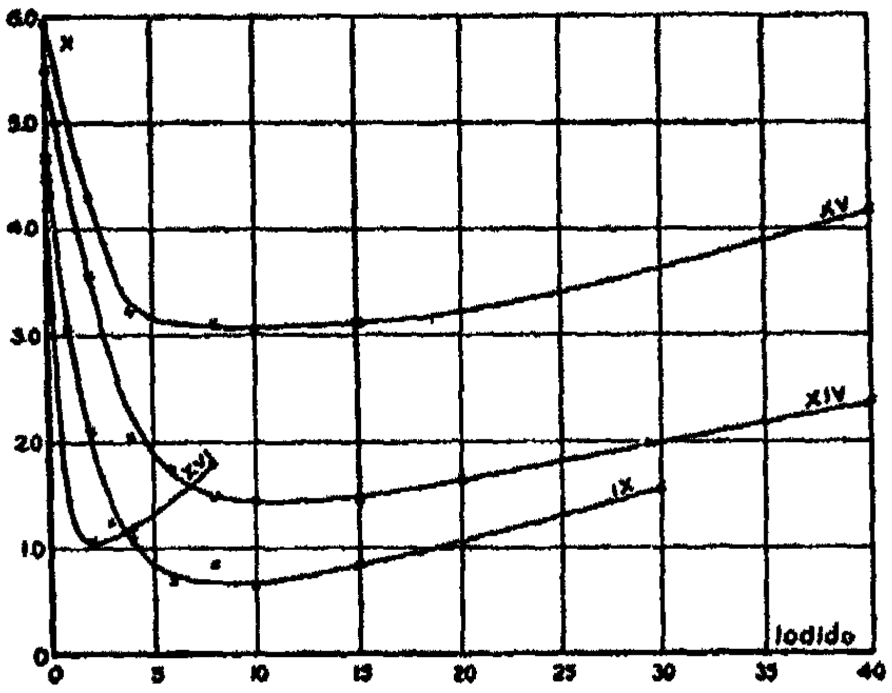

Fig. 2

TABLE XVI.

Thio., 5 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 3 min.

Iodide	0	2	4	8 cc
x	4.5	1.05	1.2	1.8

TABLE XVII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C.; Time, 2 min.

Salt added.	x
none	3.95
20 cc F/20 KCl	3.5
20 cc F/20 K_2SO_4	2.5
20 cc F/20 KI	0.6

TABLE XVIII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C.; Time, 3 min.

Bromide	0	2	5	10	20	(100)	(200) cc
x	4.65	4.4	4.25	4.15	4.05	3.4	3.1

Experiments with potassium sulphate and chloride (Table XVII) show that these salts also retard the rate, but to a much less extent than the iodide. A series of experiments was carried out with F/10 potassium bromide (Table XVIII), but no minimum was observed.

A plausible explanation of the form of the curves in Fig. 2 is afforded by the supposition, that of the two reactions (direct oxidation of the thiosulphate and oxidation of the iodide) the former is retarded by the addition of iodide, while the rate of the second is proportional to the concentration of the iodide.

I hoped to be able to test this hypothesis by analyzing the reaction product corresponding to different points on the curve. Unfortunately for this purpose, the substance formed is always the same, viz., sodium tetrathionate, whether the oxidizing agent be iodine, chromic acid, or a mixture of the two.[1]

My attempts to reach a satisfactory explanation of the retardation itself, likewise led to ambiguous results. As the oxidation is retarded by potassium iodide, whether the oxidizing agent be chloric, chromic, or bromic acid, and as the amount of iodide that must be added to obtain a minimum rate depends upon the concentration of the thiosulphate, and not upon that of the oxidizing agent, it is natural to suppose that some complex compound of iodide and thiosulphate is formed, which reduces the concentration of the latter, and consequently the rate at which it is oxidized. The existence of crystallized compounds of thiosulphates and iodides lends support to this view. A number of freezing-point and conductivity determinations, however, gave negative results; moreover, the time elapsing before the

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[1] The absence of *tri-* and *penta-thionic acids* was proved by qualitative tests with copper salts; *sulphurous acid* is instantaneously oxidized by chromic acid of the strength used in my experiments; a series of experiments in which hydrochloric acid was substituted for sulphuric showed the absence of *sulphuric acid* in the oxidation product; and finally the presence of *tetrathionic acid* in quantity equivalent to the thiosulphate oxidized was established by boiling with silver nitrate, dissolving the silver chromate and iodide with potassium cyanide, and reducing the residual silver sulphide in hydrogen. Details of the method and test analyses will be published elsewhere.

appearance of a precipitate of sulphur in acid solutions of sodium thiosulphate was found to be unaffected by the addition of potassium iodide, whereas von Oettingen has shown that the interval in question depends on the concentration of the thiosulphate. For the present, therefore, the explanation suggested lacks confirmation.

Series G — Rate of oxidation of thiosulphate by chromic acid

In conclusion I append a few measurements of the rate of oxidation of sodium thiosulphate by chromic acid. In Tables XIX–XXII the initial composition of the reacting mixture is

TABLE XIX.

Thio., F/1200; Bichr., 2F/1200; Acid, 7F/1200; Temp., 0° C.

θ	$A-x$	k
0	10.0	—
1.25	9.55	16
5	7.8	22
8.5	6.05	26
12.5	4.75	26
17.5	3.73	25
26.5	2.65	22

TABLE XX.

Thio., F/1200; Bichr., 4F/1200; Acid, 7F/1200; Temp., 0° C.

θ	$A-x$	k
0	10.0	—
1.0	9.54	21
3.75	3.45	20
7.5	7.48	17
12.5	5.34	22
20.0	3.72	22
27.5	2.88	20
35.0	2.27	18

Table XXI.

Thio., F/1200; Bichr., 2F/1200; Acid, 14F/1200; Temp., 0° C.

θ	$A-x$	k
0	10.0	—
1.08	9.3	29
4	7.45	32
9	5.34	30
15	3.25	33
21	2.34	30
28	1.74	29
31	1.38	28
38.5	1.08	25

Table XXII.

Thio., F/1200; Bichr., 2F/1200; Acid, 28F/1200; Temp., 0° C.

θ	$A-x$	k
0	10.0	—
1	9.24	34
3.5	7.56	35
7.25	5.4	37
11	4.08	35
15.5	2.76	36
22	1.98	32
37	1.08	26

given at the head of each table: "Thio., F/1200," for instance, signifying 1/1200 gramme formula weight per liter. For each analysis 100 cc were taken; the iodine reading is entered under $A-x$, and under θ the duration of the reaction in minutes. The "Acid" used was sulphuric acid.

The constancy of $k_t = 1000/\theta . log\ [A/(A-x)]$ shows that the rate of oxidation is proportional to the concentration of the thiosulphate.

Ferrous sulphate and copper sulphate accelerate the reaction; ferric, nickel, and cobalt salts slightly retard it, while starch, sodium tungstate, and ammonium molybdate are without effect. Direct sunlight exerts a very appreciable accelerating influence.

Doubling the concentration of the bichromate slightly retards the rate (Tables XIX and XXI); doubling that of the acid increases the rate by 20 percent or so (Tables XIX, XXI, and XXII).

Summary

In the *Introduction* the Compensation Method is described, the assumptions on which it is based are analyzed, a number of cases in which it has been employed are detailed, and the consequences of the hypothesis that the oxidation of thiosulphate and of iodide proceed independently in the same solution, are developed (pp. 61–68).

Experiments with *Hydrogen Peroxide* show that with this oxidizing agent the Compensation Method probably gives reliable results (pp. 68–70).

Experiments with *Chloric Acid* show that sodium thiosulphate is rapidly attacked by this substance, and that its rate of oxidation is retarded by potassium iodide. Thus the assumptions on which the Compensation Method is based, both in its original form, and as modified on p. 65, are untenable when chloric acid is the oxidizing agent (pp. 70–75).

The retardation itself, however, is obviously a distinct advantage where thiosulphate is employed as a "compensator."

Experiments with *Chromic Acid* (and one with *Bromic Acid*) lead to the same conclusion as those with chloric acid. Closer examination of the retardation produced by potassium iodide resulted in the discovery of a minimum rate; hypotheses have been advanced to account for the minimum, and for the retardation itself (pp. 75–83).

In addition, the paper contains a number of measurements of the *rate of oxidation of sodium thiosulphate* by chloric and chromic acids, with particular reference to the effect produced by adding catalytic agents, and by changing the concentrations of the thiosulphate, the acid, and the oxidizing agent. The results do not suggest any simple "mechanism" for the reaction.

In conclusion, I wish to express my thanks to Professor W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

The University of Toronto,
July, 1902

ON THE ELECTROLYTIC PREPARATION OF IODOFORM FROM ACETONE

BY HOWE ABBOTT

In 1884 E. Schering[1] patented a process for the preparation of iodoform, bromoform and chloroform by the electrolysis of the corresponding halogen compound of an alkali or an alkaline earth metal in warm aqueous alcohol, aldehyde or acetone solution with the simultaneous introduction of a current of carbon dioxide.

Elbs and Herz[2] have conducted experiments to determine the most favorable conditions for the preparation of iodoform from alcohol. They suggest that if an alkali carbonate is added to the anode solution the introduction of carbon dioxide is unnecessary.

When they tried to substitute acetone for alcohol, using as anode solutions 3, 6 and 12 grams of sodium carbonate, 10-15 grams of potassium iodide, 93 cc of water, 27 cc acetone, at temperatures from 20°-40° C and current densities from 0.5-4.0 amperes per square decimeter, they obtained no iodoform during the electrolysis, but instead a dark brown body and free iodine. If, however, they added a warm solution of sodium hydrate to the body it dissolved and, on cooling, a small quantity of iodoform together with some impurities precipitated.

This led them to substitute the hydrate for the carbonate in the anode solution. Under otherwise similar conditions after one ampere hour no solid separated and only the odor of the anode solution showed the formation of a small quantity of iodoform. In this case they state that there was no free iodine, but that the solution was colored brown by condensation products of acetone.

From their experiments they conclude that iodoform cannot be successfully prepared from acetone.

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[1] D. R. P. 29, 771, May 6, 1884.

[2] Zeit. Elektrochemie, 4, 113 (1897).

I duplicated their conditions with the same experimental result.

Knowing from experiments in this laboratory that a temperature of 75° C gave the best yield of iodoform from alcohol, I next tried to prepare iodoform from acetone at this temperature.

The apparatus was constructed as follows: The cathode chamber consisted of an ordinary beaker of about 500 cc capacity. In this was placed a porous cup, of about 120 cc capacity, containing the anode solution of 6 grams sodium carbonate, 10 grams potassium iodide, 80 cc water and 20 cc acetone. A cork with two perforations was placed in the mouth of the porous cup. Through one of these passed a thermometer and through the second a reflux condenser to prevent loss of acetone by distillation. The cathode was a cylinder of iron wire gauze and the cathode liquid a 10 pct solution of sodium carbonate. The apparatus was maintained at a constant temperature by means of a water-bath.

After electrolyzing for two hours with a current density of one ampere per square decimeter, the anode solution contained a small quantity of iodoform, an excess of free iodine and but little of the brown body described by Elbs and Herz.

Thinking that possibly the acetone could be kept from oxidizing and from forming condensation products (thus increasing the yield of iodoform), if only a small quantity was present in the anode solution at one time, the next experiment was to add the acetone gradually during the electrolysis. The result was that a considerable quantity of fairly pure iodoform was obtained. The concentration of the anode solution was next varied. Instead of 100 cc of water 250 cc were used. With the other conditions the same, the yield was perceptibly increased and the anode solution was little colored with free iodine.

In all these cases, however, the iodoform was more or less colored from the presence of a small quantity of the brown body mentioned above. Seeing that the temperature had a great influence on the quantity of the brown body formed, I next tried a temperature of 90°–95° C with the hope of either decomposing this body or preventing its formation altogether. The result was that the iodoform obtained was of a beautiful yellow color and no trace of the other body was found.

These preliminary experiments were not quantitative, but indicated the most favorable conditions for a good yield of iodoform.

I next tried by a systematic series of experiments to determine the most favorable conditions for the preparation of iodoform from acetone.

The apparatus was the same as that used in the preliminary experiments with the exception that a copper voltameter and an ammeter were placed in the circuit in addition to the resistance and the electrolytic cell. The sodium carbonate used was anhydrous and chemically pure as was also the potassium iodide and acetone.

The effect of all conditions of experiment, namely: current density, temperature, the amount of sodium carbonate and potassium iodide, the concentration of the anode solution and the gradual addition of definite amounts of acetone at regular intervals during the electrolysis, were tried and the results are given in the tables below.

A temperature of 90°–95° C was used in the first five series of experiments, as the preliminary test indicated that this was the most favorable temperature. That this is not the case is evident from the temperature table (VI).

TABLE I.

Effect of varying amounts of sodium carbonate.

Anode solution: 10 grams potassium iodide, 10 cc acetone, 250 cc water and varying amounts of sodium carbonate.

No.	Sodium carbonate.	Ampere hours.	Current density.	Temp.	Voltage.	Yield grams.	Current yield.
1	3 grams	1.675	0.85	93° C	1.95	1.4079	34.7 pct
2	5	1.692	"	92°	1.90	1.2511	30.2
3	6	1.654	0.9	92°	2.0	1.4323	35.3
4	12	1.456	"	91°	1.9	0.9002	25.2

TABLE II.

Effect of varying amounts of potassium iodide.

Anode solution: 6 grams sodium carbonate, 10 cc acetone, 250 cc water and varying amounts of potassium iodide.

No.	Potassium iodide	Ampere hours.	Current density.	Temp.	Voltage.	Yield grams.	Current yield.
1	5 grams	2.16	0.9	93° C	2.0	0.5323	10.05 pct
2	10	1.654	"	92°	"	1.4323	35.30
3	15	1.85	"	94°	1.9	1.3784	30.45

TABLE III.

Effect of current density.

Anode solution: 6 grams sodium carbonate, 10 grams potassium iodide, 10 cc acetone and 250 cc water.

No.	Ampere hours.	Current density.	Temp.	Voltage.	Yield in grms.	Current yield.
1	0.794	0.45	93° C	1.7	0.3538	18.1 pct
2	1.654	0.9	92°	2.0	1.4323	35.3
3	2.64	1.35	91°	2.2	2.6285	37.0
4	3.688	1.85	94°	2.3	2.5288	28.0

TABLE IV.

The effect of the gradual addition of definite amounts of acetone.

Anode solution: 6 grams sodium carbonate, 10 grams potassium iodide, 250 cc water and varying amounts of acetone. Current density 1.3 amperes per square decimeter.

No.	Ampere hours.	Amount of acetone used.	Temp.	Voltage.	Rate of addition.	Yield grams.	Current yield.
1	2.90	11 cc	91° C	2.2	1 cc per 10 min.	2.2747	35.2 pct
2	2.64	5.5	94°	"	0.5 " " " "	2.6285	37.0
3	2.70	4.4	95°	2.4	0.4 " " " "	1.8417	27.4
4	2.69	11.6	94°	2.3	0.2 " " 2 "	1.8522	28.3
5	2.63	11.0	93°	2.1	0.5 " " 5 "	2.0483	31.1

TABLE V.

Effect of concentration of the anode solution.

Anode solution: 6 grams sodium carbonate, 10 grams potassium iodide, varying amounts of water and 5.5 cc acetone added at the rate of 0.5 cc per 10 minutes. The solution was electrolyzed 10 minutes before the first 0.5 cc of acetone was added.

No.	Water.	Ampere hours.	Current density.	Temp.	Voltage.	Yield grams.	Current yield.
1	250 cc	2.59	1.3	93° C	2.1	1.9418	30.7 pct
2	200	2.70	"	94°	2.2	2.3579	35.6
3	150	2.68	"	93°	2.3	2.3945	36.5
4	100	2.69	1.35	94°	2.0	2.7163	40.8

TABLE VI.

Effect of temperature.

Anode solution: 6 grams sodium carbonate, 10 grams potassium iodide, 100 cc water and 5.5 cc acetone added as in Table V.

No.	Ampere hours.	Current density.	Temp.	Voltage.	Yield grams.	Current yield.
1	2.80	1.35	95° C	2.0	2.5816	37.2 pct
2	2.74	1.25	85°	2.2	3.0512	45.9
3	2.71	1.35	75°	2.2	3.3996	51.2
4	2.64	1.25	65°	2.7	1.8096	28.0

TABLE VII.

Acetone yield. The acetone yield was calculated on the basis that 0.147 gram of acetone should produce 1 gram of iodoform.

Anode solution: 6 grams sodium carbonate, 10 grams potassium iodide, 100 cc water, temperature 75° C, current density 1.3 amperes per square decimeter and varying amounts of acetone. The acetone was added every 10 minutes, as in Table V.

No.	Ampere hours.	Voltage.	Acetone.	Yield grams.	Current yield.	Acetone yield pct theory.
1	2.5	1.8	5.5 cc	3.6550	59.72 pct	12.27 pct
2	2.5	"	4.4	3.4444	56.28	14.46
3	2.6	"	3.3	3.4435	54.08	19.28
4	2.6	"	2.2	3.3905	53.26	28.46
5	2.75	2.2	1.1	2.7636	41.04	46.88

From these tables it will be seen that the most favorable conditions for the preparation of iodoform by this method are: a current density of not more than 1.35 amperes per square decimeter, a temperature of 75° C with an anode solution consisting of six grams sodium carbonate, 10 grams potassium iodide, 100 cc water, and 5.5 cc acetone added at the rate of 0.5 cc per 10 minutes during the electrolysis.

The best yield obtained by Elbs and Herz was 1.434 grams of iodoform per ampere hour. Considering that 0.116 gram of alcohol produces 1 gram of iodoform only 2 percent of the alcohol used was converted into iodoform.

In preparing iodoform from acetone the best acetone yield is 46.88 percent, which is as important as the current yield. In estimating the value of the process the amount of iodoform obtained per watt hour is also important. Taking their highest yield as a basis, Elbs and Herz obtained 0.3585 gram of iodoform per watt hour. The relatively low yield is due to the high voltage required. If acetone is used the voltage is but 2.2 and the yield 0.57 gram per watt hour.

The formation of iodoform from alcohol was explained by Elbs and Herz by assuming a direct action of the iodine upon the alcohol. O. Dony-Hénault, in a recent paper,[1] has given a new theory for the iodoform synthesis. He explains the reaction in two steps, (1) the hydroxyl ions act on the iodine ions forming hypoiodous acid, (2) the hypoiodous acid reacts with the alcohol forming iodoform.

In this case the hypoiodous acid has a tendency to form iodate as well as to react with the alcohol, and the speed of these two reactions determine the yield of iodoform. To prevent the formation of iodate and increase the yield of iodoform Doney-Hénault saturated the solution with the iodate before the electrolysis.

In either case the final equation representing the reaction is as follows:

$$C_2H_5.OH + 10I + H_2O = CHI_3 + CO_2 + 7HI.$$

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[1] Zeit. Elektrochemie, 7, 57 (1900).

The reaction in the case of acetone takes a different course. According to Richter[1] tri-iodo acetone is first formed, which is unstable, and breaks down on heating into iodoform. The fact that a high temperature, up to a certain point, increases the yield of iodoform seems to support this view. It is not probable that the reaction takes place according to Dony-Hénault's theory, as all attempts on my part to increase the yield by adding iodate to the anode solution led to negative results. The yield was, on the other hand, perceptibly decreased.

The generally accepted equation for the preparation of iodoform from acetone is as follows:

$$CH_3.CO.CH_3 + 6I + H_2O = CHI_3 + CH_3.COOH + 3HI.$$

That acetic acid is formed during the electrolysis is certain but its detection is difficult. The ordinary test with sulphuric acid and alcohol gave no result. The cacodyl test as generally applied was also of no avail from the fact that cacodyl iodide and not cacodyl was formed in the presence of the iodine.

To overcome this difficulty the residue from the electrolysis was placed, together with some As_2O_3, in a dry retort (non-tubulated) which was connected with a wash-bottle containing a strong solution of sodium hydrate to decompose the cacodyl iodide formed. The retort was then heated over a free flame and immediately the cacodyl gas began issuing from the outlet tube of the wash-bottle, proving conclusively that acetic acid had been present in the residue as sodium acetate.

From the above experiments we see that there are two possible courses for the reaction. The acetone may be converted directly into iodoform, or tri- iodo- acetone may be first formed, which undergoes hydrolysis, breaking down into iodoform and acetic acid, according to the following equation:

$$CI_3.CO.CH_3 + H_2O = CHI_3 + CH_3.COOH.$$

The fact that a rather high temperature increases the yield of

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[1] "Organic Chemistry," Vol. I., page 235.

iodoform and that no iodized acetones remain in the solutions when a high temperature is used, would lead me to accept the latter view.

In conclusion, I take this opportunity to thank Mr. O. W. Brown, who suggested the subject and who has given valuable assistance during the entire course of the work.

Electrochemical Laboratory,
Indiana University,
May 29, 1901.

THE RATE OF REACTION IN SOLUTIONS CONTAINING POTASSIUM IODIDE, POTASSIUM CHLORATE, AND HYDROCHLORIC ACID

BY W. C. BRAY

The rate of the reaction between potassium chlorate, potassium iodide, and hydrochloric acid in aqueous solution has already formed the subject of more than one research; but, as yet, no simple relation has been found between the concentrations of the reagents and the rate at which iodine is liberated in the solution.

The earliest data are contained in five tables at the end of an article by O. Burchard,[1] "*On the Oxidation of Hydrogen Iodide by the Oxyacids of the Halogens.*" His measurements are few in number; and, in the author's own opinion, "in spite of the precautions taken" (to exclude air) "the influence of the spontaneous decomposition of the hydrogen iodide is evident in all the experiments."

The next paper dealing with the subject, is W. H. Pendlebury and M. Seward's "*Investigation of a Case of Gradual Chemical Change.*"[2] The method employed — Harcourt and Esson's "Compensation Method" — is, however, quite unsuited to the reaction studied,[3] and the results of their measurements are widely different from those obtained by direct analysis.

The most recent contribution to the literature of this subject, "*The Chemical Kinetics of Oxidation,*"[4] by H. Schlundt and R. B. Warder, contains a large number of careful experiments; unfortunately, the plan of the work is of such a nature, that, failing the existence of simple relations of a preconceived form, the results of the investigation do not lend themselves

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[1] Zeit. phys. Chem. 2, 823 (1888).

[2] Proc. Roy. Soc. 45, 396 (1889).

[3] J. M. Bell. Jour. Phys. Chem. 7, 61 (1903).

[4] Am. Chem. Jour. 17, 754 (1895); 18, 23 (1896).

readily to the discovery of the relations actually existing. In reviewing their work, the authors come to the conclusion that a "satisfactory application of the law of mass has not yet been made to this reaction".[1] This paper is again referred to on page 114.

Plan of the experiments

The object of my own work has been to trace the effect on the rate produced by *changing the concentration of each one of the reagents individually.* With this end in view two methods of experimenting were employed.

First Method.— In making up the solutions in which the rates of reaction were to be determined, one of the reagents was added in much less quantity than the others; the percentage change in the concentration of the latter (caused by chemical change in the solution) was thus rendered almost negligibly small, and the diminution in rate as the reaction progressed was due altogether to decrease in the concentration of the reagent present in small quantity.[2] The effect on the rate caused by changes in the concentration of this substance was therefore easily ascertained. The relation between the rate and the concentrations of the other reagents was determined by comparing the results of a number of experiments in which the concentrations of the substances present in excess were varied. This is the plan pursued by Harcourt and Esson in their classical researches;[3] it differs from Ostwald's "Isolation Method"[4] by providing a means of determining the "order of the reaction" with respect to every reagent, without imposing the condition that each in turn must be present in (relatively) small quantity.

The *Second Method,* which may be called "the method of Constant Rates," is based upon the fact that, while the rate is dependent only on the concentrations, the total amount of

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[1] Am. Chem. Jour. 18, 27 (1896).

[2] For the effect of the products of the reaction, see Series C, page 101.

[3] Jour. Chem. Soc. 20, 460 (1867).

[4] Ostwald, Lehrbuch, 2 Ed. II, 2, 238 (1897).

change in any interval depends upon the scale on which the experiment is carried out. It is thus often possible so to arrange matters, that while the amount of change accomplished in a suitable interval is sufficient for the requirements of an accurate analysis, yet the fractional alteration in the concentrations of the reagents involved is so small that the rate may be treated as practically constant during the interval. The amount of change divided by the time then gives the rate $dx/d\theta$ directly. This method is singularly applicable in the case of a reaction where the rate passes through a maximum or minimum, or where for any other reason the rate does not vary greatly with changes in the concentration; and in general whenever the substance produced can be determined accurately in the presence of relatively large quantities of the substances from which it is formed. As the concentrations of the products of the reaction are small in comparison with those of the reagents, complications may often be avoided by the use of the method of constant rates.

The effect of varying the concentration was studied through as wide an interval as possible, the limits being: — potassium chlorate F/240[1] to 3.3F, potassium iodide, F/40 to 2F, hydrochloric acid, F/30 to 2/F. As hydrochloric acid may be regarded as a mixture of chlorine-ion and hydrogen-ion, further experiments were necessary to determine the effect of the concentration of each of these individually.

The following series of experiments were carried out: —

Series A. — In connection with the method of analysis employed in Series B, a number of experiments on the acceleration of the reaction by iron salts.

Series B. — The concentration of the potassium chlorate much less than those of the other reagents. A method of determining chloric acid without the use of a pressure bottle is described.

Series C. — Experiments to determine the magnitude of the retardation caused by the iodine set free during the reaction.

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[1] One gramme Formula weight in 240 liters.

Series D. — The concentration of the potassium iodide much less than those of the other reagents.

Series E. — The concentration of the acid much less than those of the other reagents.

Series F. — The chlorate and iodide present in comparable amounts, the acid in excess.

Series G. — The influence of the concentration of the chlorine-ion on the rate. Experiments with sodium chloride.

Series H. — The influence of the concentration of the hydrogen-ion on the rate. Experiments with sulphuric acid.

Series J. — The influence of the concentration of the potassium iodide on the rate.

Method of operation

Evaporation of iodine. — Even comparatively dilute solutions of iodine lose strength rapidly when exposed to the air at 30° C; for instance 200 cc of a $n/1000$ solution in a 300 cc beaker lost 5 percent of its iodine in ten minutes. The reacting mixture was consequently kept in small glass-stoppered bottles, and measurements were interrupted when the bottle was half empty. Even under these circumstances the last of a series of titrations is slightly affected by error due to loss of iodine.

Oxidation of hydriodic acid by air. — In order to avoid error from this source, all water used was boiled, cooled in a vacuum, kept under carbon dioxide, and delivered through a siphon. The pipettes, and the bottles in which the experiments were carried out were filled with carbon dioxide before using, and whenever the stopper was taken out of the bottle (to remove a portion for analysis) a slow current of carbon dioxide was passed in. The solutions used in making up the reacting mixtures were also freed from air, except in Series G and J, where the total duration of an experiment seldom exceeded ten minutes, and where the concentration of the potassium iodide was almost always small. In Series E, where the experiments extended over a period of several days, the reacting mixture was divided among a number of small bottles, which were completely filled, and each of which held enough for two titrations only.

In a blank experiment, where the concentrations of both acid and iodide were greater than in most of my measurements, the iodine set free after five hours (during which the bottle had been opened five times to remove portions for titration) was equivalent to one drop only (0.05 cc) of the volumetric solution of sodium thiosulphate; when one unit of potassium chlorate was added to the same mixture, 24 cc of the thiosulphate solution were needed to neutralize the iodine liberated. Thus, even under unfavorable conditions, the error due to oxidation by the air, may be set at less than one-half of one percent.

Details of a set of measurements.[1] — All solutions were brought to the temperature 30° C. A stoppered bottle (120 cc) was placed on a shelf in the thermostat and filled with carbon dioxide. Thirty-five cc of water, and 50 cc of 2F hydrochloric acid were pipetted in, then 5 cc F/3 potassium chlorate, and immediately afterwards 10 cc F potassium iodide. The stopper was inserted and the bottle shaken. As soon as possible (within a minute) 10 cc were pipetted into 100 cc of cold distilled water, and the iodine determined by sodium thiosulphate. Other titrations were made at known intervals. The time at which the first portion was removed was taken as $\theta = 0$ in the calculations, and the thiosulphate reading (0.1 or 0.2 cc) was subtracted from all subsequent readings; the readings thus corrected and expressed in cc F/100 thiosulphate, are recorded in the table under "$100x$."

Temperature. — All experiments were carried out at 30° C in a thermostat whose temperature did not vary more than 1/10 degree.

Chemicals and solutions employed. — The stock solutions of hydrochloric acid were standardized gravimetrically (silver chloride). The sodium chloride was prepared from the commercial salt by precipitation with hydrochloric acid and ignition. The titre of the volumetric solution of iodine was redetermined

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[1] Expt. 27.

at intervals by comparison with weighed quantities of iodine sublimed with potassium iodide, or by titration against a solution of sodium arsenite; and the ratio between thiosulphate and iodine was determined before each set of analyses. The potassium chlorate was obtained from the commercial salt by recrystallizing and drying in a vacuum over sulphuric acid. The potassium iodide employed in Series A to E was weighed out for each experiment, and was free from alkali. For the other series two stock solutions were made up, 5 cc of which gave 1.1345 and 2.2650 grams AgI respectively, corresponding to 0.965 F and 1.938 F. These solutions contain free alkali, 10 cc requiring for neutralization 1.4 cc and 2.8 cc F/10 HCl respectively.

Measuring instruments. — The pipettes and burettes were calibrated for delivery, and only those which agreed within 0.1 percent among themselves were employed.

Explanation of the tables

At the head of each table is given the initial composition of the reacting mixture. The number following the letter A, multiplied by 2.0416, gives the weight in grammes of potassium chlorate per liter of the reacting mixtures; the number following B, multiplied by 16.6, gives the weight of potassium iodide; that after C, multiplied by 3.64, the weight of hydrogen chloride;[1] that after D, multiplied by 3.545, the weight of chlorine added as hydrochloric acid and sodium chloride; and that after $FeSO_4$, multiplied by 15.2, the weight of ferrous sulphate — all in grammes per liter. For example, A = 1, B = 10, C = 10 signifies that the solution was F/60 (decinormal) with regard to the chlorate, and F (normal) with respect to iodide and acid at the beginning of the experiment.

Under θ is entered the time in minutes from the first measurement, and under $100x$ the number of cc F/100 thio-

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[1] In a few cases an alkalimetrically equivalent quantity of sulphuric acid was used. (Tables 35 and 36).

sulphate equivalent to the free iodine liberated in 10 cc of the reacting mixture during that period.

The numbers under "T(1)," "T(5)," etc., are obtained from Tables, 1, 5, etc., by interpolation, and give the number of minutes in which the amount of iodine entered under "100x" was liberated in the experiments of those tables.

R = 100 $dx/d\theta$ is the initial rate, *i. e.*, the number of cc n/100 iodine liberated per minute in 10 cc of a reacting mixture of the composition given at the head of the table. It is obtained by multiplying the concentration of the substance present in small quantity by k_1. Finally, k_1 is the "constant of the first order"; if the potassium chlorate be present in small quantity, $k_1 = 1/\theta \log \text{nat}\ A/(A-x)$.

Results of the Experiments

Series A. Acceleration by iron

In Expts. 1 and 2 the initial concentrations of the chlorate, iodide, and acid were the same, but in Ex. 2 a little ferrous sulphate (equivalent to 2½ percent of the chlorate) was added. This slight addition multiplied the rate by 13.

In the case of Expts. 3 and 4 the acceleration is still more marked.

EXPTS. 1 AND 2.

A 1.0; B 8.75; C 8.85; $FeSO_4$ Ex. (1) none, Ex. (2) 0.025.

1.	100x.	$k_1 \times 10^4$	k_1 corr.	2.θ	100x	T(1)	T/θ
42	3.2	7.80	6.97	10	8.6	120	12
122	9.3	8.00	—	34	28.1	445	13
188	13.4	7.66	7.28	75	49.4	950	13
194	13.9	7.73	—	108	65.08	1580	14
287	19.9	7.73	—	141	71.3	1840	13
335	22.5	7.61	7.25	172	77.5	—	—
454	28.9	7.52	7.25	204	72.6	—	—
655	38.5	7.41	—	—	—	—	—
733	41.5	7.30	7.25	—	—	—	—
1484	63.6	6.79	—	—	—	—	—
1493	63.9	6.84	—	—	—	—	—
1863	72.3	6.70	7.34	—	—	—	—

EXPTS. 3 AND 4.

A 0.25; B 2.44; C 2.46; $FeSO_4$ Ex. (3) none, Ex. (4) 0.05.

3.	One reading only ; θ, 4410 ; $100x$, 4.0						
4. θ	21	(55)*	62	1395	1588	2881	3126
$400x$	5.2	(16)	55.6	91.3	92.9	93.7	95.1

Series B. Potassium chlorate in small quantity

Effect of the Chlorate. — The (approximate) constancy of k_1 (Expt. 1) shows that the rate is proportional to the concentration of the potassium chlorate in the reacting mixture. This conclusion is supported by the constancy of k_1 in the experiments of this section, by the identity of k_1 in Expts. 5 and 6 (where the initial concentrations of the chlorate were different), and by the experiments of Series D, where the chlorate was doubled in excess. The only exception is referred to in Series E. The slight but regular decrease in k_1 as the reaction proceeds, is due to the slight decrease in the concentrations of the reagents present in excess. In the case of Expt. 1, I have applied the correction due to this cause, assuming that the rate is proportional to the first power of the concentration of the potassium iodide, and to the cube of that of the acid (see page 100). The constancy of "k_1 corr." leaves nothing to be desired.

EXPTS. 5 AND 6.

5. A 1.00; B 8.77; C 8.85.			6. A 0.5; B 8.77; C 8.85.		
θ	$100x$	$k_1 \times 10^4$	θ	$100x$	$k_1 \times 10^4$
15	1.4	9.2	30	1.35	9.2
72	6.7	9.5	83	3.5	8.7
106	9.4	9.3	162	6.7	8.7
139	11.05	8.5	241	9.45	8.5
213	15.2	7.8	332	13.1	8.3
262	19.8	8.2	593	21.5	9.2
1317	64.9	8.0	1413	39.4	10.8*
1462	67.15	7.8	1691	42.3	11.0*
	R = 0.092			R = 0.046	

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* Interpolated.

Experiments 1, 2, 3, and 4 were carried out with stock solutions whose composition is not known with accuracy; they cannot be compared directly with the other experiments of this paper.

EXPT. 7.

7. A 1.0; B 17.5; C 8.85.				
θ	$100\,x$	$k_1 \times 10^4$	T (5)	T/θ
20	3.4	17.5	37	1.9
53	8.5	16.6	95	1.8
117	17.8	16.8	213	1.8
201	28.1	16.3	387	1.9
291	36.9	15.6	555	1.9
549	37.1	15.4	1050	1.9
1346	39.7	17.0	—	—
1609	44.6	17.7[*]	—	—

R = 0.175

Effect of the Iodide. — From a comparison of Expt. 6 with Expt. 7 and of Expt. 8 with Expt. 9, it follows that doubling the concentration of the potassium iodide multiplies the rate by about 1.8.

EXPTS. 8 AND 9.

8. A 0.98; B 9.8; C 9.9.			9. A 1.0; B 5.0; C 10.0.				
θ	$100\,x$	$k_1 \times 10^4$	θ	$100\,x$	$k_1 \times 10^4$	T (8)	T/θ
20	2.0	9.9	27	1.57	5.8	16	1.7
97	8.9	9.7	65	3.7	5.7	38	1.7
142	12.7	9.5	130	7.1	5.6	75	1.7
194	16.8	9.4	373	18.5	5.5	216	1.7
256	21.7	9.4	385	19.2	5.3	225	1.7
1347	74.0	9.9	1456	53.0	5.1	800	1.8
—	—	—	1640	57.2	5.3	899	1.8
—	—	—	2935	77.5	4.9	—	—

R = 0.99 R = 0.058

Effect of the Acid. — Increasing the amount of the acid present from 4.42 units to 8.85 multiplies the rate by 4.5 or 5.0 (Expts. 10 and 5). A further increase from 8.85 to 17.7 multiplies the rate by 7.7 or 8 (Expt. 11) so that the rate is proportional to

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[*] The temperature of the thermostat rose during the night. (Expts. 6 and 7.)

the second or to the third power of the concentration of the acid depending on circumstances.

EXPTS. 10 AND 11.

10. A 1.0; B 8.77; C 4.42.					11. A 1.0; B 8.77; C 17.7.				
θ	$100x$	$k_1 \times 10^4$	T (5)	θ/T	θ	$100x$	$k_1 \times 10^4$	T (5)	T/θ
40	0.83	2.0	9	4.4	34	19.6	64	263	7.7
99	1.90	1.9	21	4.7	60	32.4	65	472	7.8
323	5.4	1.7	60	5.4	93	47.14	68	791	8.5
481	8.4	1.8	95	5.1	172	66.3	63	1390	8.1
631	10.5	1.7	120	5.2	295	81.4	57	—	—
—	—	—	—	—	461	95.8	—	—	—
R = 0.020					R = 0.64				

Series C. Influence of iodine on the rate

The difficulty experienced in finding a simple formula to describe the progress of reactions involving the oxidation of iodides, has been generally ascribed to the effect exerted upon the rate by the iodine liberated during the reaction.

Ostwald[1] showed by direct experiment that the reaction between bromic and hydriodic acids was retarded by the addition of iodine; Meyerhoffer[2] set up a formula to express the retardation as a function of the amount of iodine liberated, which was found to be inconsistent with the subsequent experiments of Burchard.[3] Finally, Judson and Walker[4] expressed the opinion that "the action of hydriodic acid on the oxygen acids of the halogens is of too intricate a nature to give any satisfactory numerical results."

Comparing Expt. 12 with Expt. 5, it will be seen that the retardation brought about by saturating the reacting mixture with iodine (8.7 units) is at the outside 15 to 20 percent; the effect of the iodine liberated in Expt. 5 (0.7 unit after 1500 minutes) may therefore safely be neglected. As in Expt. 12, the amount of

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[1] Zeit. phys. Chem. 2, 127 (1888).

[2] Ibid. 2, 585 (1888).

[3] Ibid. 2, 796 (1888).

[4] Jour. Chem. Soc. 73, 410 (1898).

iodine dissolved was sufficient to convert one-half of the iodion into triiodion, the retardation is considerably less than might have been anticipated.

EXPT. 12.

A 1.0; B 8.77; C 8.85; Iodine 8.7.

θ	$100x$	$k_1 \times 10^4$
29	1.7	5.7
50	5.6	9.6
83	5.6	6.9
152	12.5	8.7
203	12.7	6.7
285	20.6	8.0
360	25.0	7.8
1454	59.2	6.8
1577	63.7	6.4

Method of Analysis. — Every precaution was taken to exclude air from the solution. A little potassium iodide was added to dissolve precipitated iodine. The iodine was next reduced by $0.25n$ sodium sulphite, added slowly from a burette with constant shaking (blank experiments having shown that otherwise there was a loss of chlorate by reduction), starch serving as indicator. A drop or two of dilute solution of potassium permanganate were then added to restore the blue color; this was necessary in order to make sure that there was no excess of sulphite. The chloric acid in this mixture was then determined by reducing it with hydriodic acid, and titrating the iodine liberated.

The reduction may be effected by adding strong hydrochloric acid and heating the mixture in the special digesting bottle described by Mohr;[1] in the presence of a trace of iron (¼ cc normal ferrous sulphate), however, the reaction takes place so quickly at 30° C that the determinations were made in ordinary stoppered bottles standing in the thermostat in which the rates of reaction were being measured.

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[1] Mohr's "Titrirmethode," 7 ed., page 364. The use of the digesting bottle could probably be avoided in other cases by the same means.

Blank experiments showed that the results of chlorate determinations carried out as described are independent of the amount of iron salt added, and that they are in agreement with those obtained by help of the digesting bottle, or by the use of ferrous sulphate and potassium permanganate.[1] The ferrous sulphate added is probably oxidized, in part, at all events, by the chloric acid; but if so, it is again reduced by the large excess of hydriodic acid present in the solution.

Series D. Potassium iodide in small quantity

Effect of the Iodide. — If the rate were proportional to the concentration of the potassium iodide, the rate of Expt. 13 (A 9.8; B 1.0; C 10.23) would be almost the same as that of Expt. 5 (A 1.0; B 8.77; C 8.8). In reality the former is much greater. Moreover, k_1 in Expt. 13 is in no sense a constant, in fact the average rate of the reaction, as measured by the quotient x/θ, only changes 20 percent, while the concentration of the iodide falls from 1.0 to 0.05 unit. Another peculiarity is revealed by Expts. 18, 19, and 20, viz; that either increasing or decreasing the initial concentration of the iodide over that in Expt. 13 accelerates the reaction.

Expt. 13.

A 9.80; B 1.0; C 10.23.

θ	$100x$	$100x/\theta$	$k_1 \times 10^4$
24	5.9	0.245 (R)	25
81	19.6	0.242	26
123	28.5	0.232	27
194	42.8	0.221	28
201	42.8	0.213	28
264	56.9*	0.214	32
305	65.4*	0.211	35
337	72.0*	0.211	37
479	94.7*	0.200	44

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* The rate decreases until iodine is precipitated from the reacting mixture and then remains much more constant. In the last four measurements iodine separated out The reacting mixture was sealed in glass tubes, 10 cc in each, and after the proper interval the top of the tube was broken and the contents poured into 100 cc of cold water. The iodine was dissolved with a little potassium iodide, and added to the rest, and the titration proceeded with in the usual manner.

[1] Mohr. l. c. page 270.

Effect of the Chlorate. — Expts. 13, 14, and 15 show that the rate is proportional to the concentration of the potassium chlorate.

Effect of the Acid. — Expts. 13, 16, and 17 show that doubling the concentration of the acid multiplies the rate by 6 or by 7 respectively.

EXPTS. 14 AND 15.

14. A 19.60; B 1.0; C 10.23.					15. A 4.90; B 1.0; C 10.23.				
θ	$100x$	$100x/\theta$	T (13)	T/θ	θ	$100x$	$100x/\theta$	T (13)	θ/T
21.5	8.4	0.390 (R)	36	1.7	33	3.8	0.115 (R)	15.5	2.1
58	22.4	0.384	95	1.7	70	8.0	0.114	33.0	2.1
88	32.8	0.370	142	1.7	161	17.7	0.109	74	2.2
115	41.96	0.356	187	1.7	182	18.7	0.103	78	2.3
—	—	—	—	—	207	22.2	0.107	92	2.2
—	—	—	—	—	311	31.5	0.100	137	2.2
—	—	—	—	—	359	35.7	0.100	155	2.3

EXPTS. 16 AND 17.

16. A 9.80; B 1.0; C 20.46.					17. A 9.80; B 1.0; C 5.11.				
θ	$100x$	$100x/\theta$	T (13)	T/θ	θ	$100x$	$100x/\theta$	T (13)	θ/T
5	8.72	1.74 (R)	35.5	7.1	28	1.51	0.054	6.2	4.5
17	27.6	1.60	119	7.0	142	5.6	0.040 (R)	23	6.1
20	31.6	1.58	136	6.8	201	8.0	0.040	32	6.3
26	40.46	1.55	183	7.0	267	11.1	0.041	45	5.9
—	—	—	—	—	361	15.3	0.042	63	5.7
—	—	—	—	—	1332	45.5	0.034	215	6.2

EXPTS. 18, 19 AND 20.

18. A 9.80; B 0.5; C 10.23.			19. A 10.0; B 1.93; C 10.0.			20. A 10.0; B 2.9; C 9.81.		
θ	$100x$	$100x/\theta$	θ	$100x$	$100x/\theta$	θ	$100x$	$100x/\theta$
19	5.3	0.279 (R)	21	6.2	0.296 (R)	24	9.5	0.395 (R)
39	11.3	0.290	72	19.9	0.270	70	24.4	0.350
59	17.1	0.289	164	41.0	0.250	120	41.2	0.343
74	20.7	0.280	241	53.5	0.222	196	62.6	0.320
—	—	—	338	71.3	0.211	275	81.3	0.296
—	—	—	408	81.3	0.197	360	100.4	0.274
—	—	—	—	—	—	460	116.4	0.253

Series E. Hydrochloric acid in small quantity

Owing to the alkalinity of the potassium iodide, the concentrations of the acid in the experiments of this series are not simple multiples.

Effect of the Acid. — The rate is proportional to the concentration of the acid when 0.37 to 1.81 units are employed (Expts. 22, 21, 23).

Effect of the Chlorate. — Doubling the concentration of the potassium chlorate only slightly increases the rate (Expts. 21 and 26).

Effect of the Iodide. — Increasing the concentration of the potassium iodide from 10 to 18 units adds 20 percent to the rate (Expts. 21 and 25).

EXPTS. 21, 22 AND 23.

21. A 10; B 10; C 0.88.			22. A 10; B 10; C 0.37.			23. A 10; B 10; C 1.81.		
θ	$100\,x$	$k_1 \times 10^4$	θ	$100\,x$	$k_1 \times 10^4$	θ	$100\,x$	$k_1 \times 10^4$
1206	12.4	1.24	1320	5.7	1.29	83	2.1	1.40
1525	16.7	1.40	1413	6.7	1.40	1163	26.8	1.38
1555	16.9	1.36	2546	10.9	1.36	2562	53.1	1.33
2592	26.0	1.34	5336	14.5	1.04	5432	80.2	1.27
5452	46.8	1.38	5725	14.6	0.90	5832	94.5	1.27
5848	49.0	1.38	9691	15.0	0.53	7209	105.9	1.24
9905	66.1	1.40	19795	15.1	—	—	—	—
12672	66.6	1.10	—	—	—	—	—	—
19896	79.6	1.17	—	—	—	—	—	—
R = 0.0109			R = 0.0047			R = 0.0253		

EXPTS. 24, 25 AND 26.

24. A 10; B 10; C 3.85.			25. A 10; B 18; C 0.77.			26. A 20; B 10; C 0.88.		
θ	$100\,x$	$k_1 \times 10^4$	θ	$100\,x$	$k_1 \times 10^4$	θ	$100\,x$	$k_1 \times 10^4$
60	6.9	3.11	22	0.3	1.77	303	4.1	1.34
312	33.4	2.9	1040	10.3	1.38	1320	16.3	1.54
1383	107.0	2.34	4120	32.2	1.31	1730	20.1	1.49
2896	160	1.86	14246	39.2	—	—	—	—
3396	203	2.14	—	—	—	—	—	—
R = 0.119			R = 0.013			R = 0.012		

Series F. Potassium chlorate and potassium iodide in comparable quantities; hydrochloric acid in excess

Effect of the Chlorate and of the Iodide.—Throughout each experiment of this series, k_2 is fairly constant.[1]

Comparing the values of k_2 for the different experiments, it will be seen that doubling the initial concentration of the chlorate leaves k_2 unaltered (Expts. 27 and 29; 28 and 30), while doubling that of the iodide diminishes k_2 (Expts. 27 and 28; 29 and 30; 31 and 27). Hence the rate is proportional to the concentration of the chlorate, and less than proportional to that of the iodide.

Effect of the Acid.— Increase from 4.98 to 10.1 units (Expt. 33) multiplies the rate by 4 or 4.8; further increase from 10.1 to 15.2 multiplies it by 3.5 (Expt. 32).

EXPTS. 27, 28 AND 29.

27. A 1.0; B 0.965; C 10.10.			28. A 1.0; B 1.93; C 9.95.			29. A 2.0; B 0.965; C 10.1.		
θ	$100x$	$k_2 \times 10^4$	θ	$100x$	$k_2 \times 10^4$	θ	$100x$	$k_2 \times 10^4$
150	3.3	2.29	1072	24.6	1.49	90	3.8	2.16
1085	18.5	2.09	1195	26.7	1.40	171	6.9	2.13
1262	21.2	2.13	1396	29.3	1.36	1168	35.1	2.05
1390	23.0	2.18	2441	44.1	1.36	1269	36.5	2.00
2448	33.7	2.08	2541	45.0	1.35	—	—	—
—	—	—	5321	66.6	1.48	—	—	—
—	—	—	5730	69.7	1.33	—	—	—
R = 0.0229			R = 0.0298			R = 0.0432		

EXPTS. 30 AND 31.

30. A 2.0; B 1.93; C 9.95.			31. A 1.0; B 0.482; C 10.16.	
θ	$100x$	$k_2 \times 10^4$		$100x$
126	7.5	1.56	129	2.4
243	12.9	1.42	279	5.05
360	18.5	1.42	385	6.7
1366	54.8	1.41	1362	18.5
R = 0.062			R = 0.0186	

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[1] $k_2 = 1/(A - x) - 1/A$.

EXPTS. 32 AND 33.

32. A 1.0; B 0.965; C 15.2.					33. A 1.0; B 0.965; C 4.98.				
θ	$100x$	$k_1 \times 10^4$	T (27)	T/θ	θ	$100x$	$k_1 \times 10^4$	T (27)	θ/T
100	7.0	7.53	360	3.6	185	1.07	0.584	47	4.0
160	10.6	7.41	370	3.5	331	1.7	0.522	76	4.3
1181	48.5	7.98	—	—	1136	5.8	0.462	300	4.4
—	—	—	—	—	4275	15.7	0.436	880	4.8
—	—	—	—	—	14385	37.9	0.426	—	—
—	—	—	—	—	15766	42.1	0.462	—	—

R = 0.0753 R = 0.00589

Series G. Influence of the chlorine-ion on the rate

Assuming complete dissociation (or equal dissociation) of the potassium chlorate, potassium iodide, and hydrochloric acid, A, B, and C of the experiments of the preceding series represent the concentrations of the chlorate-ion, the iod-ion, and the hydrogen-ion respectively. If D stand for the concentration of the chlorine-ion, then in all the experimentsso far, C = D. In Expt. 34, however, D is varied independently of C, by adding sodium chloride to the reacting mixture. The values of R are obtained by the "Method of Constant Rates." That the acceleration is proportional to the amount of salt added, is evidenced by the agreement between the observed values of R, and those calculated by the formula $R = 0.097 + 0.009n$.

An experiment with double the amount of potassium chlorate gave double the acceleration per unit of sodium chloride added.

Series H. Influence of the hydrogen-ion on the rate

The results of the preceding series in which the influence of the chlorine-ion on the rate was determined, render it possible to calculate the effect due to the hydrogen-ion from experiments in which the concentrations of both (i. e., of the hydrochloric acid) were varied.

From Ex. 13:—

$A = 9.8$, $B = 1.0$, $C = D = 10.2$ ...... $R = 0.245$

by means of the formula of page 107 the value of R for the hypothetical experiment:—

$$A = 9.8,\ B = 1.0,\ C = 10.2,\ D = 5.1 \ldots\ldots R = 0.153$$

may be calculated, thus:—

$$R = 0.245 - 2 \times 0.009 \times 5.1 = 0.153.$$

Comparing with Expt. 17:—

$$A = 9.8,\ B = 1.0,\ C = D = 5.1 \ldots\ldots\ldots R = 0.04$$

it appears that doubling the concentration of the hydrogen-ion multiplies the rate by 4.

EXPT. 34.

A 4.967; B 0.995; C 10.01; D 10.01 + *n*.

n	D	R	R calc.
0	10.01	0.091	(0.091)
2	12.01	0.104	0.115
5	15.01	0.135	0.142
10	25.01	0.187	(0.187)
18	28.01	0.296	0.259*

EXPTS. 35 AND 36.

A 10.0; B 0.965; C (H_2SO_4) Expt. 35, 10.1; Expt. 36, 14.54.

35. θ	100 x	36. θ	100 x	T (35)	T/θ
40	2.14	21	1.98	—	—
169	6.62	65	5.6	128	2.0
360	12.9	120	9.8	262	2.2
1327	35.7	185	14.4	400	2.2
1417	38.0	222	19.6	—	—

R = 0.054 R = 0.094

Similarly, comparing Expt. 13 with Expt. 16:—

$$A = 9.8,\ B = 1.0,\ C = D = 20.46 \ldots\ldots R = 1.74$$

addition of 10.23 units of chlorine to Expt. 13 would give:—

$$A = 9.8,\ B = 1.0,\ C = 10.41,\ D = 20.46 \ldots\ldots R = 0.43$$

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* In several other experiments I have observed that when large excess of sodium chloride is used the rate is greater than that calculated by the linear formula.

and as in the former case, doubling the concentration of the hydrogen-ion quadruples the rate.

Thus, within the limits 5 and 20 units of acid, the rate is proportional to the square of the concentration of the hydrogen ion.

By way of control, in two experiments (Expt. 35 and 36) the hydrochloric acid was replaced by sulphuric acid.[1] Increasing the acid from 10.1 to 14.54 units multiplied the rate by 2.0 or 2.2; thus the rate is proportional to the square of the concentration of the sulphuric acid $(14.54/10.1)^2 = 2.07$. The rate in Expt. 35 ($R = 0.054$) is somewhat less than that calculated from the experiments with hydrochloric acid (Expt. 13), *viz*: $0.245 - 2 \times 0.009 \times 10.2 = 0.061$; a further correction of two percent, for the difference of one percent in the amount of acid in the two experiments, would bring the calculated value down to 0.060; the difference remaining may be ascribed, in part at least, to the difference between the electrolytic dissociation of the two acids.

When the amount of hydrochloric acid present is greater than 20 units, the observed rate is much greater than that calculated by the method just described, for instance:—

EXPT. 37. $A = 10$; $B = 0.965$; $C = 30.45$; R *obs.* 14; R *calc.* 5.23.

On the other hand, when the reacting mixture contains little acid and much salt (Series E) the rate is slower.

Series J. Influence of the potassium iodide on the rate

Owing to the alkalinity of the stock solutions of KI, C varies throughout the tables. The effect on the rate has been allowed for in "R *corr.*" by assuming that R is proportional to C^2.

The conclusion reached by comparing Expts. 13, 18, and 19 (page 103) is confirmed by Expts. 38, 39, and 40, which show that, as the concentration of the potassium iodide is increased, the rate falls off, passes through a minimum and rises again. After passing the minimum, the acceleration per unit of iodide added

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[1] Standardized by comparison with the stock solution of hydrochloric acid.

increases slightly with increase in the concentration of the iodide in the reacting mixture; but, as a first approximation, the acceleration per unit may be regarded as constant when $B \geqq 1$; "R *calc.*" in Tables 38, 39, 40, has been obtained on this assumption. Doubling the concentration of the potassium chlorate somewhat more than doubles the acceleration; doubling that of the acid multiplies it by 6. Increase in the concentration of either chlorate or acid causes the minimum to move towards $B = 0$.

EXPT. 38.

A 4.967; B 0.995 *n*.

n	C	R	R corr.	R calc.
1/16	10.01	0.109	0.109	—
1/8	10.01	0.097	0.097	—
1/4	10.00	0.068	0.068	—
1/2	10.00	0.088	0.088	—
1	9.98	0.097	0.097	0.097
2	9.95	0.150	0.151	0.161
4	9.84	0.271	0.277	0.289
10	9.71	0.630	0.670	0.670

(R calc. $= 0.097 + 0.064\,\overline{n-1}$)

EXPT. 39.

A 9.935; B 0.995 *n*.

n	C	R	R corr.	R calc.
1/32	10.01	0.199	0.199	—
1/16	10.01	0.176	0.176	—
1/8	10.01	0.157	0.157	—
1/4	10.00	0.163	0.163	—
1/2	10.00	0.168	0.168	—
1	9.98	0.198	0.199	0.199
2	9.95	0.290	0.292	0.305
5	9.86	0.610	0.624	0.624

(R calc. $= 0.198 + 0.106\,\overline{n-1}$)

EXPT. 40.

A 4.967; B 0.995 *n*.

n	C	R	R corr.	R calc.
1/16	5.00	0.034	0.034	—
1/8	5.00	0.028	0.028	—
1/4	5.00	0.0203	0.0203	—
1/2	4.99	0.0179	0.0180	0.0179
1	4.98	0.0228	0.0230	0.0230
2	4.95	0.0315	0.0321	0.0333
5	4.86	0.0550	0.0581	0.0655
10	4.71	0.105	0.117	0.117

$(\text{R calc} = 0.023 + 0.0103\ \overline{n - 1})$

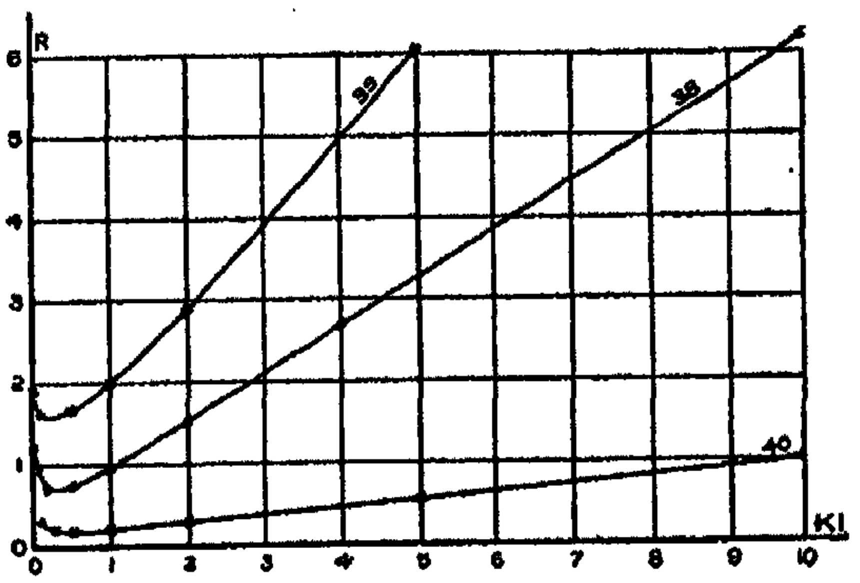

Fig. 1 Exps. 38, 39, and 40.

Summary of the results of the measurements

I. Volumetric determination of chlorates. If ferrous sulphate be added to the mixture of hydrochloric acid and potassium iodide in the iodometric determination of chlorate, the use of a digesting bottle may be dispensed with.

II. The rate at which iodine is liberated in solutions containing potassium chlorate, potassium iodide, and hydrochloric acid, is proportional to the concentration of the chlorate and to the square of the concentration of the hydrogen-ion (between $C = 5$ and $C = 20$); and is a linear function of the concentration of the chlorine-ion, and of that of the potassium iodide (when $B \geqq 1$).

Expressed in the form of an equation this statement becomes

$$dx/d\theta = (A - x)(C - x)^2[k_a(B - 1 - x) + k_b(C + 1/6x)] \,..\, \text{Eq. I.}$$

In this equation no account is taken of the retardation of the reaction by iodine.

Numerical values for k_a and k_b may be obtained as follows: In Table 35 $(A = 5,\ C = 10)$, $dx/d\theta = 0.01\,R = 0.00097 + 0.00009\,(B - 1)$; that is, $\Delta.R/\Delta.B = 5 \times 10^2 \times k_b = 0.00009$; whence $k_b = 0.00000018$. Similarly from Table 38, $k_a = 0.00000128$.

Using these numbers, I have calculated values of R for all my experiments,[1] and compared them with the observed values (Table 41). The agreement is better than could have been expected, considering that in many of the experiments the conditions of concentration differ materially from those laid down in the second paragraph of this summary.

Molecular interpretation of the results

Assuming that the rate of a chemical reaction is proportional to the concentration of each reagent, raised to a power equal to the number of molecules entering into the reaction, the kinetic equation of the preceding section corresponds to the simultaneous occurrence of the two reactions

$$\overset{-}{ClO_3} + \overset{-}{Cl} + 2\overset{+}{H} = ClO_2H + ClOH$$

$$\overset{-}{ClO_3} + \overset{-}{I} + 2\overset{+}{H} = ClO_2H + IOH$$

followed by instantaneous oxidation of hydriodic acid by the ClO_2H, $ClOH$, and IOH.

The reactions assumed are analogous to that adduced in the case of the oxidation of hydrogen bromide by bromic acid;[2] and the formation of IOH as the product of oxidation of an iodide is in accord with the results of Roebuck's research on the reaction between arsenic acid and potassium iodide.[3]

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[1] Except Expts. 1-4; see note, page 99.

[2] Jour. Chem. Soc. 73, 420 (1898).

[3] Jour. Phys. Chem. 6, 365 (1902).

TABLE XLI.

Ex.	A	B	C	R obs.	R calc.	Ex.	A	B	C	R obs.	R calc.
5	1.00	8.77	8.85	0.092	0.090	29	2.0	0.965	10.10	0.0432	0.036
6	0.5	8.77	8.85	0.046	0.045	30	2.0	1.93	9.95	0.062	0.059
7	1.00	17.5	8.85	0.175	0.178	31	1.0	0.482	10.16	0.0186	(B < 1)
8	0.98	9.8	9.9	0.099	0.125	32	1.0	0.965	15.2	0.0753	0.063
9	1.00	5.0	10.0	0.058	0.065	33	1.0	0.965	4.98	0.0059	0.0022
10	1.00	8.77	4.42	0.020	0.021	34	4.967	0.995	10.01	0.091	0.090
11	1.00	8.77	17.7	0.64	0.411	"	4.967	0.995	10.01	0.104	0.108
12	1.00	8.77	8.85	—	(iodine)	"	4.967	0.995	10.01	0.135	0.134
13	9.80	1.0	10.23	0.245	0.019	"	4.967	0.995	10.01	0.187	0.224
14	19.60	1.0	10.23	0.390	0.380	"	4.967	0.995	10.01	0.296	0.251
15	4.90	1.0	10.23	0.115	0.095	35	10.0	0.965	10.1	0.054	(H_2SO_4)
16	9.80	1.0	20.46	1.74	1.51	36	10.0	0.965	14.54	0.094	(H_2SO_4)
17	9.80	1.0	5.11	0.040	0.024	37	10.0	0.965	30.45	14.0	(B < 1)
18	9.80	0.5	10.23	0.279	(B < 1)	38	4.967	0.995	9.98	0.097	0.089
19	10.00	1.93	10.0	0.296	0.299	"	4.967	1.990	9.95	0.150	0.150
20	10.00	2.9	9.81	0.395	0.382	"	4.967	3.98	9.84	0.271	0.269
21	10.00	10.0	0.88	0.011	0.010	"	4.967	9.95	9.71	0.630	0.618
22	10.00	10.0	0.37	0.0047	0.0016	39	9.935	0.995	9.98	0.198	0.179
23	10.00	10.0	1.81	0.0253	0.0388	"	9.935	1.990	9.95	0.290	0.301
24	10.00	10.0	2.85	0.119	0.094	"	9.935	4.975	9.86	0.610	0.562
25	10.00	18.0	0.77	0.013	0.013	40	4.967	0.995	4.98	0.023	0.011
26	20.00	10.0	0.88	0.012	0.023	"	4.967	1.990	4.95	0.031	0.026
27	1.00	0.965	10.10	0.0229	0.018	"	4.967	4.975	4.86	0.055	0.070
28	1.00	1.93	9.95	0.0298	0.0295	"	4.967	9.95	4.71	0.105	0.135

In the experiments of Series E, where the quantity of acid present was small,[1] the rate is much less affected by changes in the concentration of that reagent than the formula requires. Taken alone, this fact might seem to lend plausibility to the view that the action of the hydrogen-ion is catalytic merely, i. e. that the acceleration, not the rate, is proportional to the square of its concentration.[2] As, however, in the experiments of the same series the rate is only slightly increased by doubling the concentration of the potassium chlorate, it seems preferable to ascribe the deviation to the large excess of neutral salt in the reacting mixture.[3]

The increased effect of the acid when more than twice normal (Expt. 37) may be due to the occurrence of new reactions—iodates are formed from chlorates and iodides in the presence of strong acid;—and the minimum referred to on page 109 may be compared with the retardation exerted by potassium iodide on the oxidation of sodium thiosulphate, studied by Bell;[4] experiments with potassium chlorate, potassium iodide, and sulphuric acid might throw light on this subject.

Appendix—H. Schlundt's measurements

In order to compare the results of Schlundt's measurements with those of my own, I have taken advantage of the fact that k_b is numerically much smaller than k_a to replace Eq. I by the following simpler form:

$$dx/x\theta = K(A - x)(C - x)^2(B - x) \ldots\ldots\ldots \text{Eq. II.}$$

It is true that on account of the difference between the temperatures at which the two series of experiments were carried out the ratio k_a/k_b may not be the same in both; but in view of the similarity of the two (hypothetical) reactions involved, and of

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[1] Similarly in Expt. 17, 33, and 40, where the quantity of salts is large in comparison with that of the acid, there is a marked discrepancy between *R obs* and *R calc* (Table 41).

[2] Zeit. phys. Chem. 19, 599 (1896).

[3] In one case 30 mols of salt to one of acid.

[4] Jour. Phys. Chem. 7, 79 (1903).

the equality of the temperature coefficients of the rates of most reactions, it is probable that the ratio will not be much affected by the change from 30° to 100° C.

The replacement of B - 1 by B is, no doubt, responsible for the fall in K when the concentration of the potassium iodide is increased (see below); a term of the form B - *n*, where *n* was some small number would have given better constants; but without experiments on the position of the minimum rate under the condition of Schlundt's measurements, any value selected for *n* would have been purely arbitrary.

By means of the integrated forms of Eq. II. a value of K has been computed from each of Schlundt's measurements; the results are contained in Table 42.[1] With the exception of a few scattered instances, obviously due to errors in the experiments, the lowest of the 153 values is 0.98 and the highest 2.5. In view of the fact that in Schlundt's experiments the ratio between the quantities of acid and salt never reached 3 mols of the former to one of the latter, and that in my own work "*R calc*" differed materially from "*R obs*" when the ratio fell below 5, the constancy of K is at least as good as could have been expected.

Many of the variations, moreover, can be accounted for — qualitatively at least — without introducing new hypotheses. The fall of K when A is increased, for instance (Table 42, *1a*, *1b*, *1c*), which shows that the rate is not quite proportional to the concentration of the potassium chlorate, is in accordance with those of my own experiments in which small quantities of acid were used; it may be ascribed to the influence of the large amount of salt present, either direct or by modifying the concentrations of the $\overset{+}{H}$ and $\overline{ClO_3}$ ions. Similarly with the increase of K when C is decreased (*3a*, *3b*, *3c*, *3d*; *2d*, *4c*).

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[1] The numbers of the experiments (*1a*. *1b*, etc.) are those used by Schlundt; *2a*, *3a*, and *5a* were the same as *1a*. The three figures following (for instance, 1.1,1) express the initial concentrations of the chlorate, iodide, and acid in the units defined on page 97. Under "Pct." is given the amount of iodine liberated as a percent of the total possible (in *1a*, for instance, 'Pct' = $100x$, while in *5c*, "pct" $= 25x$), and under 10^3 K are entered the values of K calculated by Eq. II. and multiplied by 1000.

TABLE XLII.

1a. 1, 1, 1.

Pct.	10^3 K
3.6	2.5
7.8	2.6
7.5	2.5
10.8	2.26
11.5	2.1
15.0	2.3
16.5	2.16
17.35	1.7
23.5	1.96
30.1	2.13
30.6	2.2
33.9	2.26
36 4	2.2
38.9	2.16
40.0	2.06
42.5	1.9
46.0	2.1
53.3	2.3
54.3	2.2
58.0	2.3
60.3	2.5

1b. 2, 1, 1.

Pct.	10^3 K
3.4	1.81
7.1	2.0
9.9	1.99
16.5	1.65
16.8	1.94
24.8	2.05
32.3	1.95
42.3	2.13
27.4	1.85
53.0	1.70
64.6	1.60

1c. 3, 1, 1.

Pct.	10^3 K
7.0	1.76
12.5	1.72
20.0	1.63
27.4	1.85
31.8	1.81
41.6	1.72
53.6	1.74
72.4	1.90

1d. 4, 1, 1.

Pct.	10^3 K
7.0	2 88
12.5	1.91
20.6	1.92
26.5	1.84
33.8	1.90
38.5	1.90
43.4	1.90
48.1	1.98
50.6	2.01
53.5	2.10
60.5	1.70
64.0	1.70
68.5	1.57
69.5	1.56
78.3	2.20

2b. 1, 2, 1.

Pct.	10^3 K
6.0	2.23
11.8	2.46
15.9	2.16
24.1	2.32
28.6	2.38
34.6	2.33
41.8	2.38
46.4	2.33
49.8	2.10
63.4	3.5

2c. 1, 3, 1.

Pct.	10^3 K
4.5	1.62
8.1	1.56
14.8	1.65
20.6	1.56
27.6	1.60
36.5	1.74
44.4	1.83
54.3	1.92
60.0	2.17
63.4	2.31

2d. 1, 4, 1.

Pct.	10^3 K
4.8	1.34
11.5	1.40
16.8	1.44
23.8	1.56
28.8	1.50
34.4	1.52
42.8	1.80
43.8	1.61
52.9	1.75
56.5	1.75
60.5	1.70

3b. 1, 1, 2.

Pct.	10^3 K
10.8	1.90
18.1	2.03
26.1	2.06
31.8	2.02
40.5	2.06
47.4	2.07
57.5	2.36

3c. 1, 1, 3.

Pct.	10^3 K
11.5	1.50
22.6	1.76
36.9	1.88
46.4	1.70
59.0	2.12
63.4	2.02
75.3	2.32
87.4	3.37

3d. 1, 1, 4.

Pct.	10^3 K
38.3	1.5
61.4	2.46
79.3	3.3
92.9	6.4

4a. 1, 2, 2.

Pct.	10^3 K
9.4	1.33
28.4	1.58
41.3	1.63
53.3	1.63
64.4	1.53
76.0	1.58
84.0	1.88

4b. 1, 3, 3.

Pct.	10^3 K
13.0	1.60
25.3	1.24
43.8	1.50
60.0	1.42
70.8	1.49
81.3	1.64
89.3	1.80
99.0	2.8

4c. 1, 4, 4.

Pct.	10^3 K
27.0	1.10
47.0	1.22
61.0	1.27
68.5	1.26
76.5	1.37
82.5	1.42
86.5	1.46

4d. 1, 2, 6.

Pct.	10^3 K
36.5	1.5
58.0	1.7
77.0	1.63
77.3	1.65
88.5	1.59
90.5	1.15

5b. 2, 2, 2.

Pct.	10^3 K
11.1	1.76
16.6	1.53
29.9	1.60
43.3	1.63
50.3	1.56
56.3	1.53
59.8	1.46
62.9	1.46
66.6	1.40
73.0	1.50
76.0	1.50

5c. 4, 4, 4.

Pct.	10^3 K
30.3	1.03
42.1	1.06
48.0	1.06
54.0	0.96
63.0	0.96
69.5	1.00
73.4	0.96
77.2	1.06
81.25	1.16

The increase of K with x observable in many of the experiments (*2c*, *2d*, *3b*, *3c*, *3d*, *4b*, *4c*) is just what would happen if K were calculated by Eq. II. from the data afforded by a reaction which in reality proceeded according to Eq. I.; the same can be said of the decrease of K when B is increased (*2a*, *2b*, *2c*, *2d*; *3d*, *4c*; *3b*, *4a*). Finally the retardation caused by free iodine accumulated in the solution shows itself in some cases by a regular diminution of K from the beginning of the experiment until iodine was precipitated; one would expect this effect to be most marked when the concentration of the potassium iodide was low (cf. *2a* with *2d*).

Temperature coefficient

If B = C, then K of Eq. II calculated from the initial rate ($x = 0$) is equal to $k_a + k_b$. For Expt. 5 then, K = 0.00000146 at 30° C. The experiment of Schlundt's where the ratios between the initial concentrations are most like those of Expt. 5, is Expt. *4c* with K($x = 0$) = 0.0011 at 100° C. Adopting the usual logarithmic formula, this corresponds to doubling the rate every 8.6 degrees.

In conclusion, I wish to express my thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

University of Toronto,
July, 1902.

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INERTIA AND COERCION[1]

BY LADISLAS NATANSON

If we cast a glance upon the universe as we see it to be, we shall be confronted with an infinite number of events, an endless variety of transformations, so that nature would at first sight look only like a confused jumble of innumerable qualities. Whether this be really so, or whether any qualitative differences at all underlie appearances, is a problem that (at the present time) we must confess ourselves unable not only to solve, but even to examine properly. However worthy of respect the various branches of science may be as a display of man's mental powers, in the full light of nature's splendour, they appear to be merely uncertain gropings: as indeed they are.

I. Accustomed as we are in natural philosophy to consider no other object but inanimate nature, we have hitherto been unable to take any other standpoint. Not only so, but we are not yet enabled to survey with a single glance the whole of the horizon thus limited by our own standpoint; as yet we have not succeeded in combining the accumulated knowledge concerning inanimate nature into a homogeneous system. We can say no more than that far as we may be from the attainment of such a goal we still are aiming to attain it.

II. The phenomena of inanimate nature may be divided into two broad categories, those which bear a character of permanence, and those which tend to subside.

We know, for instance, that the rotational and translational motion of the earth is a permanent phenomenon, like that of the moon, of the planets and comets, of the suns and planetary systems, as they move through space. The movement of terrestrial bodies is not less permanent, so long as nothing occurs to

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[1] Lecture delivered at the annual meeting of the Cracow Academy of Sciences, by Dr. Ladislas Natanson, Professor of Natural Philosophy in the Yagellonian University, Cracow.

interfere with it. Permanence in such phenomena is called inertia. In the principle of inertia, science teaches us a most important lesson in the economy of nature, though it may be no more than a first instalment, commanding a particular case, and perhaps an approximation.

Radiation affords us another example of permanence; I mean those periodic, rhythmical disturbances which are perpetually rolling through boundless, all-pervading aether. This is a fundamental phenomenon, and is, it may be, the most fundamental of all.

III. There are a great many natural phenomena of which the course runs on quite different lines. If an iron rod be heated on one end and cooled at the other, 'heat,' in popular language, will 'flow' from the hotter to the colder portion. The motion of heat, intense at the outset, becomes sluggish ere long, and at last disappears entirely; we reach at last a state of uniform temperature, or equilibrium. Various phenomena follow similar laws. In a similar manner two gases diffuse into each other, sugar diffuses in water, and gold in lead. A current of air in a closed room subsides in the same way. This is also the case with thousands of chemical reactions. An electric disturbance in any kind of matter tends to disappear, like the non-uniformity of temperature in an iron rod. In these and in many other similar cases we are confronted with something quite the opposite to inertia; we see a continuous succession of variable and transient states which tend to subside (ever more and more sluggishly, it is true), to suppress the original disturbance, to bring about equilibrium.

IV. Reverting now to the phenomena of inertia: of course they are mere abstractions, isolated from reality. Motion, for instance, is what dynamics investigates. But in nature there is no such thing as pure motion. Every real movement is intricately connected with other phenomena, either of the first category or of the second. Dynamics treats therefore of ideal phenomena; its very foundations are wanting in breadth. That is a thing understood by every scientific man; and yet we cultivate dynamics and not infrequently set it up as a standard. For we cannot do otherwise. Our aim is to grasp nature; and although nature is more complex than tongue can tell we desire it all the same. True, if we place ourselves at the standpoint of dynamics, we stand committed to a one-sided view, being thus induced to set aside quite a world of real relations; but then we at any rate can understand something of nature.

The way was shown by the master mind of Newton. He was the first to show that the motion of celestial bodies is ruled by laws which the mind of man can grasp; and by a generalization from this great achievement he discovered the universal laws of motion and thus created abstract dynamics. As we reflect upon this at the present day, we cannot help feeling perplexed. Take our solar system, for example. From the immense, coherent, and unique *totum* of phenomena with which that system confronts us, no constituent part can be separated except by a process of the nature of a fiction. How could Newton investigate gravitation without inquiring, for instance, whether the sun's heat is constant, or what changes occur in terrestrial magnetism, or what chemical reactions take place in the system? Why should electromagnetic phenomena have, *a priori*, no influence on the motion of the various parts of the system? Again, why should not the motion of the earth, for instance, react upon electromagnetic phenomena upon its surface? For almost a century physicists have sought to discover an effect of the earth's motion upon optical phenomena which they observe in their laboratories and observatories. We must change, therefore, and to some extent reverse, the position we have taken. It is, we must say, a fact that dynamics can exist as a separate, self-consistent science; the theory of pure optics, the electromagnetic theory, and other sciences, are likewise, to a certain extent, independent facts. Obviously, in the particular case on which we are engaged and to which our endeavours must conform, the problem of nature resolves itself, probably approximately, into a number of independent problems.

V. Such is the origin of every science. They have all arisen from a possibility of distinguishing, in the complexity of nature, one particular and relatively simple problem to be solved. To distinguish this is necessary at the outset of any new science; it is useful so long as that science grows in certainty and in power. Nevertheless, in presence of the close concatenation and unity which we see in nature, it is but an artifice incompatible with her intrinsic harmony. And, with the development of science, this incompatibility becomes evident; the mind of man struggles to pull down the barriers which itself had raised; a tendency arises to alter the aim of the science, to broaden its foundations and elevate its standpoint.

We say, for instance, that we observe in inanimate nature dynamical, thermal, chemical, electromagnetic phenomena. But we must not forget that all this is merely conventional language; these phenomena are abstractions, not real phenomena, nor even parts of real phenomena; rather, so to speak, sections through phenomena. As an architect represents a building by means of vertical and horizontal projection, so does the natural philosopher in his manifold theories; he gives us sections through nature, viewed from different standpoints.

VI. Thermodynamics, in a sense, is an attempt to do away with restricted standpoints. It claims not to divide problems in order to investigate them.

In the first place, thermodynamics shows that ordinary dynamics refers to one particular case only; and that infinitely many other cases of dynamics are possible. When, for instance, Newton and his followers in the XVIII. century endeavoured to discover the law of propagation of sound by ordinary dynamics, they failed. The problem belongs to the field of what we should call adiabatic dynamics; and when Laplace solved it he virtually created a second dynamics by the side of the first; this, together with numberless others besides, at present forms part of general thermodynamics.

There are, however, cases to which no form of dynamics can be made to apply. Such are those in which the two categories of phenomena — those which persist and those which tend to subside — are so connected that we cannot treat them separately without doing them violence, without breaking essential links which bind them together. And thermodynamics —as we may now define it — is a theory which discards such division of phenomena.

VII. This, therefore, is the aim of thermodynamics; it is unquestionably as great and daring as its scope is immense. No wonder then if as yet its achievement is but partial.

So far, we have established a theory of equilibrium. Though thermodynamics has not yet recognized such general laws as may govern the *course* of transformations, it has discovered one essential property, common to all those which may possibly take place, the characteristic feature which is borne by phenomena compatible with nature. Suppose a material system in which the conditions imposed are such that only changes deprived of this characteristic — and therefore contrary to nature — can occur. Then our conditional hypothesis and the laws of thermodynamics, taken together, forbid the possibility of any phenomenon occurring in the system, and since no change can take place, equilibrium must prevail. By thermodynamics, therefore, we are able to foresee the state of equilibrium towards which the so-called "subsiding" phenomena tend to approximate. A fluid, e. g., may, if certain conditions are satisfied, be in a state of equilibrium; thermodynamics, therefore, furnishes us with the foundations of hydrostatics and of the theory of capillarity. In like manner, and from the same source, the theory of elasticity receives its fundamental basis. Electrostatics and other branches of science may be likewise built up upon a thermodynamical basis. Some time ago the discovery was made that an equilibrium state of radiant energy is possible; and from this discovery a thermodynamical theory of radiation has sprung up. Ice may be in equilibrium with water, water with steam, a salt-crystal with its solution, a solution with its solvent: of all these and of innumerable other equilibria the laws have been found by thermodynamics. And by thermodynamics has chemistry been triumphantly reduced to scientific order.

VIII. As the limits to its sphere of utility recede, the fundamental ideas which underlie thermodynamics, becoming more and more general, give us an ever bolder outline of what in reality is essential. And as this great work (in which the name of J. Willard Gibbs will never be forgotten) continues to advance, we become aware, not without some surprise, that generalized thermodynamics tends more and more to similarity with the time-honoured forms assumed by ordinary statics since more than a hundred years ago. Every statical problem is, as we know, solved by the principle called the theorem of virtual work. The contents of statics is set forth here in one formula, in a single line. Nor should we consider this surprising: this knowledge sums up all essential statical knowledge accumulated from the times of Archimedes to those of Lagrange. Now, in the same manner, the thermodynamical theory of equilibria enables us to put its contents into one simple formula; and that formula is in all respects similar to the corresponding one of statics. For the sake of convenience, we frequently introduce into statical reasoning a quantity which depends upon the state of the system, and is called potential. In thermodynamics we also introduce a "thermodynamical" potential; and we find it to be as useful as the ordinary potential in statics. Finally, the thermodynamical potential is a mere generalization of the statical one; it is obtained by the consideration of the thermal aspects of equilibria. Here, therefore, is something beyond a merely formal analogy; here is the union of two sciences, one of them being absorbed into the other.

Such is at present the stage reached by the theory of equilibria. As we have remarked, it is but one fragmentary part of thermodynamics as required by natural philosophy. Equilibrium is only a limit to phenomena; when we know it, we know but the surface of reality; we have sailed around an island, but have not gone into the interior. Science never stands still, and the theory of equilibria cannot be an ultimate goal. We must go on to study the laws which preside over the *progress* of phenomena. Possibly we may not discover them; but then our successors shall profit by our failures.

IX. Let us return to the phenomena which tend to subside. Fourier, one of the masters of our science, has given in one particular department — the one which deals with thermal conductibility—a beautiful theory, a real pattern of mathematical reasoning. Other investigators have followed him in other directions, but on similar lines, so that there is now in physics quite a number of "Fourier-theories." These, however, are only a step in the right direction; nature cannot be completely mastered, even by beautiful theories.

Let us see whether we may not venture upon a scheme of generalization. Suppose, in a definite material system, a disturbance the nature of which is known, and which tends to subside. Consider, as the quantitative expression of the progress of the phenomenon, a *flux* of a certain quantity, in unit time, across unit surface. We obtain, for instance, a convenient measure of the progress of diffusion of two gases into each other if we know the flux of each of them in every part of the system. The unit flux of momentum or of energy affords likewise a convenient measure of the progress of subsidence in the motion of a fluid, or in the motion of heat. But, now, upon what does such a flux depend? It depends in general, we may say, upon the '*stimulus*' of the phenomenon. This, in the case of the diffusion of two gases into each other, is their non-uniform density: the slope or space variation of one density or the other approximately measures the intensity of the stimulus at work. In the phenomena of viscous motion-subsidence, the stimulus is, approximately, the space-variation of velocity. In thermal conductibility, it is the space-variation of temperature, or nearly so. Fourier assumes that the flux is always in direct ratio to the stimulus. This is true, but only approximately. The activity of the stimulus *is not confined to producing the flux;* it tends continually to change its intensity. Hence, the stimulus not only sets in motion the flowing quantity, it gives impetus to the flux as well. The impetus may be extremely feeble, as for instance, in Fourier-phenomena: but the fact that it had been altogether neglected was sufficient to disconnect the Fourier-theories from the remaining chapters of natural philosophy.

Why is this impetus so slight? Because it is to a great extent thwarted by coercion, a powerful though latent resistance which is always ready to act in material bodies. We do not know what its true essence is; but, Maxwell leading the way, we have found the law of coercion to be quite simple. Coercion, though powerful, is not infinitely powerful, as is implicitly assumed by the Fourier-theories. In the case of the interdiffusion of oxygen and nitrogen, for instance, the resistance of oxygen impedes the diffusion of nitrogen; but if it precluded it altogether, diffusion could not take place at all. Coercion diminishes, but does not destroy, the velocity of the flow. Now flow, in a gas, implies impetus, since a gas has inertia. Heat *also* possesses inertia, though the inertia is but slight. The inertia of heat when conducted through a gas may be regarded as the inertia of the separate molecules in motion. In a metal that conducts heat the inertia may be set down to the account of electrons; for, whatever electrons may be, they behave as (true or apparent) masses. But the important point is to notice the fact of inertia, and understand it in its bearings.

X. In the foregoing we have mentioned only one kind of stimulus, which we may call 'intrinsic.' The intrinsic stimulus is simply related to the thermodynamical potential, at least in the simpler cases; it is equal to the space-variation of this potential.

But force, as defined in dynamics, also acts as a stimulus; this we may call the accidental stimulus. The resultant of all the stimuli, of whatever kind, or ultimate stimulus, affords a convenient generalization of force as introduced by ordinary dynamics. In the case of mass-motion, the intrinsic stimulus vanishes, the rate of change of the flux is reduced to ordinary acceleration, and since in pure dynamics there is no coercion, we return, from the laws of flux and stimulus, to Newton's two first laws of motion.

To sum up: in pure dynamics, in abstract hydrodynamics and theory of elasticity, we disregard coercion. In the Fourier-theories, we take no account of inertia. But science cannot stand contented with approximations. In every phenomenon in which matter is implied, at once coercion and inertia play a part; and the quantitative ratio they bear to each other may vary to the uttermost. There is only one system from which coercion is totally absent: the vacuum or universal aether. Phenomena which take place in pure aether are the free play of unimpeded inertia.

XI. About the middle of the XIX. century we learned of Lord Kelvin to recognize in nature the universal and uninterrupted working of coercion. It may be that, in our attention to coercion, we have come to underrate inertia — that exuberance, as it were, of the activity of nature. We have just seen instances in which *some* inertia is manifested, yet which are usually considered as standard cases of coercion. Whenever a change, a phenomenon, takes place, a stimulus must be active; and its activity must create some kind of impetus — no matter how small. There is one instance of inertia without coercion; as already remarked, it is afforded by phenomena displayed in pure aether. Without inertia there is not any known instance of coercion. These two are the poles on which the world of phenomena revolves; neither is less essential than the other.

XII. Persistent phenomena interfere in an endless multiplicity of ways with those which subside. If we know the laws of both taken separately, we shall be able to elucidate the manner in which they combine, producing intricate compound phenomena.

Let us again return to dynamics. Newton formulated the laws of motion, but in a concrete form which bore traces of the way that led to their discovery. After Newton came Lagrange and other great philosophers who extended the scope of his doctrine. In Newton's dynamics the independent variables are true space-coordinates. In Lagrangian dynamics we may adopt any independent variables we choose; the rules of generalized dynamics shall not cease to apply. Now we may express these rules in various ways. If we have chosen variables (it may be, in the most general manner), we write down the Lagrangian equations of motion; these, in generalized dynamics, are the variability-equations. But we can avoid the very appearance of a choice of variables. In this case there are no explicit equations of variability, but we have a general method for deducing them in every case; this is Hamilton's principle of varying action.

Now, think of the case of a pendulum oscillating in a viscous fluid; or of a gas in which expansion and heat-conduction occur simultaneously; or of a crystal of salt dissolving as it drifts down a river; or of a lump of ice in which elastic vibrations are propagated while it melts. Such problems lie beyond the proper limits of generalized dynamics; and thermodynamics, as it is now, cannot solve them. They belong to the province of what has been called *Thermokinetics*; a province explored as yet by only a small band of students, with Prof. Duhem at their head. And yet it has attained a remarkable result. Thermokinetics presents us once more with Lagrangian equations and with Hamilton's principle, but in a slightly generalized and supplemented form. Now it is a most important fact, that the extension which is necessary to transfer the Lagrangian equations and Hamilton's principle from dynamics to thermokinetics is at bottom the same which (as we have said) makes of the principle of statics the fundamental proposition of the thermodynamical theory of equilibria.

XIII. In truth, all that we know concerning nature is no more than an attempt. It is plain that we are only starting on our way. And yet, even as it is, standing upon the threshold of knowledge, we are dazzled at every step we have made forwards, and then it takes time to accustom our eyes to the spectacle which expands before us. What then must be infinite nature?

NEW BOOKS

Hand und Hülfsbuch zur ausführung Physiko-Chemischer Messungen. *Zweite Auflage. By W. Ostwald and R. Luther. 15 × 22 cm; pp. xii + 489. Leipzig: Wilhelm Engelmann, 1902. Price: bound, 15 marks.*—The appearance of the second edition of this manual will be hailed with delight by every chemist. Ostwald has now joined forces with Luther, the sub-director of the Leipzig laboratory, with the result that the work, while losing none of the former good features, has gained many more.

The book follows its former arrangement of topics, while several new sections have been added, namely the relation of constitution to properties and reactions, and a short syllabus of a course detailing definite experiments. Of chapters which have been almost completely rewritten, those on the mercury thermometer, determination of migration numbers, and electrical measurements must be mentioned. In many cases the insertion of paragraphs containing later results or clearer explanations, examples, and references to recent work has been performed with rare good judgment.

It is to be hoped that translation into English will not be delayed, for the manual will lighten the labor of every teacher of chemistry.

H. R. Carveth

Text-Book of Electrochemistry. *By Svante Arrhenius. Translated by John McCrae. 13 × 21 cm; pp. xi + 344. New York: Longmans, Green, and Co., 1902. Price: bound, $3.50.*—The German edition of Arrhenius's book was reviewed in this Journal (6, 266) on its appearance. We have now to chronicle the issue of an English translation. But few changes have been made in the present edition, and these are for the most part confined to the correction of typographical errors. The lack of references to the original literature has been made up by the translator, who has collected them at the close of the book. They would be more useful if they had been introduced in the usual form of footnotes. The book is an interesting one, and in its new form will undoubtedly render positive service. *J. E. Trevor*

Galvanic Batteries, their Theory, Construction and Use. *Comprising primary, single and double fluid cells, secondary and gas batteries. By S. R. Bottone. 12 × 17 cm; pp. xvi + 376. New York: The Macmillan Company, 1902. Price: bound, $1.50.* — "This is a work in which a description of every known battery of any practical use is given; along with data as to E. M. F., internal resistance, and adaptability to particular requirements." Some two hundred and fifty forms of cells are discussed. *Wilder D. Bancroft*

Réflexions sur la puissance motrice du feu, et sur les machines propres a developper cette puissance. *Par Sadi Carnot, Ancien élève de l'École Polytechnique. 14 × 21 cm; pp. 118 + iv. Réimpression fac similé conforme a l'édition originale de 1824. Paris: A. Hermann, 1903. Price: paper, 5 francs.* — In 1824 Sadi Carnot published his famous brochure on what has since become known as the second law of thermodynamics. Guided by a desire to develop the theory of the steam engine, he discovered that the maximum work to be gained from a store of heat depends solely on the temperature at which the heat is assumed by the heat motor, and the fall of temperature that is available. Because the essay was little known and had become very rare, it was republished in 1878, together with manuscript notes which showed that Carnot had discovered the equivalence of work and heat, and had made a determination of the mechanical equivalent of heat. He found 370 kilogram-meters per kilogram calory, with which Mayer's determination of 365 kilogram-meters is in close accord.

This scientific classic now appears in a beautiful facsimile reprint of the first edition. Printed on old-style, heavy silky paper, the issue is all that it ought to be. As an appendix, it contains the letter in which Carnot's younger brother, the Senator, transmitted to the Academy of Sciences the unpublished discovery of the equivalence of heat and work. To this is added a facsimile of the page on which the determination of the mechanical equivalent is recorded.

J. E. Trevor

Technische Thermodynamik. *By Gustav Zeuner. Zweite Auflage, zugleich vierte vollständig neu bearbeitete Auflage der "Grundzüge der mechanischen Wärmetheorie" Zweiter Band: Die Lehre von den Dämpfen. 15 × 23 cm; pp. viii + 457 + xxix. Leipzig: Arthur Felix, 1901. Price: 14 marks.* — The present second volume of Zeuner's Technical Thermodynamics completes the new edition of this standard and admirable work. It is devoted exclusively to the theory of vapors and its technical applications. The exposition is arranged under four heads, which treat successively the thermodynamic behavior of saturated vapors, of superheated vapors, of air as liquid and vapor, and of mixtures. Studies of the technical applications are appended to the several sections.

The topics taken up in the first section, on the behavior of saturated vapors, are: vapor pressures; heats of vaporization, and specific heats; specific gravity of saturated vapors; the Clapeyron equation; Battelli's work on water vapor; and the thermal equations, the entropy, and the isothermal, isodynamic, and adiabatic curves of wet vapors. Then follow applications, to reversible and irreversible changes of state of wet vapors, and to streams of vapor. In the second section, on the behavior of superheated vapors, are considered: the critical temperature, and the curve bounding the liquid-vapor field; the characteristic equations of van der Waals and of Clausius; older forms of the characteristic equation; the thermal equations of superheated water vapor; and separate studies of the behavior of ammonia, sulphur dioxide, and carbon dioxide. The applications here are to reversible and irreversible changes of the state of superheated water vapor. The third section is concerned with the theory of the production of liquid air; ten pages of it are devoted to Linde's liquefying machine. The final section, on the behavior of mixtures, treats: isothermal and adiabatic changes of air and wet steam; isothermal changes of air, steam, water, and ice; the behavior of air and superheated steam; that of air, steam, and ice; the theory of the open cold air machine; and the behavior in general of mixtures of liquids and their vapors. The concluding applications are to the theory of the steam engine and the theory of refrigerating machines. The work is brought to a close by valuable tables of thermodynamic data for water and nine other fluids. *J. E. Trevor*

Die Grundlehren der mechanischen Wärmetheorie *und ihre elementaire Anwendung in den hauptsächlichsten Gebeiten der Technik. Für Techniker Machinebauer und für Schüler höherer technischer Anstalten. By Rudolf Wotruba. 16 × 23 cm; pp. 282. Berlin: Hermann Costenoble, 1902. Price: paper, 10 marks.* — This book begins with introductory chapters on the principles of mechanics and on the mechanical equivalent of heat, and proceeds to discuss the laws of ideal gases, cycles, hot air motors, refrigerating machines, compressed air motors, gas engines, irreversible changes of gases, the thermodynamic behavior of vapors, the evaporation of water, steam engine theory, and the completion of the topic of refrigerating machines.

The author's standpoint is characterized by his statement that "the mechanical theory of heat sets out from the principle that heat is motion of molecules, but without making any supposition regarding the nature of this motion." Being intended for the use of technical students, the treatise gives considerable attention to the technical applications of thermodynamics. It is stated that if the book succeeds in avoiding the difficulties of the classical works, the purpose of the author will have been completely attained. The difficulties appear to have been avoided chiefly by the simple expedient of leaving them out; for breadth and depth of view the book is certainly not to be compared with Zeuner's *Technische Thermodynamik*, for example. A lack of care in the preparation is manifested in the spellings 'Boyl' and 'van der Waal,' and in the lack of both a table of contents and an index. *J. E. Trevor*

Sichtbare und unsichtbare Bewegungen. *Vorträge auf Einladung des Vorstandes des Departements Leiden der Maatschappij tot Nut van't Algemeen, im Februar und März, 1901. Gehalten von H. A. Lorentz. Unter Mitwirkung des Verfassers aus dem Holländischen übersetzt von G. Seibert. 14 × 22 cm; pp. 123. Braunschweig: Friedrich Vieweg und Sohn, 1902. Price: paper, 3; bound, 3.80 marks.* — This is a German translation of a course of seven popular lectures given at Leiden in 1901 on dynamics and the mechanistic interpretation of the phenomena of sound, light, and electricity. The first lecture is on the principles of dynamics and on rectilinear motion, the second on curvilinear motion, the third on mechanical vibrations, and the next three on the phenomena of light, heat, and electricity; while the last is devoted to a review of the whole from the standpoint of the principle of the conservation of energy. The marked ability of the author appears in the fresh and lucid development of these topics, and in the ingenious and effective choice of simple experiments by means of which the leading points are elucidated.

Among many interesting details may be noted the author's opinion that Michelson's observation that the breadth of a spectral line of a gas approaches a definite limit as the gas is rarefied furnishes direct evidence for the motion of the gas-molecules. Another is that, if all molecular actions are referable to states of the interstitial ether, the weight of a train crossing a bridge is ultimately supported by tensions in the ether. A very interesting feature is an extended description of the electron theory of the phenomena of electrodynamics.

The translation is admirable, the book is well printed, and the proof-reading is well-nigh faultless. The author's point of view is admirably expressed by his closing paragraph: —

"In the conviction that a grasp of the mechanism of phenomena must be our aim, I have not spared you speculations on the ether, and on molecules, atoms, and electrons. The further we progress, the more conscious do we become of the incompleteness of our work, and that our theories, which continually require to be transformed, and in part perhaps replaced by others, give us only an incomplete reflection of actuality. But, however much I am convinced of this, and lay stress upon the expression of it, yet I hope that what I have been able to present to you has proved in some measure satisfying." *J. E. Trevor*

Über die Entdeckung der elektrischen Wellen durch H. Hertz, und die weitere Entwickelung dieses Gebietes. *By Ernst Lecher. 15 × 23 cm; pp. 32. Leipzig: Johann Ambrosius Barth, 1901. Price: paper, 1.20 marks.* — This masterly address is devoted to a review of the work of Hertz and his successors in the study of electric waves. Maxwell's formulation of Faraday's ideas is sketched, together with Hertz's demonstration that electric and magnetic disturbances are propagated with the velocity of light; Marconi's technical development in his wireless telegraphy is touched upon; and a running account is given of the scientific progress made since Hertz. such as the use made of the sensitive coherer of Branly, and the study of electric dispersion, especially by Drude. *J. E. Trevor*

Leçons sur la Théorie des Gaz. *By L. Boltzmann Translated from the German by A. Gallotti. 16 × 25 cm; pp. xix + 204. Paris: Gauthier-Villars, 1902. Price: 8 francs.* — This is a French translation of the first volume of Boltzmann's *Vorlesungen ueber Gastheorie*, on the theory of "gases with monoatomic molecules whose dimensions vanish as against their average path." Professor M. Brillouin, of the Collège de France, introduces it by a nineteen page essay: "The Molecular Hypothesis in the Theory of Gases: a Historical Review"; and he has appended notes on the law of distribution of velocities, Boltzmann's quantity H, electrical conductivity, and the distribution of velocities in the phenomena of diffusion. It may be recalled that Boltzmann divides his exposition into three chapters, devoted successively to the hypotheses: (1) The molecules are elastic spheres; (2) The molecules are centers of force; (3) The molecules repel one another with a force inversely proportional to the fifth power of the distance. A feature of the work is the author's insistence that such hypotheses are to be regarded solely as mechanical analogies, whose value lies in the agreement of their consequences with experience. The translator has omitted Boltzmann's beautiful preface to the German edition. The mechanical execution of the book is excellent. *J. E. Trevor*

Chemische Affinität und Energieprinzip. *By Joseph Siegrist. (Sammlung Chemischer und chemisch-technischer Vorträge). VII. Band, 5 Heft. 16 × 24 cm; pp. 137 to 158. Stuttgart: Ferdinand Enke, 1902. Price: 1.20 marks.* — In this address we have a readable account of the history of the study of "chemical affinity." Its first section begins with the assumption of Boyle and

Newton that this affinity is to be ascribed to attractive forces, traces the development of this idea by Bergmann and Wenzel, and shows how the recognition that chemical activity depends on the concentrations of reacting substances led finally to the mass law of Guldberg and Waage. The second section discusses the rise of thermochemistry, the establishment of the law of constant heat sums, the discovery of the first law of thermodynamics, Berthelot's discredited criterion, and the thermodynamic formulation of chemical equilibria by Horstmann and Gibbs. The final section sketches the development of electrochemistry up to the theory of electrolytic dissociation of Arrhenius. The Gibbs-Helmholtz conception of free energy is explained, and its significance as the measure of the affinity whose effect is a chemical reaction is pointed out. In conclusion the author contrasts the fruitfulness of the energy theory in this field with the sterility of the mechanistic interpretation of chemical phenomena.

J. E. Trevor

Populär-wissenschaftliche Vorlesungen. *By E. Mach. Third, enlarged and revised, edition. 12 × 19 cm; pp. x + 403. Leipzig: Johann Ambrosius Barth, 1903. Price: paper, 6; bound, 6.80 marks.* — The second English edition of Mach's remarkably fine Popular Scientific Lectures was published by the Open Court Company in 1898. The present German edition is enlarged by the addition of two short articles: On Scientific Applications of Photography and Stereoscopy, and Remarks on Scientific Applications of Photography. These are additions to preceding lectures on optical topics. A dozen new annotations, mostly brief, have been added to the book. Nineteen lectures, on all manner of physical topics, are collected. The one on the conservation of energy is truly magnificent, and should be familiar to every one who is interested in any way in the physical sciences.

Concerning the tendency manifested in the lectures, Mach says: "Of the ideas of the theory of knowledge, which were very foreign to the majority of investigators when I presented them years ago in these lectures, probably no one is due to me alone. Similar thoughts have been uttered with more or less distinctness by other investigators both before and since. Traces and elements of them can in part be found even in far distant times. But as these thoughts more or less lose their subjective personal stamp, and appear as natural or even necessary results of the general development of thought, they seem to me to gain in value in the same measure, and to become yet more worthy of the attention of others."

J. E. Trevor

Die Entwickelung unserer Naturanschauung im XIX. Jahrhundert, und Friedrich Mohr. *By Ch. Jezler. 15 × 23 cm; pp. 44. Leipzig: Johann Ambrosius Barth, 1902. Price: paper, 1.20 marks.* — This brochure is devoted to the contention that Friedrich Mohr should head the list of names — Mayer, Joule, Colding, Helmholtz — of those to whom the discovery of the conservation of energy is to be ascribed. The reason assigned is that Mohr early arrived at the idea of regarding heat as a mode of motion, and expressed corresponding convictions in regard to the essential unity of natural forces. This seems to the author to be equivalent to the discovery of the energy law. Extracts from Mohr's writings are cited to support the position. *J. E. Trevor*

Lehrbuch der Physik. *By O. D. Chwolson. Erster Band. Einleitung: Mechanik; Einige Messinstrumente und Messmethoden; Die Lehre von den Gasen, Flüssigkeiten und festen Körpern. Übersetz von H. Pflaum. 14 × 22 cm; pp. xx + 791. Braunschweig: Friedrich Vieweg und Sohn, 1902. Price: paper, 12 marks; bound, 14 marks.* — In its dimensions this treatise on physics is a monumental affair. Originally published in Russian, and intended to serve as a textbook for Russian university students, its qualities attracted so much favorable attention that the present German translation, from the second Russian edition, was promptly arranged for. The purpose of the book is to provide the student with an accurate and sharply drawn picture of the present state of physics. In the execution a truly enormous amount of matter is presented, as may be gathered from the fact that the present first volume consists of some eight hundred large octavo pages of relatively small, though clear, type, containing about four hundred and forty words per page. This volume contains a general introduction, a discussion of mechanics, a description of many instruments and methods of measurement, and separate treatments of the properties of gases, liquids, and solids. The subsequent volumes are to appear promptly; the second is to treat Sound and Radiation, the third Heat, including Thermodynamics, and the fourth Magnetism and Electricity.

In the present volume, the treatment of mechanics includes chapters on motion, force, work and energy, harmonic motion, radiation, gravitation, the potential theory, gravity, and dimensions. After introductory generalities, the section on measurement considers some auxiliary apparatus, and the measurement of lengths, surfaces, angles, volumes, force and masses, time, gravitation, and the average density of the earth. The section on gases considers density, pressure, barometers, manometers and pumps, gases in contact with gaseous, liquid, and solid bodies, the kinetic gas theory, and dissociation. In the section on liquids we find fundamental properties of liquids, density, compressibility, surface tension, adhesion and capillarity, solutions, diffusion and osmosis, viscosity, motion of liquids, and colloids. The concluding section, on solids, treats of crystallography, density, deformation, and friction and concussion.

The author's point of view is frankly atomistic. For example, he defines heat (p. 121) as "A form of energy; work can be done at the expense of a store of heat. The thermal energy is measured by the *Wucht* [*vis viva*] of the irregular molecular motions in a body; in these motions the neighboring particles can possess velocities varying in amount and direction. When work is done at the expense of the thermal energy of a body, a part of this energy disappears, the motion of the molecules is retarded, and the body cools itself off. Doubtless thermal energy is a finite quantity, although it has not yet been found possible to exhaust this energy store, i. e., to take from a body all its thermal energy." Again, under the heading Structure of Liquids (p. 532): "The inner structure of liquids is more complicated than that of gases, * * * In liquids the molecules are so close together that their collisions must occur far more frequently than in gases; wherefore every single molecule must move about a certain average position, which changes with relative slowness." These familiar speculations are thus regarded throughout as fundamental facts, and are so presented.

The German text is very readable. Numerous well-drawn diagrams, and many pictures of apparatus, illustrate the text. Each section is concluded by a list of references to original papers and standard treatises; and extensive name and subject indices complete the whole. *J. E. Trevor*

The Elements of Physics. *A College Text-Book. By Edward L. Nichols and William S. Franklin. In three volumes. New edition, revised, with additions. Vol. I., Mechanics and Heat; xiii + 209 pp. New York: The Macmillan Company, 1901. Price: bound, $1.50.*—The present book is an extensively revised and improved edition of the first volume of Nichols and Franklin's three-volume college textbook of Physics. The matter included is well chosen and arranged; it is explained in a succession of brief and clearly written paragraphs; and the accompanying illustrations, 143 of them, mostly diagrammatic, are well drawn and very helpful. Much compactness and clearness are attained through use of the calculus wherever continuous changes come into consideration. The treatment of Mechanics contains a chapter on Hydrostatics, Hydraulics, and Capillarity, and one on Chemical Action, Crystallography, and Diffusion. The treatment of Heat is arranged in four chapters: Temperature and Thermal Expansion; Calorimetry and Changes of State; Properties of Gases; Thermodynamics and Heat Conduction. It is significant that about twenty pages are devoted to thermodynamics

J. E. Trevor

Physics. *A Text-book for Secondary Schools. By Frederick Slate. 12 × 18 cm; pp. xxi + 414. New York: The Macmillan Company, 1902. Price: bound, $1.10, net.*—This exposition of the rudiments of physics is planned to serve as a textbook for secondary schools. It begins, not as usual with a formal treatment of mechanics, but with a discussion of the "Properties of Solids, Liquids, and Gases." By this is meant the more obvious characteristics of solid, liquid, and aeriform phases, the ideas of weight, specific weight, buoyancy, and pressure, and the phenomena of diffusion, solution, and capillarity. Under the caption Heat and Energy is given a more than usually sensible treatment of thermal phenomena, with introduction of the concepts of work and energy, and, and by way of balancing accounts to date, of the topic of Sound. Light, Magnetism, and Electricity then follow. The author has evidently given careful attention to the order of his topics, and there is much to be said for the arrangement that he has chosen. The most striking feature of this is the distribution of his mechanics. In the first section of the book, ideas concerning force are gained from weight; the rest of the mechanics, the definition of work, center of weight, levers, potential energy, free fall, kinetic energy, gravitation, inertia, mass, etc., is introduced after thermal and thermodynamic phenomena have been studied. This may not be the most natural arrangement; but it has certainly been made effective in the present case.

The book abounds in references to familiar phenomena. Every discussion is led up to in a natural way, and the facts of the subject are nowhere lost sight of by viewing a topic through the spectacles of a mechanistic hypothesis. The author is everywhere careful to say exactly what he means; and yet there is a severity about his style that is likely to lead the schoolboy to regard it as hard reading.

An excellent set of references to collateral reading, which will at least profit the teacher, and an outline of 180 experiments, complete the book. On the whole, it seems fair to say that Professor Slate has produced a thoughtful and well-balanced elementary treatment of his subject. *J. E. Trevor*

Ostwald's Klassiker der exakten Wissenschaften. *No. 131. Experimental-Untersuchungun über Elektricität. By Michael Faraday. XIV. und XV. Reihe. pp. 48. Price: 0.08 mark.*

No. 132. Über die Continuität der gasförmigen und flüssigen Zustände der Materie (1869) und Über den gasförmigen Zustand der Materie (1876). Von Thomas Andrews. pp. 82. Price: 1.40 marks. 12 × 18 cm. Leipzig: Wilhelm Engelmann.

The first of the two new numbers of Ostwald's *Klassiker* contains, in German translation, Andrews's two famous Bakerian Lectures on the critical phenomena of fluids. These first appeared in the London Philosophical Transactions in 1869 and in 1876. The customary annotations and a good biographical sketch of Andrews are appended. The little volume will be very convenient to those who do not possess Andrews's Scientific Papers.

The second number is a continuation of the series reproducing Faraday's experimental researches in electricity. It is particularly interesting, in that it contains a summary of the views to which Faraday was led by his experimental work, and which eventually formed the basis of the theoretical researches of Maxwell and his successors. *J. E. Trevor*

Congrès Internationale d' Électricité. (*Exposition universelle internationale de 1900*). *Rapports et Procès-verbaux. Publiés par les soins de M. É. Hospitalier, Rapporteur général. 16 × 25 cm; pp. 525. Paris: Gauthier-Villars, 1901.* — This handsome volume is the official report of the doings of the International Congress of Electricity, instituted by the French Government in connection with the Paris Exposition. The Congress was organized in five sections, of which the third dealt with electrochemistry. Over half of the large volume is devoted to the Preliminary Reports presented to the sections. Only two of these relate to electrochemistry. The first is a short statement regarding certain aspects of the electrolytic deposition of metals, by H. Bouilhat; and the second is a report on various types of electric furnace, by M. Kellar. The discussions of the third section were limited to electric furnaces, the principles of electrolytic analysis, and the utilization of sea-water for the production of electric energy. A list of the members of the Congress is appended. The papers presented at the meetings are to be published, either in full or in abstract, in a second volume now in preparation. *J. E. Trevor*

Travaux du Congrès Internationale de Physique. *Réuni a Paris en 1900 sous les Auspices de la Société française de Physique, rassemblés et publiés par Ch.-Ed. Guillaume et L. Poincaré. Tome IV. Procès-Verbaux—Annexes—Liste des Membres. 16 × 24 cm; pp. 168. Paris: Gauthier-Villars, 1901.* — The *Travaux* of the International Congress of Physics are completed by the present fourth volume, which contains the minutes of the meetings, some dozen supplementary notes on various subjects, and a list of the members of the Congress. The minutes state what papers were presented at the meetings of the sections, and give an outline of the discussions. They also contain the two addresses by which the president, Cornu, opened and closed the general sittings. Among the supplementary notes may be mentioned the following: On photogalvanography, by N. Piltschikoff; On the distinction that should be maintained between contact electromotive force and the difference of potential at a contact, by H. Pellat; Resistivity and fluidity, by G. Gouré de Villemontée; Galvanometric methods for the measurement of high liquid resistances, by D. Negreano; Note on the report on the normal scale of temperatures, by P. Chappuis.

J. E. Trevor

Vector Analysis. *A Text-book for the Use of Students of Mathematics and Physics. Founded upon the lectures of J. Willard Gibbs. By Edwin Bidwell Wilson. 15 × 22 cm; pp. xviii + 436. New York: Charles Scribner's Sons, 1901.* — Because of the continual appearance of directed quantities in various branches of mathematical physics, a simple means of reckoning with these quantities has long been a desideratum. This need has been responsible for the strenuous efforts made during the past half century and more to introduce the method of quaternions into the study of physics. These efforts have not been widely successful; and it has become increasingly apparent that some more practical form of analysis is wanted. Such a practical vector analysis has been worked out by Gibbs; but it has been hitherto made public only in Gibbs's lectures at Yale University. Some twenty years ago an outline of Gibbs's theory was printed in a small pamphlet for private distribution. Its striking excellences gave rise to a wide demand that the substance of these lectures be issued in book form; but Gibbs has not found the leisure to satisfy this demand. An account of the theory has been given by Heaviside in a chapter of his Electromagnetic Theory; but this exposition was avowedly a makeshift, printed to serve as a stopgap until a suitable special treatise should appear. This treatise we now have; for on the occasion of the issue of the Yale Bicentennial Publications, Dr. E. B. Wilson, an instructor in mathematics in Yale University, was entrusted with the preparation of a work embodying Gibbs's theory. This presentation is based on the lectures given by Gibbs in the academic year 1899–1900. It is cast into the form of an introductory textbook, in which much space is devoted to applications of the method to problems of geometry, mechanics, and physics, for the double purpose of elucidating the theory itself and of making apparent its practical bearing.

The subject-matter of the book is arranged in three parts. The first of these is an elementary exposition of the addition and subtraction of vectors, scalar multiplication, and the scalar and vector products of vectors. It presupposes only an acquaintance with the elements of trigonometry and analytical geometry. The second part considers the calculus in its relations to scalar and vector functions. This part has especial interest for the student of physics. The third part deals with the theory of the linear vector function; and a concluding chapter is concerned with the development of certain higher parts of the theory, a number of applications, and an outline study of the introduction of imaginary or complex variables.

The work is timely, and of great importance. Like the other volumes of the series, it is beautifully printed and bound. It contains a good table of contents, but no index. A prefatory note has been contributed by Gibbs.

J. E. Trevor

A Primer of Calculus. *By Arthur S. Hathaway. 12 × 18 cm; pp. viii + 139. New York: 1901. Price: bound, $1.25.* — This little book is much more than a rudimentary outline of the principles of the calculus. It affords a sound, yet brief, exposition of all that need be contained in an introductory course. The author's method is essentially Newton's method of fluxions. The point of view adopted is that differentiation is an arithmetical process; and that the resulting differentials are numbers like other numbers, and are to be classified as independent or dependent variables according to the like character of the variables from which they are derived. The treatment is, accordingly, thoroughly modern; and it is presented with great clearness and vigor. Curve tracing, partial differentiation, and successive integration are among the topics taken up.

J. E. Trevor

Higher Algebra. *By George Egbert Fisher and Isaac J. Schwatt. 13 × 19 cm; pp. xviii + 615. Philadelphia: Fisher and Schwatt, 1901.* — In this excellent college algebra a very successful effort has been made to develop the subject in a simple and clear manner. Yet all difficulties have been honestly faced and explained. The reason for every step is made clear, and each principle is first illustrated by particular examples. Numerous problems for practice are provided. The treatment is quite comprehensive, including the theory of limits, the convergency of series, the summation of series, and chapters on determinants and the theory of equations.

J. E. Trevor

Joseph Bertrand. Éloges Académiques. *Nouvelle série, avec un éloge historique de Joseph Bertrand, par Gaston Darboux. 11 × 18 cm; pp. xlix + 398. Paris: Hachette et Co., 1902.* — In this new series of the academic eulogies of Bertrand have been incorporated a number of reviews of biographies and of collected works of noted men of science, and several articles of eulogistic character originally published in the *Journal des Savants*. Among the formal eulogies are those on Poinsot, Chasles, Cauchy, and Tisserand. Among the reviews of books are essays relating to the life and works of Papin, Lagrange, Abel, and Galois. The eulogistic articles are on Clairaut, Euler, and Faraday. One of the most interesting of the papers is an analysis of the published record of the trial of Galileo by the Inquisition.

The collection is prefaced by Darboux's eulogy of Bertrand, given in the public sitting of the Academy of Sciences, in December 1901. This is an admirable biographical sketch, and it contains a somewhat detailed analysis of Bertrand's scientific work. The volume is illustrated by a striking portrait in photogravure; and is concluded by a complete bibliography of Bertrand's publications.

J. E. Trevor

Les Eaux souterraines. *Eaux potables; Eaux thermominérales; Recherche; Captage. By F. Miron. (Encyclopédie scientifique des Aide-Mémoire). 11 × 18 cm; pp. 186. Paris: Gauthier-Villars. Price: paper, 2.50; bound, 3 francs.* — This gives a very readable account of the waters of the earth. It is believed that a knowledge of the facts given in this book forms a valuable preparation for the chemist or engineer who has to deal with the problem of a water supply for a large city.

Wilder D. Bancroft

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

On the atomic weight of radium. *S. Curie. Comptes rendus,* 135, *161* (*1902*). — A sample of radium chloride, which is believed to be pure, gives an atomic weight for radium of 225. Mme. Curie believes that this value is correct to within one unit. *W. D. B.*

A contribution to the theory of the sun. *R. Emden. Drude's Ann.* 7, *176* (*1902*). — The present theory is based on Helmholtz's theory in regard to the general circulation of the atmosphere, which explains the passage of heat from the equator to the poles in rapidly moving air layers resulting in air waves. Balloon observations have enabled the author to verify this. The idea of moving layers is applied to the interior of the sun. The theory of sun spots is dealt with at some length. *H. T. B.*

Remarks on the paper by Kahlbaum on mercury air pumps. *F. Neesen. Drude's Ann.* 7, *693* (*1902*). — Exception is taken to Kahlbaum's claim for superiority for his mercury air pump (6, 276). With four pumps under test a Kahlbaum appeared to give the poorest results and required the longest time to pass an X-ray vacuum in a Geissler tube. *H. T. B.*

Reply to F. Neesen. *G. W. A. Kahlbaum. Drude's Ann.* 8, *466*(*1902*). — The author claims that Neesen in testing his pump (preceding review) together with a number of others of different types, does not give the results correctly. By taking Neesen's own numbers the author shows that his pump works faster than all the others, although the tests from which Neesen's figures were taken apparently show the reverse. *H. T. B.*

Two-Component Systems

On the alloys of copper and magnesium. *O. Boudouard. Comptes rendus,* 135, *794* (*1902*). — The freezing-point curve for magnesium and copper has three maxima and four eutectics. The maxima correspond to the compounds $CuMg_2$, CuMg, and Cu_2Mg. *W. D. B.*

On mixtures of sulphur and phosphorus below 100°. *R. Bouloch. Comptes rendus,* 135, *165* (*1902*). — Sulphur and phosphorus form two series of solid solutions and no compounds. The temperature of the quadruple point is 9.8° C. The instable portion of the curve at the phosphorus side has been followed to − 20°. *W. D. B.*

Gypsum. *J. H. van 't Hoff. Zeit. Elektrochemie,* 8, *575* (*1902*). — After a discussion of the equilibrium between $CaSO_4 2H_2O$ and $CaSO_4 \frac{1}{2} H_2O$ (5, 531), the author calls attention to the fact that the dissociation pressure for gypsum and anhydrite is considerably higher than that for gypsum and plaster of Paris. The author states that he believes this to be the first case where a difference of pressure has been observed, depending on the nature of the dissociation. This is incorrect, since Roozeboom found the same thing years ago for the dissociation of calcium chloride hexahydrate into the two tetrahydrates. In a saturated sodium chloride solution, gypsum changes to anhydrite at about 30°.

W. D. B.

Anhydrous ammoniacal cupric chlorides. *A. Bouzat. Comptes rendus,* 135, *292* (*1902*). — The author has determined the heats of dissociation of $CuCl_2 6NH_3$, $CuCl_2 4NH_3$, and $CuCl_2 2NH_3$. *W. D. B.*

Anhydrous ammoniacal copper sulphates. *A. Bouzat. Comptes rendus,* 135, *534* (*1902*). — The author has measured the heats of dissociation of $CuSO_4 5NH_3$, $CuSO_4 4NH_3$, $CuSO_4 2NH_3$, and $CuSO_4 NH_3$. *W. D. B.*

Study of the simultaneous distillation of two non-miscible substances. *E. Charabot and J. Rocherolles. Comptes rendus,* 135, *175* (*1902.*) — Increasing the external pressure increases the relative amount of the less volatile component when one is distilling two non-miscible liquids. *W. D. B.*

On atmospheric hydrogen. *A. Leduc. Comptes rendus,* 135, *860* (*1902*). — The author's measurements confirm the conclusions of Lord Rayleigh (7, 47) as to the amount of hydrogen in the air. *W. D. B.*

Preparation and properties of a vanadium silicide. *H. Moissan and Holt. Comptes rendus,* 135, *78* (*1902*). — The authors have prepared VSi_2 in the electric furnace and by means of Goldschmidt's aluminum reduction. The compound has a density of 4.42, scratches glass, and fuses in the electric furnace.

W. D. B.

Preparation and properties of a new silicide of vanadium. *H. Moissan and Holt. Comptes rendus,* 135, *493* (*1902*). — In the electric furnace, the authors have prepared the compound V_2Si, which is white like silver, and has a density of 5.48 at 17°. *W. D. B.*

Study of cerium silicide. *J. Sterba. Comptes rendus,* 135, *170* (*1902*). — The author has made, in the electric furnace, the compound $CeSi_2$, having a density of 5.67 at 17°. He did not obtain the compound Ce_2Si, which had previously been made electrolytically by Ulik. *W. D. B.*

On the compounds of silicon with cobalt and on a new silicide of cobalt. *P. Lebeau. Comptes rendus,* 135, *475* (*1902*). — In the electric furnace it is possible to make $SiCo_2$, SiCo, and Si_2Co. Of these, the last is new. *W. D. B.*

On the hydration of zinc oxide. *R. de Forcrand. Comptes rendus,* 135, *36* (*1902*). — The heat of hydration of zinc oxide depends upon the temperature at which the oxide has been formed. The author believes that zinc oxide polymerizes with rising temperature. *W. D. B.*

Multi-Component Systems

Electrochemical determinations of the constitution of silver salts. *H. Ley. Zeit. Elektrochemie*, 8, *694* (*1902*). — In the tautomeric nitrogen compounds, the base may be attached to nitrogen or may be attached to oxygen. It is generally accepted that the latter is the case with the sodium salts. It is now found that the solubility of the silver salts is decreased by the theoretical amount when the sodium salt is added. From this the author concludes that the anions are the same in the two cases. *W. D. B.*

On the formation of complex mercury salts. *R. Abegg. Zeit. Elektrochemie*, 8, *688* (*1902*). — From the solubility relations of mercurous bromide, iodide, and sulphocyanate in solutions of the potassium salts of the corresponding acids, the author concludes that the dissolved mercury is not present entirely as mercuric salt, but that a complex salt is formed of potassium mercurous bromide, for instance. *W. D. B.*

On the precipitation of cupric chloride and bromide by sulphuric acid. *G. Viard. Comptes rendus*, 135, *168* (*1902*). — Concentrated sulphuric acid in excess precipitates anhydrous cupric chloride and cupric bromide, very little hydrochloric acid or hydrobromic acid being set free. This would seem to be a case in which there was a decrease of solubility with no common ion. The author recommends the method as a qualitative test for chloride or bromide, the cupric chloride being yellow and the bromide black. *W. D. B.*

Precipitation of chlorides and bromides of cadmium, mercury, and tin by sulphuric acid. *G. Viard. Comptes rendus*, 135, *242*(*1902*). — Excess of concentrated sulphuric acid precipitates the anhydrous chlorides and bromides of cadmium, mercury, and tin. These anhydrous salts are all whitish.

W. D. B.

Synthesis of the anhydrous hydrosulphites of the alkalies and alkaline earths. *H. Moissan. Comptes rendus*, 135, *647* (*1902*). — At low temperatures sulphur dioxide acts on potassium hydride, etc , setting free hydrogen. Quantitative measurements show that the resulting compound is $K_2S_2O_4$, as claimed by Bernthsen, and not $K_2H_2S_2O_4$, as claimed by Schützenberger. *W. D. B.*

On a general process for making metallic nitrides. *A. Guntz. Comptes rendus*, 135, *738* (*1902*). — By the action of lithium nitride on metallic chlorides, lithium chloride is formed and the nitride of the metal. It seems probable that hydrides can be prepared in a similar manner, starting from lithium hydride.

W. D. B.

On barium ammonium and barium amide. *Mentrel. Comptes rendus*, 135, *740* (*1902*). — At 280° the following reaction takes place :

$$Ba + 2NH_3 = Ba(NH_2)_2 + H_2.$$

At higher temperatures there is a reversible formation of nitride from the amide. At ordinary temperatures, ammonia combines with barium, forming $Ba(NH_3)_2$. *W. D. B.*

Direct hydrogenization of acetylene hydrocarbons by the contact process. *P.*

Sabatier and J. B. Senderens. Comples rendus, 135, *87* (*1902*). — Finely divided nickel reduces heptylidene to heptane in presence of an excess of hydrogen and phenyl acetylene to ethyl pentahydrobenzene. Copper reduces phenyl acetylene to ethyl benzene. *W. D. B.*

Reduction of nitro compounds by direct hydrogenization in presence of finely divided metals. *P. Sabatier and J. B. Senderens. Comples rendus*, 135, *225* (*1902*). — Studies on the reduction of α-nitronaphthalene, nitro-methane, and nitro-ethane. With copper the reduction proceeds quietly with formation of the amine. The reduction is more thorough when nickel is used. *W. D. B.*

Direct hydrogenization of the oxides of nitrogen by the contact process. *P. Sabatier and J. B. Senderens. Comples rendus*, 135, *278* (*1902*). — Nickel or copper and hydrogen reduce N_2O to N_2, NO to a mixture of ammonia and nitrogen, NO_2 to ammonia. *W. D. B.*

The reaction in reducing with calcium carbide. *B. Neumann. Zeit. Elektrochemie*, 8, *772* (*1902*). — Contrary to the view of von Kügelgen (5, 414), the author believes that the reduction of oxides by calcium carbide leads to the formation of carbon monoxide. He ascribes the appearance of carbon dioxide to the subsequent reduction of metallic oxides by carbon monoxide. To test this view, he examines the gases given off during the reaction, and finds considerable quantities of carbon monoxide. *W. D. B.*

The reaction in reductions with calcium carbide. *F. v. Kügelgen. Zeit. Elektrochemie*, 8, *781* (*1902*). — An answer to Neumann (preceding review). *W. D. B.*

On the properties and constitution of the zinc peroxides. *R. de Forcrand. Comples rendus*, 135, *103* (*1902*). — From a study of the heat effects the author inclines to the view that the hydrated zinc peroxides are really zinc oxide with water and hydrogen peroxide of crystallization. *W. D. B.*

Artificial production of rubies. *A. Verneuil. Comples rendus*, 135, *791* (*1902*). — The author describes the conditions which must be observed in making rubies weighing over a gram. *W. D. B.*

The precipitation of colloids by electrolytes. *W. R. Whitney and J. E. Ober. Zeit. phys. Chem.* 39, *630* (*1902*). — Reviewed (6, 71) from Jour. Am. Chem. Soc. 23, 842 (1901).

Osmotic Pressure and Diffusion

A consequence of the kinetic theory of diffusion. *J. Thovert. Comples rendus*, 135, *579* (*1902*). — The author deduces that the molecular weight times the square of the diffusion constant should be a constant for any particular solvent. He shows that this is very nearly true for a number of non-electrolytes in water. *W. D. B.*

On the diffusion of hydrogen through platinum. *A. Winkelmann. Drude's Ann.* 8, *388* (*1902*). — The present paper is a continuation of the author's previous paper on the diffusion of hydrogen through palladium (6, 279). Similar experiments are tried for glowing platinum, and it is shown that the diffusion is not proportional to the pressure. It is also shown that the hydrogen molecule is in all probability dissociated, the gas passing through in the atomic state.

H. T. B.

Velocities

On the time constant characteristic of the disappearance in a closed space of the radio-activity induced by radium. *P. Curie. Comptes rendus*, 135, *857* (*1902*). — The author puts forward the formula

$$\log_{nat} (I_0/I) = At,$$

where I is the intensity of radiation at any time t, I_0 is the initial intensity of radiation, and A is a constant. *W. D. B.*

Electromotive Forces

Electrical double layer and absolute potential. *J. Billitzer. Zeit. Elektrochemie*, 8, *638* (*1902*). — The author suspends a metal in a solution and then determines what charge must be given it in order to prevent its moving when a current is passed through the solution. The suspended metal will not move when the potential difference between it and the solution is zero. This gives another method of measuring single potentials, and the values thus obtained differ radically from those obtained by the surface tension methods. Nernst believes that the value hitherto assumed for the calomel electrodes is wrong, but he does not yet claim that the new value is absolutely right. *W. D. B.*

On contact differences of potential. *P. Boley. Comptes rendus*, 135, *454* (*1903*). — The author measures the electromotive force of the cell,

$$M_1 \mid L_1 \mid L_2 \mid M_2,$$

where M_1 and M_2 are amalgams of different metals, and L_1 and L_2 are solutions. He next measures the single potential differences between $M_1 \mid L_1$ and $M_2 \mid L_2$ by the surface tension method, calculates the potential difference $L_1 \mid L_2$, adds the three values together and finds that the sum does not differ appreciably from the electromotive force of the cell. He therefore concludes that the potential difference between the two amalgams is practically zero. If he had chosen his solutions differently he could have found a difference of potential of about 0.1 volt between pure mercury and pure mercury by his method. Consequently its accuracy is not very great. *W. D. B.*

On the potential of alloys and the formation of surface films. *F. Haber. Zeit. Elektrochemie*, 8, *541* (*1902*). — The author applies his view that the reaction determines the potential and shows that an alloy may have a definite potential against the solution with respect to the nobler metal as well as with respect to the less noble metal. This leads to a consideration of the cases in which a true measurement of the potential is not possible, owing to the formation of a surface film having a different concentration from that of the mass of the electrode. *W. D. B.*

On amalgam potentials. *M. Reuter. Zeit. Elektrochemie*, 8, *801* (*1902*). — The author has measured the potentials of sodium amalgams at − 80°. There is a point of discontinuity corresponding to the existence of the compound KHg_{12}. The author draws no conclusion in regard to the rest of the curve, but his data

point to the existence of two series of solid solutions with this compound intervening.
W. D. B.

On the Hall phenomenon and the thermo-electric force. *E. van Aubel. Comptes rendus*, 135, *786* (*1902*). — According to v. Oettinghausen and Nernst, there is a relation between the Hall phenomenon and the thermo-electric force. An alloy of bismuth and antimony has a higher thermo-electric force than pure bismuth, and so has a mass of bismuth and bismuth sulphide. Experiment shows that the Hall phenomena is more marked in these two than in pure bismuth.
W. D. B.

Electromotive behavior of hypochlorous acid and chloric acid. *R. Luther. Zeit. Elektrochemie*, 8, *601* (*1902*). — The author calculates that the normal electromotive force of a hypochlorous acid chlorate electrode is about 1.65 volts; that of a chloride chlorate electrode 1.7 volts, and that of a chlorine chlorate electrode about 1.75 volts.
W. D. B.

Cathodic polarization in dilute sulphuric acid. *J. Tafel. Zeit. Elektrochemie*, 8, *604* (*1902*). — It is found that a very constant potential for each current is obtained when a large polished platinum anode (crucible) and a small platinized cathode are used in dilute sulphuric acid, the distance between the electrodes being fixed. The author first determines this "platinum" value and then replaces the platinum cathode by the lead or other cathode which he wishes to study.
W. D. B.

On the chemistry of the cuprous compounds. *G. Bodländer. Zeit. Elektrochemie*, 8, *514* (*1902*). — The author observes that the electric potential of cuprous copper is −0.454 volt when the normal hydrogen electrode is taken as zero. On the same scale, he puts the electric potential of cupric copper as −0.328 volt. For dilute solutions, cupric copper, on the other hand, is a nobler metal than cuprous copper. Cuprous chloride is more readily soluble in chlorides than cuprous bromide in bromides. This is contrary to the Abegg-Bodländer rule.
W. D. B.

On the relation between the intensity of the voltaic current and an electrolytic yield. *M. Berthelot. Comptes rendus*, 135, *5* (*1902*). — The author shows that cells can be found with such an electromotive force that they will not set free hydrogen in a sulphuric acid voltameter to which pyrogallol has been added when the hydrogen is to be set free under atmospheric pressure, while hydrogen will be set free when there is a reduced pressure in the voltameter.
W. D. B.

Electrolytic actions caused by an alkali-acid cell. *M. Berthelot. Comptes rendus*, 135, *129* (*1902*). — The author arranges combinations of alkali-acid cells so that they will set free hydrogen in a sulphuric acid-pyrogallol voltameter under diminished pressure, but will not when the voltameter is under atmospheric pressure.
W. D. B.

New experiments on the limiting intensity of current corresponding to a visible electrolytic yield in a voltameter. *M. Berthelot. Comptes rendus*, 135, *485* (*1902*). — This is practically a study of residual currents. The importance of it lies in the remark that currents of the same order could produce some of the changes actually going on in the human body. *W. D. B.*

On the use of the Fuchs method in accumulator practice. *C. Liebenow. Zeit. Elektrochemie,* **8,** *616* (*1902*). — In recent years it has become the universal practice to determine the polarization at any moment at each plate by means of an auxiliary electrode, as first suggested by Fuchs in 1875. As such an auxiliary, the author recommends a cadmium plate which, however, must not be allowed to dry in the air. A small spongy lead or peroxide plate may also be used, but must of course be completely charged shortly before using. This method can be used satisfactorily in case the positive and negative electrodes have different capacities, but the author points out in detail the sources of error when the two sets of plates have the same capacity. He also cites an interesting case of a reversal of the poles in one instance due to a bad connection. A temporary short circuit would apparently have a similar effect. *W. D. B.*

Contributions to the theory of some technical reduction and oxidation processes. *G. Bodländer. Zeit. Elektrochemie,* **8,** *833* (*1902*). — The author calculates the change of the free energy with the temperature for the three oxidations, carbon to carbon monoxide, carbon to carbon dioxide, and carbon monoxide to carbon dioxide. He shows that the ordinary technical reductions become intelligible when we consider the free energy while they are quite unintelligible when we consider the heats of reaction. *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the preparation of aluminum. *F. Haber. Zeit. Elektrochemie,* **8,** *607* (*1902*). — This is a lecture on the laboratory preparation of aluminum with special reference to its bearing on technical work. Stress is laid very properly on the importance of a fine adjustment for the anode. The statement that aluminum is always baled out of the bath does not hold for American practice. It is believed by the author that the molten aluminum does not wet the cathode and that there is always a film of pasty electrolyte between the aluminum and the cathode. When the temperature rises too high, the current efficiency may easily drop to 30 percent. *W. D. B.*

Process for obtaining metallic calcium. *W. Borchers and L. Stockem. Zeit. Elektrochemie,* **8,** *757* (*1902*). — Metallic calcium can easily be obtained by the electrolysis of fused calcium chloride. The calcium precipitates as a porous mass, but this lumps together under pressure, giving material containing about 90 percent metallic calcium. Metallic calcium acts on calcium chloride to a certain extent, forming red crystals having the formula CaCl. *W. D. B.*

On the preparation of metallic calcium. *K. Arndt. Zeit. Elektrochemie,* **8,** *861* (*1902*). — The author reports that he has made metallic calcium electrolytically in a much simpler apparatus than that described by Borchers and Stockem (preceding review). *W. D. B.*

On electrolytic precipitation of pure strontium. *W. Borchers and L. Stockem. Zeit. Elektrochemie,* **8,** *759* (*1902*). — Metallic strontium can be obtained by electrolyzing fused strontium chloride with an iron cathode and carbon anode. The iron cathode is placed in a hollow and cooled. *W. D. B.*

Electrolytic deposition of new alloys. *A. Coehn. Zeit. Elektrochemie*, 8, *591* (*1902*). — The author finds, as Berzelius had found before him, that no ammonium alloy can be obtained with a cathode of fusible metal, although ammonium amalgam can be made at the same temperature when a mercury cathode is used. When magnesium and nickel salts are electrolyzed together, magnesium is precipitated with the nickel and improves the deposit. This explains the grounds for Kugel's patent. *W. D. B.*

The electrolysis of fused caustic soda and potash. *M. LeBlanc and J. Brode. Zeit. Elektrochemie*, 8, *697, 717, 817* (*1902*). — The following conclusions are drawn: —

(1) Fused caustic soda containing water shows two decomposition voltages, at 1.3 and 2.2 volts. In anhydrous melts the lower decomposition value disappears.

(2) Quantitative measurements of the gases evolved under different voltages show that each decomposition value has a real significance. At 1.3 volts, hydrogen and oxygen are set free, and sodium and oxygen at 2.2 volts. The current yield of oxygen is never quantitative but increases with increasing current density. The evolution of hydrogen is quantitative below 2.2 volts, provided no free sodium is present. In an anhydrous melt, above 2.2 volts, sodium alone precipitates and not a sodium hydride. It follows, therefore, that pure fused caustic soda contains $Na^{\cdot}$ and OH' ions only, and no $H^{\cdot}$ and no O'' ions.

(3) Fused caustic soda absorbs water readily up to the point of equilibrium and is therefore very hygroscopic.

(4) In fused caustic soda which contains free sodium both hydrogen and oxygen are given off at the anode when the current density is high. This proves that the formation of water at the anode can only be due to the discharge of hydroxyl ions.

(5) A general discussion is given of the phenomena occurring during the technical production of sodium by the Castner process.

Special experiments with fused caustic potash showed that more oxygen dissolved in it than in fused caustic soda, and that it is practically impossible to obtain metallic potassium by means of the Castner process. *W. D. B.*

On the electrolysis of fused caustic soda. *R. Lorenz. Zeit. Elektrochemie*, 8, *873* (*1902*). — The author corrects what seems to be a misunderstanding in the paper of LeBlanc and Brode (preceding review) in regard to some results previously obtained by Sacher. *W. D. B.*

On a new silver voltameter. *P. Farup. Zeit. Elektrochemie*, 8, *569* (*1902*). — The usual current efficiency with a silver potassium cyanide solution varies from 50 percent upwards. It is shown that the loss in efficiency is due to the presence of oxygen and that a cyanide solution may be used as a voltameter for very low currents provided no oxygen is present. It was found that hydrogen which had been purified in the ordinary manner contained enough oxygen to vitiate the results, and that hydrogen must be passed over heated platinum asbestos in order to obtain satisfactory data. *W. D. B.*

On the electrolysis of silver nitrate. *A. Leduc. Comptes rendus*, 135, *23*

(*1902*). — The author finds that an equilibrium concentration tends to be established when silver nitrate is electrolyzed between silver electrodes. Starting with neutral silver nitrate solution, the solution becomes acid, while the acidity decreases somewhat if we start with a distinctly acid solution. The author believes that there is a counter-electromotive force of about 0.03 volt; but does not state whether the solutions were stirred. *W. D. B.*

The electrolysis of mixtures of salts. *A. Leduc. Comptes rendus*, 135, *395* (*1902*). — It is shown that the addition of small amounts of potassium or copper nitrate to a silver nitrate solution has no appreciable effect on the amount of silver precipitated at the cathode. *W. D. B.*

On the electrochemical equivalent of silver. *A. Leduc. Comptes rendus*, 135, *237* (*1902*). — "The amount of silver deposited at the cathode by a coulomb depends usually on a number of factors. It appears, however, that one can obtain an accuracy of 1/10,000 in the determination of the electrochemical equivalent of silver provided one works with a neutral or even slightly basic bath and avoids the formation of acid." It does not appear from this paper how much silver is actually precipitated by one coulomb. *W. D. B.*

A voltameter for small currents. *R. A. Lehfeldt. Phil. Mag.* [*6*] 3, *158* (*1902*). — A glass tube from 0.5 to 1.5 mm bore with platinum electrodes fused in each end is filled with mercury. A drop of mercurous nitrate solution is placed in the middle of the mercury column during filling. It is found that holding the tube vertical and making the upper electrode the anode the drop of nitrate moves upward slowly, the rate proportional to the intensity of the current. The movement may be measured by a scale preferably etched on the glass. For a current density of 0.010 amp/cm^2 the movement would be about 1 mm per day. Practical details are given for its construction. *H. T. B.*

Contribution to the theory of the direct determination of ion velocities. *R. Abegg and W. Gaus. Zeit. phys. Chem.* 40, *737* (*1902*). — The authors discuss the question why the values of Steele (6, 441) for potassium chloride differ slightly from those obtained by the other methods, and show that this is due to cataphoresis through gelatine and that accurate values are obtained when a correction is made for this. *W. D. B.*

The transport number of very dilute solutions. *B. D. Steele and R. B. Denison. Jour. Chem. Soc.* 81, *456* (*1902*). — The authors have used a modification of Noyes's method (5, 275). They studied calcium sulphate, calcium nitrate, calcium chloride, and potassium chloride. The same value for the migration velocity of calcium is obtained from the experiments with calcium chloride and with calcium nitrate; but a high value was calculated from the experiments with calcium sulphate. *W. D. B.*

On the electrolytic preparation of alkali and chlorine by the Solvay-Kellner mercury process. *F. Glaser. Zeit. Elektrochemie*, 8, *552* (*1902*). — The author has worked with a laboratory reproduction of the Solvay-Kellner apparatus. With a distance of 3.5 cm between the electrodes and a 20 percent potassium chloride solution he finds the decomposition voltage at 3.1 volts. His experiments show that the loss in current efficiency is due chiefly to the action of chlorine on the amalgam and not to the action of water on it. High current densities are essential to a high current efficiency unless a diaphragm is used.

W. D. B.

On the electrolysis of alkali chlorides with platinized electrodes. *F. Foerster and E. Müller. Zeit. Elektrochemie*, 8, *515* (*1902*). — More hypochlorite is formed with platinized anodes than with smooth anodes in spite of the fact that platinum black increases the rate of decomposition of hypochlorous acid. The authors have made experiments on the effect of platinizing the anode; on the electrolysis of neutral sodium chloride solutions both with and without addition of potassium chromate; on the lowering of the voltage due to platinizing the anode; on the lowering of the voltage in other solutions. They also give a general description of the behavior of platinized and smooth electrodes.

W. D. B.

On the behavior of hypochlorous acid and its salts during electrolysis. *F. Foerster and E. Müller. Zeit. Elektrochemie*, 8, *633, 665* (*1902*). — The following conclusions are drawn:

(1) On electrolyzing equimolecular solutions of sodium hydroxide, hypochlorite and chloride with increasing voltage, a definite current strength is obtained in the hydroxide solution with the lowest anode potential and with the highest anode potential in the chloride solution.

(2) The discharge of chlorine ions takes place at intermediate values for the anode potential, characteristic for electrolysis of hypochlorites.

(3) At the moment of the anodic discharge there are formed ClO′ ions, chlorate, oxygen, chloride, and oxygen.

(4) This anodic formation of chlorate occurs both in the electrolysis of solutions of free hypochlorous acids and of neutral or alkaline hypochlorite solutions.

(5) In addition, primary chlorate formation is possible in so far as unchanged ClO′ ions are brought into contact with anodic oxygen at potentials greater than — 1.1 volts. This reaction is of slight importance.

(6) Secondary formation of chlorate occurs during the electrolysis of hypochlorite when a fair percentage of hypochlorite oxygen is present as free hypochlorous acid in a considerable portion of the electrolyte; in other words, when the electrolyte has been made acid.

W. D. B.

Electrochemical preparation of ammonium plumbic chloride. *K. Elbs. Zeit. Elektrochemie*, 8, *512* (*1902*). — By using a lead anode and a carbon anode there is no difficulty in preparing plumbic chloride. The carbon anode should carry three-fifths of the current and the current density should be 4 amp/qdm, while the lead anode should carry two-fifths of the current with a current density of 3 amp/qdm. The solution must be cooled.

W. D. B.

On the behavior of lead as anode in sodium hydroxide solutions and on the electrolysis of alkaline sodium plumbate solutions. *K. Elbs and J. Forssell. Zeit. Elektrochemie*, 8, *760* (*1902*). — (1) A lead anode dissolves in caustic soda always as bivalent lead.

(2) When an alkaline sodium plumbate solution is electrolyzed with in-

soluble anodes, lead oxide and oxygen are the primary products at the anode, while lead peroxide is formed secondarily. In consequence, the current yield of peroxide increases rapidly with rising temperature. The rate of formation of lead peroxide depends on the nature of the anode. The anion is chiefly $HPbO'_2$.

(3) Lead peroxide is formed on a platinum anode at 20° at a potential which is 0.23 volt lower than that necessary for the formation of lead oxide and oxygen; this latter precipitation takes place at the same potential as that for the discharge of other oxygen acids on platinum (lead-formic acid anion $HPbO'_2$ according to Hantzsch). Lead peroxide, like platinum and some other metals, has the property of occluding oxygen, and it is probable that the pressure of the occluded oxygen at a given voltage is the same as with platinum.

(4) The single potential of the system $PtPbO_2 \mid n NaOHPbO$ is approximately 0.3 volt lower than the potential at which lead peroxide forms. Therefore, the formation of lead peroxide and the reverse formation of ions of bivalent lead is not a reversible process in alkaline solutions. *W. D. B.*

Experiments on the preparation of tetramethyl-ammonium. *W. Palmaer. Zeit. Elektrochemie*, 8, *729* (*1902*). — When tetramethyl-ammonium hydroxide or chloride is electrolyzed in liquid ammonia a blue color is observed at the cathode, analogous to the blue color obtained by dissolved sodium in liquid ammonia. It seems probable, therefore, that this blue color is due to a solution of tetramethyl ammonium in liquid ammonia. *W. D. B.*

On the electrochemical reduction of ketones. *K. Elbs and K. Brand. Zeit. Elektrochemie*, 8, *783* (*1902*). —

(1) The electrochemical reduction of ketones in alkaline solutions with a lead cathode gives the same products as the chemical reduction with sodium amalgam or with zinc dust and alkali; the process is suitable in many cases as a method of preparing benzhydroles.

(2) The electrochemical reduction of ketones in acid solution (dilute sulphuric acid or phosphoric acid) with lead cathodes leads to pinacones; in case these are instable in presence of acids, the corresponding α- and β-pinacolines are obtained. For this reason the electrochemical reduction is not so generally applicable a method of preparing aromatic pinacones as the process of Elbs and Schmitz of reduction with glacial acetic acid and zinc dust On the other hand, the electrochemical reduction is more intense than that with zinc dust and glacial acetic acid and the two reductions do not therefore run strictly parallel. Both aliphatic and aromatic ketones are reduced, but both secondary alcohols and pinacones are obtained from aliphatic and aliphatic aromatic ketones, while practically only pinacones are obtained from pure aromatic ketones. *W. D. B.*

On the electrochemical reduction of *o*- and *p*-nitrobenzene sulphonic acid in alkaline solution. *K. Elbs and T. Wohlfahrt. Zeit. Elektrochemie*, 8, *789* (*1902*). — When *p*-nitrobenzene sulphonic acid is reduced in alkaline solution, the first product is the potassium salt of azobenzene-*p*-disulphonic acid, and the second the potassium salt of hydrazobenzene disulphonic acid. When *o*-nitrobenzene sulphonic acid is reduced in alkaline solution, there are formed

o-aminobenzene sulphonic acid, benzidine-*o*-disulphonic acid and other substances.
W. D. B.

Electrochemical reduction of *m*-nitrophenol in alkaline and acid solution. *E. Klappert. Zeit. Elektrochemie,* 8, *791* (*1902*). — In a sodium acetate solution, *m*-nitrophenol reduces to *m*-azophenol; in acid solution to *m*-aminophenol sulphonic acid.
W. D. B.

Electrolytic preparation of tetra-alkyl diamido benzhydrols. *F. Esherich and M. Moest. Zeit. Elektrochemie,* 8, *849* (*1902*). — The authors show that, under suitable conditions, tetramethyl diamido benzophenone can be reduced either to the hydrol or to a high melting base which is presumably the corresponding pinacone.
W. D. B.

On the action of the cathode in the electrolytic reduction of aromatic nitrogen compounds. *W. Löb. Zeit. Elektrochemie,* 8, *778* (*1902*). — A brief outline of the experiments which are to be carried out in the author's laboratory to clear up the effect due to the nature of the metallic cathode in laboratory reductions.
W. D. B.

Experiments on the electrolytic oxidation of naphthalene. *A. Panchaud de Bottens. Zeit. Elektrochemie,* 8, *673* (*1902*). — By oxidizing naphthalene in an acetone sulphuric acid solution with platinum or lead electrodes, traces of α-naphtho-quinone were obtained. Traces of phthalic acid were also obtained in the form of the α-monosulphonic acid.
W. D. B.

Determinations of traces of metals in food-stuffs by electrolysis. *L. Medicus. Zeit. Elektrochemie,* 8, *690* (*1902*). — The author decomposes the food-stuffs with concentrated sulphuric acid and precipitates the metals electrolytically after addition of the appropriate salts.
W. D. B.

On the electrical resistance of lead sulphide at very low temperatures. *E. van Aubel. Comptes rendus,* 135, *734* (*1902*). — The resistance of lead sulphide increases with falling temperature. One sample had a resistance of 28 ohms at + 22° C and of 67000 ohms at the temperature of liquid air.
W. D. B.

On the conductivity of solutions at low temperatures. *J. Kunz. Comptes rendus,* 135, *788* (*1902*). — The resistance of solutions of sulphuric acid, caustic soda, and calcium chloride increases with falling temperature. The author believes that the chief cause of this is the increasing viscosity.
W. D. B.

On a new indicator for acidimetry. *L. J. Simon. Comptes rendus,* 135, *437* (*1902*). — Ferric isopyrotritarate shows two color changes, one similar to methyl orange and one to phenolphthaleine. With this single indicator one can therefore titrate each of the first two hydrogens in phosphoric acid, a mixture of zinc sulphate and sulphuric acid, etc., etc.
W. D. B.

On the ionization of salt flames. *G. Moreau. Comptes rendus,* 135, *898* (*1902*). — It is found that the degree of ionization decreases when the distance from the electrodes increases. This is in harmony with Wilson's views and not with those of Arrhenius.
W. D. B.

On the pyrogenic formation of anthranilic acid from *o*-nitrotoluene. *W. Löb.*

Zeit. Elektrochemie, 8, *775* (*1902*). — When the vapor of *o*-nitrotoluene is brought into contact with a red hot wire, the reaction is almost explosive. The reaction runs nicely with the formation of anthranilic acid when the vapor of *o*-nitrotoluene is mixed with water vapor. This is done by distilling the two liquids in a flask with a reverse cooler. *W. D. B.*

Note on the pyrogenic preparation of diphenyl by means of the electric current. *W. Löb. Zeit. Elektrochemie*, 8, *777* (*1902*). — Diphenyl is prepared from benzene by passing the vapor of the latter over a red hot carbon filament. If the carbon filament is too hot, charring takes place, thus increasing the cross-section of the filament and cutting down the current and the temperature. By working with a constant voltage, the temperature of the filament is kept automatically just at the point at which no charring occurs. It is, of course, essential that no oxygen shall be present. *W. D. B.*

On the behavior of bromine under the influence of high potential discharges. *K. Kellner. Zeit. Elektrochemie*, 8, *500* (*1902*). — The author works with a Tesla transformer, giving 250,000 to 300,000 volts. A solid yellow mass is formed from the liquid bromine, but it is not yet known what this is. *W. D. B.*

The purification of water by ozone. *H. J. van 't Hoff. Zeit. Elektrochemie*, 8, *504* (*1902*). — A description of the Vosmaer-Lebret processes. The capacity of the machine is 2,500 watts with a voltage of 10,000 volts, and a special arrangement secures the silent discharge and eliminates the possibility of sparks or arcs. An ozone concentration of 3 mgs per liter is found sufficient for sterilizing purposes. *W. D. B.*

The Siemens Ozone Water Works at Wiesbaden and Paderborn. *G. Erlwein. Zeit. Elektrochemie*, 8, *881* (*1902*). — A description of the new water works at Wiesbaden and Paderborn where the water is purified by means of ozone. To purify two hundred and fifty cubic meters of water per hour, forty-eight ozonizers are used. These work under a potential difference of 8,000 volts. *W. D. B.*

Electrically heated furnaces with platinum foil covering. *E. Haagn. Zeit. Elektrochemie*, 8, *509* (*1902*). — A description of some of the newer Heraeus furnaces which are covered with platinum foil only 0.007 mm in thickness. The furnaces here described are only 2 cm in internal diameter, but have since been made running up to 20 cm internal diameter. *W. D. B.*

Dielectricity and Optics

The absorption of ultra-violet, visible and ultra-red rays in thin metal layers. *E. Hagen and H. Rubens. Drude's Ann.* 8, *432* (*1902*). — The present paper stands in close relationship with the authors' work on the reflection from metal surfaces. An attempt is made to prove Maxwell's electromagnetic theory for the relation between the absorption constant for long waves, as defined, and the electric conductivity of the metal. Silver, gold, and platinum surfaces, deposited from cathode discharge, are used in the experiments. Curves for the absorption coefficient for different wave-lengths from 0.2 to 1.5μ are given. A historical sketch of previous work and a comparison with the authors' work is included, but no definite conclusions can as yet be arrived at in relation to Maxwell's theory on account of the small number of metals tried and the limited number of observations for the long waves. *H. T. B.*

The effect of self-induction in the ultra-violet part of the spark spectra. *E. Néculcéa. Comptes rendus*, 135, *25* (*1902*). — The effect of self-induction is to cut out a number of the tin lines in the ultra-violet spectrum. *W. D. B.*

On the velocity of the X-rays. *P. Blondlot. Comptes rendus*, 135, *666, 721, 763* (*1902*). — The author shows that the velocity of the X-rays is the same as that of the Hertz waves or of light in air. He concludes that the hypothesis of Stokes and of Wiechert is the best. "The Roentgen rays consist of a succession of independent pulsations, starting from the points where the molecules hurled from the cathode meet the anti-cathode and beginning at the moment of this meeting; these pulsations are transversal and move through the ether like the waves of light and with the same speed. What distinguishes the Roentgen rays from the spectrum rays is that they consist of isolated, very brief pulsations instead of continuous vibrations of the ether." *W. D. B.*

On the analogy between the X-rays and the Hertz waves. *P. Duhem. Comptes rendus*, 135, *845* (*1902*). — Attention is called to the theory of Helmholtz, which recognizes the possibility of longitudinal waves having the same velocity as light. The suggestion is made that the X-rays are these longitudinal waves of Helmholtz and not the transversal waves of Stokes (preceding review). *W. D. B.*

On the formation of cathode and Roentgen rays. *T. Tommasina. Comptes rendus*, 135, *319* (*1902*). —

1. The diffuse reflection of the anode flow is sufficient to create cathode and Roentgen rays.
2. The phenomenon occurs even when the anti-cathode is grounded.
3. The multiple reflection from a vacuum tube at the desired degree of exhaustion causes the partial change of the anode flow into cathode and Roentgen rays. *W. D. B.*

On the note of T. Tommasina. *J. Semenow. Comptes rendus*, 135, *457* (*1902*). — The author claims that Tommasina's apparatus is one in which the poles are reversed and that therefore he means cathode when he says anode (preceding review). *W. D. B.*

On Becquerel rays and radio-active substances. *F. Giesel. Zeit. Elektrochemie*, 8, *579* (*1902*). — A brief exposition of our knowledge of the subject. The author distinguishes three groups of substances, those which are intensely and constantly radio-active, those which are slightly and constantly radio-active, and those whose activity decreases with time. Radium, actinium and Giesel's unnamed element belong to the first group, uranium and thorium for the present to the second group, polonium and all others to the third.
W. D. B.

The magnetic and electric deflection of the Becquerel rays and the electromagnetic mass of the electrons. *W. Kaufmann. Comptes rendus*, 135, *577*

(*1902*).—The author has confirmed the theoretical conclusions of Abraham. He finds $e/\mu_0 = 1.84 \times 10^7$. The electron is therefore an electric charge distributed over a very small volume or surface (10^{-13} cm^3). *W. D. B.*

Dissociating action of different parts of the spectrum on matter. *G. Le Bon. Comptes rendus*, 135, *32* (*1902*).—The author divides substances into three groups depending on their ability to discharge an electroscope when they are illuminated by particular rays. The first group consists of substances sensitive to radiations not exceeding 0.295μ. These are amalgamated tin, amalgamated copper, amalgamated zinc, aluminum, magnesium, zinc, amalgamated lead, and mercury containing traces of tin. As a less sensitive subdivision of the same group, come gold, cobalt, pure mercury, tin, cardboard, wood, and the phosphorescent sulphides.

The second group is sensitive only to radiations having a wave-length less than 0.295μ. These are cadmium tin, silver, lead, etc. The third group is very sensitive only to radiations less than 0.252μ in length. These substances are gold, platinum, copper, iron, nickel, organic substances, and many salts. *W. D. B.*

Crystallography, Capillarity and Viscosity

The spontaneous lowering of the surface tension of water, water solutions and emulsions. *A. Pockels. Drude's Ann.* 8, *854* (*1902*).—A freshly formed surface shows the normal surface tension, but this rapidly sinks to an abnormally low value as the surface becomes contaminated. The surface tension in the abnormal state increases or diminishes with an increase or diminution of the surface. Convection currents are set up in the liquid on account of the difference in tension arising from a contaminated surface. The impurity may be imparted to water either from the glass-containing vessel, the dust in the air, or substances diffusing from the interior of the water to the surface. Experiments show that the spontaneous lowering of the surface tension takes place for organic solutions as well. *H. T. B.*

On the use of stationary capillary waves as a diffraction grating, and the surface tension of water and mercury. *A. Kalahne. Drude's Ann.* 7, *440* (*1902*).—Matthiessen's method of stationary capillary waves is used. Instead of employing the formula of Kelvin for determining the capillary constant from the measurement of the waves as in the experiments of Grunmach, the author, at the suggestion of Quincke, employs the waves as a diffraction grating. To do this the middle portions of the hyperbolas which approach nearly to a series of straight lines are used and a small correction is added for curvature. The hyperbolas result from the impinging of the circular waves sent out from two equal tuning forks placed opposite each other. The measurements were made for water and mercury, and the results, the author claims, are of an order of accuracy of 1 part in 1000. The surface tension of pure water against moist air at atmospheric pressure and 18° C is found to be 7.520 mg per mm, or 73.77 dynes per cm. That of mercury is found to be variable, but the greatest value obtained was 44.0 mg per mm. *H. T. B.*

ACTION UPON METALS OF SOLUTIONS OF HYDROCHLORIC ACID IN VARIOUS SOLVENTS[1]

BY HARRISON EASTMAN PATTEN

INTRODUCTION

There is an erroneously prevailing idea that chemical action cannot take place unless the substances which are to react constitute a system capable of conducting the electric current. Little is said as to the limits, either of the E. M. F. to be employed to pass this current, or of the quantity of current which this E. M. F. must produce in order that the system may be in a proper condition to undergo chemical action. The function of temperature in facilitating chemical action is left somewhat vague, too; especially as to the range of temperature within which substances are or are not "ionized." Some go so far as to assert that no chemical action can take place without "ionization", meaning by the term "ion", a small body, an element or a complex, which bears a charge of electricity. On this basis it would follow that chemical action must take place whenever a system is capable of conducting electricity, whether a current be actually passing through the system or not. Other chemists use the term "ion" in the sense that it is that part of a chemical compound which retains its identity while undergoing chemical change. Thus, ferrous iron is not to be called a radical, yet to say that iron is reacting does not express the whole truth. The word "ion" used in this sense may be helpful, but is sure to be confused with the conception of free charged ions, as put forth by Arrhenius, unless careful discrimination be made.

The facts, that water gives numerous solutions which conduct electricity, and that certain reactions were found to be

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[1] A paper read at the Washington meeting of the American Chemical Society, December 30, 1902.

peculiar to aqueous solution led Ostwald to state[1] without adequate investigation that non-aqueous solutions do not conduct the electric current. The fact that a number of reactions take place instantaneously in aqueous solutions which conduct, led others to promulgate the idea (*very* slightly qualified) that chemical action cannot go on in absence of water, since water alone gives "ions" and "ions" are needed for reaction to take place; and then when it was shown that instantaneous chemical reaction[2] takes place in solutions which conduct less than a dry air-gap, it was suggested[3] that benzene itself possesses dissociating properties; and that the evidence is not clear that every precaution was taken to dry the substance and exclude moisture in Prof. Kahlenberg's experiments; and finally that "the experiments have no bearing on the theory of electrolytic dissociation."

HISTORICAL

In this connection a review of the work done upon the influence of moisture upon chemical reaction is of interest. In 1802 Mrs. Fulhame[4] observed that presence of moisture is necessary for the reduction of salts of gold by "phosphorated ether" or by hydrogen. Higgins[5] in 1814 found that "dry muriatic acid has no action on dry calcareous earth, while these substances readily unite if moisture is present." In 1837 Bonsdorf[6] showed that dry air free from carbon dioxide does not act upon clean, dry, potassium, arsenic,[7] bismuth, lead (commercial or pure), zinc, cadmium, iron, or copper. In 1838 Regnault[8] found that dry chlorine and dry olefiant gas would not unite in diffused day-

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[1] Grundriss der Allgemeinen Chemie, 390, 391.

[2] L. Kahlenberg. Jour. Phys. Chem. 6, 1 (1902).

[3] Lectures delivered before the Brooklyn Institute, and published in the American Druggist and Pharmaceutical Record, Oct. 27, 1902, by H. C. Jones.

[4] Thomson. A System of Chemistry, Vol. II., 544 (1802).

[5] Higgins' Experiments and Observations on the Atomic Theory (1814).

[6] Pogg. Ann. 1837, 41, 293; 42, 325 (1837).

[7] Bergmann is given the priority in the case of arsenic.

[8] Ann. Chim. Phys. (2) 60, 176 (1838).

light. It was shown by E. A. Parnell[1] that dry hydrogen sulphide will not act upon dry salts of lead, mercury, or copper. In a footnote Andrews[2] states that dry chlorine at ordinary temperatures does not act upon zinc, copper, or iron filings; and that dry bromine at ordinary temperatures does not act upon dry metals. In 1867 Kolb[3] found that dry oxides and hydroxides of calcium, barium, magnesium, sodium, and potassium do not gain weight in an atmosphere of dry carbon dioxide.

Wanklyn[4] in 1869 noted that sodium and chlorine do not unite, but he did not state whether moisture alone added would cause combination. Dubrunfaut[5] thought that water favors the combustion of carbon; but Dumas[6] showed that pure graphite is completely consumed in oxygen dried by sulphuric acid.

The work of Dumas, however, loses significance since it has been experimentally demonstrated[7] that gases dried over sulphuric acid still give up a weighable amount of water to phosphorus pentoxide. In 1876 Cowper[8] allowed dry chlorine to act upon metals and found that presence of moisture was necessary for action to take place. Pringsheim[9] in 1887 and Dixon and Harker[10] in 1890 showed that dry hydrogen does act upon dry chlorine in absence of moisture, though more slowly than with water present. Dixon[11] and Victor Meyer[12] have shown that the union of hydrogen and oxygen is facilitated by presence of

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[1] B. A. Reports, 1841, 51.

[2] Trans. Royal Irish Acad, 19, 398 (1842); also Scientific Memoirs, 1889, 90.

[3] Comptes rendus, 64, 861 (1867); also De Bray, Ibid. 26, 603 (1848).

[4] Chem. News, 20, 271 (1869).

[5] Comptes rendus, 73, 1395 (1871).

[6] Ibid. 74, 13 (1872).

[7] 0.000002 gram H_2O per liter of air. Morley. Amer. Jour. Sci. [3] 30, 140 (1885).

[8] Jour. Chem. Soc. 43, 153 (1883). Cf. Wanklyn. Chem. News, 20, 271 (1869).

[9] Ann. Chim. Phys. 1887, 421.

[10] Owens College Researches, 1.

[11] Phil. Trans. 1884.

[12] Ber. chem. Ges. Berlin, 1893.

water vapor. Holt and Simms[1] find that dry oxygen does not act upon dry sodium or dry potassium; and Baker[2] finds the same for carbon, phosphorus, sulphur, and tellurium, while he also finds that boron, arsenic, antimony, and selenium are acted upon by oxygen in absence of moisture.

Sabatier and Senderens[3] in 1893 found that dry nitrogen peroxide does not act upon dry sodium at ordinary temperatures, but on heating, the sodium is gently oxidized. Nickel, cobalt, and iron reduced by hydrogen burn with incandescence in dry nitrogen peroxide to Fe_2O_3, Co_4O_5, and $NiO + Ni_2O_3$; while copper, cobalt, and nickel give with dry N_2O_4 — greatly diluted with dry nitrogen to avoid the oxidation mentioned above — the compounds Cu_2NO_2, Co_2NO_2, and Ni_2NO_2; iron is acted on similarly, but the compound is not well established as yet. The copper used may be reduced by carbon, or by hydrogen, so that the action is not due to the formation of a hydride of the metals. The authors state definitely that moist air immediately acts upon these metallic nitroxyls, giving nitrous vapors.

In 1884 Dixon[4] observed that the union of carbon monoxide with oxygen is influenced by the presence of moisture, but in 1896 found[5] that freshly prepared carbon monoxide unites with oxygen in absence of moisture. In 1894 Baker[6] showed that dry nitric oxide and oxygen will not combine. Dixon[7] first found that moisture is necessary for the decomposition of cyanogen by oxygen, but later[8] succeeded in exploding a mixture of dry cyanogen in dry oxygen. Baker[9] was able to burn dry carbon bisulphide in dry oxygen; he also showed that dry carbon

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[1] Jour. Chem. Soc. 65, 432 (1894).

[2] Ibid. 65, 611 (1894).

[3] Bull. Soc. Chim. Paris, 9, 669 (1893).

[4] Phil. Trans. 1884; B. A. Report, 1880, 503; Jour. Chem. Soc. (Abstr.) 1903.

[5] Jour. Chem. Soc. 69, 774 (1896).

[6] Ibid. 65, 611 (1894).

[7] Ibid. 49, 384 (1886).

[8] Ibid. 69, 759 (1896).

[9] Phil. Trans. 1888.

unites with dry oxygen but with no accompanying glow.[1] Cohen[2] states that dry hydrogen chloride is without action upon aluminum or sodium.

In 1892 Veley[3] showed that calcium oxide does not combine to any appreciable degree with carbon dioxide or with sulphur trioxide at temperatures below 300° C. And in 1894 he found that dry chlorine does not combine with dry calcium oxide at ordinary temperatures to form the so-called bleaching powder, up to 300° C, at which temperature a partial replacement of oxygen by chlorine takes place.[4] Baker[5] states that moisture is needed in order that the following substances may unite: lime with sulphur trioxide; cupric oxide with sulphur trioxide; ammonia with hydrogen chloride. Hughes and Wilson[6] showed that dry hydrogen chloride probably does not act upon calcium carbonate, and Hughes[7] showed that dry hydrogen sulphide does not act upon metallic salts, but does act upon mercuric chloride dissolved in absolute alcohol, giving a greenish yellow precipitate; and that dry hydrogen chloride *does* act upon manganese dioxide. Baker[8] sublimed dry ammonium chloride from dry lime without liberating ammonia, but in the same research showed that dry nitrogen tetroxide decomposes on heating; likewise he decomposed dry carbon disulphide, potassium chlorate, silver oxide, and lead acetate, and changed dry amorphous phosphorus to the yellow modification by heat, and the dry yellow phosphorus back to the amorphous state by the action of sunlight. Shenstone and Cundall[9] changed dry oxygen to ozone by application of electrical energy.

In January, 1902, Kahlenberg[10] showed that the oleates of

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[1] Phil. Trans. 1888; (Abstr.) 571.
[2] Chem News, 54, 102 (1886).
[3] Jour. Chem. Soc. 63, 831 (1893).
[4] See also F. Winteler. Zeit. anorg. Chem. 33, 161 (1902).
[5] Jour. Chem. Soc. 65, 611 (1894).
[6] Phil. Mag. 34, 117 (1892).
[7] Ibid. 35, 533 (1893).
[8] Jour. Chem. Soc, 1894, 611.
[9] Ibid. 51, 610 (18 7).
[10] Jour. Phys. Chem. 6, 1 (1902).

copper, nickel and cobalt dissolve in benzene to form non-conducting solutions and that dry hydrochloric acid gas precipitates instantly the chlorides of these metals; the same result is obtained by adding a benzene solution of $SnCl_4$, PCl_3, $AsCl_3$, or $SiCl_4$, although all of these solutions are as good insulators as benzene itself. Dry hydrogen sulphide passed into these dry oleate solutions precipitates the sulphide of the metal; arsenic and tin sulphides were similarly formed by the action of dry H_2S on a benzene solution of $AsCl_3$ and of $SnCl_4$; a petroleum ether solution of $AsCl_3$ gives with H_2S arsenic sulphide more readily than the benzene solution. Dry hydrogen chloride does not unite with dry ammonia, but in the presence of dry benzene vapor ammonium chloride is instantly formed. Similarly dry pyridine unites with dry hydrogen chloride in benzene solution. He does not state whether dry hydrogen chloride will not unite with dry pyridine in absence of a third substance.

In 1902 W. D. Patton[1] showed that dry hydrogen chloride dissolved in dry benzene will not react with dry soda lime; and that an infinitesimal amount of water is not sufficient to cause the reaction to go. J. W. Mellor and E. J. Russel[2] find that an electric spark causes combination of dry hydrogen with dry chlorine instantaneously and completely. While neither heat nor sunshine causes this action, action between the two dried gases does go on though slowly. Clearly moisture is not needed. Jatindrath Sen[3] has shown that dry ammonia gas acts upon dry mercurous chloride.

To study further the action of chemicals upon each other in solutions where the conduction of electricity is extremely slight, I have dissolved gaseous hydrochloric acid in various solvents and brought the resulting solutions into contact with a number of metals and carbonates. In some cases hydrogen or other gas was evolved from the metal and a chloride of the metal formed. In others one metal was attacked, and this metal

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[1] In this laboratory.

[2] Jour. Chem. Soc. 81, 1273 (1902).

[3] Zeit. anorg. Chem. 33, 201 (1902).

deposited from solution upon a second metal. In still others, no gas appeared and no deposition of metals upon each other was noted, but still some metals were corroded. Some solvents of themselves attack the metals. The experimental work was conducted as follows: —

EXPERIMENTAL METHOD AND APPARATUS

The hydrochloric acid gas was evolved by dropping an aqueous solution into concentrated sulphuric acid; the gas then passed over fused calcium chloride contained in a tower 30 cm high and 3 cm in diameter, through two wash-bottles containing concentrated sulphuric acid; over phosphorus pentoxide spread on dry pumice stone contained in (1) a tower 40 cm high and 4 cm in diameter, (2) a bottle 10 cm high and 5 cm in diameter, and (3) through a tower of the same dimensions as No. 1. From here the gas was passed into the bottle which contained the clean, dry metals and the anhydrous solvent. From this bottle the gas was led away through three tubes 2 cm in diameter and 15 cm long, containing phosphorus pentoxide, connected in series, then through a sulphuric acid wash-bottle, and finally absorbed in potassium hydrate solution. No cotton was used in any of this work since phosphorus pentoxide decomposes it. Where necessary, glass wool which had previously been heated, served to keep particles of phosphorus pentoxide from being carried over by the gas.

Two methods of preparing the solvent were used. 1. The dehydrated redistilled solvent was sealed up in a test-tube, placed in a clean, dry bottle which contained the clean, dry metals and the bottle closed with a rubber stopper, through which passed two tubes; one reached to the bottom of the bottle so that the hydrochloric acid gas when passed in might bubble through the solvent, the other tube served as an exit for the gas. Before any hydrochloric acid gas was run through into this bottle (with the test-tube containing the solvent still unbroken), was run a stream of hydrogen purified by the usual means and dried over sulphuric acid, calcium chloride and phosphorus pentoxide as rigorously as the hydrochloric acid just described. This hydrogen was left running all night and the experiment finished in the morning, when the bottle was closed by screwing down the pinch-cocks, connected to the hydrochloric acid generator and the pinch-cocks next the generator opened first and allowed to stand for fifteen minutes in order that any moisture from the air in the tube by which connection had been made might be absorbed.

Before taking hydrochloric acid from the generator at all the gas was allowed to run through all the train until there could be no question that all air had been displaced. Then the gas was run into the bottle under considerable pressure in order to prevent the solvent rushing back into the drying towers — hydrochloric acid gas is much more soluble in some of the solvents used than might be supposed.

2. The second method of preparing the solvent is that given in detail under the experiment in which benzene is used as solvent. Owing to the controversy concerning the action of a solution of hydrochloric acid gas in this solvent, I have given every point. To save repetition, the reader is referred to this experiment. In other cases, to relieve all doubt as to the conditions of experiment, I have been very explicit even at the risk of repetition.

Method 1 is more satisfactory for solvents which are self dehydrating; that is, which decompose water with formation of oxychlorides and hydrogen chloride gas. While it is true that the oxychlorides might promote chemical action, the conductivity measurements show that at least no electrolytic dissociation exists in these solutions.[1]

Method 2 was used for solvents which dissolve water without undergoing decomposition. It was found that method 1 was not satisfactory for these liquids. The first, second and third experiments with chloroform were carried out according to

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[1] I mean simply that it would be carrying the theory of electrolytic dissociation to an extremity to claim ionization in a solution or solvent which conducts electricity less well than a dry air-gap. That we do get a current even across the air-gap is unquestionable, since the voltmeter used as ammeter is deflected. But that this current is carried *electrolytically* is a point which requires experimental proof more rigid than any yet at hand.

method 1; also the first experiment with carbon tetrachloride. The action of the hydrogen chloride solutions upon magnesium and aluminum indicates that all moisture had not been eliminated, especially as the last experiments with carbon tetrachloride and chloroform as solvents gave evolution of gas upon zinc alone; and the electrical conductivity of the last solutions was much less than that of the solutions prepared by method 1.

RESULTS

Chloroform as Solvent. — Chloroform from Kahlbaum was dried for some weeks over a large surface of fused calcium chloride and distilled from a dry flask and condenser into a receiver protected by a calcium chloride tube. The first runnings of the chloroform were rejected and the final portion, which boiled at 60° C under 741.7 mm, was quickly sealed up in dry glass tubes. The moisture taken up during the necessary transfer through the air is extremely slight. The metals used were carefully cleaned by scraping with a sharp knife, heated, and placed in the bottle along with a tube of the sealed up chloroform and treated as described in full under method 1.

The chloroform had no action upon the metals. When hydrochloric acid gas was run in, gas was evolved upon zinc, cadmium, and magnesium. The approximate degree of violence of this action as estimated by my eye is given in Table I. by the subscripts to the H's used to denote evolution of gas. As this action progressed, a black deposit, fine and sooty, appeared on magnesium, aluminum, chromium, manganese, lead, tin, bismuth, and antimony, and small aggregations of this black deposit floated about in the solution. Doubtless it was carbon. This black deposit did not appear in either of the other three chloroform experiments. An accident happened in carrying out this experiment. The hydrochloric acid gas was admitted under slightly reduced pressure so that the solvent was drawn back up the tube by which the gas entered, into the P_2O_5 drying tower. When extra pressure was put on to force the solvent back into its flask, the stopper was blown from one of the drying towers and some air got in, but no moisture could have reached to the flask containing the metals and chloroform, since it was well protected by the remaining phosphorus pentoxide drying towers, two on each side. The chloroform came for a short time in contact with the rubber tube connecting the flask to the drying tower; however, the negative results of this experiment will stand: Iron, nickel, copper, silver, gold, platinum, arsenic, tellurium, and palladium remain perfectly bright in presence of the chloroform solution of hydrogen chloride; aluminum, chromium, manganese, lead, tin, and antimony evolve no gas. Magnesium gives off very much less gas than comes from the zinc. Calcite and witherite are not attacked. Contact of the metals with each other makes no difference in the rate at which gas is evolved. This experiment was carried out at room temperature, 22° C. Finally the solution was siphoned out of the flask under pressure into a platinum crucible and its electrical conductivity tested. Using a direct current of 110 volts pressure and a Jewell voltmeter of 20,000 ohms resistance as an ammeter, I got a deflection of 5 volt divisions, which corresponds to a current of 0.00025 ampere. The bottom of the crucible served as one electrode; the platinum disk serving as the other electrode was 1.75 cm in diameter, and the distance between electrodes was about one millimeter.

Experiment 2. — A second sample of dried chloroform was treated exactly as in the first experiment. The results are given in Table I. Zinc, aluminum, magnesium, tin, and lead are acted upon by the HCl solution with evolution of gas. The violence of action is in the order just given. No black deposit was observed; possibly it came from dissolved rubber in the first experiment. The other metals were not acted upon.

Experiment 3. — A third sample of dried chloroform was treated as in experiments 1 and 2. The hydrogen chloride solution acted upon zinc, aluminum, magnesium, tin, and lead, in the order given, with evolution of gas. Nickel, lead, and tin are very slightly corroded. Antimony turns black. See Table I.

Experiment 4. — This sample of chloroform was prepared independently of the other three samples just described. It was dried two weeks over a large surface of fused calcium chloride, the edges of which remained perfectly sharp, and then distilled from fresh fused calcium chloride out of contact with air in an apparatus which had been dried in a current of clean air and then allowed to stand twenty-four hours in contact with the phosphorus pentoxide drying train. The metals, magnesium, aluminum, zinc, and cadmium, used were polished by scraping and left in the receiver (into which the chloroform distilled) during the process of drying. No tarnish was observed on any one of them. The chloroform distilled at 59.9° C under 746 mm.

Thus the solvent was prepared dry and by means of tubes fitted with glass stopcocks attached to the receiver, dry hydrochloric acid gas was run in and its action upon the metals observed. Magnesium and aluminum show no evolution of gas; a very minute quantity of gas comes off upon cadmium; zinc is vigorously attacked, rather more hydrogen being evolved than in a normal HCl solution in water. The conductivity of this solution is very much less than that of a dry air-gap. Using the platinum crucible before described, 110 volts sent 0.00003 ampere through it. On standing twenty-four hours both magnesium and aluminum were considerably corroded, though I saw no evidence of evolution of gas upon them at any time. A qualitative analysis of the chloroform solution — which was siphoned off by pressure of dry air — showed zinc and aluminum in quantity, a fair amount of magnesium, and a slight trace of cadmium. This indicates that the corrosion of magnesium and aluminum is facilitated by the solution of zinc chloride in the chloroform.[1] Probably the hydrogen is united with the carbon of the chloroform to give hydrocarbons. See Table I.

Carbon Tetrachloride as Solvent. — Schuchardt's C. P. carbon tetrachloride was dried over fused calcium chloride for three days. It boiled at 75° C under 741.7 mm, and was sealed

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[1] Compare this with the action of aqueous solutions upon magnesium, aluminum, sodium, and sodium and potassium amalgams as treated by L. Kahlenberg and by G. Perneckes in the Transactions of the Wisconsin Academy of Sciences, 1903.

up in a glass tube as described under "Method 1." The solvent itself is without action upon the metals used. As soon as the hydrogen chloride gas was run in, an active evolution of gas upon the zinc was noticed. Magnesium was not acted upon, remaining perfectly bright for two hours, when a black deposit appeared upon it. Aluminum was attacked less vigorously than the zinc, but maintained a steadier evolution of gas. The evolution of gas upon zinc gradually decreased, a white coating forming upon the metal. At first tin was merely corroded, but after about twenty minutes gas was given off upon it and finally a brisk evolution set in which proved to be steadier than that upon the zinc. Lead was corroded, a white crust, doubtless $PbCl_2$, forming upon it. Iron was attacked with the formation of a red crust — $FeCl_3$. Cadmium was very slightly attacked, some minute bubbles rising from it at long intervals. Nickel, copper, silver, antimony, bismuth, manganese, chromium, arsenic, tellurium, platinum, palladium, gold, and calcite and witherite were not acted upon; no gas was evolved, and their luster remained undimmed. The conductivity of this solution after being siphoned off through the air was less than that of a dry air-gap. Contact of one metal with another made no difference in any of the above reactions.

Experiment 2. — A sample of the same carbon tetrachloride was left drying for two weeks over fused calcium chloride and then distilled from fresh calcium chloride in a dried apparatus (as given in method 2) and dry hydrogen chloride run in. The metals magnesium, zinc, cadmium, and aluminum were used. Zinc is immediately attacked and evolves gas with considerable rapidity, but after an hour a protective coating begins to form on the zinc, $ZnCl_2$ in all probability. After twenty-four hours, the metals, except zinc, are still unacted upon, while the zinc is completely coated over with a white crust. The solution was siphoned off and its conductivity tested: 110 volts across one millimeter in the platinum crucible passed a current of 0.000066 ampere; a dry air-gap allows 0.0001 ampere to pass, using the same pressure and electrodes. Before this test it is unquestionable that a trace of moisture was taken up while the solution was being poured through the air into the crucible where the conductivity was tested. The anhydrous solution which acted upon the metals had in all likelihood a still lower conductivity.

Ethyl Chloride as Solvent.—I. Schuchardt's c. p. ethyl chloride was treated as in method 1. The bottle containing the metals and the ethyl chloride tube was cooled to 0° C and the ethyl chloride broken from the tube. Of itself ethyl chloride has no action upon the metals at that temperature. When dry hydrogen chloride gas is passed in, the solution acts upon zinc at once with brisk evolution of hydrogen. Magnesium is attacked, but gas is not given off from it so fast as from the zinc. Gas comes off upon cadmium in small quantity, somewhat more than comes from the aluminum, which at first showed no action at all. A slight bubbling was observed upon the manganese. The following metals remained perfectly bright: Iron, nickel, bismuth, tin copper, silver, gold, platinum, and palladium. Lead was slightly tarnished. Calcite and witherite were not acted upon. The flask was opened to the air so that a trace of moisture might get in, but no more metals were corroded, and no acceleration in the liberation of gas upon any metal was observed. The order of violence with which the gas is evolved upon each metal is given in Table I. The conductivity of the ethyl chloride and of the solution of hydrogen chloride in ethyl chloride is less than that of a dry air-gap.

II. Lest question be raised as to the dryness of Schuchardt's preparation of ethyl chloride, a second experiment was undertaken. The ethyl chloride was distilled and passed in gas form through c. p. sulphuric acid of specific gravity of about 1.8, then through four wide-mouth, eight-ounce bottles connected in series and containing phosphorus pentoxide and dry pumice, and finally condensed by a freezing mixture of ice and salt in a glass bottle with a double stopcock ground in. The dry metals scraped bright had been placed in this dried bottle and allowed to stand in connection with the phosphorus pentoxide drying tube for six hours before the ethyl chloride was distilled in upon them. The

HCl gas used was dried through two sulphuric acid wash-bottles, one calcium chloride tower and two phosphorus pentoxide towers (of the dimensions given in the first paragraph under the head "experimental"), and four eight-ounce, wide-mouth bottles, and three six-inch calcium chloride tubes, in series, all filled with phosphorus pentoxide. When the HCl is run into the ethyl chloride, zinc is rapidly tarnished, a white coating, undoubtedly $ZnCl_2$, is formed and a steady evolution of gas is observed. Lead is corroded to a marked degree but no gas is evolved. Tin becomes covered with a white coating — $SnCl_2$. Magnesium was blackened in spots but no evolution of gas was observed for one hour when minute bubbles began to come off, and at the end of eleven hours, the magnesium was very considerably corroded. Aluminum was first only corroded, but after ten minutes an evolution of gas began which was steadily maintained. During the first two hours manganese, chromium, silver, antimony, copper remained bright, but the next day after eleven hours had elapsed, pink $CrCl_3$ appeared on the chromium; manganese was covered with a dark coating; antimony was slightly darkened; silver was black in spots; and copper had a very slight tarnish, such that its luster was merely dimmed. Shortly after running in the HCl, iron began to corrode red in spots, but no gas was evolved. Cadmium also was corroded white. Cobalt was tarnished but no action whatever was observed upon nickel. Arsenic, bismuth, gold, palladium, platinum and tellurium remained perfectly bright after standing eleven hours. Witherite and calcite were not attacked by the HCl solution in ethyl chloride.

The conductivity of the ethyl chloride and of a saturated solution of HCl in ethyl chloride was tested as follows: — Ethyl chloride was distilled over through the drying apparatus containing phosphorus pentoxide (mentioned in the paragraph above) and condensed in a conductivity cell of special pattern which had been dried by hot, clean air and by standing five hours in contact with phosphorus pentoxide. 120 volts from a direct current dynamo was then applied to the terminal of this cell and a Jewell voltmeter of 20,000 ohms resistance was placed in series and used as an ammeter. The deflection of the voltmeter was the same for the pure solvent and for the HCl solution, namely: one-third of a volt division which corresponds to 0.0000165 ampere. Opening the HCl solution to the air for a minute did not increase the conductivity. It still remained one-third of a volt deflection. The insulating material between the electrodes of this cell was, the glass of the cell and upon the outside an insulating wax ordinarily used for induction coils. The insulation was tested with 120 volts, but the voltmeter in series showed no deflection whatever.

Benzene as Solvent.—To ascertain if HCl gas dissolved in benzene will act upon zinc, cadmium, aluminum, or magnesium, Schuchardt's c. p. benzene was treated with phosphorus pentoxide in quantity and allowed to stand forty-eight hours. Meanwhile a distillation apparatus, dried by clean, hot air, was set up with tightly-fitting connections; the receiver was protected by a phosphorus pentoxide tube which in turn was protected by two more phosphorus pentoxide tubes and beyond them was a wash-bottle containing concentrated sulphuric acid. This apparatus was put together hot and stood forty-eight hours, thus removing the last traces of moisture. Then the benzene was poured off from the phosphorus pentoxide over which it had been standing, into the distilling flask, and the stopper quickly replaced.

Sodium was taken from the petroleum in which it is ordinarily kept, thoroughly freed from petroleum by washing repeatedly with Schuchardt's c. p. benzene, and finally cut into small, bright pieces under benzene and quickly transferred to the distilling flask which contained the benzene to be used in the experiment. About four grams of sodium were taken to 50 cc of benzene and the distilling apparatus was allowed to stand in contact with phosphorus pentoxide drying tubes for seventy-two hours before distilling the benzene.

In making the distillation the joints of the apparatus proved to be so tight that on removing the flame below the distilling flask a vacuum was caused by the condensing of the benzene vapors. When the receiver containing the benzene was disconnected from the distillation apparatus some benzene was left in the part of the glass tubes beyond the glass stopcocks. This was evaporated off by heating and blowing in air through a capillary tube. Then the receiver was connected to the hydrogen chloride apparatus and allowed to stand one-half hour in connection with the phosphorus pentoxide towers on each side before the stopcocks of the receiver were opened to let in the HCl gas. Thus it is not possible that any moisture from the air entered the receiver.

The HCl gas was now run in under pressure. Zinc was acted upon in one minute from the opening of the stopcock, a gas, presumably hydrogen, being evolved with considerable vigor. Magnesium and aluminum were not touched but remained perfectly bright. Contact with the metals makes no difference in the rate of action on zinc. After one and one-third hours the zinc was still being acted upon with a steady evolution of gas and showed signs of corrosion, a white crust forming on it, doubtless $ZnCl_2$.

Cadmium gave off no bubbles of gas at any time, but after two hours showed a very faint tarnish. Neither magnesium nor aluminum showed signs of corrosion after standing twenty-four hours. *A trace of water let in by opening the receiver to the air did not cause action upon the aluminum or magnesium.* The benzene solution was siphoned off under pressure without coming into contact with the air before it left the metals, evaporated to dryness and left not the slightest solid residue. This shows that the action upon metals of these non-aqueous solutions of HCl does not depend solely upon the solubility of the salt of the metal in the solvent used, but rather is to be attributed primarily to the chemical individuality of the metal as well as to that of the solution.[1]

The solution of HCl in benzene conducts the electric current approximately one-fifth as well as a dry air-gap when tested with 110 volts direct current with electrodes one millimeter apart.

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[1] Compare L. Kahlenberg. Jour. Phys. Chem. **6**, 1 (1902); also M. Gomberg. Am. Chem. Jour. **25**, 324 (1901).

Tin Tetrachloride as Solvent. — Schuchardt's $SnCl_4$ was treated as described in method 1. The pure solvent is without action upon magnesium, chromium, manganese, aluminum, zinc, cadmium, iron, nickel, tin, lead, copper, antimony, bismuth, arsenic, silver, gold, platinum, palladium, tellurium, calcite, or witherite. The solution of HCl in this solvent is also without action upon the above metals and carbonates. The conductivity of the HCl solution was tested with 110 volts across one millimeter and gave a deflection of one volt division on the Jewell voltmeter corresponding to a current of 0.00005. Attention is called to the fact that this solution exhibits a higher conductivity than either benzene or ethyl chloride, and yet the benzene solution and the ethyl chloride solution act vigorously upon the zinc and slightly upon the cadmium, while the $SnCl_4$ solution of HCl is entirely without action.

Silicon Tetrachloride as Solvent. — Schuchardt's $SiCl_4$ was treated as described in method 1. The pure solvent does not act upon magnesium, aluminum, zinc, cadmium, iron, nickel, tin, lead, cobalt, copper, silver, platinum, palladium, or tellurium. No gas was evolved upon any of the metals when HCl was run in. Copper was blackened, and after standing three hours and fifteen minutes, lead was corroded white. All the other metals remained perfectly bright during eight hours and fifteen minutes after the HCl was run in. The $SiCl_4$ alone, and the HCl solution conduct electricity less than a dry air-gap as tested by 110 volts across one millimeter.

Calcite and witherite are not acted upon by the HCl solution.

Phosphorus Trichloride as Solvent. — Schuchardt's phosphorus trichloride was distilled over phosphorus pentoxide from a dry retort into a dry Erlenmeyer eight-ounce flask containing the metals. The pure solvent has no action upon any of the metals used. See summary in Table I. When dry HCl gas is run in, lead is slightly tarnished; tin is very slightly darkened; bismuth is darkened; but beyond this there is no action upon any of the metals used. The conductivity of the pure solvent and of its HCl solution is less than that of a dry air-gap as tested by 110 volts across one millimeter.

Arsenic Trichloride as Solvent. — Schuchardt's $AsCl_3$ was treated as in method 1. Magnesium is blackened by $AsCl_3$ alone, very likely by a deposit of arsenic. Aluminum, chromium, manganese, zinc, cadmium, tin, copper, silver, gold, platinum, palladium are turned black by the solvent alone. Iron is corroded red, but the coating is not very thick. A white crust, doubtless $PbCl_2$, is formed on lead. When the HCl gas was run in, gas was evolved upon magnesium and zinc in about equal amount, but only about one-seventh as fast as from zinc or aluminum when acted upon by a solution of HCl in chloroform. This is simply *my judgment* as to the respective rates *as observed by my eye* and is not to be thought of as a rigid quantitative relation. No further action was observed upon the other metals except bismuth and nickel, which were very slightly corroded. Calcite and witherite were not acted upon. The arsenic trichloride alone, allowed a current of 0.002735 ampere to pass when subjected to 65 volts pressure; the electrodes were five millimeters apart and approximately 1 cm square.

Antimony Pentachloride as Solvent. — E. de Haën's $SbCl_5$ was treated as described in method 1. The pure solvent acted upon iron, coating it red; tin was slightly darkened; bismuth, copper, and antimony were blackened; the other metals remained bright. When HCl gas was run in, lead was very slightly tarnished; silver was blackened; beyond this there was no action upon any of the other metals. Those which were bright in the pure solvent remained bright; those which were corroded or deposited upon by the solvent alone appeared to undergo no further action when HCl was present. No gas was evolved upon any metal. Calcite and witherite were not acted upon. See Summary in Table I.

II. A second sample of $SbCl_5$ was treated as in method 1. The pure solvent acted upon iron, coating it red; upon tin, forming a white crust. Bismuth, copper, antimony, and tellurium were darkened; arsenic turned gray. Magnesium, aluminum, chromium, manganese, zinc, nickel, cadmium, silver, gold, platinum, and palladium were not acted upon, as was the case in Experiment I. above. When the HCl gas was run in, the corrosion on the iron was increased slightly. No further action was observed on any of the metals except silver, which was blackened. By a separate experiment it was shown that no silver goes into solution in this antimony pentachloride and HCl solution. A qualitative analysis of this solution showed traces of lead, cadmium, iron, zinc and magnesium. A large quantity of the solution was operated upon — 10 cc — so that the test shows that the solubility of chlorides of the metals found is extremely slight. By another experiment it was shown that silver may be kept indefinitely without blackening in a solution of HCl in $SbCl_5$ provided no other metal be present. This means that we have here a case of plating out of one metal upon another from a solution which is as non-conducting toward the electric current as a dry air-gap. Calcite and witherite were not attacked. No bubbles of gas were given off from any of the metals. This may be explained by assuming that nascent hydrogen reduces the $SbCl_5$, regenerating HCl, which dissolves in the solvent.

Sulphur Monchloride as Solvent. — Schuchardt's S_2Cl_2 was treated as described in method 1. The pure solvent blackened antimony immediately, copper was blackened and tellurium turned dark. Magnesium at first was coated a yellowish white and after ten minutes the action upon the magnesium became so violent that sufficient heat was generated to crack the bottle containing the solvent and the metals. A separate experiment showed that magnesium alone acts upon S_2Cl_2 when both are dry, giving free sulphur and the chloride of magnesium.

A second experiment with S_2Cl_2 was undertaken, leaving out magnesium, cobalt, copper, antimony, tellurium, which were acted upon by the pure solvent. In this second experiment S_2Cl_2 did not act upon aluminum, chromium, manganese, zinc, iron, nickel, lead, cadmium, tin, bismuth, silver, gold, platinum, or palladium, which metals also remained bright in the first experiment with S_2Cl_2, as shown in Table I. When the HCl gas was run in, aluminum was coated white; zinc was slightly corroded white; cadmium showed a white crust; there was a red coating upon iron; tin was corroded white; and bismuth was darkened. The other metals remained bright. The solution of HCl in S_2Cl_2 shows a conductivity less than that of dry air. 110 volts direct current across one millimeter gave one and one-half volt deflection of a Jewell voltmeter, corresponding to a current of 0.000075 ampere. Calcite and witherite are not acted upon.

Thionyl Chloride as Solvent. — Schuchardt's $SOCl_2$ was treated as in method 1. The pure solvent acted upon magnesium, coating it gray; aluminum, lead, and tin were coated white; iron, copper, bismuth, and antimony were coated black; arsenic was coated gray, and a very slight evolution of gas was noticed; tellurium was corroded; chromium, manganese, zinc, nickel, cadmium, silver, gold, platinum, and palladium remained bright. The solution of HCl in $SOCl_2$ gave zinc a white coating, slightly darkened silver, and dissolved away the black coating which had been formed upon the iron by the $SOCl_2$ alone. Probably this coating was FeS and gave $FeCl + H_2S$. Very likely the silver was darkened by the H_2S thus formed. No further action upon any of the metals mentioned above was noticed. Both calcite and witherite were vigorously attacked with evolution of gas. 73 volts caused 0.00235 ampere to flow through the $SOCl_2$ with electrodes approximately 5 mm apart and 1 cm square.

All of the above experiments were carried out at room temperature (22° C) except the one with ethyl chloride, which necessarily was done at 0° C on account of its low boiling-point. With the exception of $AsCl_3$ and $SOCl_2$, none of the above solvents or solutions conduct electricity; rather they are most excellent insulators. It is established beyond question that chemical action may and does take place in solution at ordinary temperature without the presence of moisture and without concomitant electrolytic conduction. Contact of one metal with another has no effect upon any of the above actions. The colors

TABLE I

	1		2		3		4		1		2		1		2												1		2		1		2					
	$CHCl_3$ + HCl								CCl_4 + HCl				C_2H_5Cl + HCl				C_6H_6 + HCl		$SiCl_4$ + HCl		$SnCl_4$ + HCl		PCl_3 + HCl		$AsCl_3$ + HCl		$SbCl_3$ + HCl				S_2Cl_2 + HCl				$SOCl_2$ + HCl		H.F.	
Mg		H_γ		H_β		H_γ				CB after 2 hours				H_α		H_β									C?X PB	H_β					X	Solvent decomposed by magnesium before HCl could be run in.	—	—	CG	NF	75,505	Mg
Al		PB		H_α		H_α				H_α				H_β		H_β CW									PB	NF								CW	CW	NF	53,660	Al
Cr		PB					—	—	—	—	—	—	—	—		CP_κ	—	—	—	—				—	PB	NF												Cr
Mn		PB					—	—	—	—	—	—		H_β		CD	—	—	—	—			—	—	PB	NF											55,995	Mn
Zn		H_α		H_α		H_α		H_α		H_α		H_α		H_α		H_β CW		H_α CW							PD	H_β								C WT		CW	48,605	Zn
Fe							—	—		CR	—	—				CR	—	—					—	—	C RT	NF	CR	CI	CR	CI				CR	C or P B		41,025	Fe
Co	—	—	—	—	—	—	—	—	—	—	—	—	—	—		CD	—	—			—	—			—	—			—	—	—		—	—	—	—	38,740	Co
Ni						CT	—	—			—	—					—	—								CT											37,260	Ni
Pb		PB		H_γ		H_γ C WT	—	—		CW	—	—		C WT		CW	—	—		CWT after 3¼ hrs				CW T	CW	NF		T	C TW	NF				CW	CW	NF	41,385	Pb
Cd		H_γ PB						H_Δ		H_γ				H_β		CW		CWT after 2 hours							PD	NF											46,620	Cd
Sn		PB		H_β		H_γ C WT	--	—		H_α	—	—				CW	—	—						C DT	CD	NF	CD	NF	CW	NF				CW	CW	NF	31,812	Sn
Bi		PB					—	—			—	—					—	—	—	—				CD		CD T	CB	NF	CD!	NF				CD	CD	NF	30,210	Bi
Cu							—	—			—	—				T	—	—							CD T	NF	CB P?	NF	CB!	NF	PB		—	—	C or P B	NF	25,815	Cu
Ag							—	—			—	—				PB	—	—							PT	NF		PB		PB						C or P D	29,380	Ag
Sb		PB				CB	--	—			—	—		H_β		T	—	—	—	—							CB	NF	PD	NF	T PB!		—	—	CB	NF	20,974	Sb
Au							—	—			—	—					—	—	—	—					PB	NF											7,607	Au
Pt							—	—			—	—					—	—							PB	NF												Pt
As							—	—			—	—	—	—			—	—	—	—			—	—					PG	NF					CP GH_β	NF	23,796	As
Te							—	—			—	—	—	—			—	—											CD	NF	CD		—	—	C	NF	19,345	Te
Pd							—	—			—	—					—	—							PB	NF												Pd

of the coatings formed upon the various metals indicate that the chlorides of the metals have been formed. In many cases the formation of a protective chloride coating causes the corrosion of the metal to cease.

Table I.

Table I contains a summary of results obtained in this research. At the top of each column is given the formula for the solvent used. Above this formula is given the number of the experiment with that solvent. The symbols placed in the squares directly below the solvent formula denote what action the pure solvent had upon the metal which stands in the horizontal column with this square. The symbols in the squares below the formula HCl indicate the action of the solution of HCl in that solvent upon the respective metals.

The following symbols are used to indicate what action took place upon the metal:—

Square left blank = Metal remained bright.

C = Metal corroded; no gas given off. An ! after the C means that the action is instantaneous.

W = White. B = Black. R = Red. D = Darkened.

G = Gray. Pk = Pink. I = Corrosion increased.

T = Slight tarnish. NF = No further action.

P = Metal seems to be plated upon. — = Metal not present.

X = Solvent is broken down.

H = Bubbles of gas given off.

The subscripts H_α, H_β, H_γ, etc., indicate the order of violence of action, H_α being most violent, and H_Δ the least. The *estimation* was made *by my eye* and is merely my judgment as to the rate at which gas was evolved.

H. F. = Heat of formation of anhydrous chlorides for chemical equivalents taken from Thomson.[1]

$\sqrt{B}$ = Black coating removed upon running in HCl gas.

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[1] Thermochemische Untersuchungen, 3, 503–522.

Discussion

The results given in Table I show that solutions of hydrochloric acid which are good insulators will in some cases act vigorously upon metals, and even permit the deposition of one metal upon another. Further investigation would in all likelihood show that for each solvent there exists a definite concentration of HCl for which the action upon the metal is a maximum. That this concentration would be the same for all metals is unlikely. The factors which determine whether or not action will take place at the temperature, pressure and concentration studied are, the metal and the solvent.

The conductivity of these solutions, slight as it is, gives no basis for predicting action upon the metals.[1] As an instance

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[1] The conductivity of 0.1*n* HCl in water is $3,250 \times 10^{-9}$. In the first chloroform experiment where the conductivity was greatest (save for the arsenic trichloride and for the thionyl chloride, which solvents themselves exhibit a slight conductivity), 0.00025 ampere was obtained with 120 volts across 1 mm. This gives for the conductivity of this solution of HCl in chloroform $8,700 \times 10^{-13}$ approximately. If 120 volts were kept on this solution for ten hours, according to Faraday's law, we should get 2.06 cc of hydrogen. A 0.1*n* HCl solution in water would give under the same conditions 7,700 cc of hydrogen, assuming no counter E. M. F., since the aqueous solution has a conductivity 3,750 times that of the chloroform solution. If now the action of the chloroform solution of HCl upon zinc were in proportion to its conductivity, we should expect hydrogen to be evolved upon the zinc 3,750 times slower than in 0.1*n* HCl in water. The fact is, the aqueous solution of HCl acts slower than the chloroform solution. But this chloroform solution was not dried to my entire satisfaction. The conductivity of the fourth chloroform solution was 1/8 of that given above. In this case hydrogen should be evolved 30,000 times slower in the chloroform than in the aqueous solution of HCl, speaking in round numbers. Compare L. Kahlenberg. Jour. Phys. Chem. 6, 1 (1902).

Approximately the same figures and reasoning apply to the other solvents in which zinc or other metals was acted upon. The so-called period of induction appears to be of slight duration in these non-aqueous solutions. The metals are acted upon, where action takes place, with great promptness, although slower action was noted in the case of some metals. The part played by protective coating on the metal in bringing the action to a stop is important. Even in solvents where the chloride of the metal is soluble, the solution becomes saturated with that metallic chloride, refuses to clear away the freshly formed chloride from the surface of the metal, and in consequence a coating is *formed. The acid solution cannot get at the metal, and corrosion ceases.* Mr. G. Ferneckes has recently shown that an aqueous solution of sodium hydroxide which has been saturated with the caustic will not act upon sodium continuof this, compare the action of the ethyl chloride solution and of the benzene solution with that of the tin tetrachloride solution and of the silicon tetrachloride solution, taking into consideration the conductivity of these solutions as given under the detailed description of each solvent's action.

The heat of formation of the chloride of the metal also does not determine the action upon that metal, or even the order of violence of the action.

The solubility of the chloride in the solvent used does not of itself enable prediction as to action upon the metal. This is shown by the experiment with benzene as solvent, in which zinc is attacked, although its chloride is insoluble in benzene to any appreciable extent. Chemical individuality — the fact that different substances act differently — appears vividly throughout this work.

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ously. A coating forms and the action ceases. (Part of an unpublished research now in progress in this laboratory.)

The fact that speed of reaction is not proportional to the electrical conductivity has been noted in many cases. For example ammonium cyanate is transformed into urea 30 times faster in ethyl alcohol than in water, although the conductivity of the alcoholic solution is considerably lower than that of the aqueous solution. Certainly the degree of electrolytic dissociation here is not even a main factor in the reaction ; yet on the basis of that theory we ought to find our main explanation in the activity of the ions.

T. Ericson-Aurèn found that the speed with which zinc dissolves in aqueous solutions of HCl and of SO_3 is not proportional to the electrical conductivity of these solutions ; that presence of non-electrolytes in solution lessens the speed of solution of zinc, but not in proportion to the mass of non-electrolyte added, rather in the proportion of the number of gram-molecules added ; and that the presence of the zinc salt in solution increases the speed of reaction. (Zeit. anorg. Chem. 27, 251 (1901).) He attributes this acceleration produced by the zinc salt to the increased conductivity of the solution ; but when it appears that presence of zinc chloride in chloroform solution facilitates the corrosion of magnesium and aluminum by dissolved HCl, it seems that this explanation is not sufficient. The conductivity of the chloroform solution containing $ZnCl_2$ and HCl was approximately 30,000 times less than that of the $0.1n$ HCl in water with which Ericson-Aurèn worked. According to the idea of solution tension of metals, the more zinc chloride dissolved the less should be the solution tension, and the slower the solution of the metal. The facts indicate that this is not the case either in electrolytes or in non-electrolytes. The existence of chemical affinity between the zinc and the solution seems to be the simplest explanation of the facts. If it be objected that the very object of our researches is to analyze chemical affinity, it may be said that a satisfactory explanation or analysis must fit the salient facts.

The tendency of the so-called new chemistry, the chemistry of infinitely dilute solutions and the gas equations $PV = iRT$, is to separate the particles of matter in solution so far from each other that whatever characteristic individual attraction (chemical affinity) they may possess for each other may be minimized. Then every substance in solution is to act like every other substance, since there will be so little of its own peculiar attraction for its neighbors exerted when it is so far from them. Any attraction which the particle of matter may have for the particles of solvent about it is neglected.

It is true the mathematician or physicist argues that the simple laws of motion and of attraction grow complicated when the bodies acting are numerous and close together. But in the case of solution, this diluting of chemical affinity does not destroy it, and when we begin to concentrate we get back chemical affinity as certainly as if it had not been cast away. The problem may be complicated, but it must be faced. Furthermore, these laws which were developed to hold for infinitely dilute solution, by neglecting chemical affinity, do not serve even reasonably well for concentrated solutions, in spite of numerous additional assumptions. However much the physicist or mathematician may desire to get all matter to act alike, the fact of chemical individuality remains to be dealt with.

The facts show that presence of water is not a necessity in order that chemicals may react upon each other. A chemical system need not conduct electricity electrolytically in order that chemical action take place. Chemical individuality and chemical affinity are the main factors in chemical reactions, while temperature, pressure, surface conditions, and the masses of the acting substances also exert great influence upon the nature, direction and extent of the reaction. In general a chemical action goes on in such a way that the potential energy of the system is reduced to a minimum. The impulses which initiate chemical action require further study: the probability is that a vibration of proper period must be set up in the system before chemical reaction will take place. On this basis we can understand why certain reactions require a definite temperature; likewise why substances are stable between definite limits of temperature.

Some have taken the position that two pure substances cannot unite — an easy thesis to defend if one assumes that man cannot make pure substances. Water has been conceived of as forming a complex electrolyte with the reacting substances. Where it was found that water would not cause chemical reaction to go on, it was suggested that the proper impurity to cause water to conduct was not at hand.

In order to conceive of water as forming an electrolyte in the case of gaseous systems where presence of moisture facilitates reaction, it was found necessary to suppose the water to be liquefied, thus forming a little globule of solution. This attempt to reduce all chemical action to a case of electrolytic dissociation in aqueous solution loses its point when it is shown that chemical action in solution is not dependent upon the electrical conductivity of that solution.[1]

In a recent address, Prof. H. E. Armstrong[2] says: "It is premature to conclude that gases undergo ionization — using the word in its modern sense. I also venture to think that the question whether mere molecules cannot form conducting systems has not yet received in any way the attention it deserves from those engaged in these inquiries." His suggestion that radioactivity may be due to ether vibrations induced by a rapidly vibrating atom of the radio-active substance, is full of interest, too.

Regarding the presence of ions during the union of gaseous hydrogen with gaseous chlorine, Prof J. J. Thomson[3] says: "The object of these experiments was to see whether there were any free ions present either in the preliminary stage when the expansion discovered by Draper is occurring, or (2) when the hydro-

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[1] Kelvin's researches, too, on contact E. M. F. show that an electrolyte is not necessary to produce a difference of potential between substances.

[2] Chem. News, 85, 2218, 254; see also H. E. Patten. Jour. Phys. Chem. 6, 554 (1902). Also Phil. Mag. 45, 172 (1898).

[3] Proc. Camb. Phil. Soc. 11, 90 (1901).

gen chloride is being produced (from Cl_2 and H_2). At neither stage could I detect any free ions amounting to anything like one in 10^{14} of the molecules present. I then tried whether the rate of combination was affected when ions were produced by external means, *e. g.*, Röntgen rays, thorium radiation, etc. The results were negative. I could not detect the slightest effect." Evidently then it is well established that hydrogen and chlorine unite without ionization, and even when actually conducting an electric current no increase in their rate of combination is observed. Also, as Mellor and Russel[1] have shown, these gases unite when dried by the best known means.

Changes of color, such as chromium and cobalt salts exhibit in aqueous solution, have been attributed to change in their ionization. But Kahlenberg[2] has shown that cobalt oleate dissolved in benzene shows the same color change on heating and cooling as in aqueous solution, though the benzene solution is a most excellent insulator. Similarly it has been claimed that the absorption spectra of solutions depend only upon one colored ion. But G. D. Liveing,[3] in a most careful research, has shown that the absorption spectra of erbium salts in aqueous solution do not change with changing concentration in the manner required by the theory of Arrhenius. He found, too, that the spectra varied with the acid radical and with the solvent used.

The mass of evidence, then, effectually disposes of the idea that chemical reactions go on, even in the commonest instances, because of the previous splitting up of the substance into ions.[4] It remains to explain the fact that a third substance facilitates chemical action. In many cases the union of reacting substances into a complex compound, and their subsequent splitting off in altered form is a demonstrated fact. The union of solvent and solute in solution, and the many reactions which takes place in

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[1] Loc. cit.

[2] Loc. cit. See also Lachman. Jour. Am. Chem. Soc. 25, 50 (1903).

[3] Proc. Camb. Phil. Soc. 1899.

[4] Consult further L. Kahlenberg. Jour. Phys. Chem. 6, 1 (1902); also Bull. Univ. Wiss. 47, Science, Series Vol. 2, No. 5, 297-351; also H. E. Patten. Jour. Phys. Chem. 6, 554 (1902).

solution fall directly in line with this explanation of the function of a third substance.

In conclusion I wish to thank Prof. Kahlenberg for valuable suggestions given during the progress of this work. Also Mr. Wm. Brinsmaid, Mr. Eckern, and Mr. Mott for careful assistance rendered me.

NOTE ADDED JAN. 19, 1903

At the Washington meeting of the American Chemical Society, December 30, 1902, President Ira Remsen stated that he had been unable to get hydrogen by acting upon dry zinc with hydrogen chloride dissolved in dry benzene. He said that the zinc was acted upon very slightly for a period not exceeding two minutes, after which the zinc remained unacted upon. His interpretation was that as soon as the surface layer of moisture on the zinc[1] was used up, the action ceased for lack of ions.[2] He further stated that upon opening the flask containing the benzene solution to the air, moisture was at once taken up and action upon the zinc recommenced, but stopped again when the moisture was gone.

After the close of that session I told Dr. Remsen that I should be in Baltimore during the next week and would be pleased to see wherein the difference in our experiments lay. On Monday, Jan. 5, I presented myself to Dr. Remsen and he sent me into the laboratory to meet Mr. K. G. Falk, who had done the experimental work. Mr. Falk put together the apparatus given in Figure 1.

Flask 1 contained c. p. concentrated acid into which c. p. concentrated aqueous hydrochloric acid was dropped. The hydrogen chloride gas evolved passed through wash-bottles 2, 3,

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[1] The zinc had been heated to 120° C for at least half an hour, as I afterwards learned from Mr. Falk, a graduate student at Johns Hopkins University, who did the experimental work.

[2] If the water ionizes the hydrochloric acid gas we should expect the action to continue indefinitely as in the case of the union of dry ammonia with dry hydrogen chloride when a trace of moisture is introduced. The mere formation of zinc chloride and its solution in the small amount of water should not stop the action.

and 4, which contained c. p. concentrated sulphuric acid; and then through a phosphorus pentoxide drying tube, 5, into the bottle, 6, about two inches in diameter and three inches high, containing the benzene and the zinc or other metals. Tube 7 is a phosphorus pentoxide protection tube, and 8 is a wash-bottle containing c. p. concentrated sulphuric acid.

The sulphuric acid used was the ordinary c. p. concentrated acid and the phosphorus pentoxide was a sample from Bender & Hobein, which had been standing some time in a common stock bottle and was balled together in spots from having taken up moisture. Mr. Falk was unable to get a better sample and so used this one. The benzene had been shaken with concentrated acid till the thiophene was removed, as shown by the isatine test, washed with dilute aqueous caustic soda, then with water, then dried over calcium chloride. The benzene was then frozen, the residual liquid discarded and the crystals of benzene melted and allowed to stand over phosphorus pentoxide (commercial from Bender & Hobein) for at least four months. For this ex-

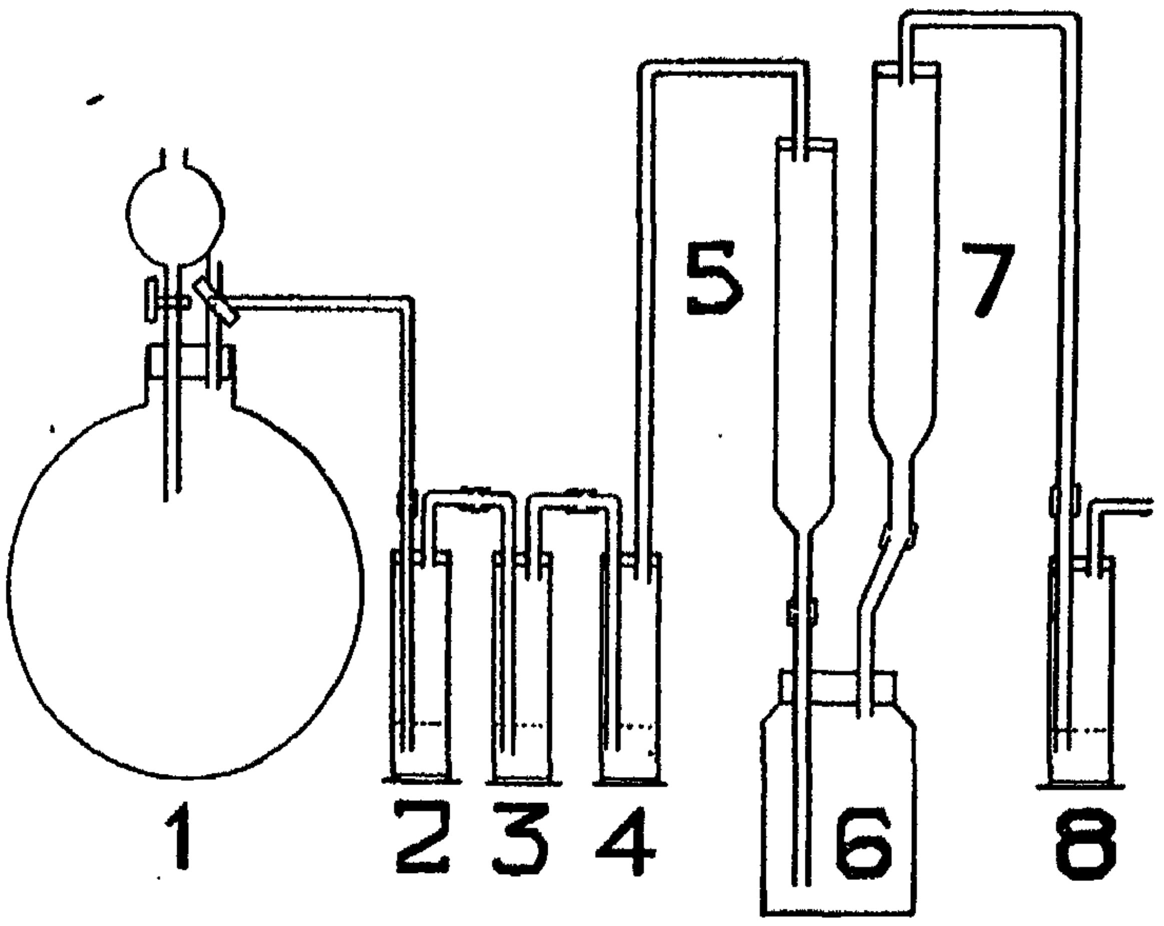

Fig. 1

periment a portion (about 600 cc) of the above benzene stood over sodium chips till used; in addition, bright sodium chips were introduced a few hours before the experiment. The benzene was poured off through the air into the bottle (6 in Fig. 1) still hot after being dried at 120° C in an air-bath for an hour or more. The zinc was quickly introduced into the benzene and the bottle (6) fitted in place as shown in Fig. 1, and the hydrogen chloride gas run into the benzene.

In order that the train might be filled with hydrogen chloride gas, the lower ends of the tubes 5 and 7 were joined (before inserting them in bottle 6) by a glass tube connected on by rubber tubes and the gas passed until the air in the apparatus might reasonably be considered expelled. When bottle 6 containing the benzene was placed in position this glass tube was removed and the hydrogen chloride gas necessarily came in contact with the air and took moisture from it.

I have described this manipulation carefully because it makes clear that moisture was not excluded in this experiment. The phosphorus pentoxide drying tubes used were not longer than 6 inches, and about 1 inch in diameter, and cotton plugs of about ⅜ to ½ inch depth were used between the layers of pentoxide. The hydrogen chloride was run in at a rapid rate, too. Mr. Falk assured Dr. Jones in my presence that the experiment was conducted in every way like the one Dr. Remsen described at the Washington meeting, and Dr. Remsen himself, on seeing the apparatus, passed no criticism.

The zinc used was c. p. wire from Merck. One piece, cleaned with emery cloth, was cut in two, and one-half heated half an hour at 120° C in an air-bath; the other piece was not heated. This variation was made to see if the action upon the zinc were due to a surface layer of moisture upon it.

The results obtained were as follows: At first the zinc was vigorously attacked, no difference in action being observed upon the heated or the unheated samples. This evolution of gas gradually decreased, and at the same time a white coating formed on the zinc, growing thicker and thicker. After ten minutes the action had abated considerably, and after thirty minutes very minute bubbles were coming off at long intervals. I detected these bubbles rising from the zinc after forty minutes had elapsed, and without the aid of a lense, but Mr. Falk could not see them, so I have set aside the forty minute period, though I am not at all sure that the action ceased even then. That is as long as I watched it.

The bottle was then opened to the air, but the zinc was not acted upon immediately after opening, as Dr. Remsen stated at Washington; this first experiment I did not time by a watch, but it took several minutes of contact with the air before the zinc was attacked. This long time and considerable amount of moisture required to start the action upon zinc is not due to slow diffusion of water from the top of the benzene solution down to the zinc — as I showed in an experiment to be described later, by shaking up the solution from time to time. The bottle was then corked and left till Tuesday morning, when all action had ceased. The bottle was again opened and after about five or six minutes contact with the air, gas began to come off from the zinc; as more and more water came in, this action increased in violence. The water is used up here before the hydrogen chloride is exhausted.[1]

On Tuesday morning, at my suggestion, Mr. Falk platinized one end of a piece of zinc wire (Merck's) and dried it for two hours at 120° C in an air-bath; magnesium from Bender & Hobein was scraped clean, but not heated; aluminum and cadmium, obtained from Eimer & Amend were treated like the magnesium and all four metals were placed in benzene dried over sodium as before described, all the manipulations being exactly the same as on the preceding day (Monday, Jan. 5, 1903); and hydrogen chloride gas was passed into the benzene. The

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[1] In my first experiment upon the action of hydrogen chloride upon zinc in benzene solution, in this paper, I stated that upon opening the flask to the air no acceleration in the rate at which zinc is attacked was observed. This observation is correct. I merely took out the stopper of the flask containing the benzene and immediately replaced the stopper. The interior of the flask filled with the white cloud usually seen when dry hydrogen chloride is brought in contact with moisture, so that presence of water is certain. And yet I could detect no further action upon the zinc.

phosphorus pentoxide in the drying and protection tubes was not renewed; the same had been used the day previous and a considerable quantity of gas passed through it. No one in the laboratory would maintain that it was efficient in removing the moisture from the hydrogen chloride gas.

The results. — Zinc was acted upon vigorously for three minutes, then the evolution of gas decreased till in ten minutes no action upon the zinc could be detected by Mr. Falk. The zinc was covered by an even white coating. No greater evolution of gas was observed near the platinized portion of the zinc than upon the rest of it. Magnesium, aluminum, and cadmium were not acted upon; no gas was evolved and the metals remained perfectly bright. During the experiment the hydrogen chloride gas was passed into the benzene very rapidly.

At 12:28 P.M. the bottle containing the metals and the benzene solution of hydrogen chloride was opened to the air. After two minutes standing no action on the zinc was seen; at 12:31 no action on the zinc, although I shook up the benzene solution to distribute the moisture taken up from the air evenly throughout the liquid. At 12:32½, on shaking up the solution, evolution of hydrogen upon the zinc commences, but magnesium, aluminum and cadmium remain bright for a long while; gradually the magnesium appears tarnished.

As the bottle remained open to the air, up till 12:43½, zinc gave off gas with increasing rapidity, but thereafter less and less gas came from it till at 1:12 P.M. the rate of gas evolution was quite slow. Up till this time the magnesium, aluminum, and cadmium still appeared bright.

The thought immediately occurs, that the hydrochloric acid was exhausted, consequently further addition of water did not accelerate the rate of gas evolution. But addition of a drop of water caused an immediate and vigorous evolution of hydrogen upon zinc, while no hydrogen was given off from the other metals. The hydrochloric acid, then, was present in quantity, but with moisture being absorbed from the air at a steady rate at the surface of the benzene solution, we get first an increased action and then a decrease.

The explanation of all this is at hand. The hydrochloric acid solution in benzene acts upon zinc, forms zinc chloride and this forms a protective coating upon the zinc. In this same paper I have shown that zinc chloride is insoluble in benzene. When moisture is allowed to enter the solution slowly no action is observed till four and one-half minutes have elapsed, since sufficient moisture must be present to dissolve away the protective coating and allow the hydrochloric acid solution to attack fresh zinc surfaces.

The tendency of zinc chloride to combine with water is well known. The first portions of water added, then, do not clear away the zinc chloride but unite with it. The latter portions of water dissolve off the coating, fresh zinc is acted upon and the zinc chloride thus formed again coats the zinc and the action ceases.

It is worthy of note that the zinc was acted upon for a shorter time on Tuesday than on Monday in the experiments conducted by Mr. Falk. The first day the drying materials were less saturated with moisture than on the second day. This is why the action was shorter; the less moisture, the better the action went, since there was less chance to form the compound of zinc chloride and water, which is a more sticky coat than the dry zinc chloride. Reference to my first experiment with zinc, benzene and hydrogen chloride will show the excessive precautions taken to dry all apparatus and materials, and that the time during which gas is evolved from the zinc is one hour and twenty minutes certainly, but much longer in reality, since I neglected to watch the experiment to see exactly when the action stopped, being at that time unaware of the part duration of action was to play in the present needs of the discussion.

From the work of Mr. Falk, then, it appears that the action upon zinc of hydrochloric acid gas dissolved in benzene does not cease because of lack of moisture to form HCl into H and Cl ions, but simply because the zinc coats over and the acid solution cannot get at it. Mr. Falk thought this coating too thin to protect the zinc, but it is well known that extremely thin coatings serve as impervious coverings on some metals, for example, the coat which forms upon metallic aluminum when exposed to the air. In fairness to Mr. Falk, it should be said that he approached this problem from the standpoint of utility, wishing to perform an organic reduction under Dr. Remsen's guidance. While I have criticized severely the method used by him in its bearing upon this discussion, I would not be understood as reflecting in the least upon Mr. Falk's efficiency as an open-minded, clear thinking and painstaking chemist.

It is a fact that at the present writing no worker in the Johns Hopkins University chemical laboratory has brought dry benzene into contact with dry hydrogen chloride and dry zinc. Consequently any statement from that laboratory can be only speculation.

There is then no difference in our results save the length of time during which the zinc is acted upon. I took back to Madison with me samples of the zinc used at Johns Hopkins by Mr. Falk, and, using them with my zinc and with a bright bar of magnesium from Schuchardt, repeated my experiment, using an entirely new set of apparatus in which extraordinary precautions were taken to dry all the parts. The only possible points open to criticism were the use of rubber connections where glass tubes join, of rubber stoppers, and of phosphorus pentoxide from E. de Haën which had not been resublimed. Dr. Remsen thought the use of pumice (which had been thoroughly heated) in the drying towers might account for the action I got upon zinc in my first experiment. So in this last one I used glass wool in all my phosphorus pentoxide drying tubes, first heating it nearly to the melting-point of glass before loading the tubes and towers. All the glass with which the benzene and metals came into contact was steamed, treated with sulphuric acid and chromic acid, washed with distilled water repeatedly and dried by heating the outside and blowing dust-free air through it. The dried containers were allowed to cool in contact with phosphorus pentoxide tubes after the metals had been introduced hot. A stream of air dried by the phosphorus pentoxide train was drawn through while the containers were cooling.

A drawing made from a photograph of the apparatus is given in Fig. 2. Number 1 is the evolution flask containing c. p. concentrated sulphuric acid into which concentrated c. p. aqueous hydrochloric acid was allowed to drop. Z is a two-way stopcock for relieving pressure. 2, 3, and 4 are wash-bottles containing c. p. concentrated sulphuric acid. Q is a stopcock to protect the towers 5, 6, and 7 from moisture if it be desired to break the train. These towers, 5, 6, and 7, are of the same dimensions: 40 cm high and 4 cm in diameter and were filled with alternate layers of phosphorus pentoxide and glass wool rammed fairly tight and approximately 2 cm in depth each. At V is a by-pass. Opening of stopcock Y permits the gas to go through 8, a tube 15 cm long and 2 cm in diameter, filled with alternate layers of phosphorus pentoxide and glass wool, then through pinchcock R into the protection train 14, 15, 16, and 17, which consists of empty trap bottles alternated with concentrated sulphuric acid and caustic soda solution. The end of the train is attached to a suction pump. When the train is filled with hydrochloric acid gas, cocks Y and R are closed, X, S, T, and N opened and the gas absorbed in the benzene in flask 9, which was fitted with a securely fitting three-hole pure gum rubber stopper. The benzene had previously been gently distilled over from the retort 10 into flask 9, where it was condensed by external application of snow. The benzene used was Schuchardt's thiophene-free preparation. It stood one month over a large quantity of phosphorus pentoxide from E. de Haën and then was poured into retort 10, where it stood twenty-four hours over bright sodium chips before being distilled from them. In order to displace the air in the retort 10 and flask 9, suction was applied to the end of the train and benzene evaporated to take its place. Oxidation of the metals which remained in flask 9 over night was thus prevented. The stopper of retort 10 was specially ground in by myself, set in with vaseline and wired tightly to the retort. The distillation was conducted with a very small flame. The phosphorus pentoxide tubes 11, 12, and 13 protect flask 9. They are of the same dimensions and filled in the same manner as tube 8 already described.

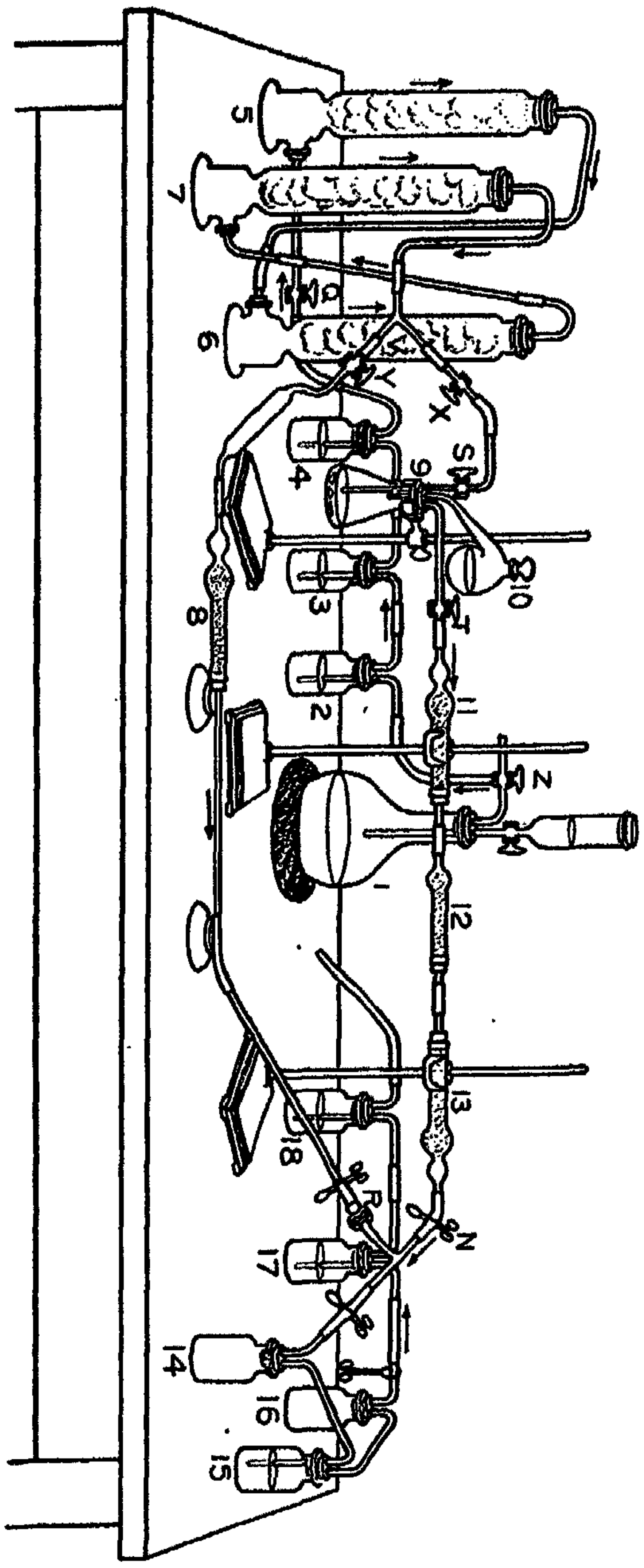

Fig. 2

The hydrogen chloride was passed slowly into the benzene after running for fifteen minutes through the by-pass. At 9:42 A.M., Thursday, Jan. 15, all the zinc — both the c. p. wire and stick given me by Mr. Falk and the Schuchardt's stick zinc which I used originally — gave off gas. For a time gas came off faster and faster, the platinized zinc acting exactly like the other zinc except where the platinum coating protected it, and there no gas was evolved. No action was visible upon the magnesium: neither a tarnish nor gas evolution. The gradual formation of a protective coating upon all the zinc was seen, not a mere tarnish, but a thick white coat.

At 10:04 — 22 minutes from the start — there was still a decidedly brisk evolution of gas upon all the zinc.

At 10:10 — 28 minutes — less gas was coming off.

At 10:20 — 38 minutes — very slow evolution of hydrogen. By shaking the flask about and getting a fresh zinc surface by abrasion of one piece of metal upon another, gas was again evolved upon all the zinc in spots, not uniformly, showing that the zinc ceased acting because of this protective coating and not because there was an insufficient quantity of water present to "ionize" the hydrochloric acid.

At 10:30 gas still came slowly from all the zinc in spots, showing that where the coating was open the acid solution acted upon the zinc. The coating upon the zinc is thicker.

At 10:40 gas coming from all the zinc at intervals of about 20 seconds between bubbles.

At 11:00 minute bubbles from all the zinc at long intervals.

At 1:45 P.M. gas still coming slowly in tiny bubbles from all the zinc.

At 3:18 P.M. gas was evolved in small bubbles at long intervals on all the zinc. Confirmed by G. M. Wilcox of Armour Institute, and L. Kahlenberg.

At 5:00 P.M. all the zinc was covered with a thick even coating of white zinc chloride, which could not be dislodged by shaking the metals together, since no further action of zinc on the acid solution could be detected.

During all this time a slow steady current of hydrogen chloride was passed into the benzene. The magnesium is not acted upon so far as could be detected by use of a large hand lense, either as to gas evolution or diminution of luster, after three days contact with the acid solution. In view of the important part which thin films play in the corrosion of metals it would be advisable to subject the magnesium and aluminum to the more delicate optical methods while in contact with this acid solution. So far as my observation goes the magnesium is not acted upon. The reason for this lack of action appears to me — in the absence of further experimental proof to the contrary — to be due to the same cause which underlies all differentiation of substances and which, the better to conceal our lack of knowledge, we call chemical affinity.

This action of hydrochloric acid gas dissolved in dry benzene upon dry zinc endured then five hours and thirty-six minutes, possibly longer. Dr. Remsen wished to get nascent hydrogen for reducing purposes in a solvent containing neither water, oxygen nor chlorine. While the hydrogen produced in my experiments may or may not serve this purpose,[1] the fact is established that we do get a gas evolved from the zinc; and within certain limits the dryer the materials the longer the action endures.

The following gentlemen were present at this last experiment:— Prof. W. W. Daniells, Prof. L. Kahlenberg, Prof. G. M. Wilcox, of Armour Institute, Mr. Shinn, Mr. Fernеckes, Mr. Huddle, and Mr. Brinsmaid. Prof. Lenher and Prof. C. F. Burgess examined the coating on the metals after the action had ceased.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
Jan. 19, 1903.

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[1] I propose to try the reducing power of the hydrogen thus obtained at an early date.

ELECTROLYSIS OF WATER

BY W. R. WHITNEY

The purpose of this article is to briefly discuss the continual electrolysis of water at voltages below the so-called decomposition value. On reading the article by Dr. Bigelow,[1] entitled "On the Passage of a Direct Current through an Electrolytic Cell", I was impressed with the idea that a strict application of the Nernst formula for E. M. F. of polarization would explain all the phenomena observed and described by him without the necessity of an introduction of any such corpuscular theory as he introduces. I am confident that this is the view held by others and is in accord with the theory as advanced by Helmholtz. Dr. Bigelow has repeated the early experiments of Helmholtz in which water, in closed vessels, is shown to continually conduct the current when the potential difference across the cell is only one volt. For visible decomposition, about 1.7 volts is necessary, and this is approximately the value calculated by the erroneous process of considering the heat of the chemical reaction to be exactly equal to the electrical energy obtained from the reaction when generating a current, or equal to the electrical energy necessary to bring about the decomposition of water into its component gaseous products at atmospheric pressure. It seems to me that the recent advances in our electrochemical knowledge lead us to conclude that whenever an electromotive force is applied to a pair of electrodes in an electrolyte, if its value is too small for visible electrolysis, there immediately occurs at least such an amount of real electrolysis as is capable of changing the poles into electrodes whose characteristic E. M. F. is equal and opposite to the impressed E. M. F. The earliest experiments on polarization point to this as a fact. In the case then of an aqueous solution, the electrodes at one

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[1] Jour. Phys. Chem. 6, 603 (1902).

volt impressed electromotive force are so charged with oxygen and hydrogen that they are to be considered as gas electrodes of low gas concentration or pressure. I see no reason for not accepting this conception as representing a condition to be expected. The gases could escape as bubbles only when the concentration had at least reached that value at which a gas pressure equal to that upon the liquid was reached, i. e., the atmospheric pressure. Helmholtz[1] certainly recognized this principle when he drew the conclusion that with gas electrodes the electromotive force should be different for each different pressure of the gas. This he then expressed in the form,—

$$A - A_1 = C \log p/p_1.$$

If these electrodes represent the gases at low pressure these gases should certainly dissolve in the water and tend to reach a condition of saturation corresponding to the above concentration. In an open vessel this might never be attained, owing to the continual escape of the gases into the air, where their partial pressures are low. As it is well known also that these gases when dissolved in the electrolyte are capable of depolarizing the electrodes, especially the hydrogen the oxygen electrode, a current at very low voltages seems a necessary result. It should depend largely on diffusion and convection, as the actually studied current very evidently does.

Considered from the point of view of energetics, there is also no transgression of a law. A molecule of water certainly could not be decomposed by an expenditure of less total energy than would be generated in its formation, nor is such an assumption necessary to the case in hand.

In the decomposition of water by the current in general, electrical energy and heat are both absorbed, but the quantitative relation between the two varies with the conditions. Moreover, at a given temperature it varies with the pressure so that at low pressures less electrical energy should be necessary than at high, although the total energy should be the same in all cases.

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[1] Wied. Ann. 34, 737 (1888).

The total energy-difference between the water and its gases will be the same at a given temperature for all concentrations because of the constancy of the value of the product of pressure and volume for these gases, but the difference in free energy will depend upon the pressure and volume of the gases, for the greater the volume the less the free energy they contain. The electrical energy obtainable from these gases under ideal conditions is a measure of the free energy they contain. At great attenuations this would become very small, though the heat of reaction would be the same as before, conversely the decomposition of water into these attenuated gases requires the application of but little work.

The quantity factor of the electrical energy necessary to decompose the water is the constant of Faraday's law, but the intensity factor by which this must be multiplied to give the energy necessary, is the electromotive force of polarization. This, in accord with the Helmholtz-Nernst conceptions, is a function of the concentration of the active electrodes. This has been shown to be the case with cadmium and zinc amalgams, and it is natural to assume that it applies to the case of gas electrodes.

Dr. Bigelow's experiments really support this view. For example, the minimum current reached in his various cells when corrected for size and resistance of electrolyte is practically a constant whatever precautions were taken to previously remove gases from the electrolyte. In fact in the single case where he could have observed the actual production of gas at low pressure above the electrolyte he apparently did so, but attributed it to a leakage of air. It seems most probable that a low rate of electrolysis existed in each of the several experiments described, that this started without the introduction of dissolved gases and probably reached a condition of equilibrium in which the diffusion of one dissolved gas to the other electrode in both cases caused continual depolarization. In such a case there should also have been some gas pressure above the electrolyte and this while not demonstrated, was really indicated by the experiments. It would seem a radical step to adopt the theory of Dr. Bigelow that simple dissolved gases conduct the current and the facts hardly warrant it. To build upon this theory the additional theoretical structure involving the mysterious corpuscles of Thomson would be still more dangerous. If all the phenomena of this particular subject seem on careful investigation to be in accord with our present theories it is simply fortunate. Such I believe is the case.

Massachusetts Institute of Technology.

THE OPTICAL ROTATING POWER OF CAMPHOR WHEN DISSOLVED IN CARBON DISULPHIDE, SULPHUR MONOCHLORIDE, PHOSPHORUS TRICHLORIDE, AND SULPHUR DIOXIDE

BY HERMAN SCHLUNDT

The influence of different solvents on the optical rotating power of camphor has received careful study by several investigators. The effect of concentration on the specific rotation of camphor solutions has also been extensively studied, and a few observations have been made on the effect of temperature on the rotation. Landolt,[1] working at 20° C, determined the specific rotation of camphor at different concentrations in the following solvents: — Methyl alcohol, ethyl alcohol, benzene, acetic acid, ethyl acetate, monochlorethylacetate, and dimethylaniline. His results show that the specific rotation increases with the concentration in all of the solvents mentioned, and that the solvent exercises a marked influence on the rotation. The curves[2] representing the variation of the specific rotation with the concentration converge, and when extended, meet the axis on which the values for the specific rotation are plotted at points lying between 54 and 56. Hence by determining the specific rotation at several concentrations in different solvents, Landolt, by extrapolation, arrived at the value $+ 55.4 \pm 0.4$ for the specific rotation of pure camphor at 20°.

The optical rotating power of camphor was further investigated in Landolt's laboratory by H. Vogel.[3] Solutions of camphor in the fatty acids, — formic, acetic, propionic, N-butyric, isovalerianic, and caprylic were studied. In general, Vogel's results confirm the regularities observed by Landolt, but additional relations appeared. In the first place, it was found that

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[1] Liebig's Ann. 189, 333 (1877). See also Landolt. "Das Optische Drehungsvermögen," 2 Auflage, pp. 167–171.

[2] Landolt. "Drehungsvermögen," p. 169.

[3] Inaug. Diss., Berlin, 1892. Landolt. "Drehungsvermögen," p. 176.

the specific rotation of solutions containing the same percent of camphor is least in formic acid, and increases with increase of molecular weight of the acids. Then it was found that isovalerianic and caprylic acids exert a singular influence on the rotation. First, the solution containing about 37 percent camphor has a minimum value for its specific rotation in these solvents, and secondly, solutions containing less than 15 percent camphor have a specific rotation considerably greater than the specific rotation of pure camphor, 55.4. Moreover, in these dilute solutions the specific rotation increases with the dilution.

Several other important investigations on the optical rotating power of camphor solutions are noted on p. 564 of Landolt's work — "Das Optische Drehungsvermögen" (2 Auflage). Rimbach[1] measured the rotation of camphor when dissolved in mixtures of benzene and ethyl acetate; and Förster[2] studied the effect of temperature on the specific rotation of camphor solutions in benzene. Hesse,[3] in measuring the rotation of camphor dissolved in a solution of water and ethyl alcohol, containing 80 percent alcohol by volume, found that the specific rotation decreases with the concentration, — a result in contrast to the general behavior of camphor solutions in pure solvents.

While the foregoing references are not exhaustive, still a further presentation of results would disclose no other solvents in which a systematic study of the rotation of camphor has been carried out. It appears then that the rotation of camphor has been studied in an extensive number of solvents. The list is however made up entirely of organic solvents.

Camphor, as is well known, dissolves readily and without undergoing decomposition in several inorganic solvents. The present investigation was undertaken with the view of studying the influence of some inorganic solvents on the optical rotation of camphor, and to determine the effect of concentration and, to some extent, the effect of temperature on rotation. Measurements were made in the following solvents, — Carbon disulphide,

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[1] Zeit. phys. Chem. 9, 698 (1892).

[2] Ber. chem. Ges. Berlin, 23, 2981 (1890).

[3] Liebig's Ann. 176, 119 (1875).

sulphur monochloride, phosphorus trichloride, and sulphur dioxide.

Apparatus and method

Polariscope. — A half-shadow instrument provided with a Lippich polarizer was used for the measurements. In form and construction it resembles the type of polariscope[1] figured and described by Landolt, l. c., p. 324. The large circular scale was divided into quarter degrees, and verniers permitted readings to be made to hundredths of a degree. The dimensions of the instruments were such as to permit the use of tubes 4 dcm long.

Polariscope Tubes. — Three types of tubes were employed. The nature of the solvent and the temperature at which it was desired to make measurements determined the form of tube that was best suited for the measurements. All of the tubes used were made of glass, and were mounted and supplied with water jackets. The ordinary plain form of tube provided with cover glasses and screw caps was used for a few of the measurements at 20° C.

Since some of the solvents used are quite volatile the solutions were cooled before transferring them to the tubes. The rotation of some of these solutions was measured in a tube[2] provided with a short side-tube, which affords space for the subsequent expansion, and serves, moreover, for filling the tube and for holding a thermometer bulb in the solution above the line of sight. The tube was 40 cm long at 20° C, and was fitted with spring fastening caps, as recommended by Landolt. I am indebted to Prof. Kahlenberg for the loan of this tube.

In working with solutions of camphor in phosphorus trichloride, it was found that the spring fastening caps allowed the solution to creep out. A thin film soon formed on the outside of the cover glasses, which causes a blurring of the field. The phosphorus trichloride also injures the brass mountings. The rotation of the solutions in this solvent was measured in a form

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[1] It was not supplied with the micrometer attachment described by Landolt.

[2] This form of tube is figured and described by Landolt, l. c., p. 396.

of tube with which cover glasses are not used. The ends of the tube were continuous with the body of the tube.

The tube was constructed from ordinary glass tubing of 1 cm internal diameter. It was made in three sections and these were finally fused together. For the end pieces tubes about 5 cm long were closed at one end, so as to have a flat bottom like a Nessler tube. By preparing a number of such tubes, several were obtained that had a bottom section of nearly uniform thickness. The outer and inner surfaces of the bottom were then ground down with fine emery and emery flour. The ground surfaces were polished with a mixture of stannic and lead oxide — the "putty powder" used by glass polishers. The inside grinding and polishing was done on a speed lathe. A rotating glass rod about 0.5 cm in diameter served for the grinding with emery, and a wooden rod was used for the polishing. No difficulty was experienced in obtaining excellent transparency, but a slight curvature of the inner surface could not be avoided. To the body of the tube two side tubes were fused at an angle as shown in Fig. 1. Finally the end sections and body were fused together.

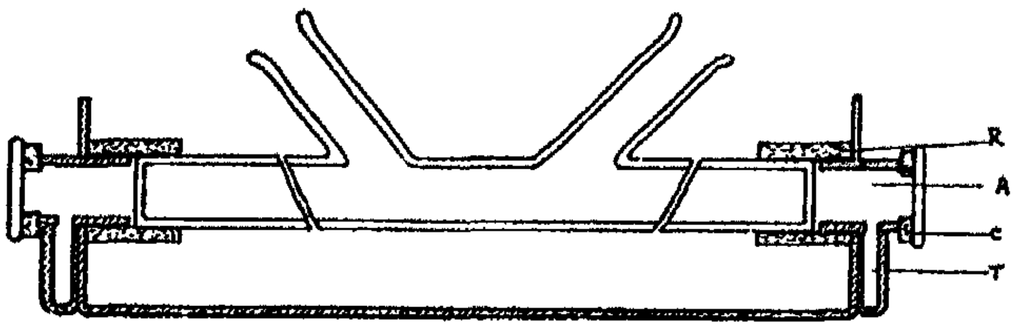

Fig. 1

The accompanying figure is a cross-section drawing of the tube and its mountings. The tube was held in position in a metallic trough by means of the two pieces of rubber tubing R. To prevent the condensation of moisture on the ends of the tube when measurements at temperatures lower than the dew-point were in progress, the following accessories were fitted to each end of the trough, — a small tube T, for fused calcium chloride, a cork washer C, to retard the conduction of cold, and a cover glass fastened to the cork with wax so as to form a small closed chamber A. The inside length of the tube was found by filling it with a solution of potassium permanganate and measuring the length of the liquid column with a cathetometer. The length was found to be 3.420 dcm at 20° C.

The field obtained with the tube in position for observations, was not quite as clearly defined as with the ordinary form of tube operated with cover glasses; but a series of test readings — the tube containing phosphorus trichloride, — gave differences between successive readings that rarely exceeded those obtained with the ordinary form of tube when filled with water.

The tube served for all the measurements made with camphor solutions in phosphorus trichloride, and it was also used for some of the other solutions studied. The angle at which the side tubes were set greatly facilitated the cleaning and drying of the tube by permitting the easy introduction of rubber tubing.

Miscellaneous Accessories. — Sodium light was used for all the measurements except for the solutions in sulphur monochloride. Sodium chloride was volatilized in the flame of a simple form of Bunsen burner[1] adapted for polariscope work. The light was filtered in its passage through a crystal of potassium dichromate of about 1 mm thickness. In working with sulphur monochloride, the luminous gas flame was used as the source of light, as sodium light is absorbed by this solvent. A layer of sulphur monochloride 40 cm in thickness transmits a narrow band of light including the lithium line, but its region of greatest intensity is nearer the C line of the solar spectrum. Hence the specific rotations obtained for camphor in this solvent are expressed as $[\alpha]^{t}_{C}$.

In the preliminary experiments the densities of the solutions were determined by means of an Ostwald-Sprengel pycnometer of 10 cc capacity. But on account of the volatility of some of the solvents as well as the marked affinity that others have for moisture, it seemed desirable to determine the densities

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[1] Landolt. l. c. Fig. 62, p. 356.

by a method involving less manipulation. The densities given in the tabulated results below were determined by means of a "test-bottle"—a type of flask in general use for determining the percent of butter fat in milk. The capacity of the flask was 50 cc. It had a graduated stem of small bore 10 cm long with a capacity of 2 cc. Each scale division on the stem represented 0.02 cc, and by estimating tenths the volume readings may be expressed to three decimals. The flask was calibrated for the temperatures at which most of the density determinations were made, namely—0°, 20°, 40°. The calibrations were made by weighing out different volumes of boiled distilled water in the flask. The weights thus obtained were converted into volume readings by multiplying them by the factors[1] representing the specific volume of water at the temperatures at which the scale readings were taken.

Method.—The solutions were prepared directly in the flask used for the density determinations. After weighing the flask with stopper, the camphor was introduced and another weighing made. The solvent was then added and a final weighing made. The flask was then placed in a bath at 20°, and the volume noted. From the data thus obtained the percentage strength of the solution and its density were calculated. Before transferring the solution to the observation tube, the densities desired at other temperatures were determined. When the solution in the tube had reached the desired temperature five settings were made, and the average taken for the reading.

The specific rotation, $[\alpha]^t_D$, was calculated from the usual formula,—

$$[\alpha]^t_D = \frac{\alpha^t_D \times 100}{l \times p \times d},$$

in which α^t_D represents the observed rotation at the temperature $t°$, l, the length of the tube in decimeters, p, the number of grams of camphor in 100 grams of solution, and d, the density of the solution at the temperature $t°$.

In connection with each solvent some determinations were

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[1] Landolt and Börnstein. Tabellen, pp. 38, 39.

made to ascertain the effect of temperature on the rotation. For the measurements at 0° the trough was filled with melting ice, and lower temperatures were obtained by means of the usual freezing mixture of snow and salt. For 20° and higher temperatures, the trough was kept supplied with water maintained at the desired temperature in a small tank.

To test for birotation and to ascertain whether any of the solvents act chemically on camphor, a solution was prepared directly in the polariscope tube, and its rotation noted at intervals during twenty-four hours. A solution of camphor in phosphorus trichloride was kept for a week, but no change in rotation occurred. These preliminary tests showed that the solvents studied have no action on camphor. In the case of the phosphorus trichloride solutions the air apparently exerts a slight oxidizing action. A slight decrease in the rotation — less than 0.5 percent — was observed with a solution which had been kept for several days in a flask containing considerable air.

Reagents. — A sample of refined camphor was sublimed and the sublimate was used for most of the determinations. Its melting-point was 175.8°. The camphor used for the solutions in carbon bisulphide was from the same lot; but it was purified by crystallization from 50 percent alcohol. Its melting-point was 176.3°.

The phosphorus trichloride and carbon bisulphide were Kahlbaum's preparations. The sulphur monochloride was of Merck's manufacture. These solvents were redistilled and found to have very constant boiling-points.

Experimental results

The greater portion of the experimental results obtained is presented graphically in Fig. 2, to which Landolt's curve for benzene solutions has been added for comparison. The experimental data then follow in tabular form. The values given for the specific rotation of pure camphor were obtained for the most part, by extending the curves representing the effect of concentration on the specific rotation to the axis of ordinates.

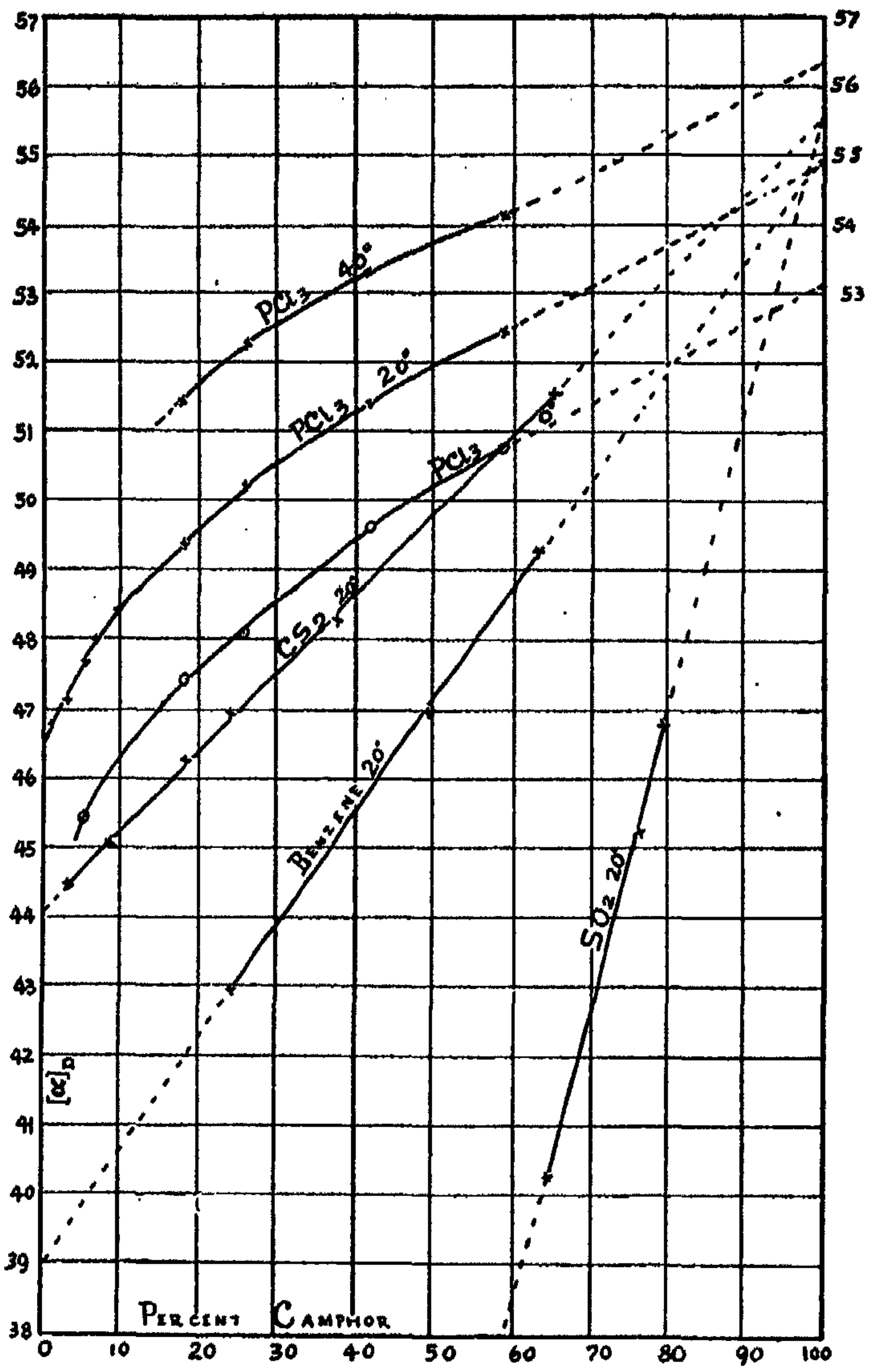

Fig. 2

Solvent — Carbon Disulphide. — Its boiling-point was 45.3° under a pressure of 752 mm. Its density at 20° compared with water at 4° was found to be 1.2633. The following results were obtained:

Percent of camphor	Density of solution	l	α_D^{20}	$[\alpha]_D^{20}$
3.5402	1.2487	4	7.87	+44.51
8.6954	1.2269	4	19.26	45.12
18.455	1.1910	4	40.69	46.26
24.119	1.1704	4	53.01	46.95
37 7975	1.1260	2	41.12	48.31
65.198	1.0461	2	70.31	51.54

The specific rotation of camphor at 20° when dissolved in carbon disulphide is expressed by the formula,

$$[\alpha]_D = 44.006 + 0.11402\,C,$$

where C represents the number of grams of camphor in 100 grams of solution. The formula holds for values of C from 3 to 65. By assuming it to hold for $C = 100$, the specific rotation of pure camphor is found to be 55.41. The value obtained is the same as the one assigned to it by Landolt on the basis of his determinations.

Solvent — Sulphur Monochloride (S_2Cl_2). — The boiling-point of the sample used for the measurements was 136.9° under a pressure of 756 mm. Its density at 20° = 1.6768. A 4 dcm tube was used for the measurements. Solutions of greater strength are readily prepared, but a uniform field could not be obtained with the stronger solutions. An attempt to measure the rotation with lithium light proved but a partial success. The results here given were obtained by using the luminous gas flame.

Percent of camphor	Density of solution	α_C^{20}	$[\alpha]_C^{20}$
3.4362	1.6345	8.38	+37.30
9.8907	1.5620	24.29	39.31
20.1721	1.4562	49.85	42.43

The temperature coefficient of these solutions is positive.

Solvent — Sulphur Dioxide. — According to Schulze[1] sulphur dioxide is absorbed quantitatively by camphor at 0°. The gas is also readily absorbed at room temperatures. The first liquid solution prepared contained 76 percent camphor, but a solution containing 85 percent camphor is still liquid at room temperatures.

Three solutions were prepared and their rotation measured. The sulphur dioxide, prepared by the action of concentrated sulphuric acid on copper turnings, was passed into a weighed quantity of camphor contained in the flask used for the density determinations. The resulting solution was weighed and its volume noted at 20°. From these data the concentration and density were calculated. By cooling and continuing the flow of gas for a time after the camphor has dissolved solutions containing a relatively small percent of camphor may be prepared. The measurements were not extended to more dilute solutions owing to a considerable loss of solvent incurred when the solutions were transferred to the tube. The following results were obtained:

Percent of camphor	Density of solution	l	a_D^{20}	$[a]_D^{20}$
64.515	1.0924	4.0	113.63	+40.31
76.595	1.0449	4.0	145.44	45.24
79.492	1.0345	4.0	153.55	46.77
79.492	1.0345	3.42	131.58	46.78

By extrapolating these results the value 55.64 is obtained for the specific rotation of pure camphor at 20°.

To ascertain the effect of temperature on the rotation a qualitative test was made with a solution containing approximately 77 percent camphor. The following readings were obtained in a tube 3.42 dcm long:

$$\begin{aligned} \text{At } 20^\circ\ a &= 127.24^\circ \\ 0^\circ\ a &= 125.12^\circ \\ -12^\circ\ a &= 123.60^\circ \end{aligned}$$

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[1] Jour. prakt. Chem. [2] 23, 351 (1881).

Solvent — Phosphorus Trichloride. — The boiling-point of the solvent used was 75.8° under a pressure of 750 mm. The following densities of the pure solvent were determined:

Temperature	50°	20°	0°	—15°
Density	1.5232	1.5794	1.6146	1.6655

All but one of the measurements were made with the tube figured, $l = 3.42$ dcm. The following results were obtained:

Percent of camphor	Density of solution	t	α_D^t	$[\alpha]_D^t$
1.0468	1.5714	20	2.63	+46.81
1.1887	1.5678	"	2.99	46.80
3.0745	1.5519	"	7.69	47.13
"	1.5865	0	7.52	45.08
5.5447	1.5274	20	13.82	47.71
5.1442	1.5255	25	12.83	47.80
"	1.5680	0	12.53	45.42
6.7257	1.5190	20	16.77	48.00
"	1.4825	40	17.06	50.08
"	1.5538	0	16.43	45.97
10.028[1]	1.4878	20	28.91	48.44
18.296	1.4199	"	43.86	49.37
"	1.3870	40	44.68	51.47
"	1.4498	0	43.07	47.48
26.1346	1.3601	20	61.05	50.22
"	1.3311	40	62.24	52.28
"	1.3888	0	59.70	48.09
"	1.4031	—10	58.90	46.96
42.075	1.2516	20	92.66	51.43
"	1.2304	40	94.40	53.31
"	1.2753	0	91.14	49.65
"	1.2865	—10	90.49	48.87
59.114	1.1716	0	119.78	50.65
"	1.1510	20	121.58	52.29
"	1.1281	40	123.88	54.19
"	1.1165[2]	50	125.00	55.38
"	1.1048[2]	60	125.95	56.39
"	1.0943	70	126.46	57.16
"	1.0816[2]	80	127.12	58.13
"	1.0709	90	127.11	58.71
"	1.1510	20	121.62	52.31

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[1] $l = 4$ dcm.

[2] The density was determined by interpolation.

The foregoing measurements are recorded in the order they were made.

By extending the curves expressing the relation between specific rotation and concentration, the following values are obtained for the specific rotation of pure camphor: —

At 0° $[\alpha]_D = 53.1$
20° $[\alpha]_D = 54.8$
40° $[\alpha]_D = 56.4$.

Solvent — Nitrogen Peroxide (N_2O_4). — Liquid nitrogen peroxide dissolves camphor very readily. A solution containing 40 percent camphor was prepared, but it does not transmit light sufficiently well even when cooled to 0° to make measurements possible in a tube 1 dcm long. Probably by further cooling, measurements may be obtained.

Summary

A comparison of the results obtained with the results published by former investigators shows that the regularities observed for the rotation of camphor when dissolved in organic solvents obtain for solutions in inorganic solvents: (1) The specific rotation increases with the concentration; (2) the rotation increases with rise of temperature; (3) the values obtained for the specific rotation of pure camphor at 20° confirm the value 55.4 ± 0.4 first assigned to it by Landolt; (4) for solutions of the same concentration, the specific rotation follows the order of the molecular weights of the solvents,[1] increasing with increase of molecular weight.

The results obtained with the 59 percent solution of camphor in phosphorus trichloride, and the 77 percent in sulphur dioxide show that no abrupt change occurs in the rotation as the boiling-point of the solvent is passed. The temperature coefficient remains positive, but its value is less at the higher temperatures.

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[1] On account of the different wave length of the light used the measurements with sulphur monochloride are not included in the above comparisons.

The following values were deduced for the specific rotation of pure camphor:—

Solvent	t	$[\alpha]_D$
Carbon bisulphide	20°	55.41
Sulphur dioxide	20	55.64
Phosphorus trichloride	20	54.8
" "	40	56.4
" "	0	53.1

Camphor is quite soluble in other inorganic solvents. Arsenic trichloride, phosphorus tribromide, thionylchloride, hydrocyanic acid[1] dissolve camphor readily. The further investigation of camphor when dissolved in inorganic solvents is in progress.

I desire to express my thanks to Prof. W. G. Brown for the interest he has taken in this work during its progress.

Chemical Laboratory,
University of Missouri,
Columbia, Mo.,
Jan., 1903.

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[1] Kahlenberg and Schlundt. Jour. Phys. Chem. 6, 450 (1902).

NEW BOOKS

Vorlesungen über Naturphilosophie. *Gehalten im Sommer 1901 an der Universität Leipzig. By Wilhelm Ostwald. 15 X 23 cm; pp. xiv + 457. Leipzig: Veit und Comp, 1902. Price: paper, 11 marks.* — For some years Ostwald has advocated the view that the only known thing which persists, and at the same time underlies all phenomena, is energy. Energy, in other words, is the universal *substance.*

Ostwald devoted the summer semester of 1901 to the delivery of a course of lectures on the system of philosophy that seems to him to be the outcome of this view. These lectures, revised for publication, are now issued in book form. They constitute what may perhaps be best described as an energistic view of existence. We shall attempt to give, as briefly as may be, some account of the contents of the work.

The matter is arranged in two fairly distinct parts. The first, occupying about one-third of the book, is given up to a preliminary discussion of the development of elementary and complex concepts from experience. The second fills the remainder of the space, and is an exposition of the energistic philosophy.

The introductory lecture contrasts the *Naturphilosophie* of Schelling with the mechanistic-materialistic view which caused its downfall. The fundamental idea of the nature philosophy was that thought and being are identical; whence it was concluded that the processes of the world can be excogitated. But this procedure proved ineffective; and, on the other hand, the adherents of the opposing view actually advanced knowledge by calculation and experiment, and so won the day. Their derision of the nature philosophy as 'speculative' provided a word that has remained a term of abuse to this day. Yet Ostwald resuscitates the name Nature Philosophy, to denote a philosophy attained through the study of nature. Ostwald acknowledges great indebtedness, in his philosophical thinking, to J. R. Mayer and to Ernst Mach. And he emphasizes that in the philosophy of the man of science *absolute* certainty has *no* place; like physics, chemistry, and biology, philosophy is an empiric science.

Since our philosophy must be tested by reference to experience, we are led to ask what we mean by experience. This is the subject of the second lecture. Experience must consist of processes in our consciousness. Its most essential feature is our capacity to construct a view of the future. This capacity is attained through comparison of past and present facts with one another, as in our anticipation of continual alternations of day and night. In this comparison we are aided by the use of *concepts* — rules according to which we attend to certain peculiarities of given phenomena. This idea of concepts is most interestingly discussed at length, and its bearing on formal logic is examined.

The third lecture is on Language. In order to hold and to communicate a concept once formed, we associate with it some sign recognizable by the senses. Thus arise spoken and written languages, one appealing to the ear, the other to the eye. Mathematical and chemical symbols are included here. The written language serves to preserve records. It might seem that examination of words would yield the essence and laws of concepts. Aristotle proceeded in this way. Slavish imitation of this method gave rise to the Scholasticism of the Middle Ages. The scholastic error lay in overlooking the fact that both concepts and words continually change. Yet an artificial international language might be devised, through the establishment of clearly defined concepts, like those of an hour and a meter. The significance of the parts of speech in Teutonic languages is examined. In particular, it is remarked that the possibility of making any word a noun by prefixing an article leads to subconsciously ascribing reality to such formations; and that, since adjectives serve to add or subtract concept-elements to or from a concept, a somewhat free disposition of qualities in this way has led to the idea that properties are removable from bearers of properties. Both are fruitful sources of error.

Sense Impressions is the title of the fourth lecture. We have noted that the results of the formation of concepts are but vaguely and incompletely crystallized in words. So the examination of words has but little value in the study of the formation of concepts. Another path lies in examination of the character and origin of concepts. Concepts, as for example that of 'man,' are usually complex. By analysis of them we reach concept-elements, which have an obvious analogy to the chemical elements. In chemical analysis one starts from 'pure substances' — a railroad train would not be subjected to chemical analysis. In like manner we must analyze pure concepts. Those are supplied by the sciences.

Two things are concerned in the establishment of a concept: sense-impressions, and certain operations of the mind. We might expect the analysis of both to lead to elementary concepts. Beginning with the sense-impressions, Ostwald distinguishes sight, hearing, skin, inner, and muscular sensations; and he subdivides skin-sensations into sensations of smell, taste, pressure, and temperature. As general result of the analysis of the sensations, it appears that we have to do with a *flux* of phenomena, and that the characterization of the elementary character of sensations is variable — with extended practice we analyze more deeply. The other path toward concept-elements lies in study of the operations of the mind. By way of introduction hereto, Ostwald defines the 'outer world' as the totality of the experiences that we can voluntarily call up or dismiss; or as the sum of the experiences in whose origin the sense-apparatus participates. The distinction between the outer and the inner worlds, though arbitrary, is convenient.

The search for concept-elements, through the study of the operations of the mind, is begun in the fifth lecture. The more 'elementary' a concept — as 'thing' — the more individuals it embraces, and the fewer characteristics. (Overlapping concepts together designate what is common to both — 'Peter is here'). The concept-elements sought are to be found in the operation of the Formation of Concepts, which consists in: (1) grasping, (2) distinguishing, (3) compounding, (4) comparing, (5) concluding — i. e., testing the concept by application to the future. The most general concept is 'thing'; for it is applicable to *all* our experiences. The second step in our formation of concepts from experiences consists in arranging distinguishable things. The totality of any arrangement is a 'manifold'. The laws of manifolds are represented by time and space; for all our experiences stand to one another in chronological or spatial relationships, and in these only. Time is a continuous, simple, directed manifold without multiple points; space is a continuous, multiple, isotropic manifold.

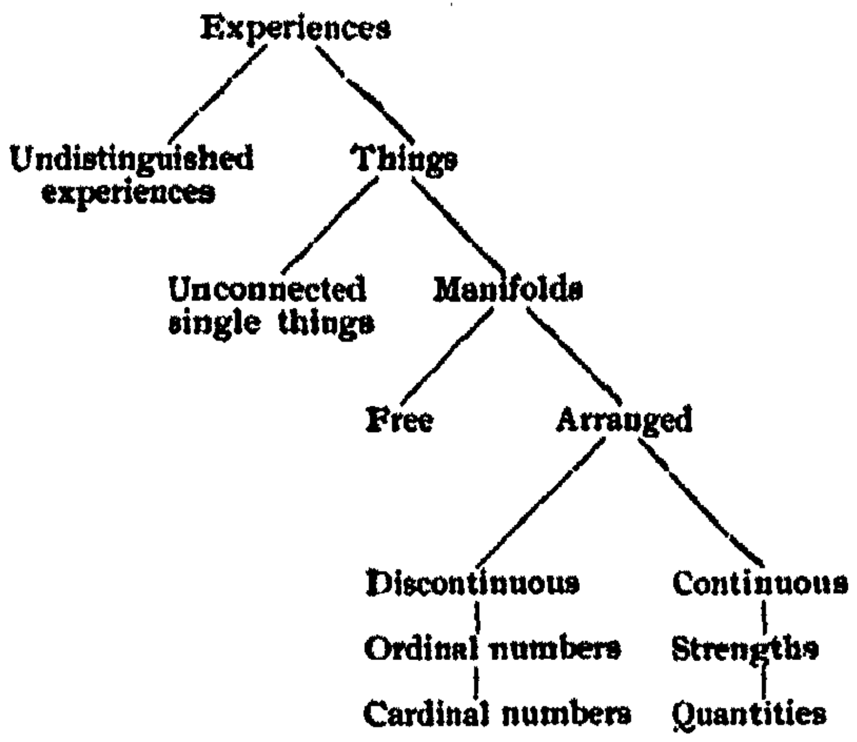
We see then that time and space, though always constituents of our thinking, are composite: we have only approached our goal. Since both are manifolds, the concept 'manifold' is more elementary than either. 'Manifold', on the other hand, stands next to 'thing', the first concept won from the flow of experience; for it is the result of assembling things. A discussion of manifolds occupies the sixth lecture.

A manifold is an assemblage of things; the contents of a boy's trousers pocket is a manifold. A manifold can be divided into poorer manifolds, whose sum is the original one. A manifold can be arranged, e. g., the letters of the alphabet. But it cannot always be arbitrarily arranged; a series of experiences, for example, occur in a definite order. Indeed, all our experiences occur in time and space; wherefore all real manifolds are continuous and ordered.

In the formation of the concepts 'thing' and 'manifold', we have executed the necessary operations up to that of comparison. In comparing two manifolds we can *establish a correspondence between each element of the one and an element of the other*, — as between theatre seats and theatre tickets, or their holders, or between concepts and the words that denote them. An ordered manifold of the simplest type is the series of positive whole numbers. Every unarranged manifold can be made to correspond with this series. Two uses are made of it: those of the cardinal and of the ordinal numbers. Arranging successive manifolds to correspond to the successive members of a simple manifold, we obtain a twofold manifold of the simplest type. The process can be indefinitely extended, to yield multiple manifolds of higher orders.

At this point in the investigation of the formation of concepts, through examination of the relations which the experiences denoted by the thing-concept bear to one another, we have arrived at the concepts of manifold, correspondence, and number; and we are now engaged in the study of the Comparison of Things, which is the subject of the seventh lecture, on Magnitudes.

Ostwald begins with the definition, "we set two things *equal* when, in any definite operation, each can replace the other." Thus two manifolds are equal when they have the same number of members; and two pieces of marble are equal for the chemist, who considers their chemical reactions, and are not so for the physicist, who weighs them. Equality or inequality of things can be asserted only with reference to definite operations. Furthermore, a determination of equality, since it reduces to a determination of the equality of certain actions, has ever but a limited accuracy. Using) to indicate greater than, higher than, stronger than, etc., it may be asserted that every simple manifold, even if continuous (for continuous manifolds can be divided in any arbitrary way), can be arranged in a series so that from A) B and B) C follows A) C, which is the general law of these manifolds. This is illustrated by thermometry. A straight line can be divided into equal parts, a continuous series of tones cannot. The former is typical of a manifold of "quantities", the latter of "strengths". Quantities can be represented by cardinal numbers, strengths by ordinal numbers. Quantities are measured in terms of "units". A view of the argument to this point is afforded by the following tabular arrangement:



Now that we have recognized the concepts of the manifold and its arrangement as the most general in which things — the individual constituents of our experience — can be included and used, we pass, in the eighth lecture, on Time, Space, and Substance, to the *application* of these concepts. This yields the concepts of time and space. For the manifold presented by time and space together serves for the comprehension and arrangement of all our outer and inner experience — of all possible events. Under the assumption that spatial displacement of solids does not alter their dimensions, it appears that space is a 'quantity'. Time elements occur in a definite order; so time is a 'strength'. Yet we *measure* times. This apparent contradiction is resolved by the consideration that for phenomena assumed to be constantly periodic time is a quantity, otherwise it is a strength. Although we arrange all our experiences in space and time, yet in the peculiarities of things we distinguish different spaces and times. Such distinctions cannot lie in space and time, for they are uniform; so other, narrower, manifolds must be sought in our experiences.

Here, after 144 pages of preliminaries, we come to the considerations that give to the book its distinctive character. In our experience of the outer world certain impressions continually recur. These seem therefore to have an existence more permanent than that of the shifting accompanying elements. Hence has been concluded that a thing has a permanent part, its *substance*, and a variable part, its *accidence*. The question as to what renders possible the formation of the thing-concept may be resolved into the questions, what is the most general substance and what the most general accidence in the things of the outer world. Ostwald answers 'energy' to both questions, since "energy is that which is present in time and space, and is that which is distinguishable in time and space." This answer is given merely as a form of words; its meaning is to appear in the subsequent lectures.

The 'substance' of the present physics and chemistry is termed 'matter'. No one satisfactorily defines it, and it fails to embrace important optic and electric phenomena. An 'ether' invented to fill this gap leads to insoluble contradictions. Summarizing, Ostwald maintains that the only known thing that persists, and at the same time underlies all phenomena, is energy; wherefore it is the universal substance. Our knowledge of the outer world results from the action of energies upon the sense-organs, and it can all be presented in statements concerning energies. Energy is defined as "work, or all that arises from work or can be converted into work". The purpose of the book is to construct "an energistic view of the world", in which the concept of matter is superseded by that of energy.

A sketch of The Energistic View of the World constitutes the ninth lecture. The work absorbed in the deformation of an elastic body depends on the form of the body. Ostwald terms this "form energy", and work of compression "volume energy". In touch we experience the spatial relations of volume and form energies. Wherever form energy is present, weight and mass are also observed. In a body at rest, equilibrium obtains between its form energy and "distance energy". Form energy and distance energy are always associated on the earth for the reason that a body without gravity would not be retained here. *Bodies without form energy, if present, would be imperceptible.* Ostwald holds that we have information only of spaces in which energies are associated. A body breaks when the form energy imposed upon it exceeds a definite amount per unit volume: every solid has a specific capacity for form energy.

Breaking and tearing develop new surfaces; the work in excess of that stored as form energy is converted into a "surface energy", on which capillary phenomena depend. In a falling body, distance energy is converted into "motion energy". When equal amounts of work induce equal velocities in two bodies, the bodies have equal masses. "The usual definition of mass as quantity of matter is pernicious nonsense." For the measurement of energies, the units of time, length, and mass are fundamental. Inertia is viewed as a consequence of the conservation law, the motion energy being conserved in amount and character. The '*riddle of gravity*' is merely the fact that a form of energy depends on the distances between bodies.

The form energy of a solid changes greatly in small changes of form. Liquids have volume, surface, and distance energies, i. e., require work for compression, surface extension, and change of relative position. A melting solid assumes (usually) thermal energy, and loses its form energy. Aeriform bodies have no form energy, and their volume energy is always positive.

In the tenth lecture, on Heat, Ostwald attacks the somewhat widely prevalent view that all energy is mechanical, or even kinetic. A gas cools as it expands. Ostwald says that the thermal energy of the gas is partly converted into work; according to the mechanistic hypothesis invisible mechanical energy is converted into visible. The contention that the second view goes deeper into the reality is incorrect. We should aim to give hypothesis-free representations of the observed facts. "The task of science is to represent the observed manifolds in such wise that only the actually observed elements of the phenomena appear in the representation." This excludes mechanical analogies, and admits only the general means of representation of manifolds—numbers and algebraic expressions. Ostwald here presents a very sound and readable sketch of the attitudes assumed by Mayer, Joule, and Helmholtz toward the principle of the conservation of energy; and of the parts played by Mayer and Joule in the determination of the mechanical equivalent of heat. He concludes with the statement that, since things are equal in so far as they can replace one another, equal quantities of different energies are equal only in the one respect that they can be converted into equal quantities of some other energy form.

The eleventh lecture treats The Other Energies. Electric energy, and the allied magnetic energy, are distinguished from the others considered by the circumstance that we have no senses for the immediate recognition of their action, we recognize them chiefly by their transformation into either mechanical or radiant energy. Their great technical significance rests on the readiness with which they can be conducted to places of application, and with which they can be converted into other forms, as work, heat, light, and chemical energy. 'Chemical energy' is liberated or absorbed in the transformations of substances. Its most important properties are its permanence and its high concentrations, as in coal and food stuffs. The great technical problem of the future is the immediate production of mechanical energy from chemical energy. Direct measurement of chemical energy is impossible; for the purpose of measurement it is usually transformed into heat. While form, volume, motion, and chemical energies always occur together, and together form 'matter', thermal and electric energies are separable from the others. 'Radiant energy' is yet more independent of matter. It need not involve the assumption of a carrying ether; for it may be regarded simply as a periodic transformation of electric and magnetic energies in space. The radiant energy from the sun is the chief source of the 'free energy' whose transformations constitute terrestrial phenomena. This current of radiant energy maintains terrestrial activity much as a mill stream maintains the action of a mill. Summarizing the energistic view of the world, Ostwald says: "Everything that occurs in the outer world is exhaustively characterized by assigning in kind and amount the energies that are displaced and transformed. Even the physiological operations, including sense-impressions and thought, are to be viewed in this way. "An especially important result is the resolution of matter into a spatially arranged complex of certain energies."

The conservation law, the 'first law of energetics', does not answer the question, "What assumptions must be satisfied in order that a transformation of energy shall occur?" This question is attacked in the twelfth lecture, on The Second Law or the Law of Events. It was first investigated in mechanics. In mechanical systems spontaneous changes lead to states of equilibrium. The energy thereby lost is of necessity converted into motion energy, which leads to periodic changes resulting in heat-development and consequent cessation of motion. That all things do not come to permanent rest is due to the activity of the sun as a disturber of the peace.

An event may involve changes of motion, changes of temperature, chemical changes, radiation, etc. Thermal, electric, or mechanical equilibrium subsists in spaces of uniform temperature, electric tension, or pressure, respectively. These things are the "intensity-factors" of the energies in question. Conversely, in order that processes shall occur, there must exist differences of intensity of energies present (Helm). Intensities are 'strengths', not 'quantities'. From the theorem that when two intensities are equal to a third they are equal to each other, it follows that a store of energy of uniform intensity is inconvertible, that a 'perpetual motion of the second kind' is impossible. This is the 'second law of energetics'. Most non-thermal forms of energy are readily interconvertible; but all easily pass into heat, whereupon uniformity of temperature is established by heat conduction. For this reason, terrestrial processes proceed in a direction of decreasing 'free energy'.

In order that different energies may hold one another in equilibrium, they must be so connected that a change of one involves a change of the other. Energies can appear as spatially distinguished phenomena only when such connections yield a composite equilibrium in which intensity differences of one form compensate those of another. "For anything to occur, uncompensated differences of intensity must arise." What occurs is a change in which the uncompensated intensity decreases. The intensities of distance, form, and volume energies are compensated readily, that of electric energy with difficulty, and that of thermal energy not at all. Every energy equalization requires time. An equalization cannot, therefore, be complete; the world consists of instable systems. In a change in time we may observe: a continual slowing up, as in heat conduction; an increasing rate followed by a decreasing one, as in a conflagration; an increasing rate followed by a steady one and then a decreasing one, as in the burning of a candle; or an alternation of increasing and decreasing rates, as in the action of an autoregulated steam engine. There are two sources of the time concept, a mechanical one, — motion, — and the dissipation phenomena.

The thirteenth lecture considers Substances. A substance is something that persists during changes. Mass, energy, quantity of electricity, the chemical elements, centers of gravity, are conserved, and so are substances. In the search for the most general substance, the most general concepts of natural science, time, space, and energy, are examined. Time is deduced from the phenomena of change; so we cannot directly speak of its conservation. That space is conserved has a meaning only under the assumption that solids maintain their size and form on displacement. "The comprehensive significance of energy for the conception of natural phenomena as a whole justifies us, in view of the law of its conservation, in regarding it as the most essential substance."

The other substances mentioned are the "capacity factors" of energies. The energies are the products of the capacity and intensity factors. These capacity factors are 'quantities', not 'strengths'. In isolated systems all the capacity factors except the entropy remain constant; the entropy increases because of heat conduction. Possibly the other capacity factors vary as well. The intensity of chemical energy about coincides with 'chemical affinity'; and the conservation of the corresponding capacities appears in the conservation of the elements. In those assemblages of energies that we term matter, equal chemical capacities of different substances are associated with simple rational multiples of other capacities. This appears in the equality of the molecular volumes of gases, and in Faraday's law of electrolysis.

Ostwald holds that the differences between energies, and between their factors, lies in the fact that no two of these magnitudes are manifolds of the same kind. Tabulation of all possible kinds of intensity manifolds and of capacity manifolds, and formation from the table of all combinations of an intensity with a capacity, should yield all possible energies. Unknown energies could then be foreseen, as unknown chemical elements were foreseen by Mendelejeff. Ostwald adds that his struggles with this problem have indicated that the number of possible energies considerably exceeds the number of those known.

The Law of Causality is the subject of the fourteenth lecture. Hume saw in this law only the chronological connection of occurrences. But the effect would not follow if the cause were absent: the law asserts a relation further than sequence in time. Such relations are found only in energistic relationships. From the idea that the effect must be equal to the cause, and must be completed when the cause ceases, Mayer regarded the law of causality as identical with the law of transformation and conservation of energy. In Ostwald's formulation: "Nothing occurs without equivalent transformation of one or more energy forms into others." When and how anything occurs is determined by the second law of energetics; so both laws together state the content of the law of causality.

Yet the time-rate of a process remains undetermined. It can be varied by varying the resistances, catalyzers, etc. Such 'causes' Ostwald terms the chronological 'conditions' of the occurrences. Similar *spatial* conditions can be recognized. Causes of another class remove the compensations of existing differences of intensity, as does a spark in gunpowder. Terming these 'releasings', the conclusion is reached that the law of causality "lies in the experience that a one-valued functional relation obtains between the causes, the conditions, and the releasings of a system on the one hand, and the course of its phenomena on the other. Extensive scholia follow.

The remaining lectures are on: Life; Purposes and Means of Living Organisms; Sensitiveness and Memory; The Spiritual Life; Consciousness; The Will; The Beautiful and the Good. In brief abstract their contents are somewhat as follows:

Through a living being passes a current of energy by which it is maintained in a steady state. An energistic description of the processes of life would furnish all the knowledge of life that can be asked for. This is the answer to those who maintain that vital phenomena are inexplicable. The organism is essentially a complex of chemical energies, which it converts into other forms. The velocities of its chemical reactions are regulated by its temperature, the concentrations of its fluids, and by catalysis. As disturbances accumulate, the dissipative actions outweigh the accumulative ones, and the organism goes out of commission.

It is not impossible that inorganic processes may exhibit "a typical resemblance to the adaptive behavior of organisms." And as spontaneous production of crystals of Glauber's salt occurs at the limit of metastability of their solutions, so may it be that organisms are produced at the limit of metastability, with respect to organic life, of nourishing solutions.

Our senses have developed to correspond to our practical needs. Thus it is that we are not sensitive to the intensity of every form of energy. Touch and hearing are related to volume energy, sight to radiant energy, the temperature sense to heat, taste and smell to chemical energy, — though in but slightly developed degree, — while no sense reacts upon the intensities of electric and magnetic energies. The action of nerves is ascribed to the transformations of a 'nerve energy'. A "chemical theory of memory" is suggested.

Inquiry into the relation between mind and matter is formulated in the question, how are the intellectual phenomena related to the energy concept? Ostwald suggests the assumption of an intellectual energy, identical with nerve energy, which is transformed into heat. He holds that it may prove possible to put this view to a direct test. Sensation, thought, and action are discussed from this standpoint. It is proposed to regard consciousness as a property of the 'intellectual energy'. "It seems to me no more difficult to think that energy of the central nerve system involves consciousness than that kinetic energy involves motion." The will is regarded as a discharge of energy, presumably from a chemical source.

The problems of science and the problems of art reduce, alike, to the comprehension of the infinite manifold of phenomena through the formation of suitable concepts. Tangible concepts are formed by art, concepts in thought by science.

Some idea of the argument embodied in Ostwald's book should be apparent from the above abstract. But the abstract conveys no impression of the marked literary quality of the work, which appears in the mental alertness that the author continually exhibits, and the remarkable fluency with which he handles the German language. Yet this fluency does not mislead him into becoming diffuse; his writing is a steady flow of systematic exposition. The details, further, of each successive topic are worked up in ingenious and well-rounded fashion; and the points made are frequently illuminated by striking and unexpected illustrations in which often appears a play of humor and delicate fancy delightful in itself and exceedingly effective for its purpose. This is especially apparent in the severe chapter on experience.

But what must one say of the actual content of the book, irrespective of its form? The view advanced is purely metaphysical, a hypostasizing of the energy of the world. This speculation is unquestionably interesting, but is not new. In an essay of great impressiveness and wonderful literary beauty (The Idea of God, *Atlantic Monthly*, 56, 642, 791 (1885); also in book form, Boston), John Fiske develops the idea that the 'energy' of the physicist is the one reality, the animating principle of the universe, the eternal source of phenomena. He contends that this conception is no metaphysical abstraction; and that, following the definition of God as that power, not ourselves, that makes for righteousness (through the development of high psychical life), it is to be identified with the Athanasian Indwelling Deity. Apart from this formal theological interpretation, it is hard to see that Ostwald's view differs in any essential way from

Fiske's. Both regard energy as something that persists and at the same time underlies all phenomena. But before allowing ourselves to be carried away by the enthusiasm of the protagonists of this metaphysical view, let us turn to the following sensible remark by Mach (in his famous lecture in 1872 on the energy law) on the tendency to regard energy as a substance.

"The law of causality presupposes a dependence between the natural phenomena $\alpha, \beta, \gamma, \dots$ It is the task of the investigator to find the form of this dependence. In what manner, now, these dependence-equations are written cannot be essential. One will grant that it makes no especial difference, in which of the three forms,

$$f_1(\alpha, \beta, \gamma, \dots) = 0$$
$$\alpha = f_2(\beta, \gamma, \delta, \dots)$$
$$f_3(\alpha, \beta, \gamma, \dots) = \text{const.}$$

an equation is written, and that the last of these forms contains no especially higher wisdom than in either of the others.

"But the law of the conservation of energy is distinguished from other laws of nature solely by this form. ... However beautiful, simple, and viewable many things appear in the form of the principle of the conservation of energy, I cannot grow enthusiastic over the mysticism that is often connected with it."

In fact, metaphysics aside, the modest aim of the man of science is to obtain in simple form a description of the observed relationships between measurable quantities of physical phenomena. What is really wanted at present is a philosophical study of the genesis of the ideas of work, the work-equivalents of physical changes, and energy; a study of the development of the formulation of the functional relations between allied physical variables. Inductive reasoning will then furnish the justification for the use of any auxiliary quantities employed, or a quantity of entropy or store of energy; and metaphysical speculation concerning them will be regarded as an entirely extraneous affair. Something has been done in the direction indicated, most notably by Mach, but not yet enough; the general aspects of the matter are as yet but imperfectly understood. The problem is more a logical one than an experimental one; it is not that we do not know enough facts, the vagueness lies in our imperfect combination of them in a general scheme. This difficult task Ostwald has not attacked, save in so far as his admirable initial analysis lays a foundation for it. An adequate investigation, building up the theory in a step-by-step fashion, would doubtless show the energy theory to be a more complex affair than Ostwald assumes it to be. But one would avoid the objections to be made to Ostwald's off-hand definition of energy in general, to 'volume energy' as a product of two factors, and the like; and clearness in regard to the foundation of the mathematical treatment of physics and chemistry would be attained.

As a matter of curiosity, I have assembled Ostwald's swarm of 'energies', in the order in which he introduces them. They are:

1. Form energy
2. Volume energy
3. Distance energy
4. Surface energy
5. Motion energy.
6. Thermal energy
7. Electric energy
8. Magnetic energy
9. Chemical energy
10. Radiant energy
11. Nerve energy
12. Intellectual energy

Apart from the pulpy paper on which it is printed, the mechanical execution of the book is good. It is printed in a generous, widely-leaded page, from a new font of a compressed heavy-face type of large size and of a curious cut. The tail-pieces, which occasionally reduce to a mere wiggly line, are a disfigurement. But few typographical errors are noticeable. An analytical table of contents serves the purpose of the missing index. The work is dedicated to Ernst Mach. *J. E. Trevor*

The General Principles of Physical Science. *An Introduction to the Study of the General Principles of Chemistry. By Arthur A. Noyes 15 × 23 cm; pp. viii + 172. New York: Henry Holt and Company, 1902.* — The purpose of the book is to present the general concepts and laws of physics and chemistry which lie at the basis of the modern science of theoretical chemistry. The arrangement of the subject-matter is as follows: the object of science; the methods of science; the subdivisions of science; the fundamental concepts; space and time; the concepts of matter and energy; matter, its quantitative measurements, and the law of its conservation; the states of aggregation and other physical states of matter; chemical substances and mixtures; elementary and compound substances; law of the conservation of the elements; the law of definite proportions; the law of multiple proportions; the law of combining weights; determination of the combining weights; numerical values of the combining weights; elementary composition as a means of distinguishing chemical substances from mixtures; chemical formulas and chemical equations; definition of equivalent weights; general significance of the properties of gases; relation between the pressure and volume of gases; relation between the pressure-volume product and temperature; relation between the pressure-volume product and combining weight; general expression of the pressure-volume relations of gases; the forms of energy and other classes of energy manifestations; the quantitative measurement of energy; the law of the conservation of energy, the factors of energy in general; the factors of kinetic and gravitation energies; the factors of surface, volume, and elastic energies; electricity and magnetism; the factors of electrical energy; Faraday's law of electrolytic conduction; heat energy; chemical energy; radiant energy; the internal energy of gases; the second law of energetics; application of the second law to changes taking place at a constant temperature; application of the second law to changes taking place at different temperatures.

The general plan of the book is excellent and the details are fairly well worked out, with one striking exception. By introducing atomic or combining weights before molecular weights, the author has complicated the subject and has made his treatment unnecessarily arbitrary. For a systematic presentation one should begin with the volume relations between reacting gases. This gives the conception of molecular weights. Weight relations are then substituted for volume relations as being more exact. Next comes the choice of the unit. The introduction of the atomic or combining weight is made to avoid the difficulties due to hydrochloric acid, water vapor, etc. There are a few minor slips. It is a pity to class amorphous substances with the solids, p. 24. If one is to use the law of Dulong and Petit as showing that the elements are of the same degree of complexity, p. 35, one should be logical and classify carbon, for instance, as a probable compound.

On the other hand, the discussion of hypotheses and theories on page 8 is one that we should all read at least once a year and ponder over. There is not a sentence in it at which any one will cavil in the abstract, but the application is always to our friends and not to ourselves. "It is highly important that the student of science should constantly keep in mind the radical distinction between facts and laws on the one hand, and hypotheses and theoretical principles on the other; for the history of science and education proves that there is a great tendency to attribute to the latter an undue importance, so that a theory, especially one which has already proved of great scientific value, may come to be a hindrance to increase of knowledge and to further progress of the science, by causing facts inconsistent with the theory, or not comprehended by it, to be ignored, thus giving to the science a one-sided development."

The strong points of the book are the uniformity of treatment and the conception of the subject as a whole. The weak points are to be found in the treatment of some of the chapters. The volume will therefore be valuable to the student who has already been over the ground, rather than to the elementary student. The style could have been improved by shortening the sentences and placing the adverbs differently. *Wilder D. Bancroft*

Elektro-Metallurgie. *Die Gewinnung der Metalle unter Vermittlung des elektrischen Stromes. By W. Borchers. Dritte vermehrte und völlig umgearbeitete Auflage. Erste Abtheilung. 16 × 23 cm; pp. iv + 289. Leipzig: S. Hirzel, 1902. Price: paper, 9 marks.* — The first section of the third edition contains the chapters on magnesium, lithium, sodium, potassium, calcium, strontium, barium, beryllium, aluminum, cerium, lanthanum, praseodymium, neodymium, copper, nickel. There is much that is new. The work of Fischer on the electrolysis of fused sodium chloride and that of Stockem on the preparation of calcium, strontium, and the cerium metals was carried out in the Aachen laboratory. Darling's process for the electrolysis of fused sodium nitrate is given and there is also a discussion of the Bradley patents for aluminum. It is recognized at last that the Castner process for making metallic sodium is a commercial success and that aluminum is made by the process of Hall and Héroult. There are some very interesting paragraphs on the use of chloride in copper refining and there are details in regard to some of the American plants.

On the other hand there are no analyses of electrolytic copper; the information in regard to the Hayden system is ten years old; pages are wasted on the early Hall patents while little or nothing is said of the modern practice. There is an unnecessary polemic against Muthmann, the Borchers air cell receives its usual extended notice, and there is a painful want of proportion. The Castner sodium process gets half a page, and the Hall aluminum process practically only a cut. The Héroult process fares a little better; but the Hayden process for copper refining receives half a page, no more than is given to the other patents for a series system. The remainder of the two hundred and eighty pages is devoted to the multiple system of copper refining and to descriptions of processes which are commercial failures. *Wilder D. Bancroft.*

Jahrbuch der Elektrochemie. *Berichte über die Fortschritte des Jahres 1901. Herausgegeben von Heinrich Danneel. VIII. Jahrgang. 16 × 24 cm; pp. viii + 725. Halle: Wilhelm Knapp, 1902. Price: bound, 24 marks.* — This year the volume is edited by Danneel, Nernst and Borchers having retired. The new editor shows no less skill than his predecessors and the new volume is a fitting continuation of the admirable series. It may even be said that there is a greater uniformity of plan under the single editors than under the dual control. There are 372 pages devoted to pure electrochemistry and 326 to the applied science. A chapter on radiant energy and the behavior of gases is new, as is also a chapter on the treatment of metallic surfaces. It is interesting to notice that the attitude toward Kahlenberg's experiments is that of a frank admission that the results are entirely unexpected, tempered by the hope that these results will some day be interpreted in such a manner as to make them overwhelming arguments in favor of the electrolytic dissociation theory.

The reviewer is somewhat skeptical as to the Siemens-Halske electrolytic process for gold being in full swing in South Africa. The reports that reach this country are to the effect that the Siemens-Halske people or their licensees have bought the Andreoli patents and are working under them.

Wilder D. Bancroft.

Vorlesungen über hydrodynamische Fernkräfte nach C. A. Bjerknes' Theorie. *By V. Bjerknes. Band II. 16 × 25 cm.; pp. xvi + 313. Leipzig: Johann Ambrosius Barth, 1902. Price: paper, 10; bound, 11.50 marks.* — The second volume of the lifework of the Bjerknes, father and son, on hydrodynamic forces or action at a distance, is of a character quite different from the first volume. While the latter worked out the subtle dynamical effect of pulsation, oscillation, etc., in a homogeneous frictionless fluid, mathematically, often demanding very abstruse investigation, the present volume takes up the whole subject from an experimental point of view. To give the book coherence, however, the experimental part is introduced by an elementary mathematical theory, sufficient to explain the nature and purpose of the experiments, while the remarkable analogy between the forces and torques hydrodynamically found and the electric and magnetic field, is prefaced by a brief but interesting treatment of these subjects. Bjerknes here follows Heaviside's suggestion of rationalizing the electrical units as a whole, by beginning fundamentally with an irrational unit of charge. In other words, two unit charges (or poles) repel each other with one dyne, if their distance apart is the radius of a sphere of unit area. The equations which result have an unfamiliar aspect, but they have been simplified in the manner so often discussed.

The contents of the volume are within the reach of every one who has the usual elementary knowledge of mathematics, but they are none the less strikingly original. The degree of detailed similarity which exists between these hydrodynamic, electric, and magnetic fields is surprising; and yet nobody today believes that this analogy is more than a coincidence. The ether is daily becoming more complex and further removed from the state of the so-called ideal fluid. An ether model is a nightmare. The kinetic theory of gases which recently invaded chemistry is to-day becoming more obtrusive in its insistance upon the all-important pervasiveness of the corpuscle. The reviewer recalls vaguely the severe strictures which Thomson and Tait, in the earlier edition of their dynamics, cast upon Weber's electrical theory. In later editions the passage seems to have been expunged. All the worse, said they, if a theory is beautiful, and Weber's theory is beautiful. Surely a battering ram would not have done more effective execution! To-day, however, Weber's theory crops out serenely again in its ministrations to the ubiquitous corpuscle, and nobody calls for the battering ram.

Meantime the beautiful researches of the elder Bjerknes stand apart, something like what Lord Kelvin on another occasion calls a "mathematical poem;" and whoever finds pleasure in the contemplation of a model piece of physical research, completed without haste and without rest, both in its experimental and its mathematical aspects, will here find a rare and most fascinating volume.

C. Barus

Die Elektrizität in Gasen. *By Johannes Stark. 14 × 22 cm; pp. xxviii + 509. Leipzig: Johann Ambrosius Barth, 1902. Price: paper 12; bound, 13 marks.* — The author has given an excellent presentation of the phenomena bearing on the passage of electricity through gases, in so far as these phenomena interest the physicist. Practically no attention is paid to the chemical reactions taking place in gases under the influence of electricity. While this may seem a limitation, it is a natural one and, perhaps, a necessary one. The simplest case is the one which should be studied first and the simplest case is the one in which no permanent chemical change takes place. The chemist takes up the work where the physicist leaves it: but he must know what the physicist has done if he is to continue the work intelligently. It is for this reason that this book is valuable to the chemist, although written by a physicist for physicists. *Wilder D. Bancroft*

The Theory of Heat. *By Ernst Mach.* — Some time ago (1, 430) we had occasion to speak with interest and enthusiasm on Mach's notable treatise on the Theory of Heat. The book is a model of the way in which a scientific topic should be presented; wherefore we note with pleasure the appearance, in the Open Court for November, of the first installment of an English translation of it. It is to be hoped that the enterprising Open Court Company will soon complete and issue this English version; for it will certainly be very helpful to English-speaking students of physics and chemistry, and will undoubtedly contribute to a spread in general circles of an appreciation of the actual content of physical science and of the paths of induction through which it has arisen. Many who cannot find the time to read the completed book may find it readily possible to read the separate parts as they appear in the Open Court. The accurate translation into idiomatic English is the work of Mr. Thomas J. McCormack, one of the editors of the Open Court and the translator of the same publishers' admirable edition of Mach's Mechanics. *J. E. Trevor*

Plattner's Manual of Qualitative and Quantitative Analysis with the Blowpipe. *Translated by Henry B. Cornwall and John H. Caswell. Eighth edition, revised, after the sixth German edition from Friedrich Kolbeck. 15 × 22 cm; pp. xvii + 463. New York: D. Van Nostrand Company, 1902. Price: bound, $4.00 net.* — Plattner's classical work has gone through a number of editions as was to be expected. Richter edited the fourth and fifth editions and now Professor Kolbeck, for many years his assistant, has given the sixth German edition. There have been seven American editions, the translation having been ably done by Professor Cornwall, who now gives us the eighth edition from the latest German copy. The work is thus brought up to date, many new minerals have been added with approved tests, while some superfluous ones have been omitted. Modern chemical notation has been adopted and the spectroscopic methods have been dropped out, very properly. There is little for one to say of recent editions of standard works except to make such notes as are given above, yet some little curiosity is aroused to know why the use of metallic sodium, as given by Parsons and Moses, is not mentioned. *C. Baskerville*

Annuaire pour l'an 1903. *Publié par le Bureau des Longitudes. 9 × 15 cm; Paris: Gauthier-Villars, et Fils. Price: 1.50 francs.*—The current *Annuaire* of the Bureau of Longitudes, with its extensive tabulations of scientific data, appears promptly as usual. The special features of the present issue are the following appended articles: Shooting Stars and Comets, by R. Radeau; Science and Poetry, read before the annual public sitting of the five academies on October 25, 1902, by J. Janssen; the addresses delivered at the funerals of Cornu and of Faye. *J. E. Trevor*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Report of the international committee on atomic weights. *F. W. Clarke. Jour. Am. Chem. Soc.* 25, *1* ; *Zeit. anorg. Chem.* 33, *241* (*1903*). — The followlowing changes are made: Sb 120.2 ; Ge 72.5 ; H 1.008; La 139.04; Hg 200.0; Pd 106.5 ; Rd 225 ; Se 79.2 ; Sn 119.0 ; U 238.5 ; Zr 90.6. *W. D. B.*

The atomic weight of lanthanum. *B. Brauner. Zeit. anorg. Chem.* 33, *317* (*1903*). — This is a reply to a review by Jones. The author claims that the experiments of Jones were made with impure material and without proper care, and that his results and conclusions are therefore wrong. The author's value of 139.04 for lanthanum was obtained after he had discovered the error in the method by which both Jones and himself found 138.78. The same error—of the acid sulphate—occurs in the praseodymium determinations, where the true value is 140.95 and not the 140.46 of Jones. *W. D. B.*

On selenium, II. *J. Meyer. Zeit. anorg. Chem.* 31, *391* (*1902*). — The first paper (6, 498) dealt with the relations between phosphorus and selenium this one with the atomic weight of selenium. The author determined the silver in silver selenite by electrolysis. The results for the atomic weight of selenium vary between 79.17 and 79.28, the mean for the five experiments being 79.21. These results were checked by precipitating the selenium from the selenious acid solution by means of hydrazine sulphate. *W. D. B.*

The calculation of atomic weights. *F. W. Clarke. Zeit. anorg. Chem.* 32, *219* (*1902*). — Reviewed (6, 429) from *Am. Chem. Jour.* 27, *321* (*1902*).

On the position of the rare earth elements in the periodic system of Mendelejeff. *B. Brauner. Zeit. anorg. Chem.* 32, *1* (*1902*). — A general discussion of the rare earth elements. The author proposes to put all the elements with atomic weights, 140-178, in the fourth group below tin. These are to be treated as a single individual or zone, just as we now treat iron, cobalt and nickel, or ruthenium, rhodium, and platinum for instance. *W. D. B.*

On the position of tellurium in the natural system of the elements. *K. Seubert. Zeit. anorg. Chem.* 33, *246* (*1903*). — The author gives his reasons for believing that tellurium must be placed before iodine in the periodic table even though this is not in accordance with the atomic weights. He holds that the agreement of properties is too striking to permit of any other arrangement and that we must frankly accept the atomic weight as "abnormal." *W. D. B.*

The significance of changing atomic volume.—III. *The relation of changing heat capacity to change of free energy, heat of reaction, change of volume and chemical affinity. T. W. Richards. Proc. Am. Acad.* 38, *293; Zeit. phys. Chem.* 42, *129* (*1902*).—From the fact that the heat capacity of a system usually changes in the course of a chemical change, the author is led to inquire whether a relation exists between this change of heat capacity and the change of free energy and the heat of the (reversible) reaction. On tabulating the change of heat capacity, the output of electric energy, the heat of reaction, and the difference of the last two quantities, for ten reversible cells, he observes that the first and last of these quantities have the same sign and similar magnitude. From the data he concludes that "the change of the free energy with the temperature must have some fundamental connection with the change of the total energy with the temperature," and that this connection is

$$\frac{\partial \Delta F}{\partial \theta} = - M \frac{\partial \Delta E}{\partial \theta},$$

using a notation of obvious meaning. The factor M is "about 2" in the units employed.

Defining an "attracting energy" as "the sum of the work done by all those tendencies which exert a positive attraction," with the explanation that these tendencies may be chemism, gravitation, electric attraction, and perhaps others, the author interprets the observed facts in the statement that "when the heat capacity of a system changes during a reaction, and concentration influences are balanced, it seems reasonable to suppose that the attracting energy lies between the free-energy and the total-energy change, one being too small and the other too large."

Let us examine the equation given above. In normal variables we have

$$E = F - \theta \frac{\partial F}{\partial \theta},$$

E, F, and θ denoting energy, free energy, and absolute temperature, of the system. By differentiation

$$\frac{\partial E}{\partial \theta} = - \theta \frac{\partial^2 F}{\partial \theta^2};$$

whence, for a finite reversible isothermal change, by subtraction,

$$\frac{\partial \Delta E}{\partial \theta} = - \theta \frac{\partial^2 \Delta F}{\partial \theta^2},$$

which is the correct form of the relation in question. But let us return to the original question as to the relation between ΔF, ΔE, and the alteration of heat capacity in the change. In the equation

$$\frac{\partial E}{\partial \theta} = - \theta \frac{\partial^2 F}{\partial \theta^2},$$

the first member is the heat capacity C for constant parameters. If, for example, the state of the system is fixed by the two variables volume and temperature, this member represents the heat capacity at constant volume. So we have

$$C = - \theta \frac{\partial^2 F}{\partial \theta^2}$$

which is the relation sought. In a finite reversible isothermal change,

$$C(\theta, x_{12}, x_{22}, \cdots, x_{n2}) = -\theta \frac{\partial^2}{\partial\theta^2} F(\theta, x_{12}, x_{22}, \cdots, x_{n2})$$

$$C(\theta, x_{11}, x_{21}, \cdots, x_{n1}) = -\theta \frac{\partial^2}{\partial\theta^2} F(\theta, x_{11}, x_{21}, \cdots, x_{n1})$$

wherefore, by subtraction,

$$C_2 - C_1 = -\theta \frac{\partial^2}{\partial\theta^2} (F_2 - F_1),$$

which expresses the relation between the change of heat capacity and the simultaneous change of free energy.

The paper is concluded by an examination of "systems involving appreciable concentration effect." An interpretation of the facts is offered, on the basis of a hypothesis of compressible atoms. *J. E. T.*

On the nature of the metallic state. *H. Erdmann. Zeit. anorg. Chem.* 32, *404* (*1902*). — The author defines metals as elements whose molecules contain but one atom while metalloids are elements whose molecules consist of several atoms. *W. D. B.*

One-Component Systems

On yellow arsenic. *H. Erdmann and M. v. Unruh. Zeit. anorg. Chem.* 32, *437* (*1902*). — The authors prepare yellow arsenic by distilling it into carbon bisulphide and then evaporating the carbon bisulphide. At temperatures below – 60° the crystalline yellow arsenic keeps for quite a while when in contact with glass and in the dark. When in contact with metal, it blackens at any temperature, and the same change takes place under all circumstances when exposed to light. Boiling-point experiments with yellow arsenic dissolved in carbon bisulphide gave results indicating a formula As_4. *W. D. B.*

Some constants for carbon bisulphide. *M. v. Unruh. Zeit. anorg. Chem.* 32, *407* (*1902*). — Carbon bisulphide boils at 46.25° under 760 mm. Between 740 mm and 765 mm, the change of boiling-point per millimeter is practically constant at 0.04144°. The specific gravity is 1.22093 at 46.25°. The boiling-point constant, referred to 100 grams, is 2370. *W. D. B.*

Note on the law of the rectilinear diameter. *A. Batschinski. Zeit. phys. Chem.* 41, *741* (*1902*). — The author points out that Mathias's law of the rectilinear diameter can be deduced from the van der Waals formula. *W. D. B.*

Note on the Clapeyron-Clausius equation for latent heat. *K. Hällstén. Zeit. phys. Chem.* 42, *369* (*1902*). — The author deduces the value of the "internal" pressure from a consideration of the Clapeyron-Clausius equation for the latent heat. *W. D. B.*

Note on determination of vapor-densities under diminished pressure. *H. Erdmann. Zeit. anorg. Chem.* 32, *425* (*1902*). — The apparatus is very similar to that of Bleier and Kohn (4, 144). *W. D. B.*

Two-Component Systems

The nature of cadmium amalgams and their electromotive behavior. *H. C.*

Bijl. Zeit. phys. Chem. 41, *643* (*1902*). — In the system mercury and cadmium, a solid solution is solid phase from the melting-point of cadmium to 188°. At lower temperatures, two series of solid solutions are possible. A study of the electromotive forces of the amalgams showed that they varied with the concentration in the manner called for by the theory. The difficulties in regard to the 14.3 pct amalgam were cleared up. *W. D. B.*

Mix-crystals of sulphur and selenium. *W. E. Ringer. Zeit. anorg. Chem.* 32, *183* (*1902*). — A careful study of the system, sulphur and selenium. The following conclusions were drawn: —

1. Fused selenium and liquid sulphur are miscible in all proportions. The fused mass crystallizes with difficulty when the amount of selenium exceeds ten atomic percents. Even with slow cooling, the mixture changes to an amorphous mass and mixtures rich in selenium are obtained crystalline only after several hours heating near the melting-point.

2. The crystalline mixtures are probably composed only of mix-crystals and no evidence of a chemical compound has been found.

3. From the fused mixtures there separate three series of mix-crystals:

(*a*) A series of monoclinic mix-crystals (of the monoclinic sulphur type) with 0–27 atomic percents of selenium).

(*b*) A series of monoclinc mix-crystals (the third sulphur modification ?) with about 50–82 atomic percents of selenium.

(*c*) A series of hexagonal-rhombohedric mix-crystals (of the metallic selenium type) with ca.87-100 atomic percents of selenium.

4. The crystals of the first series change below certain temperatures into rhombic crystals, just as monoclinic sulphur changes to the rhombic form. These temperatures lie between 95.5° and ca.75°. No such change occurs with the other series of mix-crystals.

5. At ordinary temperatures there exists:

(*a*) A series of rhombic mix-crystals with 0–ca.10 atomic percents of selenium.

(*b*) A series of mix-crystals of the second type with 55-75 atomic percents of selenium.

(*c*) A series of mix-crystals of the hexagonal selenium type with 90-100 atomic percents of selenium. *W. D. B.*

Succinic and phthalic anhydrides in their behavior towards water. *E. van de Stadt. Zeit. phys. Chem.* 41, *353* (*1902*). — Determinations of the freezing-point curves for succinic anhydride and phthalic anhydride with water. The author finds that equilibrium is reached at once and that the melting-points of the acids is not a function of the time of heating. The author also finds a eutectic point, or what appears to be one, with phthalic acid and phthalic anhydride as solid phases. These results are exactly the reverse of those found in the reviewer's laboratory (3, 72) and differ markedly from those of all other investigators. While the experiments seem to have been made carefully, a further investigation seems to be called for. It seems very improbable that the dissociation of solid phthalic acid takes place instantaneously. *W. D. B.*

The hydrates of perchloric acid. *H. J. van Wyk. Zeit. anorg. Chem.* 32, *115* (*1902*). — The author has determined the freezing-point curve for water and perchloric acid up to 90 molecular percents of perchloric acid. There are five compounds, each stable at its melting-point, with, one, two, three, four, and six of water, melting respectively at + 50°, — 20.6°, — 47°, — 40°, and — 45°. The monohydrate is stable over the widest range of concentration.

W. D. B.

The compounds of tellurium and iodine. *A. Gutbier. Zeit. anorg. Chem.* 32, *108* (*1902*). — Tellurium and iodine do not form two liquid layers. The author has isolated TeI_4, but could not obtain the TeI_2 described by Berzelius.

W. D. B.

The relation between freezing-points, boiling-points and solubility. *M. Wildermann. Zeit. phys. Chem.* 42, *481* (*1903*). — The author starts with the concentrations at the eutectic point and boiling-point of a binary system as given and deduces the solubility curve on the assumption of constant heat of solution.

W. D. B.

On the extrapolation for the melting-point of chemically homogeneous substances from measurements of the volumes on the isobar near the melting-point. *V. Ssobelewa. Zeit. phys. Chem.* 42, *75* (*1902*). — The author determines the volume change and corresponding temperature at three points during the solidification of an impure melt and extrapolates from these values to the freezing-point of the pure substance. Experiments are described, showing the accuracy of the method. *W. D. B.*

On the solubility of ammonium nitrate in water between 12° and 40°. *W. Müller and P. Kaufmann. Zeit. phys. Chem.* 42, *497* (*1903*). — Schwarz found a lesser solubility for ammonium nitrate at 36° than at 35°. Experiments by the authors show that this very unexpected result is to be attributed to experimental error. *W. D. B.*

The solubility of red and yellow mercuric oxide and its dissociation. *K. Schick. Zeit. phys. Chem.* 42, *155* (*1902*). — When equilibrium is reached, there is no difference in the solubility of the red and yellow mercuric oxides. On heating, the yellow oxide changes to a red color above 35°-45°, the yellow color returning on cooling. A solution of mercuric oxide conducts only slightly better than water. Hydroxyl as ion increases the solubility of mercuric oxide in water. While a solution of mercuric oxide has no action on ethyl acetate, saponification takes place when a neutral salt is added to the solution.

W. D. B.

Addition to my paper: Preliminary communication on a method for calculating solubilities. *A. Findlay. Zeit. phys. Chem.* 42, *110* (*1902*). — The author points out that a term has been overlooked in the formula given by him (6, 431) and that this formula is therefore only to be used under definite limitations. *W. D. B.*

On the discoverer of the "breaks" in solubility curves. *W. Meyerhoffer. Zeit. phys. Chem.* 42, *501* (*1903*). — It is claimed that Kopp's views on the solubility curves, and on the change of direction when the solid phase changes, were practically the same as those of the present day. It is also claimed that Kopp was the first to be clear as to the cause of the breaks. *W. D. B.*

The doctrine of solubility curves. *W. Ostwald. Zeit. phys. Chem.* 42, *503* (*1903*). — Kopp's view about the breaks in the solubility curve (preceding review) was not entirely correct because he assumed a sudden change in the unsaturated solution at the temperature of the quadruple point. Ostwald maintains that the first complete statement of the facts is to be found in the first edition of his *Lehrbuch*. He attributes the discovery of the breaks in the solubility curve to Gay-Lussac and not to Kopp. *W. D. B.*

On the nature of the metastable state. *F. W. Küster. Zeit. anorg. Chem.* 33, *363* (*1903*). — The solubility of a solid at a given temperature increases with decreasing size of crystals. The author claims that there is an upper limit to the solubility because there is a limit below which the size of the crystal cannot go and yet have that crystalline substance. The author places the field for metastable solutions between this limiting solubility and the 'normal' solubility. This is atomistic to the last degree. *W. D. B.*

Molecular weight determination of solid and liquid substances in Weinhold's vacuum vessels. *H. Erdmann and M. v. Unruh. Zeit. anorg. Chem.* 32, *413* (*1902*). — It is claimed that the Dewar vacuum tubes were invented by Weinhold in 1881. This paper describes molecular weight determinations by Landsberger's method, using a vacuum-jacketed boiling flask. Sulphur in carbon bisulphide gave results corresponding to S_8. *W. D. B.*

On colloidal tellurium. *A. Gutbier. Zeit. anorg. Chem.* 32, *51*, *91* (*1902*). — When tellurium dioxide is treated with dilute hydrazine hydroxide, a brown colloidal solution of tellurium is formed which can be purified by dialysis. When telluric acid is treated in the same way, the colloidal solution may be either brown or blue. An excess of hydrazine hydroxide leads to the formation of the gel only. The brown hydrosol can also be prepared by the action of sulphur dioxide, sodium bisulphite, hypophosphorous acid, or hydroxylamine hydrochloride on suitable solutions of tellurium salts. *W. D. B.*

On the liquid hydrosol of selenium. *A. Gutbier. Zeit. anorg. Chem.* 32, *106* (*1902*). — When selenium dioxide is treated with dilute hydrazine hydroxide, a solution of colloidal selenium is formed which can be purified by dialysis. The solution is red by transmitted light and shows a blue fluorescence by reflected light. The gel is red selenium. *W. D. B.*

Studies on colloidal sulphides. *A. Gutbier. Zeit. anorg. Chem.* 32, *292* (*1902*). — By passing hydrogen sulphide into solutions of tetravalent tellurium, of telluric acid, and of selenium dioxide, the author has prepared the liquid hydrosols of tellurium bisulphide, tellurium trisulphide, and selenium sulphide respectively. *W. D. B.*

Contributions to our knowledge of inorganic colloids. *A. Gutbier. Zeit. anorg. Chem.* 32, *347* (*1902*). — The author describes the preparation, chiefly by means of hydrazine hydroxide, of the hydrosols of gold, selenium, tellurium, silver, platinum, mercury, and copper. *W. D. B.*

The liquid hydrosol of gold. *A. Gutbier. Zeit. anorg. Chem.* 31, *448* (*1902*). — If dilute neutral gold chloride be reduced by hydrazine hydroxide with suitable precautions, a dark-blue solution is obtained. If too much hydrazine hydroxide be added, a blue gel separates. The blue sol, when dialyzed, will keep indefinitely. *W. D. B.*

On aqueous ammonia solutions. *C. Frenzel. Zeit. anorg. Chem.* 32, *319* (*1902*). — The author discusses at length the reasons for and against the assumption that aqueous ammonia consists chiefly of aqueous ammonium hydroxide. He decides against this assumption, largely on the strength of some electrolytic experiments herein described. *W. D. B.*

Multi-Component Systems

The formation and solubility of sodium copper sulphate. *J. Koppel. Zeit. phys. Chem.* 42, *1* (*1902*). — The curious results obtained by Massol and Maldes (6, 354) have been explained by the author who finds that a double sulphate of copper and sodium, $Na_2SO_4CuSO_42H_2O$, exists with an inversion temperature at 16.7°. This same double salt has been found in the desert of Atacama and has been described under the name of Kröhnkite. *W. D. B.*

The system $SbCl_3$, HCl, H_2O. *J. M. van Bemmelen. Zeit. anorg. Chem.* 33, *272* (*1903*). — The author has determined the solubility curve with $SbCl_3$ as solid phase and isotherms at 20° and 50°. At 20° the solid phases are $SbCl_3$, a compound of $SbCl_3$ and SbOCl, SbOCl and $Sb_4O_5Cl_2$. The compound referred to appears to have the formula $(SbOCl)_3SbCl_3$; but this is not yet definitely determined. *W. D. B.*

Vapor-pressures of ternary mixtures. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 36, *257*, *412*, *711*; 37, *129*; 38, *227* (*1901*). — This is a consideration of ternary systems, based on the ζ surface of van der Waals. It is first shown that, at constant temperature, the vapor surface and the liquid surface both rise with rising pressure, the vapor surface faster than the liquid surface. At constant pressure, both surfaces fall with rising temperature, the vapor surface falling faster than the other. The author then discusses the form of the evaporation and condensation curves for a number of typical cases and shows how these curves are displaced by changing the temperature or pressure.

Next comes the form of the distillation curves when one distils at constant temperature, or at constant pressure. This is followed, in the third article, by a discussion of the evaporation and condensation curves in dineric systems, while the fourth article treats of distillation in these same systems. In the fifth article there is a consideration of systems forming three liquid phases, and then the author takes up the question of the change of vapor pressure when a third component is added to a binary system.

This last section is the least satisfactory because the author treats his three components as three abstract substances, A, B, and C, without reference to the behavior of these substances taken by pairs. In a ternary system, it makes all the difference in the world whether one component tends to precipitate another or not. The author neglects this point and is probably led into at least one error thereby. He deduces the conclusion that a binary mixture having a constant boiling-point will behave like a pure substance when a third component is added. It seems to the reviewer that the tacit assumption has been made that the addition of the third component does not change the ratio of the other two in the vapor phase. *W. D. B.*

Vapor-pressures in the system: water, acetone, and phenol. *F. A. Schreinemakers. Zeit. phys. Chem.* 39, *485*; 40, *440*; 41, *331* (*1902*). — The author has determined a binodal curve for water, acetone, and phenol at 56.5°; and a whole series of pressure-temperature curves for different ternary mixtures. He then discusses the evaporation and condensation curve at 56.5° and also the composition of the vapor in equilibrium with two liquid phases at this temperature.

In the third article there is a discussion of the evaporation and condensation curves at the constant pressure of 380 mm; of the dineric system at 380 mm; and of the evaporation curve at 760 mm.

If we add water to a mixture of phenol and acetone, the boiling-point may be raised or lowered, depending on the relative masses of phenol and water. If we add phenol to an aqueous acetone solution, the sign of the change of the boiling-point will depend on the relative masses of water and acetone. If we add acetone to a homogeneous mixture of phenol and water, the boiling-point will be lowered, regardless of the relative masses of water and phenol.

W. D. B.

The solubility equilibrium between silver chloride, silver oxide, and solutions of potassium chloride and hydroxide. *A. A. Noyes and D. A. Kohr. Jour. Am. Chem. Soc.* 24, *1141*; *Zeit. phys. Chem.* 42, *336* (*1902*). — The determination of the solubility of AgOH by analytical methods gave 2.16×10^{-4} mols per liter at 25°. *Experiments on the ratio of the concentrations of chlorine and* hydroxyl as ion in solutions of potassium chloride and hydroxides, which are simultaneously saturated with silver chloride and oxide, point to a solubility of silver oxide ten times that of silver chloride. The analytical results indicate a solubility of 14.4 times as great. This discrepancy is eliminated if we assume seventy percent dissociation of silver hydroxide. *W. D. B.*

On the dissociation of the mercuric halides. *H. Morse. Zeit. phys. Chem.* 41, *709* (*1902*). — From experiments on the solubility of silver chloride, bromide and iodide in mercuric nitrate solutions and from distribution experiments with mercuric salts, the author deduces the existence of a cation $HgX^{\cdot}$ in solutions of mercuric halides. Transference experiments confirmed these conclusions. Some new double salts were isolated. *W. D. B.*

The freezing-point of dilute mixed solutions. *Y. Osaka. Zeit. phys. Chem.* 41, *560* (*1902*). — Experiments were made with potassium sulphate in mannite and phenol solutions, and with sodium chloride in urea and phenol solutions. The lowering of the freezing-point for the mixtures is very nearly the sum of the depressions for the single substances, if anything a little less. Potassium sulphate in phenol solution gives a smaller depression than in water, though the reverse effect had been expected from the solubility relations. The author concludes "that the action of the ions of a salt on the undissociated salt is small and that this action cannot be the main cause of the variations from the dilution law in the case of the strong electrolytes." In none of the experiments did the lowering of the freezing-point reach 0.06°. *W. D. B.*

On the behavior of sodium sulphate in aqueous solution. *A. Hantzsch. Zeit. phys. Chem.* 42, *202* (*1902*). — Wyrouboff has claimed that the precipitation of sodium sulphate from aqueous solution by alcohol gives different solid phases depending on the solution having been made by dissolving hydrated or anhydrous sodium sulphate in water. Experiments in the author's laboratory show that Wyrouboff's solutions were probably not all at the same temperature and that he overlooked the temperature changes due to adding alcohol. *W. D. B.*

On the molecular state of potassium iodide in phenol. *E. H. Riesenfeld. Zeit. phys. Chem.* 41, *346* (*1902*). — Potassium iodide distributes itself between phenol and water pretty nearly so that the ratio of the concentrations is constant. This became more intelligible when it was found that potassium iodide in aqueous phenol conducts fairly well. In pure phenol potassium iodide conducts much less well. *W. D. B.*

The solubility of boric acid in hydrochloric acid. *W. Herz. Zeit. anorg. Chem.* 33, *355* (*1903*). — In Dammer's handbook it is stated that hydrochloric acid increases the solubility of boric acid in water. Experiments by the author show that addition of hydrochloric acid at 26° decreases the solubility of boric acid from 0.9 *n* to the constant value of about 0.33 *n*. *W. D. B.*

On the solubility of sulphur dioxide in aqueous salt solutions. *C. J. J. Fox. Zeit. phys. Chem.* 41, *458* (*1902*). — The solubility of sulphur dioxide increases approximately proportional to the concentration of the salt in the case of many aqueous salt solutions. With NaCl, Na_2SO_4, $CaBr_2$, $CaCl_2$ and $CdSO_4$, however, there is decrease of solubility. The following solid salts were prepared: $KISO_2$, $KBrSO_2$, $KClSO_2$, $KCNSO_2$. In these salts the anion is complex. *W. D. B.*

On thallic chloride. *R. J. Meyer. Zeit. anorg. Chem.* 32, *72* (*1902*). — Thallic nitrate dissolves silver chloride readily so that the chlorine in thallium chloride can be precipitated completely only by adding an excess of concentrated silver nitrate. *W. D. B.*

The lecithans, their function in the life of the cell. *W. Koch. University of Chicago Decennial Publications*, 10, *1* (*1902*). — The word lecithan is proposed as a group name to include such compounds as egg lecithin, kephalin, myelin, paramyelin, etc. A method of determining lecithin and kephalin quantitatively is presented. According to the author, the latter substance occurs only in the living cell, possibly as an intermediary product in the metabolism of lecithin. The precipitation of an emulsion of brain lecithin is effected by acids and by salts of the following bivalent metals: Mg, Ca, Sr, Ba, Co, Ni, $Fe^{\cdot\cdot}$, Zn, Cd, Cu, Pb. Ferric salts and salts of aluminum do not cause precipitation; chromium salts give "unsatisfactory results;" from gold salts the metal is reduced to the metallic state. Salts of Na, K, NH_4, Li, Ag apparently have no effect on the emulsion; the presence of these salts, and also that of ferric and aluminum salts, prevents the precipitation by salts of the bivalent metals, while the presence of urea and glucose does not prevent it. Caustic alkalies cause the emulsion to clear up. The author leaves the reader in doubt as to which salts of the above metals he used; this follows from his attempt to express his results entirely in terms of the theory of the electrolytic dissociation. Under the head of new "facts" the author states that "the emulsion formed by the lecithans may be the substratum in which the reactions of the cell take place;" no evidence to support this statement is presented, however.

L. K.

Osmotic Pressure and Diffusion

Relation between negative pressure and osmotic pressure. *G. A. Hulett. Zeit. phys. Chem.* 42, *353* (*1902.*) — The author has repeated some of Askenasy's measurements (1, 379) with a ferrocyanide membrane at the top of the tube. In this way he succeeded in getting a negative pressure of 377 mm before the column broke. The author shows that the osmotic pressure can be considered as a negative pressure. *W. D. B.*

On chromium hydroxide. *W. Fischer and W. Herz. Zeit. anorg. Chem.* 31, *352* (*1902*). — When chromium hydroxide precipitates from an alkaline solution, there is no change of conductivity. When such a solution is subjected to dialysis, no chromium passes the diaphragm. The authors conclude that chromium hydroxide is present only as colloid in alkaline solution, that aluminum hydroxide is present as compound, and zinc hydroxide partly as compound, partly as colloid. *W. D. B.*

Dialysis experiments with metal hydroxides and sulphides. *W. Herz. Zeit. anorg. Chem.* 31, *454* (*1902*). — In alkaline solutions of lead, tin, and aluminum, the metals diffuse through parchment without precipitation of hydroxides. In alkaline solutions of zinc and beryllium, small quantities of the metals diffuse through parchment; but there is a heavy precipitate of hydroxide. In an alkaline solution of chromium (preceding review) no chromium diffuses. These experiments are in agreement with the conclusions of Hantzsch (6, 504). In a solution of nickel sulphide in ammonium sulphide, some nickel diffuses through parchment but a great deal of the sulphide precipitates.

W. D. B.

Dialysis experiments with metal hydroxides. *W. Herz. Zeit. anorg. Chem.* 32, *357* (*1902*). — When stannic hydroxide is dissolved in alkali, the tin diffuses through parchment. Antimony does the same when antimony oxide is dissolved in alkali. It is now found that if the hydroxides of zinc and beryllium are washed and then dried at 60°-70° before being dissolved in alkali, they pass readily through parchment. There is thus apparently a marked difference between the dried and the fresh hydroxide (preceding review). *W. D. B.*

Velocities

The rate of decomposition of diazo compounds, I. *J. C. Cain and F. Nicoll. Jour. Chem. Soc.* 81, *1412* (*1902*). — Following the example of Hausser and Müller and of Hantzsch (Ber. 33, 2517 (1902), the authors have determined the rate of decomposition of a number of diazo compounds of the benzene series in aqueous solution. While Hantzsch's numbers are confirmed, both the experimental results and conclusions of the former writers are severely criticized. Measurements were made with the diazo salts of the following amines and diamines : Aniline, *o*-, *m*-, and *p*-nitraniline, *p* aminoacetaniline, benzidine, *oo*-dichlorbenzidine, toluidine, and dianisidine. Except in the cases of diazo-*p*-acetaminobenzene chloride and a couple of tetrazo-compounds very good first-order constants were obtained, the deviations with the former substance being ascribed to a simultaneous elimination of the acetyl group by the free acid, and in the latter to a difference in the stability of the diazo groups and consequent occurrence of successive reactions. Free acids and (in disagreement with Hausser and Müller) phenol were found to be without influence on the velocity.

The experiments extended over a range of temperature from 20° to 60°. The temperature coefficient was unusually large, the rate being almost quadrupled by increases of 10°. *F. B. K.*

The hydrolysis of triacetylglucose by enzymes. *S. F. Acree and J. E. Hinkins. Am. Chem. Jour.* 28, *370* (*1902*) — Certain bacteria not only generate organic acids from glucose, lactose, etc., but also cause the acids to combine with the sugar to form esters. In order to determine, whether the latter reaction is a reversible one, the analogous case of the hydrolysis of triacetylglucose by enzymes has been studied. Measurements were made of the rate of hydrolysis of the following enzymes : pancreatin, amylopsin, emulsin, maltase, diastase, and takadiastase. The reactions came to a standstill at different points with different enzymes, probably on account of an inhibitory effect of the free acids on the catalyzers. The reverse change, namely the combination of acetic acid with glucose, was found to be effected by pancreatin. The experiments are to be considered as of a preliminary nature. *F. B. K.*

Intermolecular transposition in the halogen acetanilides, and its velocity. *J. J. Blanksma. Rev. Trav. Chim. Pays-Bas*, 21, *366* (*1902*). — The transformation of acetyl chloranilide into *p*-chloracetanilide in aqueous solution containing acetic acid is found to be a monomolecular reaction, catalyzed by hydrochloric acid. Doubling the concentration of the hydrochloric acid increases the rate about fourfold (1 : 3.81) When the hydrochloric acid is replaced by sulphuric acid the reaction proceeds extremely slowly, while with glacial acetic acid as solvent, the reaction is very rapid even when only small quantities of hydrochloric acid are present. In the latter case the constant increases as the reaction proceeds, owing to a setting free of hydrochloric acid during the process. The meaning of the results is unnecessarily obscured by a wanton change of the time units from one-half to one-quarter of an hour. The experiments were carried out in the dark at 25°. *F. B. K.*

The molecular decrease of the rate of crystallization by addition of foreign substances. *E. von Pickardt. Zeit. phys. Chem.* 42, *17* (*1902*). — A large number of determinations of the rate of crystallization of benzophenone and benzoic anhydride, containing very small quantities of dissolved substances, lead to a very striking relation. It is found, namely, that the decrease in the velocity of crystallization of the pure substance is proportional to the square root of the concentration of the added material, and that, for the same solvent, the proportionality constant is independent of the nature of the dissolved substance, when its concentration is expressed in molecular units. When several substances are added at the same time, proportionality to the square root of the total molecular concentration subsists, and not to the sum of the square roots of the individual concentrations. The relation holds good up to about eight mols of solute to one hundred mols of solvent.

The author points out that this relation not only affords a new method for determining molecular weights, but supplies also a means of estimating the absolute amount of impurity in a substance which cannot be prepared in the pure state. The measurements were carried out in capillary tubes at 20°.

F. B. K.

The action of blood on hydrogen peroxide. *J. Ville and J. Moitessier. Bull. Soc. Chim. Paris,* 27, *1003* (*1902*). — Experiments on the catalysis of hydrogen peroxide by blood. The amount of oxygen liberated depends on the acidity of the solution, on the concentration of the peroxide and on the kind of animal from which the blood was obtained. *W. L. M.*

The decomposition of urea. *C. E. Fawsitt. Zeit. phys. Chem.* 41, *601* (*1902*). — Measurements were made of the rate of decomposition of urea in aqueous solutions varying from 1/2 to 1/16. (1/4 to 1/32 molecular). Ammonium salts retarded, sodium salts accelerated the reaction, while ammonium carbonate had but little influence. Acids (HCl and H_2SO_4) increase the velocity greatly, although the rate was almost independent of their concentration. Alkalies, with the exception of ammonia, increased the rate even more than acids, the acceleration increasing with the concentration of the alkali. Ammonia diminished the rate. In all cases the reaction remained of the first order, except where much alkali was present, in which event the constants increased with the course of the decomposition, indicating a reaction of higher order. The author has turned his experimental data to excellent theoretical account, and explains his results satisfactorily by assuming that the urea first changes to ammonium cyanate, which is subsequently decomposed to ammonia and carbonic acid, while concentrated alkalies cause a simultaneous direct saponification of the urea. The reaction between the urea and the ammonium cyanate is a reversible one, the equilibrium point and the rate of formation of urea having been determined by Walker and Hambly. This reaction the author was able to isolate in the case of neutral solutions. He found not only that the velocity constant was of the first order, but also that it possessed the value calculated from the equilibrium constant and the velocity constant of the reverse reaction. Without going into further details, it may be said that this reaction is one of the few cases where the existence of an "intermediate substance" — assumed in order to bring the chemical equation into accord with the velocity equation — has been confirmed by sound independent evidence. The measurements were carried out at 99.2° and 90.1°. *F. B. K.*

The speed and nature of the reaction of bromine upon oxalic acid. *T. W. Richards and W. N. Stull. Proc. Am. Acad.* 38, *321* (*1902*). — Reviewed (7, 49) from Zeit. phys. Chem. 41, 544 (1902).

Rate of coagulation of colloidal silicic acid. *W. Flemming. Zeit. phys.*

Chem. 41, *427* (*1902*). — The rate of coagulation of colloidal silicic acid is the same under the same conditions. With increasing concentration of hydroxyl there is first a retarding action, then an accelerating action, followed by a retarding action. With increasing concentration of hydrogen as ion, the reverse effects are observed. The rate of coagulation increases with increasing concentration of the silicic acid and with rising temperature. *W. D. B.*

Electromotive Forces

On amalgam potentials and the monatomicity of metals dissolved in mercury. *F. Haber. Zeit. phys. Chem.* 41, *399* (*1902*). — The author points out that the ordinary formula for an amalgam concentration cell must be modified if compounds of the type Hg_nNa are formed. On the assumption of Hg_6Na the correcting term is a few tenths of a millivolt for the concentrations studied by Meyer. *W. D. B.*

On the dissociation constant of water and the electromotive force of the oxy-hydrogen gas cell. *G. Preuner. Zeit. phys. Chem.* 42, *50* (*1902*). — From the reaction between carbon monoxide and oxygen, and the reaction between carbon dioxide and hydrogen, the author deduces the dissociation constant for water and the electromotive force of the hydrogen-oxygen gas cell. The latter value comes out 1.15 volt, in close agreement with the experimental results of Bose (6, 155). *W. D. B.*

The phase rule and the difference of potential between an electrode consisting of two metals and an electrolyte containing the salts of these metals. *W. Reinders. Zeit. phys. Chem.* 42, *225* (*1902*). — A discussion of the potential differences between different types of binary electrodes and a solution. This is followed by an application of the phase rule to normal cells, which is somewhat unintelligible. The author attributes imaginary statements to the reviewer and apparently comes out with the result that the electromotive force of the Clark cell is independent of the pressure. *W. D. B.*

On the oxidation of alcohol and aldehyde. *J. Slaboszewicz. Zeit. phys. Chem.* 42, *343* (*1902*). — Experiments showed that aldehyde has a higher potential than alcohol, both in acid and alkaline solutions, contrary to the results of Dony-Hénault (4, 699). *W. D. B.*

Contributions to our knowledge of cuprous compounds, II. *G. Bodländer and O. Storbeck. Zeit. anorg. Chem.* 31, *458* (*1902*). — From solubility and electrometric measurements with cuprous bromide and cuprous iodide, the authors conclude that cuprous copper is univalent, the ion being Cu•. The experiments involve a good deal of calculation which may introduce an error. It seems to the reviewer that more satisfactory results could be obtained by studying copper amalgam concentration cells with cuprous chloride and hydrochloric acid as electrolyte. *W. D. B.*

On the asymmetry of the electrocapillary curve. *J. J. van Laar. Zeit. phys. Chem.* 41, *385* (*1902*). — The author concludes that the potential-pressure curve for mercury in any solution is not continuous; but consists of two parts, meeting at a point. He deduces a formula which represents, with accuracy, Smith's results with 0.1 *n* KCl. One consequence of this view is that we cannot determine single potentials by the maximum surface tension method or by the flowing mercury electrode. *W. D. B.*

Experimental notes on the anodic decomposition points for aqueous sodium hydroxide. *F. Plzák. Zeit. anorg. Chem.* 32, *385* (*1902*). — The cathode was always a platinum plate over which hydrogen was bubbled. The anode was a platinum point and it was found to make no difference whether hydrogen was or was not bubbled over it. The following decomposition voltages were found: both electrodes smooth, 1.08 volts; cathode platinized and anode smooth, 0.6 and 1.67 volts; cathode smooth and anode platinized, 0.4 and 0.9 volt; both electrodes platinized, 1.08 and 1.53 volts. These values are connected in some way with the 0.6 volt for hydrogen with one smooth and one platinized electrode and the 0.45 volt for oxygen with one smooth and one platinized electrode. *W. D. B.*

On bipolar electrodes. *A. Brochet and C. L. Batillet. Comptes rendus,* 135, *854* (*1902*). — A preliminary study on the behavior of interposed plates which do not fill the cross-section of the electrolytic cell. The authors seem to be a little vague as to the exact conditions under which there should be precipitation on the interposed plate. *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the accuracy of the improved voltameter. *T. W. Richards and G. W. Heimrod. Proc. Am. Acad.* 37, *415*; *Zeit. phys. Chem.* 41, *302* (*1902*). — Special experiments showed that two 'normal' or cell voltameters gave the same results when placed in series; that a zinc anode and zinc nitrate could be substituted without error; that a platinum cathode gives the same value as a silver cathode; and that doubling the current density introduced no variation. The porous cell can be dispensed with, if necessary, by placing the anode at the bottom of a beaker and the cathode above it. Another series of experiments brought out the effect of silver oxide, etc., etc., in the solution. The precipitated silver always contains some moisture which can be driven off only at a high temperature. From the electrochemical experiments with copper and silver, the authors deduce a combining weight of 63.601 for copper, while 63.604 was obtained from the chemical relations. By introducing corrections due to the form of voltameter, it is shown that the results of Rayleigh, F. and W. Kohlrausch, Kahle, and Patterson and Guthe reduce practically to the same value of 1 coulomb = 1.1175 mg. Ag. This figures out to 96580 coulombs per equivalent. This is a beautiful piece of work and illustrates anew the fact that Mr. Richards has a wonderful gift for making exact measurements and that the scientific world will be the gainer if he will give this talent full play even though this involves giving up more abstract subjects. *W. D. B.*

Studies on the formation of metal oxides. *A. Coehn and M. Glaser. Zeit. anorg. Chem.* 33, *9* (*1903*). — Since hydrogen precipitates before cobalt, it should be possible to precipitate all the cobalt in a solution at the anode without precipitating any metallic cobalt. This can be done if care is paid to the voltage, but it is slow and troublesome. By adding potassium bichromate to the solution, the range of voltage is much increased. This makes the precipitation a very easy one. A little nickel and a little sulphate is always carried down mechanically by the oxide Co_2O_3. *W. D. B.*

Oxidation by electrically precipitated fluorine. *F. W. Skirrow. Zeit. anorg. Chem.* 33, *25* (*1903*). — Since the decomposition voltage of hydrofluoric acid is well above that of hydrochloric acid, a greater oxidation should be possible in the first case than in the second. Comparative measurements on the electrolysis of chromium sulphate, manganous sulphate, and cobalt sulphate solutions, with and without addition of hydrofluoric acid, show that there was always more oxidation when hydrofluoric acid was present. On the other hand, the presence of hydrofluoric acid is detrimental to the formation of persulphates and percarbonates. *W. D. B.*

The electrolysis of fused salts. *R. Lorenz. Zeit. anorg. Chem.* 31, *385* (*1902*). — A detailed reply to a number of reviews of articles which have been carried out in the Zürich laboratory. The author makes the point that these reviews are all grossly inaccurate. *W. D. B.*

On the electrolysis of fused salts. *G. Bodländer. Zeit. anorg. Chem.* 32, *235* (*1902*). — A rejoinder to Lorenz (preceding review). *W. D. B.*

On the electrolysis of fused salts. *R. Lorenz. Zeit. anorg. Chem.* 32, *239* (*1902*). — A counter-rejoinder to Bodländer (preceding review). *W. D. B.*

Apparatus for preparing pure hydrogen. *M. Vèzes and J. Labatut. Zeit. anorg. Chem.* 32, *464* (*1902*). — The authors describe an apparatus for the electrolytic production of hydrogen under constant pressure. By an ingenious device the authors introduce a varying liquid resistance into the cell so that the electrodes do not heat. Caustic soda is the electrolyte. *W. D. B.*

On water in some relations to air. *F. Kohlrausch. Zeit. phys. Chem.* 42, *193* (*1902*). — Drying with caustic soda will change the conductivity of water from 0.9×10^{-6} to 0.5×10^{-6} and a subsequent treatment with platinum will lower this to $< 0.3 \times 10^{-6}$. The first improvement is due to the removal of carbonic acid and the second probably to the removal of ammonia. Special experiments showed that bubbling air freed from carbon dioxide through water did not cause unexpected or abnormal variations. *W. D. B.*

Conductivity of solutions in ethyl bromide. *W. A. Plotnikoff. Jour. Russ. Phys. Chem. Soc.* 34, *466* (*1902*). — In confirmation of Kahlenberg and Lincoln's results (3, 23) with ferric chloride dissolved in hydrocarbons or their halogen derivatives, the author finds that solutions of aluminum bromide in bromoform or ethylene dibromide do not conduct. Ethyl bromide, however, forms an exception, as both $AlBr_3$ and the author's complex substance, $AlBr_3.C_2H_5Br.Br_2CS_2$ [Jour. Russ. Phys. Chem. Soc. 33, 91 (1901); 34, 6 (1902)] give with it conducting solutions. These substances, carefully prepared with exclusion of moisture, were investigated by the Kohlrausch-Ostwald method in a vessel similar to that used by Walden and Centnerzwer for liquid SO_2. The specific resistance of pure C_2H_5Br was as high as that of pure water. The following (preliminary) results among others were obtained, where v and μ are calculated on the assumption that the molecules contain one atom Al.

$AlBr_3$	$v = 0.89$	$\mu = 0.23$	$v = 4.00$	$\mu = 0.084$	$v = 9.17$	$\mu = 0.065$
	$v = 1.44$	$\mu = 0.17$	$v = 6.36$	$\mu = 0.074$	$v = 17.9$	$\mu = 0.065$
	$v = 1.92$	$\mu = 0.12$	$v = 7.4$	$\mu = 0.071$	$v = 40$	$\mu = 0.082$
$AlBr_3C_2H_5Br.Br_2CS_2$	$v = 8$	$\mu = 4.5$	$v = 16$	$\mu = 4.3$	$v = 32$	$\mu = 3.8$

The great fall in μ for $AlBr_3$ (three times less for $n/10$ solutions than for normal solutions) is not exceptional for non-aqueous solutions. The greatly increased conductivity of the complex body is explained by the author by the assumption of complex cations.

A slight conductivity was observed with solutions of $FeCl_3$ and of $Ba(CCl_3.COO_2)$ in ethyl bromide, but none with solutions of KI, picric acid, trichloracetic acid or its alkaline salts.

On electrolyzing a solution of $AlBr_3$ in ethyl bromide with carbon electrodes, brilliant metallic crystals were obtained (Al) soluble in HCl with evolution of hydrogen. The complex body gave no products, as the free bromine it contained prevented the reduction of the metal. *B. B. T.*

Electrical conductivity of potassium chloride in aqueous alcohol solutions. *W. A. Roth. Zeit. phys. Chem.* 42, *209* (*1902*).—The transference number of the cation for potassium chloride in aqueous alcohol increases gradually with increasing concentration of alcohol, while the molecular conductivity decreases. The ratio of the conductivities of an aqueous and an aqueous alcohol solution is not independent of the salt concentration. No satisfactory formula could be found for the change of the dissociation with the concentration. *W. D. B.*

The electrical conductivity and the internal friction of solutions of caseine. *O Sackur. Zeit. phys. Chem.* 41, *672* (*1902*).—From measurements of the conductivity, the author concludes that caseine is a tetrabasic acid with a molecular weight of 4540. The sodium salt does not diffuse through parchment. The author has prepared from caseine a substance which he calls isocaseine. This substance is a much stronger acid than caseine. *W. D. B.*

Electrical conductivity of flames and gases. *A. de Hemptinne. Zeit. phys. Chem.* 39, *545* (*1901*).—Those factors which favor the condensation of water favor the passage of electricity through gases, and vice versa. The author concludes therefore that there are no ions in an actual reaction between gases, and that water acts only when present as liquid drops. *W. D. B.*

Outline of a broader theory of dilute solutions. *H. Jahn. Zeit. phys. Chem.* 41, *257* (*1902*).—Starting with the assumption of a specific action between the dissociation products and the undissociated substance, the author develops new formulas for the dissociation isotherm; the van 't Hoff laws; concentration cells; change of solubility; chemical equilibrium and reaction velocity. The author claims that there are no facts known which conflict with his theory, one feature of which, however, is that non-electrolytes do not affect the solubility of non-electrolytes. The real weakness in these otherwise praiseworthy attempts is to be found in the assumption that the behavior of any two substances can be described accurately without introducing any values specific to the two substances. *W. D. B.*

Numerical examples on the newer theory of solutions. *J. B. Goebel. Zeit. phys. Chem.* 42, *59 (1902).*—By the "newer theory of solutions," the author means Nernst's assumption (6, 153) as to the mutual influence of dissolved substances. He shows that formulas can be written which describe, with great accuracy, Hausrath's experiments on the freezing-points of sodium chloride solutions and the experiments of Loomis with potassium chloride solutions.

W. D. B.

On the simultaneous titration of boric acid and strong acids. *W. Herz. Zeit. anorg. Chem.* 33, *353 (1903).*—In a mixture of hydrochloric acid and boric acid, the author titrates the hydrochloric acid, using *p*-nitrophenol as an indicator. He then adds mannite and titrates the boric acid with phenolphthaleine as indicator. *W. D. B.*

Dielectricity and Optics

The effect of the radio-active substances on the luminosity of gases. *A. de Hemptinne. Zeit. phys. Chem.* 41, *101 (1902).*—Reviewed (6, 364) from Comptes rendus, 133, 934 (1901).

Crystallography, Capillarity and Viscosity

Additions to the paper on the surface tension of liquid air. *L. Grunmach. Drude's Ann.* 7, *236 (1902).*—The author points out an error in his paper (6, 286). In his eight series of observations under the heading temperature he places the same value — 190.3°, which leads to the conclusion that the boiling-point of liquid air for different strengths of oxygen and different pressures is the same. On a previous page it is pointed out that — 190.3° C is the mean value of the boiling-point. *H. T. B.*

Determinations of capillary constants. *M. Cantor. Drude's Ann.* 7, *698 (1902).*—The author severely criticizes a paper by Whatmough on a new method of determining capillary constants. *H. T. B.*

On the formation of liquid drops and on the law of Tate. *A. Leduc and P. Sacerdote. Comptes rendus,* 135, *95, 732 (1902).*—The law of Tate is that the weight of the drops of a given liquid falling from the end of a circular tube is proportional to the radius of the surface. Experiments show that this is not strictly true. For water it is approximately true with surfaces varying from 0.5 cm to 1.5 cm. For larger surfaces, the ratio of weight to radius decreases with increasing radius. For smaller surfaces the ratio increases very rapidly with decreasing radius. These measurements refer to drops allowed to form very slowly. *W. D. B.*

On the formation of liquid drops and on the law of Tate. *P. A. Guye and F. C. Perrot. Comptes rendus,* 135, *458, 622 (1902).*—The authors give their reasons for believing that the law of Tate is inaccurate. They go further than Leduc and Sacerdote (preceding review) and do not admit that it is even approximately accurate under any circumstances. Kinetoscope photographs of falling drops are given. *W. D. B.*

THE RATE OF OXIDATION OF POTASSIUM IODIDE BY CHROMIC ACID

BY RALPH E. DeLURY

The present measurements, like those of the rate of oxidation of ferrous salts[1] by chromic acid, were undertaken with a view of throwing light on the remarkable catalytic action of iron on the oxidation of iodides; and also in order to ascertain whether the irregularities observed in the oxidation of ferrous sulphate[2] and of sodium thiosulphate[3] were inherent to the use of chromic acid as an oxidizing agent.

With the exception of Series VI the measurements were carried out at 30° C. Two of the reagents, suitably diluted, were mixed in a wide mouthed Erlenmeyer flask of 200 or 300 cc capacity while the third (usually the substance present in least quantity) was pipetted into a test tube, together with enough water to make up 15 cc. Both vessels were left in the thermostat until the proper temperature was attained, when the test-tube was taken out, quickly covered with a cloth to hinder loss of heat, and at the right moment emptied into the flask. The mixture was shaken and the last drops of liquid were removed from the tube by tapping it against the walls of the Erlenmeyer.

When it was desired to stop the reaction, a "restrainer" was poured in, consisting of a solution of sodium acetate in which was dissolved sufficient sodium bicarbonate to neutralize somewhat less than nine-tenths of the sulphuric acid initially present in the reacting mixture. The iodine liberated was then determined with *n*/100 sodium thiosulphate and iodine solutions, using starch[4] as indicator; a sharp end point was ensured by

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

[2] Ibid. 7, 10 (1903).

[3] Ibid. 7, 81 (1903).

[4] If a few crystals of menthol be left floating on the starch solution, it keeps good for weeks; the solution of sodium acetate was preserved from decomposition by the same means.

adding about one cubic centimeter of a normal solution of potassium iodide before titrating.

The efficiency of the restrainer was tested by letting the mixture stand half an hour or so after titration; no blue colour, indicating liberation of iodine, was observable.

Blank experiments showed that (probably owing to the short duration of the experiments) there was no necessity for special precautions to exclude air or to prevent loss of iodine by evaporation; the mouth of the Erlenmeyer flask was simply closed by a watch glass.

The stock solutions were:—*Potassium bichromate*, $F/10$[1] (0.6 normal), made up by weighing the pure salt. *Potassium iodide*, approximately $F/10$, standardized gravimetrically with silver. *Sulphuric acid*, approximately $F/2$, standardized gravimetrically with barium. The alkalinity of the iodide solution was determined, and has been allowed for in giving the initial compositions of the reacting mixtures.

The volumetric solutions of iodine and thiosulphate were frequently compared with a solution of sodium arsenite whose titer was determined against freshly sublimed iodine.

All pipettes used were calibrated by weighing the distilled water delivered, an interval of thirty seconds being allowed for draining.

Classification of the Measurements

The experiments may be grouped in six Series.

In *Series I*, the concentration of the bichromate was much less than those of the other reagents. Expts. 1–6.

In *Series II* the concentration of the iodide was much less than those of the other reagents. Expts. 7–11.

In *Series III* bichromate and iodide were present in comparable amounts, the acid in excess. Expts. 12–14.

Series IV includes experiments on the influence of each of the three reagents, by the Method of Constant Rates; Expts. 15–17.

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[1] One formula weight in ten liters.

Series V contains experiments on the catalytic action of a number of salts; Table 18. Finally the experiments of

Series VI were carried out at 0°C, to determine the influence of the temperature on the rate; Expts. 19–27.

Explanation of the Tables

At the head of each table the total volume of the reacting mixture is given, and the quantities of the reagents initially present, in the following units. The letter *A* denotes the number of gramme-formula-weights of potassium bichromate ($K_2Cr_2O_7$) multiplied by 100,000; *B*, the number of gramme-formula-weights of sulphuric acid (H_2SO_4) multiplied by 100,000; and *C* the number of gramme-formula-weights of potassium iodide, (KI) also multiplied by 100,000. *V* is the volume in cubic centimeters. Under x is entered the amount of iodine liberated in θ minutes, expressed in cubic centimeters of *n*/100 thiosulphate. The amount of iodine dissolved in the potassium iodide of experiments *i–iii*, Table 18, is expressed in the same units.

The value of x for $\theta = \infty$ (that is, the number of cubic centimeters of *n*/100 thiosulphate equivalent to the iodine that would be liberated if the reaction were allowed to proceed until none of the reagent present in least quantity remained) was obtained by calculation from the known initial composition of the reacting mixture; in the measurements of Series I this value was controlled by direct experiment; in Series II a similar check was not feasible.

RESULTS OF THE MEASUREMENTS

Series I

The first Series were carried out with potassium bichromate in small quantity, as it was thought that the iodine liberated by the reaction might exert less influence on the rate in presence of a large excess of potassium iodide, than if the quantity of the latter were small. Experiments *i* and *ii*, Table 18, show that the retardation due to this cause would not seriously affect the results of the measurements.

The constancy of k_1[1] throughout each of the tables, and the fact that doubling the concentration of the bichromate does not affect that constant (Expts. 1 and 2; 3 and 4) shows that the rate is proportional to the concentration of the bichromate. Doubling the concentration of the iodide trebles the rate (Expts. 5 and 2), and doubling that of the acid quadruples it. Thus, the rate is proportional to the concentration of the bichromate, and to the square of that of the acid.

Expts. 1 and 2.

1. A, 1.968; B, 237.9; C, 142.4; V, 100; k_1avg, 0.0065; R, 0.18
2. A, 0.984; B, 237.9; C, 142.4; V, 100; k_1avg, 0.0066; R, 0.088

1. θ	x	k_1	2. θ	x	k_1
5	0.75	(0.0057)	10	0.75	(0.0059)
10	1.60	0.0063	15	1.21	0.0067
15	2.43	0.0067	20	1.50	0.0064
20	3.00	0.0064	25	1.90	0.0067
30	4.31	0.0066	30	2.18	0.0067
∞	11.81	—	∞	5.90	—

Expts. 3 and 4.

3. A, 1.968; B, 478.3; C, 142.4; V, 100; k_1avg, 0.029; R, 0.792
4. A, 0.984; B, 478.3; C, 142.4; V, 100; k_1avg, 0.029; R, 0.396

3. θ	x	k_1	4. θ	x	k_1
2.5	1.68	0.0307	2.5	0.82	0.0260
5.0	3.21	0.0276	5.0	1.78	0.0312
7.5	4.57	0.0283	7.5	2.42	0.0306
10.0	5.78	0.0292	10.0	2.87	0.0289
15.0	7.60	0.0299	15.0	3.71	0.0287
∞	11.81	—	∞	5.90	—

Expts. 5 and 6.

5. A, 0.984; B, 235.3; C, 284.9; V, 100; k_1avg, 0.019; R, 0.260
6. A, 0.984; B, 117.7; C, 142.4; V, 100; k_1avg, 0.002; R, 0.026

5. θ	x	k_1	6. θ	x	k_1
5	1.18	0.0194	10	0.24	0.00180
10	2.16	0.0197	20	0.48	0.00184
15	2.74	0.0181	40	1 01	0.00204
20	3.46	0.0192	—	—	—
∞	5.90	—	∞	5.90	—

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[1] $k_1 = 1/\theta \cdot \log_{10} 6A/(6A - x)$.

At the head of each Table of this Series, I have noted the average value of k_1 (omitting those enclosed in brackets). Strictly speaking, k_1 should diminish as the reaction proceeds; owing to the large excess of iodide and acid however, the diminution could never exceed a few percent, and is of the same order as the experimental errors. R is calculated from the average value of k_1 by the relation $R = dx/d\theta = 6k_1A. \times \log nat\ 10.$

Series II

In Series II the amount of the potassium iodide in the reacting mixture was much less than that of the bichromate or that of the acid. A few experiments in which iodine was dissolved in the potassium iodide before making up the reacting mixture led to the adoption of the following equation,

$$K_2Cr_2O_7 + 9KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 3KI_3 + 7H_2O$$

whence the expressions,

$$6A - x, \quad 6/7B - x, \quad 2/3C - x,$$

to represent the amounts of bichromate, acid and iodide remaining when the iodine liberated was equivalent to $x\ 10^{-5}$ gramme-formula-weights of sodium thiosulphate.

The details of the measurements in question are not published in the present paper; it is hoped that the results of an investigation of the reaction between iodic and hydriodic acids which has been undertaken in this laboratory, may throw light on the retardation caused by iodine.

EXPTS. 7 AND 8.

7. A, 19.9; B, 240.3; C, 9.45; V, 100; *Kavg*, 26×10^{-10}; R, 0.083
8. A, 19.9; B, 480.7; C, 9.45; V, 100.

7. θ	x	$K \times 10^{10}$	8. θ	x	$T(7)$	T/θ	$K \times 10^{10}$
5	0.39	26	5	1.47	20	4	26
10	0.78	26	10	2.69	44	4.4	28
15	1.13	26	15	3.85	80	5	32
20	1.45	26	20	4.66	—	—	34
30	1.93	24	25	5.37	—	—	40
40	2.54	26	30	5.80	—	—	44
60	3.32	26					
80	3.84	24					

EXPTS. 9 AND 10.

9. A, 39.8; B, 240.3; C, 9.45; V, 100; $Kavg$, 22×10^{-10}; R, 0.141
10. A, 39.8; B, 240.0; C, 18.89; V, 100; $Kavg$, 20×10^{-10}; R, 0.257

9. θ	x	$T(7)$	T/θ	$K \times 10^{10}$	10. θ	x	$T(9)$	T/θ	$K \times 10^{10}$
5	0.52	—	—	(18)	5	1.26	11	2.2	21
10	1.10	15	1.5	20	10	2.47	24	2.4	22
15	1.75	27	1.8	22	15	3.20	32	2.0	20
20	2.25	35	1.8	23	20	3.71	39	2.0	18
25	2.53	40	1.6	21	26	4.64	55	2.0	18
30	3.06	57	1.9	23	30	5.56			20
40	3.77	77	1.9	24					
50	4.32	—	—	(24)					

EXPT. 11.

A, 39.8; B, 480.7; C, 9.45; V, 100; K_1avg, 27×10^{-10}; R, 0.694

θ	x	$T(8)$	$T(8)/\theta$	$T(9)$	$T(9)/\theta$	$K \times 10^{10}$
2.5	1.31	4.5	1.8	12	5	24
5.0	2.64	10	2.0	26	5	27
10.0	4.11	18	1.8	46	4.6	27
15.0	5.15					29

Comparing Expts. 7 and 9, it is apparent that halving the concentration of the bichromate approximately doubles the time necessary for the liberation of a given quantity of iodine; $T(7)$ in Table 9 (obtained from Expt. 7 by interpolation) being the time required to free x units when $A = 19.9$, and θ the time when $A = 39.8$ (compare also Expts. 8 and 11).

Similarly, doubling the concentration of the iodide doubles the rate (Expts. 9 and 10), while doubling that of the acid somewhat more than quadruples it (Expts. 8 and 7; 11 and 9).

The values of K in Tables 7 to 11 are calculated from the integrated form of the equation

$$R = dx/d\theta = K(6A - x)(6/7B - x)^2(2/3C - x) \ldots\ldots (1)$$

Except in the case of Table 8 the values are fairly constant, affording further evidence that in first approximation at all events, the rate is proportional to the concentrations of the bichromate and of the iodide, and to the square of that of the acid.

With respect to the bichromate and the acid, therefore, the general results of these measurements confirm those of Series I. In the case of the iodide, however, the effect of doubling the concentration differs in the two Series.

The experiments of

Series III

in which the concentrations of the reagents in question were intermediate between their values in Series I and those in Series II, were undertaken in order to obtain further light on this matter.

As the concentration of the acid remained practically unaltered during the progress of the reaction, it was allowable to treat $(6/7B - x)$ as constant during the integration of Equation (1), thus obtaining

$$k_2 = 36KB^2/49 = 1/\theta(c - a).\ \log nat\ (c - x)a/(a - x)c$$

(a being written for $6A$, and c for $2/3C$).

EXPTS. 12, 13 AND 14.

12. A, 7.91; B, 239.4; C, 56.97; V, 100; k_2avg, 13×10^{-5}; R, 0.23
13. A, 7.91; B, 240.1; C, 18.89; V, 100; k_2avg, 11×10^{-5}; R, 0.068
14. A, 2.637; B, 239.4; C, 56.97; V, 100; k_2avg, 13×10^{-5}; R, 0.077

12. θ	x	$k_2 \times 10^6$	13. θ	x	$k_2 \times 10^6$	14. θ	x	$k_2 \times 10^5$
5	1.11	13	5	0.22	(7)	10	0.71	12
10	2.24	13	15	0.96	11	15	1.10	13
15	3.24	13	20	1.23	11	20	1.50	13
20	4.26	13	30	1.84	11	30	2.12	13

Reference to the Tables containing the results of Expts. 12, 13 and 14 shows that trebling the concentration of the bichromate leaves k_2 unaltered, i. e. trebles the rate, while trebling that of the iodide increases k_2, i. e. *more* than trebles the rate.

Deviation from strict proportionality between rate and concentration, therefore, occurs in the case of the iodide, and not noticeably in the case of the bichromate.

Series IV

In order to study this deviation more thoroughly, free from the restriction that one or other of the reagents must be present in relatively small quantity, the measurements of this Series were carried out by the "Method of Constant Rates" described in a recent paper by Bray.[1]

The restrainer being added, and the solution analyzed before the concentrations of the reagents had been much reduced by the progress of the reaction, the quotient x/θ gives a first approximation to the rate; the effect due to the slight decrease in the concentrations (12 percent at most), was corrected by means of equation 1.

EXPT. 15.

A, 17.79; C, 94.83 × n; V, 200.

B	n	θ	x	R	R corr.	R calc.
239.6	0.5	80	3.01	0.040	0.040	0.045
238.7	1	80	7.52	0.11	0.11	0.10
237.0	2	36	8.08	0.23	0.24	0.24
235.3	3	35	13.01	0.38	0.40	0.42
233.6	4	17	9.76	0.64	0.68	0.64
231.9	5	10	8.05	0.88	0.94	0.90
230.2	6	11	11.31	1.17	1.28	1.20
228.5	7	9	11.30	1.42	1.57	1.54
226.8	8	8	12.47	1.78	2.01	1.92
225.1	9	6	11.55	2.19	2.49	2.34
223.4	10	5	11.00	2.47	2.86	2.80

EXPT. 16.

A, 17.79; C, 94.83; V, 200.

B	θ	x	R	$R/B^2 \times 10^6$
118.5	80	2.96	0.039	2.80
238.7	80	7.52	0.11	1.87
479.2	20	7.66	0.42	1.85
729.6	10	8.59	0.95	1.80
960.0	5	8.30	1.83	1.99
1200.4	3	8.25	3.02	2.10

The results of these measurements are given in Tables 15, 16, and 17, and graphically in Fig. 1. Owing to the alkalinity of the stock solution of potassium iodide, the concentration of the acid varied from case to case in Expt. 15; under "*R corr*"

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[1] Jour. Phys. Chem. 7, 93 (1903).

is given the rate calculated for $B = 240.4$, on the assumption that R is proportional to B^2. The corrected values of R are plotted in the figure.

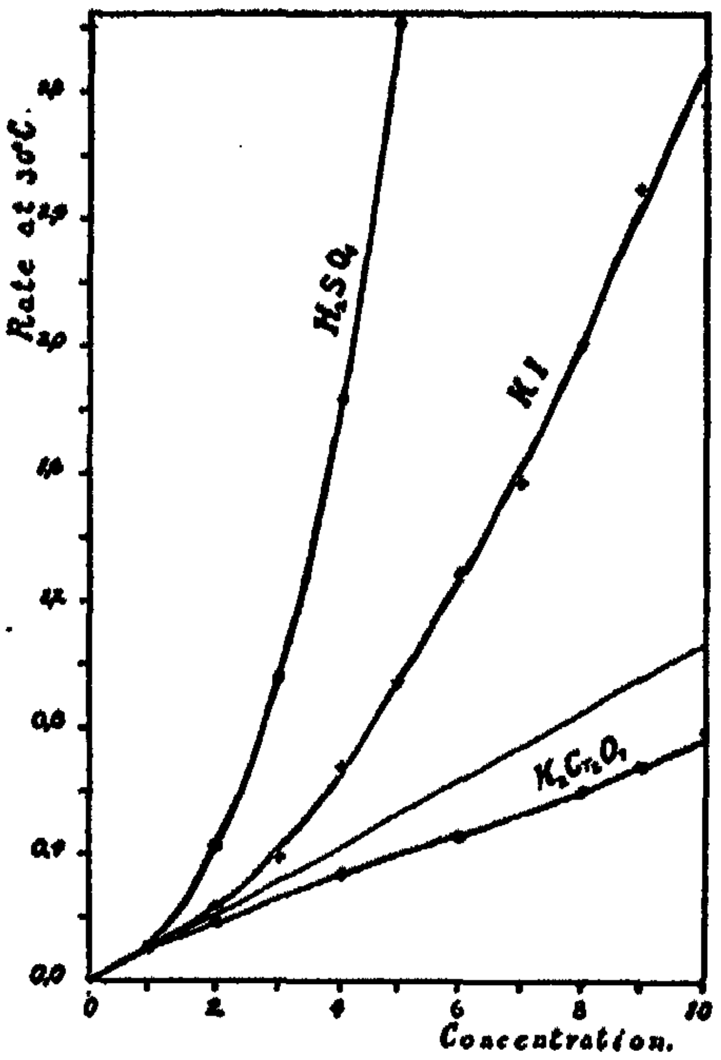

Fig. 1

EXPT. 17.

A, 17.79 × n; B, 238.7; C, 94.83; V, 200.

n	θ	x	R	R/n
0.5	80	4.43	0.06	0.12
1	80	7.52	0.11	0.11
2	40	6.70	0.18	0.09
4	20	6.26	0.34	0.08
6	15	6.22	0.45	0.08
8	10	5.85	0.59	0.07
9	10	6.24	0.67	0.07
10	8	5.82	0.77	0.08

If the rate were strictly proportional to the concentrations of the bichromate and of the iodide, the values of R from Expts. 15 and 17 should all lie on the straight line drawn through the first two measurements in Fig. 1. As may be seen by a glance at the figure, the rate is somewhat less than proportional to the concentration of the bichromate, and much more than proportional to that of the iodide. It is very closely proportional to the square of the concentration of the acid (see the quotient R/B^2 in Table 16).

The deviation in the case of the bichromate may be ascribed to decrease in the dissociation of the chromic acid attendant on increase in its concentration, the rate being supposed proportional to the concentration of the ion Cr_2O_7. It is only necessary to assume that in Expt. 17 ($n = 1$) ten percent of the chromic acid is undissociated, in order to account for the difference between the observed values and those of the straight line in Fig. 1.

That the potassium ions added with the bichromate are not responsible for the retardation is evidenced by Expt. *vi*, Table 18, in which potassium nitrate was present. In the absence of bichromate, no iodine was liberated; thus the possibility that retardation by the potassium was offset by action of the nitric acid, is excluded.

In the case of the iodide, the rates are reproduced with considerable accuracy by the formula

$$R\ calc\ (\text{Expt. } 15) = 0.08n + 0.02n^2.$$

An explanation, in conformity with the prevalent theories connecting rate and mechanism of a reaction, and not in itself improbable, is afforded by the supposition that there are two different primary products of oxidation, one involving but one molecule of potassium iodide, and the other two molecules of that substance.

Bray's[1] experiments on the oxidation of potassium iodide by chloric acid (see his series J, also the foot note on page 108 of his paper), show that with this oxidizing agent as well as with chromic acid the rate increases more rapidly than the concen-

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[1] Jour. Phys. Chem. 7, 92 (1903).

tration of the iodide; but the explanation suggested in the preceding paragraph, though plausible, cannot be considered well founded until the effect of dissolving iodine in the iodide has been thoroughly studied and satisfactorily accounted for. It is hoped that the experiments with iodic acid, already referred to, may prove of service in this connection.

Series V

Under this heading are collected the experiments in which the products of the reaction, and a number of salts which often exert an accelerating effect on the process of oxidation, were added to the reacting mixture.

TABLE 18.

No.	Catalyser	*A*	*B*	*C*	*D*	*V*	θ	x(Cat.)	x
i	Iodine	9.84	233	142.	10.65	100	5	4.35	4.50
ii	"	19.9	240	9.45	7.97	100	20	1.00	1.45
iii	"	17.79	232	474.	7.56	200	10	8.11	8.05
iv	$Fe_2(SO_4)_3$	4.92	233	142.	12.5	100	10	27.5	4.65
v	"	29.8	240	9.45	12.5	100	15	2.35	1.86
vi	KNO_3	17.79	234	379.	20.	200	15	9.18	9.17
vii	K_2SO_4	17.79	232	474.	5.	200	10	8.10	8.19
viii	$Cr_2(SO_4)_3$	17.79	223	948.	1.7	200	4	9.70	9.15
ix	"	17.79	229	664.	1.7	200	7	9.60	9.31
x	"	124.5	239	94.8	1.7	200	13	7.18	7.34
xi	$UO_2(NO_3)_2$	1.968	239	94.8	1.0	100	16	2.61	2.48
xii	$Co(NO_3)_2$	1.968	239	94.8	1.0	100	15	2.51	2.47
xiii	$MnCl_2$	1.968	239	94.8	1.0	100	15	2.56	2.51
xiv	$MO_7O_{24}(NH_4)_6$	1.968	239	94.8	1.0	100	15	2.52	2.42
xv	Na_2WO_4	1.968	239	94.8	1.0	100	15	2.42	2.42

y, (iv) 4.85; (v) 0.06; (vi) 0.00.

In Table 18 the amounts of bichromate, acid, and iodide, are entered in the columns headed *A*, *B*, and *C* respectively; the total volume in cubic centimeters, under *V*. The quantity of salt, etc. added is given under *D* in 10^{-5} gram-formula weights. The iodine liberated in θ minutes is given under "x(cat)", while under x is entered the result of blank experiments in the absence of the catalyser. Finally, in a few cases, the amount of iodine set free by the catalytic agent in the absence of bichromate, has been recorded at the foot of the table, after y.

Very few of the substances experimented with had any appreciable effect on the rate. The acceleration due to the chrome alum is somewhat greater than would be caused by the acid liberated by complete hydrolysis; and in the case of the ferric salt, the acceleration is too great to be ascribed to the ferrous sulphate formed by reduction, although increase in the concentration of the iodide, which increases the amount of ferrous salt formed, also greatly increases the acceleration.

Series VI

In order to find the temperature-coefficient of the reaction, I repeated Experiment 1 at zero. The surprisingly small effect on the rate caused by a drop of thirty degrees suggested the possibility that the nature of the reaction might be profoundly modified by the change of temperature, and I accordingly carried out a number of experiments at zero. The results, contained in Tables 19 to 27, and in part in Fig. 2, show that, on the whole,

Expts. 19 and 20.

19. *A*, 1.968; *B*, 237.9; *C*, 142.4; *V*, 100; k_1*avg*, 0.0023; *R*, 0.063.
20. *A*, 0.984; *B*, 237.9; *C*, 142.4; *V*, 100; k_1*avg*, 0.0022; *R*, 0.030.

19. θ	x	k_1	20. θ	x	k_1
10	0.66	0.0025	20	0.57	0.0022
15	0.86	0.0022	30	0.83	0.0022
20	1.19	0.0023	—	—	—
30	1.72	0.0023	—	—	—
∞	11.81		∞	5.90	

Expts. 21, 22 and 23.

21. *A*, 1.968; *B*, 478.3; *C*, 142.4; *V*, 100; k_1*avg*, 0.012; *R*, 0.33.
22. *A*, 0.984; *B*, 478.3; *C*, 142.4; *V*, 100; k_1*avg*, 0.013; *R*, 0.18.
23. *A*, 0.984; *B*, 235.3; *C*, 284.9; *V*, 100; k_1*avg*, 0.0053; *R*, 0.072.

21. θ	x	$k_1 \times 10^4$	22. θ	x	$k_1 \times 10^4$	23. θ	x	$k_1 \times 10^4$
10	2.69	112	10	1.34	112	10	0.69	54
20	4.94	118	15	2.04	123	15	1.00	54
30	6.87	126	20	2.77	138	20	1.21	50
35	7.68	130	30	3.75	146			
∞	11.81		∞	5.90		∞	5.90	

TABLE 24.

A	*B*	*C*	Ex.	*R*(0°)	Ex.	*R*(30°)	*Ratio*	*Coeff.*
1.968	237.9	142.4	19	0.063	1	0.18	2.9	1.4
0.984	237.9	142.4	20	0.030	2	0.088	2.9	1.4
1.968	478.3	142.4	21	0.33	3	0.79	2.4	1.3
0.984	478.3	142.4	22	0.18	4	0.396	2.2	1.3
0.984	235.3	284.9	23	0.072	5	0.26	3.6	1.5

EXPT. 25.

A, 17.79; *C*, 94.83 × *n*; *V*, 200; *R corr.* (30°) from Expt. 15.

B	*n*	*θ*	*x*	*R corr.*	*R*(30°)	*Ratio*	*Coeff.*
238.7	1	120	4.34	0.04	0.11	2.7	1.4
235.3	3	80	8.69	0.12	0.40	3.3	1.5
230.2	6	20	5.70	0.33	1.28	3.9	1.6
223.4	10	8	4.65	0.71	2.86	4.0	1.6

EXPT. 26.

A, 17.79; *C*, 94.83; *V*, 200; T, 0°C; *R* (30°) from Expt. 16.

B	*θ*	*x*	*R*	*R*(30°)	*Ratio*	*Coeff.*
238.7	120	4.34	0.04	0.11	2.7	1.4
479.2	40	5.73	0.15	0.42	2.7	1.4
960.0	10	7.41	0.81	1.83	2.3	1.3
1440.8	4	7.69	2.09	—	—	—

EXPT. 27.

A, 17.79 × *n*; *B*, 238.7; *C*, 94.83; *V*, 200; *R* (30°) from Expt. 17.

n	*θ*	*x*	*R*	*R*(30°)	*Ratio*	*Coeff.*
1	120	4.34	0.04	0.11	2.7	1.4
3	80	6.84	0.09	(0.26)	2.9	1.4
5	50	6.36	0.14	(0.40)	2.9	1.4
7	30	5.24	0.19	(0.63)	3.3	1.5
9	20	4.17	0.22	0.67	3.0	1.4

the effect of changing the concentrations of the various reagents is the same at zero as at thirty degrees; the iodide curve is flatter, and the acid curve a little steeper at the lower temperature.

Hence the temperature coefficient increases with *C*, and falls off when *B* is increased.

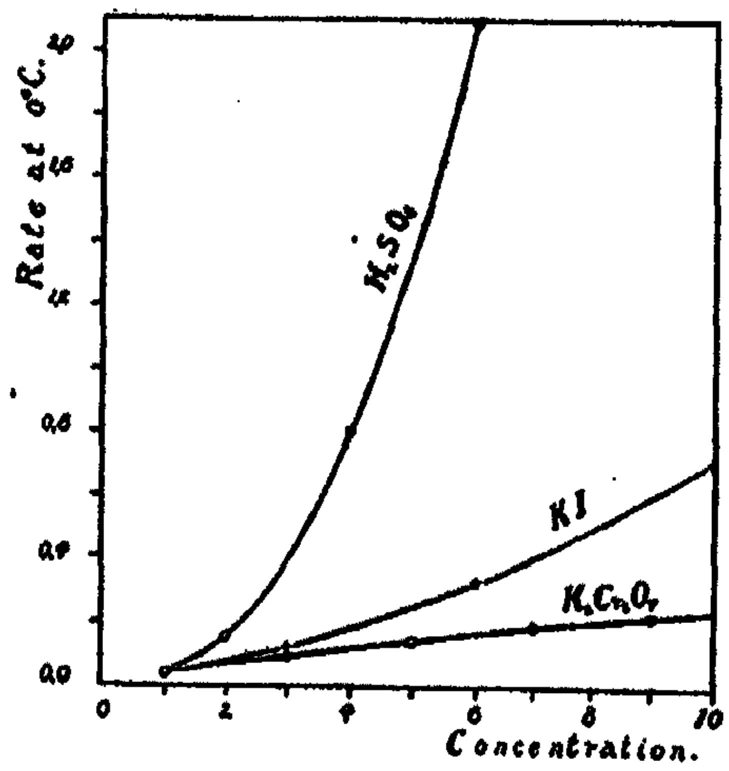

Fig. 2

Table 24 contains a résumé of the results of Expts. 19 to 23 with the rates at 30°, and the ratios of the two rates. The temperature-coefficient, that is, the cube root of this ratio, is entered under "*coeff*".

Cohen[1] gives a list of 16 reactions whose temperature coefficients have been measured; they vary from 3.6 to 1.9, all being much greater than that of the reaction studied in the present paper.

Summary

The rate of the reaction between potassium bichromate, potassium iodide, and sulphuric acid, is very nearly proportional to the concentration of the bichromate, and to the square of that of the acid.

The relation between the rate and the concentration of the iodide can be expressed by an equation of the form $R = mC + nC^2$.

The temperature coefficient of the reaction is unusually low.

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[1] "Studien zur Chemischen Dynamik," (1895).

A number of salts which usually accelerate the process of oxidation have very little effect on the rate of this reaction. Exceptions are, ferric (and ferrous) salts, and, perhaps, chromic salts.

In conclusion, I wish to express my thanks to Professor W. Lash Miller, at whose suggestion this research was undertaken, and under whose supervision it has been carried out.

University of Toronto,
February, 1903.

TABLE OF CONTENTS

ON THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN AMYL AMINE

BY LOUIS KAHLENBERG AND OTTO E. RUHOFF

Preliminary qualitative tests of the electrical conductivity of solutions in amyl amine have previously been made.[1] It seemed of interest to determine the electrical conductivity of a number of solutions in amyl amine, especially as it has a dielectric constant[2] of the order of that of chloroform, in which latter solvent no solutions have as yet been prepared that are not tolerably good insulators.

In measuring the conductivity the Kohlrausch method was employed. The resistance cell used was similar to the one employed by Kahlenberg and Schlundt[3] in their investigations of solutions in liquid hydrocyanic acid; the only difference being that the cell was fitted with a ground-glass stopper, and that the lower portion of the cell was wider, and the upper part was contracted to a rather narrow neck, which was graduated to 1/30 cc, thus enabling the volume to be estimated accurately to 0.01 cc.

The amyl amine was of Schuchardt's manufacture. It was slightly optically active, indicating the presence of an isomer. The sample was dried over fused caustic potash for several months. It was then distilled and a large fraction passing over between 95°.7 and 97°.5 at 746 mm was used in the experiments. The specific conductivity of this sample was found to be less than 8.2×10^{-8} reciprocal ohms at 25° C.

Solubility tests showed that potassium iodide and sodium oleate are not perceptibly soluble in amyl amine. Copper oleate is readily soluble but the solution conducts no better than the pure solvent. Chloride of ammonium is soluble in amyl amine,

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[1] Kahlenberg, Jour. Phys. Chem. 5, 384 (1901).

[2] The value 4.50 was found by Schlundt, Jour. Phys, Chem, 5, 503 (1901); also Bull. Univ. Wis. Science Series, 2, 353 (1901).

[3] Ibid 6, 447 (1902).

but ammonia is liberated simultaneously. Silver nitrate, cadmium iodide and ferric chloride are soluble in amyl amine and the resulting solutions are electrolytes. In tables 1 to 3 are given the results obtained by measuring the conductivity of solutions of the last three salts named in amyl amine. These salts were of a high degree of purity and were thoroughly dry. In the tables, v indicates the volume in liters in which the formula weight of the salt in grams is contained, and Λ the molecular conductivity at 25° C in reciprocal ohms.

In the case of both the silver nitrate and the cadmium iodide solutions (tables 1 and 2), the molecular conductivity passes through a maximum, being exceedingly low for the more dilute solutions. The greatest dilutions given in the tables do not indicate the most dilute solutions tested, but they are the weakest solutions whose resistance could be sufficiently accurately measured with the method used. From table 1 it appears that in the silver nitrate solutions the maximum value of Λ occurs at about $v = 1.158$; while table 2 shows that in the cadmium iodide solutions the maximum value of Λ corresponds to about $v = 1.095$. In the case of ferric chloride, the molecular conductivity diminishes steadily as the values of v increase. We have

TABLE I.

Silver nitrate ($AgNO_3$) in amyl amine.

v	Λ
0.4001	0.530
0.4351	0.639
0.5096	0.870
0.6206	1.128
0.8629	1.402
1.158	1.476
1.685	1.376
2.302	1.144
2.850	0.908
3.261	0.744
6.330	0.168
11.45	0.038
31.07	0.008
81.63	0.002

TABLE II.

Cadmium iodide (CdI_2) in amyl amine.

v	Λ
0.7810	0.465
0.8909	0.534
1.095	0.542
1.237	0.480
1.450	0.346
1.738	0.187
2.473	0.034
5.482	0.002

TABLE III.

Ferric chloride ($FeCl_3$) in amyl amine.

v	Λ
5.021	0.217
13.43	0.158
18.34	0.138
27.05	0.086

here then additional illustrations of the fact that the molecular conductivity does not always reach its maximum at infinite dilution. Cases of this kind are by no means rare; they have been found in aqueous as well as in non-aqueous solutions, and do not admit of simple explanation from the standpoint of the theory of Arrhenius, in the formation of which only such solutions were considered whose molecular conductivity reaches a maximum at infinite dilution.

The tables indicate that the solutions are rather poor electrolytes as compared with aqueous solutions, for instance. Nevertheless, the conductivity is sufficiently great to admit of ready measurement. It is particularly interesting to note that the molecular conductivity dwindles to nearly nothing in about 1/82 normal silver nitrate solution, which is by no means a very high dilution. In the cadmium iodide solution the conductivity is equally low when the solution is as strong as one gram molecule in 5.5 liters; and the ferric chloride solutions when still far from very dilute also show a low molecular conductivity. This is interesting in studying the rôle of the solvent in causing electrolytic conduction. In these amyl amine solutions the ability of the solvent to produce with the solute a liquid having electrolytic conductivity is slight. The molecular conductivity of strong solutions of silver nitrate and cadmium iodide increases as the solutions are diluted; but after passing a certain point, the maximum, the solute and solvent are no longer able to influence each other so as to give increased conductivity, and so further addition of solvent leads to lower conductivity.[1] It is possible that if solutions of ferric chloride stronger than those in table 3 were used, the molecular conductivity might also pass through a maximum in this case. But sublimed ferric chloride dissolves extremely slowly in solutions in amyl amine that already contain one gram molecule in five liters, and so further efforts to prepare stronger solutions of this salt were not made.

Of the three salts, cadmium iodide, silver nitrate and ferric chloride, the first dissolves most rapidly in amyl amine, the last by far the most slowly. All three salts first formed with amyl amine a pasty mass, which then dissolved away.[2] In the case of ferric chloride, this preliminary union was accompanied by a great increase in bulk, which may possibly have been especially noticeable in this instance on account of the compactness of this salt, which was a sublimed product. This behavior cut short the measurements with the ferric chloride before the saturation point was reached. The strongest solutions of silver nitrate and cadmium iodide were not far from saturated; the next additions of salt remaining practically undissolved. Both of these solutions became very viscous near the point of saturation, the silver nitrate solution having about the consistency of thick molasses. A lowering of the temperature of a few degrees caused needle shaped crystals to separate out from the cadmium iodide solution.

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[1] This behavior is interesting in connection with the studies of H. E. Patten, Jour. Phys. Chem. 6, 554 (1902).

[2] This action is analogous to the behavior of the solution of many salts in water, where a compound with water of crystallization or hydration is first visibly formed, and this then dissolves in excess of solvent.

These crystals did not at all resemble those of pure cadmium iodide. They were not examined further, but were probably an addition product of solvent and solute.

From the point of view of the Nernst-Thomson theory, the conductivity of solutions in amyl amine is relatively high as compared with solutions in chloroform and ether.[1] A comparison of existing data[2] on the conductivities of solutions in solvents in the series in which liquid ammonia is the first member, methyl amine the second, and amyl amine a higher homologue, would indicate that the conductivity of the solutions diminishes as the solvent occupies a higher position in the series. This behavior is similar to that found in other homologous series of solvents; the series of the primary alcohols, of which water may be considered as the first member, presents a typical example.

Laboratory of Physical Chemistry,
University of Wisconsin,
December, 1902.

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[1] The dielectric constants of the solvents in question are as follows; amyl amine, 4.50; chloroform, 3.95; ether, 4.373.

[2] Compare the data of:—H. M. Goodwin and M. deKay Thompson, Jr., Phys. Rev. 8, 47 (1899); Franklin and Kraus, Am. Chem. Jour. 23, 288 (1900), also 24, 83 (1900).

NOTE ON THE IDENTIFICATION OF BASIC SALTS[1]

BY W. LASH MILLER AND FRANK B. KENRICK

(Read May 22, 1901)

Basic salts are prepared by the action of water or of bases—potash, ammonia, etc.—on the "normal" salts of most of the metals; in composition they stand intermediate between the normal salts and the oxides (bases), hence the name "Basic Salt." Some are well defined crystalline compounds, but the greater number are known only as amorphous, muddy precipitates, whose composition varies with the concentration and temperature of the solutions and even with the order of mixing the ingredients from which they are prepared.

When the basic salt, besides being amorphous, is insoluble, non-volatile, and infusible—and this is the rule rather than the exception—it is quite impossible to purify it by any of the usual means; and as the removal of the mother-liquors by washing with water can be resorted to only when special experiments have shown that the composition of the precipitate is not affected by such treatment, even the ultimate analysis of the crude precipitate is not unattended with difficulties.

In the article "Antimoine" in the *Encyclopédie Chimique*, M. Guntz quotes analyses of an oxychloride of antimony by four different chemists; the percentage of chlorine varies from 11.25 percent to 7.8 percent. As experiments carried out by Mr. Good (referred to below) show that the substances analyzed with such discrepant results were in all probability one and the same chemical compound, M. Guntz's conjecture that the material for analysis was washed too much by some of the analysts, and too little by others, may be accepted as correct.

In such cases the allocation of formulæ is apt to be somewhat arbitrary. Some authors distribute them with a lavish hand, and appear to delight in endowing "amorphous finely-divided pre-

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[1] Reprinted from Trans. Roy. Soc. Canada, (2) 7, 35 (1901).

cipitates" with the dignity of chemical individuality; while the more conservative are content to describe the same precipitates as "impure modifications" of "compounds" which have already found their way into the text-books. Gladstone took a cautious course; after analyzing the precipitate sometimes produced when cupric chloride is dissolved in water, he says:—"Though the salt is evidently somewhat irregular in composition, it approaches nearer [within 2–3 percent] to the oxychloride $CuCl_2.2CuO$ than to any other of the eight or nine that have been described by previous investigators."

In the absence of any clearly defined principle of selection much must of necessity be left to individual taste, and as there is wide room for difference of opinion, flat contradictions are not uncommon in the literature of the subject. In Dammer's "Handbuch der anorganischen Chemie," for instance, after detailed descriptions of seven compounds of lead chloride with ammonium chloride, comes the announcement that "according to Randall, none of André's compounds exist"; while with reference to Cross and Suguira's basic oxychlorides of lead, $Pb_{12}Cl_{21}O_4$, $Pb_8Cl_{16}O$, and Pb_4Cl_7O, the editor himself ventures on the criticism, "These were obviously impure, and probably badly analyzed." But neither André nor Randall, Cross nor Dammer adduces conclusive evidence in support of his contentions. Mere complexity in the formula is in itself no bar to the genuineness of a chemical compound—Mr. Allan's experiments, referred to below, establish beyond question the existence of a basic nitrate of bismuth with the formula $BiH_9N_5O_{26}$.

Even in the case of so important an article of commerce as white lead, it is still wholly uncertain whether the different varieties are to be regarded as distinct chemical species, as mixtures of a few individuals, or as more or less saturated (solid) solutions of carbon dioxide in lead oxide or in some basic carbonate. It is consequently hardly surprising that success in the manufacture of such substances is conditioned by strict adherence to empirical recipes, any deviation from which may seriously affect the properties—and the value—of the product.

Application of the phase rule

Difficult though it might appear to find any rational basis of classification for these precipitates, there is one large group—viz., all cases where equilibrium is attained between precipitate and mother-liquor—for which the problem is completely solved by two theorems due to Professor Willard Gibbs, which form part of what is commonly known as his "Phase Rule."

These theorems may be stated as follows:—Assuming that the system has arrived at *equilibrium*, at "arbitrary" temperature and pressure, (i) The system can in general consist of no more phases than it has components, (ii) A solution can form one of a group of n phases (n is the number of the components) only if it has attained a certain composition dependent on the temperature and pressure, and on the chemical and physical nature of the other phases present.

The first theorem does not exclude the possibility of the coexistence of $n + 1$ or even $n + 2$ phases under certain conditions of temperature and pressure; but if the experiments be carried out at atmospheric pressure in a thermostat set for some temperature below the boiling-point of the solution, the chance of meeting with such special conditions is negligible.

These theorems, which were reached by Gibbs in 1876, in the course of an abstract thermodynamical study of the conditions of equilibrium in heterogeneous systems, have often been verified; their importance, however, as furnishing a means—often the only means—of discovering the chemical individuals in ill-defined muddy precipitates, is only now beginning to be generally realized.

Applied to a particular case, for instance the formation of basic salts by the action of water on the chloride of antimony or on the nitrate of bismuth (temperature and pressure fixed as above), the theorems affirm:

(i) That if the system, which consists of three components (see below), has arrived at equilibrium, not more than three phases can coexist. Of these the solution forms one, the precipitate consequently must be either *one* single homogeneous substance (one phase), or a mixture of *two* phases—for instance, of two basic salts, or of one basic salt with the oxide.

(ii) That if the observed difference in composition between two precipitates, formed by the action of different quantities of water on the same salt, is due to their being mixtures of the same pair of basic salts in different proportions, the composition of the mother-liquors will be the same in the two cases.

The possible cases are thus divided into three groups:—

1. The solutions are identical in composition in different experiments, while the composition of the precipitate varies.—The precipitate is a mixture of two phases.

2. The solutions differ in composition, but the precipitates have the same composition.—The precipitate is a single chemical compound.

3. Both solutions and precipitates vary.—The precipitate is a single phase of variable composition, a "solid solution."

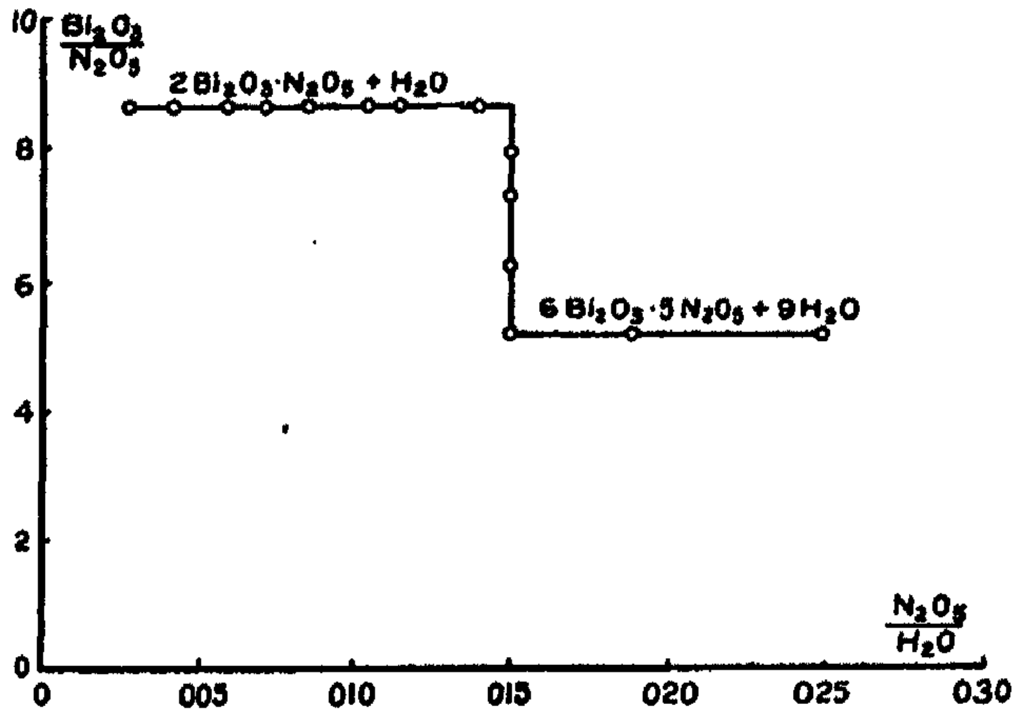
If it were possible to represent the compositions of the solutions by abscissae, and those of the precipitates by ordinates, the results of a series of experiments could be represented by a curve; perpendicular lines would then correspond to case 1 above, horizontal lines to case 2, and slanting lines to case 3. In a three-component system this is in general not possible. In many cases, however, a pair or pairs of components may be found whose ratio in the solution, or precipitate, changes whenever the composition of the solution, or precipitate, changes, and only then; and since for the interpretation of the results it is only necessary to know whether the composition of solutions and precipitates remains constant or changes from experiment to experiment, it is sufficient to plot these ratios instead of the compositions themselves. An illustration is afforded by the following curve taken from Mr. Allan's paper on the basic nitrates of bismuth. The abscissae give the ratios between N_2O_5 and H_2O in the solutions, and the ordinates those between Bi_2O_3 and N_2O_5 in the precipitates.

The mechanism

Although a great deal of use has been made of the Phase

Rule in classifying chemical reactions, and in the study of solutions and alloys, and more recently of such compounds as steel and the various commercial varieties of iron, comparatively little attention has been paid to the mechanism by means of which the results foretold by it are arrived at in the system. The subject is not only interesting in itself, but leads to an extension of the method of identifying chemical individuals among the basic salts, to the case where the precipitation is carried out by means of potash, ammonia, etc., although here the system no longer consists of three components only, and consequently the direct application of the Phase Rule in the manner just illustrated is not possible.

The precipitates produced by the action of water on the nitrate of bismuth are all of the general formula $m\mathrm{Bi_2O_3}$, $\mathrm{N_2O_5}$, $n\mathrm{H_2O}$; the compositions of the solutions also may be expressed in terms of the same substances, $\mathrm{Bi_2O_3}$, $\mathrm{N_2O_5}$, and $\mathrm{H_2O}$, which are henceforward termed the "components" of the system. The compositions of the precipitates and solutions might be expressed in terms of other groups of three, — elements, compounds, or mixtures — but three at least are necessary, and more than three are superfluous; if for example the elements Bi, N, H, and O be selected, and the quantities of three of them in the solution



be known, that of the fourth can be calculated from the stoichiometric relations.

The condition *sine qua non* for the application of the Phase Rule is that equilibrium be reached with respect to all reactions that occur in the system. There is only one sure sign of the attainment of equilibrium, namely, that the compositions of precipitates and solution are found to be independent of the order in which the components were mixed,—the composition of the precipitate must be the same whether $Bi(NO_3)_3$ be mixed with water, or Bi_2O_3 with dilute nitric acid, provided only that the same quantities of the three components be employed in each case. In other words, the quantities of the three components (together with the temperature and the pressure) are sufficient to define the state of the system.

Now, it can be shown by a simple algebraical argument[1] that if A, B, C, and D, be any four phases whatever, formed from the same three components, it is possible either

(i) to mix three of these, e. g., A, B, and C, in such proportions that the components are present in the mixture in the same proportions as they are in D, or

(ii) to prepare a mixture of A and B, and another of C and D in such proportions that the quantities of the three components are the same in both mixtures.

In other words, it is possible with these four phases to build up two systems identical with respect to the amounts of each of the three components, but differing in the nature and composition of the phases composing them, and the condition that the state of the system should be completely defined by the amounts of the components (and temperature and pressure) can be fulfilled only if one of these alternative systems changes spontaneously into the other; that is, if reactions between the phases

$$A + B + C = D \qquad\qquad A + B = C + D$$

take place whenever possible, and proceed until one at least of the reacting phases totally disappears. Which of the four will

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[1] Van der Waals, quoted by Roozeboom, Rec. Trav. chim. Pays-Bas, 6, 265 (1887).

be the first to disappear, depends obviously on the direction of the reaction and on the relative amounts of the different phases present. When the number of phases has been reduced to three, the possibility of a reaction of this nature has vanished.

The occurrence of reactions of this type, then, is the mechanism by means of which the number of phases in a three-component system is kept down to three. If it fails, the state of the system is no longer defined solely by temperature, pressure, and the masses of the components. Experimental evidence of such definition must therefore be regarded as proof that not more than three phases are present in the (three-component) system.

The result predicted by the second theorem is effected by means of reactions of a second type, which can take place in a three-component system of three phases only if one of the three is capable of continuous variation in composition (a solution).

By dissolving more or less of the solid phases in the solution, it would be possible to construct a whole series of systems —formed of the same amounts of the same components— but differing in the composition of the solutions and in the relative quantities of the solid phases. If only one of these is found to exist in fact, the disappearance of the others must be ascribed to the occurrence of reactions of this second type, which fix the composition of the solution irrespective of the relative quantities of the three phases of which the system is composed.

Extension of the Method

The two theorems which serve to interpret the experimental results, distinguishing between mixtures and single substances, and identifying the chemical individuals in the precipitates, are thus dependent on the occurrence of reactions of two types:— the first (which does not involve change of composition of any of the phases) resulting in the disappearance of all phases in excess of three; the second (which involves change of composition of the solution) keeping the composition of the solution constant so long as it is in contact with the same pair of basic salts.

The possibility of applying the same method to the study of precipitates formed by potash in solutions of metallic salts, depends on the discovery of conditions under which a fourth component may be added to the system without interfering with the occurrence of these two classes of reactions.

These conditions are:—(*a*) The quantity of water must be large in comparison with that of the second and of the third component; (*b*) The fourth component must remain in the solution and not enter into the composition of the precipitate; (*c*) In each member of a series of experiments there must be a constant ratio between the amounts of the fourth component and of the water in the system.

If the water is present in large excess (condition *a*), the mass of the solution will be much greater than that of the precipitate, and no reaction occurring in the system can have more than a very slight effect on the total mass of the water contained in the solution. In reactions of the first type (during which the composition of the solution remains unaltered), the quantities of the other components entering or leaving the solution must be still smaller than that of the water; so that reactions of this type leave the total mass of the solution (practically) unaltered.

If now a fourth component be added, the total amount of which in the solution is unaffected by the reaction (condition *b*), this slight variation in the quantities of the other components in the solution will cause such a very slight change in the composition of the latter that the effect of the change in checking the progress of the reaction may safely be neglected; so that the presence of the fourth component, under these conditions, will not interfere with the efficiency of reactions of the first type in keeping down the number of phases to three.

Reactions of the second type (involving changes in the composition of the solution) are of course just as possible when the solution contains a fourth component as when it does not. In order, however, that the solutions over a given pair of basic salts should reach exactly the same composition in different experiments, it is obviously necessary that the concentration of the fourth component in the solution should be the same from case to case. This is provided for by condition *c*. In experiments on the action of caustic potash on solutions of bichloride of copper, for example, H_2O, CuO, and $CuCl_2$ may be selected as components, with KCl as the "fourth component" of the preceding paragraphs; and condition *c* requires that if the quantity of potash added to a given volume of the copper solution should vary from case to case, enough KCl must be added to keep the total amount of potassium per cubic centimeter of water the same in each experiment.

Experiments

In the spring and summer of 1899 the writers carried out a lengthy series of experiments on the action of potash and ammonia on the chloride of lead. The less basic of the oxychlorides are formed with remarkable slowness; the reaction between N/3 ammonia and lead chloride not coming to a standstill in ten days shaking at 100° C. $PbCl_2 3PbO$, however, was formed in a few hours in the cold.

In the winter of 1900–1901, Mr. Good took up the study of the action of water on antimony trichloride, presenting his results as a thesis in competition for the 1851 Exhibition scholarship. His observations may be regarded as confirming the individuality of the oxychloride $2SbCl_3 5Sb_2O_3$ in the powder of Algaroth; although in this case also equilibrium is often not attained until days after the precipitation.

Mr. F. B. Allan, lecturer on chemistry in the University of Toronto, has just completed a series of experiments on the action of water on the nitrate of bismuth,[1] which he has presented as a thesis for the degree of Ph.D. His results, some of which are represented in the curve on page 38, establish the existence of basic nitrates of the formulæ $Bi_2O_3.N_2O_5.2H_2O$, $2Bi_2O_3.N_2O_5.H_2O$, $6Bi_2O_3.9N_2O_5.9H_2O$; while although precipitates were obtained intermediate in composition between the two last named, they were obviously mixtures. Two of these latter have found their way into the literature as the "compounds" $5Bi_2O_3.4N_2O_5.9H_2O$, and $11Bi_2O_3.9N_2O_5.21H_2O$.

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[1] Am. Chem. Jour. 25, 307 (1901).

Mr. Wilson has been engaged during the past Easter term with experiments on the precipitation of cupric chloride by potash. With N/5 solutions at 85° C. the precipitate consists altogether of $CuCl_2.3CuO.2H_2O$ until all the copper is removed from the solution ; on further addition of potash the precipitate turns black, no potash remaining in the solution until the precipitate is totally converted into the oxide.

THE RELIABILITY OF THE DISSOCIATION CONSTANT AS A MEANS OF DETERMINING THE IDENTITY AND PURITY OF ORGANIC COMPOUNDS

BY HEYWARD SCUDDER

Since the publication of the work of Ostwald[1] on the dissociation constants[2] of organic acids it has been assumed that this constant furnishes a reliable guide to the identity, strength and purity of organic compounds. Ostwald[3] states that the constant gives a satisfactory guide to the purity of analytically pure compounds showing, by a steady diminution of the value found at different dilutions, the presence of isomers or of acids of similar composition which could not be detected by analysis. Nernst[4] repeats practically the same idea in a note on the experimental work of Wakeman[5] on isohydric solutions, stating that in the case of a mixture of two acids the variation of the constant at different dilutions gives, as Ostwald had previously pointed out, a criterion of purity. The assumption that it is a suitable means of identification is not explicitly stated in text-books but will become obvious if the articles relating to conductivity measurements are studied.

Unfortunately a study of the literature has shown that the dissociation constant is of no greater reliability than the other physical constants. It is an additional and welcome aid, but can only be used as an aid and not as a crucial test for determining either identity or purity.

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[1] *Note.*—Since almost all the references to Ostwald's work are taken from one series of articles, unless otherwise stated they will be found in Vol. 3 of Zeit. phys. Chem. and only the page number will be given. Zeit. phys. Chem. 3, 173 (1889).

[2] The dissociation constant is also called the affinity constant.

[3] l. c. 173.

[4] Theoret. Chemie (3 Aufl.) 473 (1900).

[5] Zeit. phys. Chem. 15, 162 (1894).

The object of this paper is to point out the causes of the errors that may affect the value of the constant, to draw conclusions as to its accuracy as a means of identification and to show that it is not reliable as a guide to purity.

The following symbols for the Ostwald formula will be used;

$$K = 100k = \frac{m^2}{(1-m)v} \;.\; m = \frac{\mu_v}{\mu_\infty} \;.\; 100m = \text{percent dissociated.}$$

μ = molar conductivity. v = volume in liters.

The temperature at which the measurements quoted were made is 25° unless otherwise stated. The solvent used in all cases was water. For the sake of brevity complete tables will not always be given. The condensed forms will readily be understood. No essential data will be omitted. The expression "limits of K" means the maximum and minimum values found for K at the different dilutions measured. It does not indicate that the variations were regular, giving a steady increase or decrease of K with increasing dilution.

Causes of error

Measurement of conductivity.—Ostwald[1] states that on account of the difficulty of making accurate measurements, and since an error of one percent in the conductivity makes an error of at least two percent in the value of K, there is an allowable error of five percent in the value of K. All subsequent observers have accepted this as the allowable error.

Value of μ_∞.—Until within a few years the molar conductivities were expressed in terms of the Siemens unit. At the present time they are frequently expressed in reciprocal ohms. It is apparent that this change will not affect the value of K, for m simply expresses the ratio $\frac{\mu_v}{\mu_\infty}$. Since μ_∞ equals the sum of the equivalent conductivities of the anion and kation a change in the equivalent conductivity of the hydrogen or hydroxyl ion will affect the value of K only when the equivalent conductivity of the other ion (kation or anion as the case may

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[1] l. c. 173.

be) remains the same. For instance, Ostwald in his measurement of the dissociation constant of acetic acid used different values for H and $C_2H_3O_2$ from those given later by him,[1] but since μ_∞ remains the same the constant is not changed.

H.		$C_2H_3O_2$.		μ_∞	K.
320.5	+	43.5	=	364	0.00180
325	+	38.4	=	363	0.00180

l. c. 172. Lehrb. d. allgemeinen Chemie vol. II [1] 675, 677
2. Aufl.

But if the value for the equivalent conductivity of H is changed while that of $C_2H_3O_2$ remains the same, the difference in K may be considerable.

	H		$C_2H_3O_2$		μ_∞	K
(a)	320.5	+	43.5	=	364	0.00180
(b)	325	+	43.5	=	368	0.00175
(c)	345	+	43.5	=	389	0.00158

The value of H given in (c) is calculated to Siemens units from the value in reciprocal ohms found by Noyes and Sammet.[2] It will be seen that a variation in the value of H of about one and one-half percent as in (a) and (b) does not change K beyond the limits of allowable error, but that a variation of about six percent as in (b) and (c) changes K about six percent. The equivalent conductivity of H as given at present is,

H	Authority
325	Ostwald l. c. (In Siemens unit.)
345	" Calculated to reciprocal ohms by Noyes and Sammet.
346.4	" Calculated to reciprocal ohms by Muller.[3]
346	Bredig. Calculated to reciprocal ohms by Wegscheider.[4]
365	Noyes and Sammet (In reciprocal ohms).

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[1] The change in the values of the equivalent conductivity of the anions was due to a better determination of the equivalent conductivity of the sodium ion.

[2] Jour. Am. Chem. Soc. 24, 968 (1902).

[3] Bull. Soc. chim. Paris, (3) 27, 1012 (1902).

[4] Monatshefte 23, 613 (1902).

Noyes and Sammet state that their value is 3.8 percent higher than the latest value adopted by Kohlrausch and 5.8 percent higher than the value given by Ostwald. Comparison of this table with the one just given shows that the difference in the value of H calculated to reciprocal ohms by the three different observers would not affect K. But that the difference between Ostwald's value in Siemens unit and in reciprocal ohms or the difference between Ostwald's value in reciprocal ohms and that of Noyes and Sammet would correspond to (b) and (c) and change the value of K considerably.

The same difference may occur in the case of the hydroxyl ion. Bredig[1] in his work on dissociation constants of the bases states that the extrapolated value for OH calculated by Kohlrausch is about 8 percent higher than his own value derived from direct observation, and that if the Kohlrausch value is used the constants of the bases will in general be about 16 percent lower than those given by himself.

Confusion from this source of error is of slight possibility at present, since almost all constants are calculated from the values for different ions given by Ostwald and Bredig.

Temperature. — The difference caused by variation in temperature is so well understood that almost all published results give the temperature at which the measurement was made. The following table is taken from Schaller[2] omitting measurements between 50° and 90° and at 99°.

o-Toluic acid			K	
v	25°	40°	50°	90°
128	0.0135	0.0119	0.0107	0.00672
256	0.0134	0.0118	0.0105	0.00660
512	0.0130	0.0115	0.0103	0.00652
1024	0.0130	0.0115	0.0103	0.00652

Guinchard[3] gives the following measurements.

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[1] Zeit. phys. Chem. 13, 293 (1894).

[2] Ibid. 25, 517 (1898).

[3] Ber. chem. Ges. Berlin, 32, 1728, 1741 (1899).

Levulinic acid		Violuric acid
T	K	K
0°	0.00211	0.00144
25°	0.00228[1]	0.00273
35.5°	0.00229	0.00333

K = 0.00255 at 25° Ostwald.

He ascribes the considerable change in the value of K in the case of violuric acid to the fact that it is a pseudo acid, since true acids, like levulinic, show no such great differences.

It will be noted that in Schaller's table the change in value of K for a change of ten degrees in temperature is about ten per-cent, though the values found at different dilutions at each temperature agree well. In the case of other acids the change for ten degrees was in many cases as great as this, in other cases much less.

Decomposition. — Under this head will be described what is commonly known as decomposition, that is, change in molecular composition. Some compounds are decomposed quite rapidly when in solution. The decomposition may be hastened greatly by the influence of the platinized electrodes, though the weight that should be ascribed to this influence is at times a matter of dispute. Bader[2] states that, partly on account of oxidation the constants of the phenols are in doubt. Hantzsch,[3] on the other hand, states that the phenols are not oxidized if pure, and that Bader's trouble was due to the use of impure material. Bader's table for phenol will be given later under the head of Degree of Dissociation. He found that K increased with increasing dilution. Angeli[4] found that acetonedicarboxylic acid is decomposed by electrolysis, to which fact is due the diminution of the constant with increasing dilution.

Hantzsch and Miolati[5] in their work on the oximes of ketone-acids found a number of cases of decomposition due to

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[1] 0.00239 is the value given on p. 1736.

[2] Zeit. phys. Chem. 6, 289 (1890).

[3] Ber. chem. Ges. Berlin, 32, 3068 (1899).

[4] Gazz. chim. Ital. 22, II., 31 (1892).

[5] Zeit. phys. Chem. 10, 19 (1892).

different causes. The next three sets of tables are taken from their work.

v	K	
21.46	0.0787	K diminishes steadily
171.68	0.0743	
686.72	0.0671	
	K = 0.079	

α-Oximino-succinic acid (Syn-)			β-Oximino-succinic acid (Anti-)		
v	100 *m*	K	*v*	100 *m*	K
32	—	0.103	32	—	0.3861
64	—	0.113	64	—	0.3874
128	—	0.114	128	49.19	0.3749
256	43.02	0.127	256	59.60	0.3470
512	56.20	0.141	512	71.37	0.3518
1024	69.93	0.159	1024	81.90	0.3860
	K = 0.110			K can not be found	

They attribute the increase of K in the case of the *α*-acid to the effect of the second carboxyl, not to decomposition. The *β*-acid is rapidly decomposed in water to carbon dioxide, water and cyanacetic acid (K = 0.372 Ostwald). They state that under the conditions of electrolysis the acid is almost instantly decomposed, as shown by the approach of K to the value of K for cyanacetic acid.

They found that the monethyl esters of these acids were decomposed in solution, but in different ways.

Ester of α-acid			Ester of β-acid		
v	100 *m*	K	*v*	100 *m*	K
32	—	0.0188	32	—	0.5330
64	—	0.0195	64	—	0.5554
128	—	0.0196	128	54.48	0.5107
256	—	0.0194	256	63.77	0.4391
512	—	0.0193	512	—	0.3427
1024	35.27	0.0188	1024	80.39	0.3220
	K = 0.0192			K = 0.533?	

The ester of the α-acid is slowly decomposed by saponification, as shown after standing by the increase of conductivity and by titration.

	Fresh sol.	After 1 hour	After 5 hours
v	μ	μ	μ
32	26.59	27.68	33.0

The ester of the β-acid is not changed to the isomer, as was shown by measurements of conductivity and by titration of solutions that had been allowed to stand. It is rapidly saponified to the β-acid, which at once breaks down to cyanacetic acid as just shown.

It will be noted that in most of the illustrations given, except in the case of the phenols where other factors are of influence, K decreases on dilution, because of the effect of the decomposition products in the solution. But there is no regularity in the case of β-oximino-succinic acid.

Change of intramolecular constitution. — This is the change from one isomer to another. It produces in the solution a second compound that may have a value for K and a degree of dissociation quite different from the first, so that a change of K as in the case of impurities might be expected. Optical isomers, however, have the same value for K, so that if a change from one to another occurred, it would not be shown by conductivity measurements.

	K	M. p.	
d-Tartaric acid	0.097	170°	
l-Tartaric acid	0.097	170°	(From Walden)[1]
Racemic acid	0.097	205°	

In the case of all other isomers the change may affect K greatly. The next two tables are taken from Hantzsch and Miolati.[2]

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[1] Zeit. phys. Chem. 8, 465 (1891).

[2] l. c. 24.

Phenyloximino-propionic acid

Syn- or stable			Anti- or labile
v	100m	K	
64	—	0.00175	K can not be got. Comparison of μ shows that it is much stronger than the syn-acid. Syn- $v = 101.6 \quad \mu = 10.76$ Anti- $v = 100.6 \quad \mu = 17.69$
128	—	0.00182	
256	—	0.00196	
512	—	0.00224	
1024	14.21	0.00230	
K = 0.0002014			

They state that the change in K on dilution in the case of the syn-acid is due to transformation to the anti-acid.

Phenyloximino-acetic acid

Syn-			Anti-		
v	100m	K	v	100m	K
16	—	0.18	16	32.73	1.53
32	—	"	32	50.00	1.56
64	—	"	64	59.58	1.37
128	—	"	128	—	1.15
256	48.65	"	256	—	0.861
—	—	—	512	—	0.638
—	—	—	1024	82.29	0.373
K = 0.18			K = 1.55		

They state that the diminution in K in the case of the anti-acid is due to transformation to the syn-acid and not to impurity.

It will be seen from these examples that the change from one isomer to another may cause K either to increase or to diminish with increasing dilution. If the measurement for α-oximino-succinic acid given under the last head (Decomposition) is examined it will be seen that K increases steadily and shows no sudden great increase after fifty or sixty percent dissociation. This might suggest a change to an isomer.

Great degree of dissociation. — For some reason still in doubt the Ostwald formula is satisfactory only for the so-called half electrolytes, which are but moderately dissociated at ordinary dilutions. This group includes most organic electrolytes. For strongly dissociated compounds the constant varies with varying dilution. Rudolphi and van 't Hoff have proposed formulae for such cases, but these have been so little used in measurements of organic compounds that they will not be considered. The constants calculated by their use may vary widely from those obtained by the Ostwald formula.

In the following tables the names of some of the compounds have been slightly altered, so that they correspond to the names given in Beilstein's Organische Chemie (3d Aufl.) and Ergänzungsband.

Papaveric acid

Ostwald[1]			Kirpal[2]		
v	100 *m*	K	*v*	100 *m*	K
256	77.6	1.05	256	78.0	1.08
512	87.1	1.15	512	87.7	1.20
1024	—	—	—	—	—
K = 0.9 (approx.)			K not given		

4,6-Dibromanilin-2-sulphonic acid			4,5-Dibromanilin-2-sulphonic acid		
v	100 *m*	K	*v*	100 *m*	K
109.8	95.5	18	278	95.8	7.9
439.2	97.5	9	556	97.8	7.8

Both these were measured by Ostwald.[3] No constant is given.

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[1] l. c. 398.

[2] Monatshefte, 18, 466 (1897).

[3] l. c. 408.

3-Chlor-6-nitro-benzoic acid

Bethmann[1]			Holleman and de Bruyn[2]		
v	100 m	K	v	100 m	K
70.4	62.92	1.52	—	—	—
140.8	73.29	1.43	—	—	—
281.6	81.88	1.31	256	81.7	1.44
563.2	89.04	1.29	512	89.3	1.44
1126.4	94.66	—	1024	93.5	1.36
	K = 1.52			K = 1.42	

Bethmann ascribes the fall of K to extreme dissociation.

2-Brom-5-nitrobenzoic acid

v	100 m	K	Holleman and de Bruyn[3]
256	75.4	0.89	
512	85.0	0.93	
1024	91.8	1.01	
	K = 0.91		

It will be noted that K falls, rises or remains constant on dilution. Ostwald's constant for papaveric acid is an approximate value obtained by extrapolation. Since the acid is dibasic and is more than seventy percent dissociated at the first dilution measured, this value is of course very doubtful, because the effect of the second carboxyl is unknown. When K has a value much greater than 1.5 it varies greatly. Bethmann does not use an extrapolated value for K or his value would be still higher. Holleman and de Bruyn, measuring the same acid, get constant values. If the acid were as much dissociated as the dibrom-anilin-sulphonic acids such an agreement would be attributed to chance.

Small degree of dissociation. — When a compound is very

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[1] Zeit. phys. Chem. 5, 393 (1890).

[2] Recueil Trav. Pays-Bas, 20, 361 (1901).

[3] l. c. 361.

slightly dissociated the constant is so small that its value is affected greatly by small amounts of impurity or by small errors in measurement.

p-Nitro-phenol

Bader[1]			Hantzsch[2]		
v	μ	K	v	μ	K
35.6	0.75	0.000012	64	1.28	0.0000098
71.2	1.04	0.000012	128	—	0.0000102
142.4	—	0.000012	512	2.53	0.0000100
284.8	—	0.000013			
569.6	3.01	0.000013			

$\mu_\infty = 355$
K = 0.000012

(K of water used not subtracted)
K = 0.0000096

Hantzsch had this measurement repeated on other samples of the phenol with the same result. His criticism of Bader's work has already been given under the head of Decomposition.

In the case of compounds that have a smaller constant the difference is still more marked.

Phenol

Bader[3]			Observer
v	μ	K	K
25	0.14	0.00000056	0.0000005 Hantzsch[4] (K of aq. not subtr.)
50	0.23	0.00000077	0.00000042 Van Laar (calculated)[5]
100	0.41	0.0000012	0.000000013 Walker and Cormack[6]

$\mu_\infty = 357$
K = ?

Walker and Cormack state that values as small as these can be

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[1] l. c. 297
[2] l. c. 3070
[3] l. c. 291.
[4] l. c. 3069.
[5] Zeit. phys. Chem. 12, 748 (1893).
[6] Jour. Chem. Soc. 77, 5 (1900).

measured if the conductivity of the water used is not greater than 0.7×10^{-6}. In a revision of this article Walker[1] criticises unfavorably the values given by the other observers which agree in magnitude among themselves but not with the value found by Cormack and himself. He also regards the agreement in magnitude of the value of K for hydrocyanic acid as found by Ostwald, and by Morgan, and calculated by Van Laar as purely accidental.

In this group of cases if K has a value less that 10^{-5} the only possible comparison of values found by different observers is the comparison of the magnitude.

Isohydric solutions. — Wakeman[2] gives tables of measurements of isohydric mixtures of acids. The following tables are from his paper.

Acetic acid	K = 0.0018
Propionic acid	K = 0.00134

I.			II.		
Acetic acid	50 parts		Acetic acid	100 parts	
Propionic acid	1 part		Propionic acid	1 part	
v	K	K (calc.)	v	K	K (calc.)
32.4	0.00184	0.00179	32.72	0.00187	0.00179
64.8	0.00185	"	64.4	0.00188	0.00179
129.6	0.00186	"	128.8	0.00189	0.00179
259.2	0.00187	"	257.6	0.00192	0.00179
518.4	0.00190	"	515.2	0.00195	0.00180
1036.8	0.00194	"	1030.4	0.00198	0.00180

He concludes that in the case of acids as little dissociated as acetic acid and propionic the presence of impurities considerably influences the constant found, and that the presence of a small amount of propionic acid in acetic acid cannot be found by conductivity measurements. He ascribes the rise in value of K to

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[1] Zeit. phys. Chem. 32, 137 (1900).

[2] l. c. 171.

impurities in the water that were not taken into account in calculating K.

Smith[1] measured the so-called meso-camphoric acid which is a mixture of equal amounts of *d*-camphoric acid, K = 0.00229, and *l*-iso-camphoric acid, K = 0.00174, and found a constant unchanged on dilution though he had expected a change because the solution is not isohydric.

(*i*)Meso-camphoric acid

v	100 *m*	K
64	—	0.00187
128	—	0.00188
256	—	0.00187
512	—	0.00187
1024	12.82	0.00184

K = 0.00187

He also found that a mixture of equal parts of adipic acid, K = 0.00376, and pimelic acid, K = 0.00323, gave a constant K = 0.00345 (limits of K = 0.00348–0.00342).

It will be noted in the tables from Wakeman's work that the value of K as calculated and up to *v*256 the value of K as found agrees with K for acetic acid. In Smith's measurement of meso-camphoric acid the value of K is constant within the limits of the error in measurement, so that the small decrease in value could cause suspicion that an impurity was present only because the decrease is fairly regular. There was no regular decrease in the case of the second mixture.

Purity of compound. — It is frequently forgotten that mixtures form which cannot be separated by repeated crystallization from the same solvent or by repeated distillation at the same pressure, but only by crystallization from different solvents or by distillation at different pressures. The instances given under the last head show that widely varying amounts of a second compound may not affect the value of K beyond the allowable

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[1] Zeit. phys. Chem. 25, 214 (1898).

error, or in such a way as to cause a suspicion that an impurity is present. The fact that the value of K decreases regularly on dilution might tend to indicate the presence of an impurity, especially if the decrease is great. But if the decrease is within the limits of error of measurement the regularity may be accidental. Smith[1] measured suberic acid and found that K decreased from 0.00307 to 0.00295 in a fairly regular way. He decided that it was impure and recrystallized it. The limits of K then found were 0.00300–0.00294 with no regular decrease. It will be noted that in the first measurement the values of K agree within five percent. If reference is made to Smith's measurements of meso-camphoric acid and of the mixtures of adipic and pimelic acids, it will be seen that in one case there was such a regular decrease, in the other no regularity, though the agreement of the values is good in both. Walden[2] gives the following data for α-methylglutaric acid: $K = 0.0052$ (limits of K 0.0052–0.0050 at v32–512) m. p. 74°–76°. He ascribes the lack of sharpness in the melting-point to the presence of an impurity.

If the illustrations given under this and the preceding head are grouped, it becomes evident that just as there are "analytically pure" compounds which may contain small amounts of impurity that can not be shown by analysis, so there are "electrolytically pure" compounds containing variable amounts of impurity that can not be shown by conductivity measurements.

Different methods of measurements.—The apparatus used in making conductivity measurements is usually little varied. Schaller[3] used a different form, in order to measure at temperatures up to 100°. His constants from measurements at 25° agree well with those of other observers in some cases, but in other cases do not agree, although his own values of K at different dilutions agree closely. This is shown in the case of *o*-toluic acid, the table for which has been given under the head

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[1] l. c. 196.

[2] Zeit. phys. Chem. 8, 486 (1891).

[3] l. c. 517.

of Temperature. He does not give a constant, but from the data a value between 0.0130 and 0.0132 would probably be chosen. Ostwald[1] gives K = 0.0120. For *o*-nitro-benzoic acid Ostwald[2] gives K = 0.616, Schaller gives K = 0.663 at *v*128 and K = 0.640 at *v*1024;[3] the fall in value is regular but only about three and one-half percent. This is the strongest of the three isomeric nitro-benzoic acids, so that the presence of an isomer should tend to make the value less than that found by Ostwald.

When the constant is calculated by an entirely different method as by the inversion of sugar, etc., the results are satisfactory only in certain cases. Most of this work has been done with inorganic compounds. With our present limited experimental knowledge, the constants determined for organic compounds only by such means and not by conductivity measurements can not be regarded as more than approximate. Hantzsch and Miolati[4] calculate the constant for pyroracemic acid as about 0.56 by comparing its effect on the rate of inversion of sugar with that of lactic acid. Ostwald[5] found a constant of about 0.3 by conductivity measurements. He was unable to get or prepare any acid that did not give a value of K diminishing on dilution (which fact he attributes to the presence of some impurity), but states that by analogy to similar acids a much smaller constant would be expected.

Difficult solubility. — Some compounds are too insoluble to be measured at ordinary dilutions. At great dilutions the influence of impurities in the water and of errors in measurement of *v*, etc., may be considerable, and since at most only a few dilutions are measured a comparison of the values of K in order to get the best value is impossible. In the following illustration only one dilution was measured.

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[1] l. c. 269.

[2] l. c. 259.

[3] NOTE. — Schaller's table for *p*-chlorbenzoic acid, p. 522, from the context and from the value of K is obviously in error from a misprint. It should be for *o*-chlorbenzoic acid, not *p*-chlorbenzoic.

[4] l. c., p. 7.

[5] l. c., p. 192.

β-Naphthoic acid

Bethmann[1]		Bader[2]	
v	K	*v*	K
3124	0.00678	3400	0.00523

It has been pointed out in the case of papaveric acid (under the head of Degree of Dissociation) that if a dibasic acid is more than sixty percent dissociated at the first dilution measured there is an error of unknown amount, because the constants for dibasic acids are calculated just as in the case of monobasic acids and the values are rejected which are found after the increase due to the effect of the second carboxyl (this increase is usually marked after an acid is about sixty percent dissociated). But in the case of these difficultly soluble acids of such a degree of dissociation, the values that are usually rejected are the only ones that can be used for getting an approximation of K.

Judgment. — It has been stated previously that the assumption is made that for pure compounds the value of K will remain constant at different dilutions and that in the presence of impurities it will diminish with increasing dilution. But a large number of cases occur in which K changes markedly on dilution, although there is no suspicion of impurity nor is the degree of dissociation such that the formula is unsuitable. In making a choice of the constant that will best represent the compound in these cases it is necessary to consider the cause of the variation. This involves a consideration of the structure of the compound, of the possibility of associated molecules, complex ions, impurity, isomers, etc. It therefore furnishes a fruitful field for extremely ingenious speculations, some of which are of value.

Since judgment is always necessary in selecting the proper value for K from the measurements made, an attempted classifi-

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[1] l. c., p. 399.
[2] l. c., p. 311.

cation of the cases specially calling for the use of judgment is open to adverse criticism, for at best it can be but rough, and many of the examples already given could properly be put under this head. But it aids an analysis of the subject under consideration by allowing emphasis of certain conditions that often affect the choice of a constant.

(a) *Value of K increases with increasing dilution.* — This occurs in quite a large number of cases, e. g., phenols, amino-acids, etc. Ostwald[1] gives the following measurements:

Amino-benzoic acids

ortho-		meta-	para-	
v	K	K	K	
64	0.00066	0.00650	0.00072	Benzoic acid K = 0.00600
1024	0.00096	0.00806	0.00105	

The value of K increases steadily. He gives no constant. The increase of K is ascribed to the fact that the acids are at the same time both weak acids and bases and probably form intermolecular salts which dissociate on dilution. To the same cause he ascribes the strength of the meta-acid which is stronger than benzoic acid, contrary to the ordinary chemical experience that the introduction of an amino group into an acid weakens it. Berthelot[2] two years later measured these acids and found that the meta-acid is weaker than benzoic acid.

ortho-		meta-	para-	
v	K	K	K	T = 17°
100	0 00065	0.00084	0.00068	K of water not subtracted
1000	0.00099	0.00099	0.00118	

The meta-acid was measured by Bersch for Ostwald,[3] who states

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[1] l. c., p. 261.

[2] Ann. Chim. Phys. (6) 23, 95 (1891). Berthelot in this paper uses the value $K = 10^3 k$ instead of $10^2 k$, as used ordinarily. In the table in the text K has been changed to $10^2 K$ to correspond to the other tables.

[3] Zeit. phys. Chem. 8, 428 (1891).

that some error had been made in the earlier measurement and that Bersch had found K = 0.0012, bringing the meta-acid into the same relation to the ortho- and para-acids and to benzoic acid as found by Berthelot. No extended table is published, but the value of K probably is an extrapolated value or else the value of K at *v* 1024.

In a case of this sort there is no definite guide. It would not be expected that the introduction of an amino group would strengthen an acid nor would the analogy to the isomeric acids support such a supposition. But on the other hand it must be remembered that the influence of the substituting group varies greatly both with its position and with its nature. If Ostwald's constants of the nitro- and oxy-benzoic acids are considered,

Nitrobenzoic acids	Oxy-benzoic acids
o-K = 0.616	*o*-K = 0.102
m-K = 0.0345	*m*-K = 0.00867
p-K = 0.0396	*p*-K = 0.00286

it will be seen that the order of strength of the different isomers varies in the two groups and that the constant of *o*-oxy-benzoic acid is about twelve times as great as that of the next strongest isomer, while in Ostwald's measurements of the amino-benzoic acids the constant of the meta-acid is about nine times as great as that of the next strongest isomer. The introduction of the amino group caused an increase of K on dilution contrary to the usual rule for pure compounds, so that it might actually cause an increase in the strength of benzoic acid because of some unsuspected influence of space relations.

Walden[1] measured asparagic acid (amino-succinic acid).

v	100 *m*	K	
32	—	0.0067	Succinic acid K = 0.00665 (Ostwald)
1024	31.05	0.0137	

K = ?

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[1] l. c., p. 481.

The minimum value of K (which increased steadily) is slightly greater than that of succinic acid. Walden gives a clever theoretical explanation based on a structural formula for the acid different from that usually given. I have found no repetition of the measurement of this acid (Walker's work[1] is in a different direction), so that it is not possible to say whether this case will have the history of *m*-amino-benzoic acid or whether Walden's explanation is correct. [See foot-note.]

Ostwald[2] measured protocatechuic acid:

v	100 m	K	
32	—	0.00290	(K increases five units for each succeeding dilution except the last, for which the increase is six units)
1024	16.68	0.00326	

K = 0.0033

This value (which is extrapolated) he considers as correct because confirmed by its agreement with the value calculated from the constants found for the oxy-benzoic acids.

(b) *Value of K decreases with increasing dilution.* — This is characteristic of certain groups, such as the alkyl succinic acids. It also occurs in isolated cases. No definite explanation has been given. The following table is taken from Walden.[3]

NOTE. — I overlooked Berthelot's measurements which confirm those of Walden. $K = 10^2 k$ instead of $10^3 k$ as given by Berthelot.

Succinic acid		Asparagic acid	
v	K	v	K
100	0.00635	100	0.00813
500	0.00634	500	0.0114

T = 17° T = 15.4°

Conductivity of water not subtracted

Ann. Chim. Phys. (6) 23, 54, 99 (1891).

[1] Zeit. phys. Chem. 4, 332 (1889).

[2] l. c., p. 250.

[3] l. c., p. 462.

s-Diethylsuccinic acids

	Anti- M. p. 128°		Para- M. p. 192°	
v	100*m*	K	100*m*	K
32	—	0.0343	—	0.0245
64	—	0.0342	—	0.0245
128	—	0.0338	—	0.0249
256	—	0.0330	—	0.0241
512	—	0.0320	—	0.0235
1024	33.1	0.0291	37.9	0.0225

K = 0.0343 K = 0.0245

The highest value of K was taken in these cases.

3,5-Diamino-benzoic acid

v	K	Bethmann[1]
36	0.00108	(The first two dilutions are omitted here as being unessential. At $v = 9$ K = 0.00316.)
72	0.00069	
144	0.00051	
288	0.00045	
576	0.00049	

K = 0.00048

Bethmann repeated this measurement with a sample that had been recrystallized, to make sure that there was no impurity. The second measurement gave the same values with the minimum at v 248. The only explanation that he offers is that it may be due to the fact that this acid is also a base, although it is sufficiently strong to be titred.

It will be recalled that the basic nature of the amino-benzoic acids was used in explaining the increase of K on dilution in their case.

(c) *Place in a series.* — If homologous compounds are arranged in order, the difference in value of their constants is sometimes so regular that it affords a guide to the probable value

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[1] l. c., p. 388.

of constants that are in doubt. The following table of constants of monobasic fatty acids is taken from values found by Ostwald[1] and by Franke[2]. The boiling-points are from Beilstein's Organische Chemie.

Acid	Ostwald	Franke	Boiling-point
Formic	0.0214	—	100.8°
Acetic	0.00180	—	118.1° (corr.)
Propionic	0.00134	—	140.9°
n-Butyric	0.00149	0.00152	162.3°
iso Butyric	0.00144	0.00143	154°–155°
n-Valeric	(0.00161)	0.00150	186°–186.4° (corr.)
iso-Valeric	—	0.00167	173.7°
Caproic	0.00145	0.00138	205°
iso-Butylacetic	—	0.00145	200°–201° (207° corr.)
Diethylacetic	—	0.00189	190° (I. *v.*)
Heptoic	—	0.00131	223°–223.5°
Caprylic	—	(0.00144)	236°–237° (I. *v.*)
Pelargonic	—	(0.00112)	253°–254° (I. *v.*)
—	—	—	I. *v* = thermometer im-
—	—	—	mersed in the vapor.

Constants enclosed by brackets are regarded as doubtful, Ostwald's because the measurement was made before the importance of having pure water was understood and the water used contained some ammonia, Franke's for reasons which will be given. Both observers state that there is no regular difference between the constants of the acids in this series. Franke, however, doubts his value for caprylic acid, because it is stronger than heptoic acid. His measurements are

Caprylic acid. B. p. 237.5° (corr.)

v	K	
259	0.00144	(No other dilutions were measured)
512	0.00143	K = (0.00144)
1024	0.00144	

in which the values of K agree admirably.

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[1] l. c., p. 174 et seq.

[2] Zeit. phys. Chem. 16, 486 (1895).

It is not obvious why caprylic acid should not be stronger than the acid which immediately precedes it, since propionic and the butyric acids offer a striking illustration of the same sort and it is admitted that there is no regular difference in the constants for the acids in this series. The question of regularity in such a series is often a matter of arrangement. If, omitting formic acid, acetic acid is taken as the starting point and the acids are arranged in two series, placing on one side the normal acids considered as monalkyl derivatives, methylacetic acid, etc., and on the other side the acids that do not have a straight chain considered as dialkyl derivatives, dimethylacetic acid, etc., it will be seen that the difference becomes much more regular and that caprylic acid might be considered to be in its proper place when stronger than heptoic.

Franke regards Ostwald's caproic acid as iso-butyl acetic. The constants of the two acids differ slightly less than five percent, and the boiling-points are so close together that it would be difficult to tell whether the acid measured was one or the other. It will be noted that, excluding formic and pelargonic acids, the constants of these acids differ only forty-four percent between the extremes, and that the difference between any two acids is often less than ten percent. The table of dibasic acids that will be given later under Identification offers another illustration of how the place in a series influences the judgment of what the proper constant for a compound ought to be.

(d) *Analogy.* — It is found that substituting groups affect the value of K in a fairly regular way under limited conditions. Thus Ostwald found the following constants:

Benzoic acid	$K = 0.00600$
m-Oxy-benzoic acid	$K = 0.00867$
p-Oxy-benzoic acid	$K = 0.00286$

If the ratio of the constants of the substituted acids to the constant of benzoic acid is considered to be a factor representing the influence of meta- or para-hydroxyl, the value of K for a *m*-, *p*-dioxy benzoic acid could be calculated by multiplying the constant for either of the oxy-acids by the factor for the other hydroxyl,

$0.00867 \times 0.48 = 0.0038$
$0.00286 \times 1.4 = 0.0040$
K found $= 0.0033$

This acid is protocatechuic acid which has been given under (a) of this head. It will be noted that the calculated values only offer a suggestion of the real value. Wegscheider[1] in his work on the influence of constitution on the dissociation constant, in which he gives tables of factors for the different substituting groups, states that constants calculated by the help of factors do not as a rule agree very exactly with those found by direct measurement and sometimes do not agree at all.

But since these factors give approximations in closely allied cases, there is a temptation to apply the knowledge of the effect of a certain group, gained by experimental work on a small number of compounds, to all apparently similar compounds. Hantzsch and Miolati[2] finding in their work on ketone acids that the substitution of the oxime group for oxygen weakens the acid, conclude that the work of Bader[3] on the oxime of papaveric acid needs revision because the oxime could not be so strong. For papaveric acid $K = 0.9$ (Approximated. The measurement has been given under the head Degree of Dissociation.) Bader found the oxime stronger than oxalic acid ($K =$ about 10. Ostwald). But since they measured no acids of the same type containing both a benzene and pyridine ring, their judgment must be accepted with caution, for in all cases space relations may cause an unsuspected difference. In their own work they found that in the case of the α- and β-oximino-acids, there is such a difference in apparently analogous acids which they ascribe to a difference in the space relation of the oxime group to carboxyl. Engler and Hantzsch[4] give the following constants for the diazophenols:

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[1] Monatshefte, 23, 300 (1902).
[2] l. c., p. 13.
[3] l. c., p. 418.
[4] Ber. chem. Ges. Berlin, 33, 2148 (1900).

$C_6H_5NNOHK = 0.123$.
$CH_3OC_6H_4NNOH$ Nearly as strong as KOH, etc., therefore K can not be found.

They found that *p*-anisidine hydrochloride is more dissociated than aniline hydrochloride, but give no measurements by which the effect of methoxyl in the two cases can be compared.

We are in the habit of thinking loosely that the same group always has the same effect when it is substituted, the alphyl groups, CH_3, etc., for instance, weakening acids, while the aryl groups, such as phenyl, strengthen.[1] There are so many exceptions to such a principle that it can hardly be called general. The halogens and the nitro and sulphonic groups show a fairly fixed character when substituted. In the following tables, taken from Ostwald, Bethmann, and Walden, the effect is reversed.

Glutaric acid	$K = 0.00475$
α-Methylglutaric acid	$K = 0.0054$
β-Methylglutaric acid	$K = 0.0059$
Acrylic acid	$K = 0.0056$
Phenyl-acrylic acid (Cinnamic acid)	$K = 0.00355$
Succinic acid	$K = 0.00665$
anti-Dimethylsuccinic acid	$K = 0.0123$
para-Dimethylsuccinic acid (Cf. Judgment *b*)	$K = 0.0191$
Benzoic acid	$K = 0.00600$
o-Methylbenzoic acid (*o*-Toluic acid)	$K = 0.0120$

Such effects are ascribed to space relations. It is evident that here as elsewhere the argument from analogy is often weak because the analogy is only apparent and not real. It is also evident that the attempt to argue from a particular case or group of cases to all similar organic compounds will fail.

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[1] Cf. Nernst. Theoret. Chemie, p. 469 (3 Aufl.).

Frequency of errors

The error in measurement at present always may cause an unavoidable error of five percent in the value of K.

The errors from using different values of μ_∞, different temperatures of measurement, different methods of measurement and different formulae for calculating K, will not often be met with. They may cause considerable variation, so that the possibility of their occurence must be borne in mind.

This leaves, as affecting most cases, the errors due to decomposition, change of constitution, isohydric solutions, impurity of the compound, difficult solubility, degree of dissociation, and errors of judgment in selecting a proper value for K. Inspection will show the possibility of error due to degree of dissociation. Values of K outside the limits 1.5 — 0.00001 are of doubtful accuracy.

Causes affecting the value of K in one set of measurements at different dilutions

In the following classification no unusual cause such as variation of temperature is considered.

On dilution	Cause
K remains constant	Purity of compound Impurity of compound Isohydric solution Difficult solubility Inaccuracy of formula
K increases	Dissociation of associated molecules Change of intramolecular constitution Impurity of compound Inaccuracy of formula (Compound may be pure)
K decreases	Impurity of compound Decomposition Change of intramolecular constitution Isohydric solution Inaccuracy of formula Unknown reasons (Compound may be pure)

This classification is made from the examples previously given. The distinction between isohydric solution and impurity is of course artificial, since the presence in a solution of any other compound beside the one that is being measured is strictly the presence of an impurity.

Identification

If it is assumed that the value of K can be found with an accuracy of five percent and that the purity of the compound is shown by the agreement of the values of the constant found at different dilutions, yet for the same compound two observers find values of K differing by ten percent or more, although each one gets an excellent agreement for his own value of K at all dilutions measured, the question arises whether the compound actually is the same. If the difference is ten percent or less, the true value might lie between the reported values, in which case each would agree with the true value. But if the difference is greater than ten percent the conclusion is evident, either that one of the reported values is in error or that two different compounds were measured. Of course it is easy to assume that the compounds were isomers and that the difference is due to space regulations, for even such a simple acid as propionic acid gives at least three possible isomers from different space relations of the methyl and carboxyl groups. But unless the existence of such an isomer is shown directly or is shown to be probable, the *onus probandi* lies on the man making such an assumption. This leaves the other alternative, that one of the values is in error. From the illustrations already given it is evident that the agreement in the values of K at different dilutions does not exclude the possibility of impurity, so that an error is quite probable. It has also been shown that on account of a number of reasons the value of K as found by two observers may differ more than five percent. These facts make the primary assumptions invalid.

In the following table of some of the lower dibasic fatty acids, the observers are arranged in chronological order. Since each one found concordant values of K in his own measurements, extended tables will not be given. Oxalic and malonic acids are the only acids more than twenty-five percent dissociated at *v* 1024. The melting-points are taken from Beilstein's Org. Chemie. If the values given differ by more than one degree the extremes are taken, as in the case of pimelic acid.

	Ostwald[1]	Bethmann[2]	Brown & Walker[3]	Smith[4]	Melting-point
Oxalic	(10).	—	—	—	98°; 189.5° aq. free
Malonic	0.158	0.171	—	—	130°; 132°
Succinic	0.00665	—	0.0068	—	185° (corr.)
Glutaric	0.00475	—	—	0.00473	97.5°
Adipic	0.00371	—	0.00365	0.00376	149°; 153°(corr.)
Pimelic	0.00357	—	—	0.00323	114°; 118°
Suberic	0.00258	0.00311	0.00296	0.00299	140°
Azelaic	—	0.00296	—	0.00253	106°
Sebacic	0.00234	—	0.00276	0.00238	133°–133.5°

Walden[5] found for malonic acid K = 0.163. This, if correct, brings the values of Ostwald and Bethmann, which differ by about eight percent, into agreement with a mean value.

Ostwald could get no constant for oxalic acid because it is too strongly dissociated. He regards the value for pimelic acid as doubtful because it does not come in its proper place in the series which has a value of K steadily diminishing with increased molecular weight and separation of the two carboxyl groups. The poor value he attributes to the presence of impurity (although K did not diminish on dilution) which could not be removed on account of the small amount of material available.

Bethmann found that his new values for malonic and suberic acids improved the series and gave a regular difference. If a table of differences is made it will be seen that the

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[1] l. c., p. 284.

[2] l. c., p. 401.

[3] Liebig's Ann. 261, 116 (1891).

[4] l. c., p. 198.

[5] l. c., p. 448.

magnitude of the difference varies with alternate acids, not with succeeding acids as in Ostwald's table.

The work of Brown and Walker is of special interest, because they made by electrolysis the four acids given in the table and tried to identify them by the constant. The constants of succinic and adipic acids agreed well with Ostwald's, but of the other two did not agree within ten percent, and the constant of suberic acid differs a little more than five percent from Bethmann's. They measured samples of the last two acids prepared in the usual way and found for suberic acid $K = 0.00293$, for sebacic acid $K = 0.00271$, values which agreed well with their own for the synthetic acids. Ostwald[1] accepts all their constants as better than his own.

Smith found that his new values for pimelic, suberic and azelaic acids make a much better series than that of Bethmann, giving a regular decrease in K (as found by Ostwald) except in the case of suberic and azelaic acids where the difference is too great, showing a possible error. Both Bethmann and himself found that in the case of azelaic acid the value of K increases on dilution. He regards his own value as better than Bethmann's because it makes the difference between azelaic and sebacic acids more regular, and finds confirmation of the probable accuracy of this value in the fact that his constant for suberic acid agrees well with that found by Brown and Walker. In the case of sebacic acid his value fits in well in his series and agrees with that of Ostwald.

It will be noted in this series that the values regarded as most accurate are those that give desired differences between the constants of two adjacent acids, except in the work of Brown and Walker, who simply made and measured four acids without reference to any such considerations. Ostwald regards his constant for pimelic acid with doubt on this account. Smith's value would fit much better in Ostwald's series. Bethmann introduces into the series a new acid and finds a new value for suberic acid which gives a better series. Smith regards his

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[1] Zeit. phys. Chem. 7, 235 (Review).

value for suberic acid as better than Bethmann's because it makes a better series and is confirmed by its agreement with the value found by Brown and Walker. This agreement in the case of suberic acid he also regards as showing that his value for azelaic acid is better than Bethmann's. But he rejects Brown and Walker's value for sebacic acid (which Ostwald had accepted) because his own makes a better series and agrees with that of Ostwald. The difference in the value of the constant for the last three acids is so great that identification would be impossible. If the proper value for each acid from glutaric acid on is chosen, two series can be made, one corresponding to Bethmann's in which the regularity is between alternate acids, the other corresponding to Ostwald's in which the regularity is between adjacent acids. Neither series is perfect. But there is no way of deciding which series is the better one to take as a guide in selecting the most probable value of the constants. The same difficulty occurred in the series of monobasic fatty acids. It is due to imperfect knowledge.

Itaconic acid. — Ostwald[1] found K = 0.0120. Smith[2] measured preparations from different makers and found for one, K = 0.0149; for the other, K = 0.0151. This agreement makes him suppose that Ostwald may by mistake have measured the wrong acid. The difference, however, is little greater than that found in many other cases.

Oxaluric acid. — Ostwald found the acid too much dissociated to get a constant, except by approximation.

	Ostwald[3]	Trüsbach[4]
v	μ	μ
64	284	98.8
128	311	108.8
	K = 4.5 (approx.)	

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[1] l. c., p. 383.

[2] l. c., p. 211.

[3] l. c., p. 287.

[4] Zeit. phys. Chem. 16, 713 (1895).

Trübsbach found that this acid decomposes in solution, finally breaking down to oxalic acid. This decomposition is the probable explanation of the great difference between the two measurements which would seem to be of different compounds. The illustration shows the danger of depending on agreement of the molar conductivities at the same dilution as a means of identification in all cases.

The only other point that is of interest in identification is the agreement in value between the constants of compounds of closely related composition. The tables of constants of the monobasic and dibasic fatty acids give several instances of this sort in which the difference is less than five percent. The following table is from Walden:[1]

	K	M. p.	
Methylsuccinic acid	0.0086	111°	(Note that these acids are stronger than succinic acid. K = 0.00665)
Ethylsuccinic acid	0.0085	98°	
Propylsuccinic acid	0.00886	91°	

The agreement is of course accidental. It is of theoretical interest because of the slight difference caused by different substituting groups.

In conclusion it seems advisable to make a brief statement about certain points that have been brought up by inference. In the choice of illustrations care has been taken to give no isolated or unusual cases, but to select only those that can be duplicated by a number of similar cases which have been published. This has restricted the illustrations chiefly to acids, since the constants of most organic bases can not satisfactorily be found by conductivity measurements. Many of these acids are dibasic, so the question naturally arises whether some of the differences may be due to the fact that the influence of the second carboxyl varies in different cases. This hardly seems possible because the agreement found is so often good.

It will be noted that few cases have been given in which

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[1] l. c., p. 460.

different observers found values for K that agreed well, though many such cases are reported. This is because the reliability of a constant is shown by the relative number of cases in which it is found wanting. If the relative number of such cases tends to increase with increased knowledge, the reliability decreases accordingly.

The availability of conductivity measurements is greatly limited by the fact that the compound must be in solution when measured, and that the use of organic solvents gives results that are of doubtful value in our present state of knowledge.

Unless extended tables of measurements are given it is impossible to compare justly two different values for the constant of any compound, since there is no guide to the circumstances that affected the choice of each value. For instance, if one is an extrapolated value and the other is the value found at the first dilution measured, the agreement may be better or may be worse than it would be if both values were chosen in the same way.

In all cases where the value of K steadily decreases or increases with increasing dilution it is possible that the cause may be a change from one isomer to another.

Conclusions

The dissociation constant is a moderately reliable aid to identification. Its use is limited.

If, for any compound, the constants found by different observers agree within ten percent, the agreement is satisfactory.

The agreement between the values of the constants at different dilutions does not give a satisfactory guide to the purity of the compound that is being measured. This fact lessens the reliability of the constant as a means of identification.

Massachusetts Institute of Technology,
February, 1903.

NEW BOOKS

Handbuch der Spectroscopie. *By H. Kayser. Zweiter Band. 17 × 25 cm; pp. xi + 696. Leipzig: S. Hirzel, 1902. Price: 40 marks.* — The second volume of Kayser's monumental work on spectroscopy, dealing in the main with Kirchhoff's law of emission and absorption in its broadest phases, has followed the first with exemplary despatch. There can be no doubt that Kayser has put everybody interested in the progress of spectroscopic work, under a debt of lasting gratitude; for the mere marshaling of so great a wealth of experimental and theoretical research would have been an accomplishment, particularly in view of the complete and serviceable index. But Kayser and his two associates, Dr. H. Konen and Dr. C. Runge (to whom is due the excellent treatise on the concave grating in the first volume), do more than this, in endeavoring to enter critically into each of the papers presented.

In the first chapter of 66 pages, the law of the equality of emission and absorption is dealt with in its general bearings, beginning with an historical summary in which the names of Ritchie, Angström, Euler, Stokes, Stewart, Kirchhoff and others are prominent. A full presentation of Kirchhoff's famous researches is then given with a briefer outline of the correlative work. This is followed by the more recent treatment of the law associated with the name of Clausius, who, during the period of controversy over the second law of thermodynamics, published a new demonstration of the necessary dependence of emission on the square of the index of refraction, or as newer writers put it, on the specific inductive capacity of the medium. The remainder of the chapter is devoted to the experimental demonstrations of the law, and the number of investigators cited is naturally very large.

The next chapter on the emission of solids, in which the work done to determine the emission function in its dependence on temperature and wave length is detailed, is particularly valuable as a summary of the present status of the subject. The end in view was only possible after the invention of the bolometer and the realization of the importance of a black body. After his original contributions, Langley seems to have abandoned the subject, and the progress which culminated in the establishment of admirably exact equations for the energy of radiation is due to several German physicists, among whom Paschen, Lummer, Wien, and Planck may be mentioned. The two parts of the chapter discuss at length the total emission of hot bodies and the distribution of energy in the spectrum, respectively. It is curious to note how fruitfully suggestive Stefan's law of radiation has been throughout the whole of this work.

The next chapter of 74 pages on the radiation of gases, or luminosity as it is now called, is, according to the author, necessarily unsatisfactory in the view of the absence of any uniform hypothesis to account for the phenomena classified. The chapter endeavors to ascertain at the expense of what kind of energy the light of gases is produced, and therefore how this energy is converted into light. Ignition, fluorescence and phosphorescence, and organic sources offer a means of grouping the large number of investigations described. The intermediate part of the chapter shows, in an interesting way, the advantages of the transition from the older mechanisms to the more modern corpuscular mechanism, but as a whole the chapter reads like a report on a vigorous controversy still in progress.

Overlapping or combined spectra and multiple spectra are treated in the 69 pages of the fourth chapter. Roscoe and Clifton, and after them Lockyer, were the first to clearly apprehend the occurrence of spectra of compounds as distinguished from the spectra of the elements themselves. That the same substance may furnish two kinds of spectra of different character was later established by Plücker and Hittorf. The subject elicited much discussion until it was eventually cleared up by Lockyer's simple and ingenious method of producing long and short line spectra, by projecting a sharp image of the luminous source on the slit. In reviewing the theories which have been advanced for the occurrence of line, band, and continuous spectra in gases, viz., the emission hypothesis of Zöllner, the kinetic and bell theories, and Lockyer's dissociation theory, Kayser introduces much valuable discussion on the light sources of spectroscopic work. The review made of Lockyer's stellar hypotheses is appreciative, even though acknowledging that Lockyer's own experiments are not convincing and that the burden of evidence has accumulated incidentally from other sources.

The effect of temperature, pressure, electrical discharge, etc., on the spectrum is discussed in the fifth chapter (48 pages). What is here met with is not so much a change in the character of the spectrum as a modification of its details, such as may be grouped under broadening, displacement, and self-reversal of spectral lines. Kayser points out the absence of any sufficiently comprehensive theory to account for the large number of experimental results available. Michelson's researches are broadening, which show the admissibility of Döppler's principle on the basis of an argument of Rayleigh's, are given preference without, however, ignoring the frictional theories elaborated by Lommel and Jaumann. The chapter concludes with a discussion of the results of Jewell, Humphreys, and Mohler on the displacement of spectral lines due to pressure, and a final summary of the effect of temperature.

The appearance of the lines of the spectrum, whether sharp or diffuse, has been found of far-reaching importance, and a short chapter is devoted to it, largely made up of the intensity curves of Rayleigh and Michelson. Some magnificent plates due to Kayser himself are added in illustration of the phenomena of single and double reversal.

Dr. Konen begins his chapter of 92 pages on Döppler's principle with an exhaustive historical summary, which in spite of its detail will be found interesting reading. The theoretical part has also been worked out on historical lines, though here again the material is well grouped and conveys the impression of an independent treatise. The section investigates the effect of motion of the source, or of the illuminated body, or of the intervening medium on the intensity, the wave length, and the period of the light received. The earlier paragraphs are elementary and kinematic, and as such serve to introduce the more rigorous elastic and electro-optic treatment which the principle has received. The chapter concludes with a summary of the apparatus devised for verifying Döppler's principle.

The following chapter is the longest (142 pages) in the book, and in it Kayser has embodied much of his experience in practical spectrometry. The chapter treats of the laws discovered in relation to the distribution of spectrum lines. Some progress has been made to infer from these the motions of the atoms and their charges and the nature of the forces involved, though a consistent theory is as yet, naturally, very far in the future. The discussions in this chapter are necessarily of a highly technical kind, as most of the advance has been made empirically and they do not readily admit of abbreviation. Suffice it to say that in addition to the treatment of spectrum lines in general, a detailed exhibit is made of the spectra of all the important elements.

The final chapter by Prof. Runge gives a most welcome summary of the present state of our knowledge of Zeeman's discovery. It is well known that Faraday sought for the magneto-optic effect in question and that it was clearly predicted by Tait, though neither observer was able to detect it. Twenty-two years later under the improved instrumental facilities, due principally to the genius of Rowland, the effect was found by Zeeman.

The present chapter follows the general plan of the book in giving first a detailed historical account of the subject, then a description of essential apparatus, and finally an analysis of the theories of the phenomenon, among which the original theory due to Lorentz and the latter and apparently more flexible theory of Voight are prominent. The chapter concludes with a summary of the results obtained throughout the extent of the spectrum.

In reviewing a book of this encyclopedic character, it is manifestly impossible to give even an approach to an adequate account of the contents. The book will be found of incalculable value to any one whose work trenches on this vast domain of optics, which seems to have attracted the physicist, the chemist, and the astronomer about equally; and there will be very little excuse in the future for overlooking important papers or for repeating work already well done in spectroscopy. *C. Barus*

Physikalische Chemie der Zelle und der Gewebe. *By Rudolf Höber. 16 × 24 cm; pp. viii + 344. Leipzig: Wilhelm Engelmann, 1902. Price: paper, 9; bound, 10 marks.* — That physical chemistry is destined to have a very important influence upon the development of physiology is generally recognized. It is gratifying that Dr. Höber has thus early collected in book form the results so far obtained in the study of physiological problems from the standpoint of physical chemistry. The book consists essentially of a presentation of the theory of dilute solutions, the theory of electrolytic dissociation, and an attempt to utilize these to explain the various physiological activities of cells and tissues. The author has gathered together in a coherent and fairly complete manner the work that has been done in this field. The chapters on permeability of plasmic membranes, secretion, ferments, and dynamic equilibrium in organisms are of special interest. The volume is written in an admirable, enthusiastic spirit, and exhibits throughout power of original thought and ability to correlate material on the part of the author. Criticisms that might be made would fall upon the imperfections of existing physico-chemical theories rather than upon the way in which the author has sought to apply them. The book deserves the attention of those interested in physical chemistry, physiology, and medical practice. Though it will hardly prove a fruitful source of practical information to practicing physicians, it will be an aid in awakening renewed interest in physiological studies, and it certainly ought to stimulate physical chemists to further efforts toward securing more adequate conceptions of the nature of solutions. The interesting and valuable results that Quincke has published in the recent numbers of Drude's Annalen should in this connection command the attention of chemists and physiologists.

Louis Kahlenberg

Die radioactiven Stoffe nacht dem gegenwärtigen Stande der wissenschaftlichen Erkenntnis. *Bearbeitet von Karl Hofman. 15 × 22 cm; pp. 54. Leipzig: Johann Ambrosius Barth, 1903. Price: paper, 1.60 marks.* — This is a valuable compilation of the widely scattered work on radioactivity. Within but a comparatively short space of time a new branch of physical research has arisen, which, as it carries with it such an important connection with chemical phenomena, should make it of special interest to the physical chemist.

The fundamental experiments of Becquerel with the subsequent discovery of the properties of active uranium form the subject of the first part of the book, which is followed by similar sections on the other radioactive elements. These are radioactive bismuth (polonium), radium, radioactive lead and thorium.

Induced radioactivity, or, as it is more correctly called, excited radioactivity, is considered, and the methods employed in producing and studying this form of activity are carefully described. The radioactivity of the atmosphere is treated at some length. In conclusion the author discusses the general philosophical bearing of the subject, which shows him to have made a careful study of the work of the foremost investigators.

To any one desirous of gaining a good historical résumé of the work from the modern scientific standpoint, the book is sure to be of interest, while the clear way in which the matter is presented makes it of value to the student as well as to the investigator.

The subject is advancing rapidly, and since the publication of the book some important developments have taken place, notably the deviation of the α, or easily absorbed, rays by a magnetic field. It is, however, as much up to date as could be expected, and what it contains of the very latest work is accurate, although of necessity somewhat brief. *H. T. Barnes*

Die Herstellung von Metallgegenständen auf elektrolytischen Wege, und die Elektrogravüre. *By W. Pfanhauser (Monographien über angewandte Elektrochemie, Band V.). 16 × 24 cm; pp. xii + 144. Halle: Wilhelm Knapp, 1903. Price: paper, 7 marks.* — The subject is arranged under the following headings: historical introduction; galvano-plastic copper baths; physical properties of precipitated copper; behavior of anode copper; constants; technical details; special arrangements for definite purposes; preparation of metallic powders; preparation of sheet metal; preparation of wires; preparation of bulky articles; preparation of parabolic mirrors; preparation of tubes; electrolytic etchings; Rieder's method of electrogravure.

Some of the author's calculation as to cost seems to need revision. In two cases where he has estimated enormous profits from electrolytic refining of copper, the total profit is represented by the value of the gold and silver recovered. That profit goes to the original owner of the copper and not to the refiner. It is that which makes it profitable to refine copper electrolytically; but that has nothing to do with the question of making copper wire by a direct electrolytic process. Apart from this the volume is an excellent one. To the layman the chapters on the physical properties of electrolytic copper and on the preparation of pulverulent metals are perhaps as interesting as any.

Wilder D. Bancroft

The Electro-Plating and Electro-Refining of Metals. *Being a new edition of Alexander Watts' "Electro-Decomposition". Revised and largely rewritten by Arnold Philip. 13 × 19 cm; pp. xxiv + 680. New York: D. Van Nostrand Company, 1902. Price: $4.50, net.*—This new edition is divided into two distinct parts, as implied by the title, 480 pages being given to electroplating and 170 pages to electrolytic refining. In Part I. there are chapters on electrolytic deposition of copper, gold, silver, nickel, tin, iron, zinc, platinum, cobalt, bismuth, antimony, lead, aluminum, cadmium, chromium, magnesium, silicon, and alloys. Details are also given as to many non-electrolytic processes of plating; there is a chapter on the mechanical operations connected with electro-deposition; and also one on the recovery of gold and silver from waste solutions. There is a vast amount of information, stowed away in these pages, and this portion of the book is therefore valuable to the student. The practical exclusion of such words as volts and amperes from the text and of all ideas connected with such words detracts very much from the usefulness of the book. When we read that the current from a Bunsen cell is better for a certain operation than that from a Wollaston cell, we know qualitatively what the author is trying to say; but qualitative knowledge is of little value in electroplating. One must know the permissible variation in current strength and this one does not get from the book. Its value consists solely in the formulas for the plating baths and in the details of manipulation. For these we are grateful, but we would rather have seen the other data included, to the exclusion perhaps of the part on refining.

In Part II. there are the following chapters: the electro-metallurgy of copper; the cost of electrolytic copper refining; some important details in electrolytic copper refining; electrolytic gold and silver bullion refining; the electrolytic treatment of tin; the electrolytic refining of lead; the electrolytic production of aluminum and the electrolytic refining of nickel; electro-galvanizing. The chapter on the cost of electrolytic copper refining is an interesting one, though the author is wrong in concluding that a current density of 16 amp/sq. ft. is the maximum that can profitably be employed in refining copper. The Baltimore works are running at a higher rate than that to-day. While it takes four times the power to double the current density, the power per pound of copper is only doubled. The statement that the rolling mill in a Hayden plant takes about one-third of the total power is inaccurate, as is also the statement that most refineries work at a temperature of about 25° C. It is doubtful whether any works in America regularly use anode copper containing 97 pct copper.

Wilder D. Bancroft

Einrichtungen von elektrolytischen Laboratorien unter besonderer Berücksichtigung der Bedürfnisse für die Hüttenpraxis. *By H. Nissenson.* (*Monographien über angewandte Elektrochemie, Band IV.*). *16 × 24 cm; 51 pp. Halle: Wilhelm Knapp, 1903. Price: paper, 2.40 marks.* — The first part contains a statement of the general needs of a laboratory for electrolytic analysis, while the second part shows how the need has actually been met at Aachen, Breslau, Clausthal, Darmstadt, Freiburg i. S., Giessen, Hoboken (near Antwerp), Königsberg, Leoben, Liège, Munich, Philadelphia, and Stolberg. The subject is to be treated further in a later number. Since there are only fifty-one pages in this volume, it is a pity that the two should not have been combined. It is rather tantalizing to be told that the recent improvements by the author are not included in this pamphlet.

Wilder D. Bancroft

Specielle Elektrochemie. *By H. Danneel.* (*Handbuch der Elektrochemie.*) *Lieferung I. 17 × 26 cm; pp. 80. Halle: Wilhelm Knapp, 1903. Price: paper, 3 marks.* — The publishing house of Wilhelm Knapp is to issue a complete handbook of electrochemistry. The work will give all possible information about every known electrochemical reaction, including the discovery, theory, and application of it. All articles on such kindred subjects as methods of measurement and of electromagnetic concentration are to be included. The subject is to be divided into the following parts in charge of the following men: theoretical electrochemistry, Nernst; measurements, Bose; special electrochemistry, Danneel; batteries and accumulators, Elbs; electrolytic analysis, Küster; electromagnetic concentration, Langguth; technical inorganic electrochemistry, Borchers; technical organic electrochemistry, Elbs; plating, Stockmeier. It is expected that the publication will be completed inside of two years.

The part on the special electrochemistry of the elements and the inorganic compounds is to appear in about fourteen numbers, of which the first is now ready. The subjects treated are hydrogen, water, hydrogen peroxide, hydrofluoric acid, hydrochloric acid, hypochlorous acid, chloric acid, perchloric acid, hydrobromic acid, bromic and perbromic acids, hydriodic acid, iodic acid, hydrogen sulphide, sulphuric acid, persulphuric acid, sulphurous acid, hydrogen selenide, selenious acid, hydrogen telluride, nitric acid.

Wilder D. Bancroft

Notions fondamentales de Chimie organique. *By Ch. Moureu. 13 × 22 cm; pp. 292. Paris: Gauthier-Villars, 1902. Price: paper, 7.50 francs.* — The earlier part of this volume bears a considerable resemblance to the little book of somewhat similar title by Hjelt. The first chapters take up the analysis and composition of organic substances, the determination of formulas and molecular weights, isomerism, unsaturation, substitution, homologous series, stereochemistry, etc.; after this general treatment of theoretical matters a discussion of single groups of compounds begins, taking up first the hydrocarbons, both fatty and aromatic, then the alcohols, phenols, aldehydes, and so on.

It is not very plain to what class of students the work is intended to appeal. It would be very difficult for the beginner to understand the sixty large pages of purely abstract considerations before he had become familiar with a single organic compound ; on the other hand the advanced student would find the treatment of theoretical matters neither full nor suggestive. The book would be useful for reference in connection with some more simply arranged text, though the addition of an index to the table of contents at the back would have been very desirable.

As far as the general plan of the work is concerned it might just as well have been written twenty years ago ; there is no sign that general chemistry has since then contributed anything to organic chemistry, unless it be a few more structural formulas ; and so this volume, while it is as good as most of those we already have, shows no advance upon them. *A. P. Saunders*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Investigations on the atomic weight of tellurium. *G. Pellini. Gazz. chim. Ital.* 32, *I., 131* (*1902*). — From the oxidation of tellurium the author obtains the value Te = 127.65. From the reduction of the oxide to tellurium, there is obtained the value Te = 127.62. The single determinations vary from 127.30 to 128.05. *W. D. B.*

A redetermination of the atomic weight of lanthanum. *H. C. Jones. Am. Chem. Jour.* 28, *23* (*1902*). — From an analysis of the sulphate, the author deduces an atomic weight for lanthanum of 138.77. This value has been questioned by Brauner (*7*, 222). *W. D. B.*

A thermochemical constant. *F. W. Clarke. Jour. Am. Chem. Soc.* 24, *882*; *Zeit. anorg. Chem.* 33, *45* (*1902*). — The author finds the following equation to hold for a number of aliphatic hydrocarbons and their non-oxygenated derivatives.

$$\frac{4K}{12a + 6b - c - 8n} = \text{const.}$$

In this formula 4K is the heat of combustion, all the initial and final substances being in the gaseous state; *a*, is the number of molecules of CO_2 produced; *b*, the number of molecules of water; *c*, the number of oxygen molecules dissociated; and *n*, the number of atomic unions or linkings in the compound burned. The 'constant' has the value 13,773 cal, agreeing very closely with the heat of neutralization of strong bases by strong acids. The following general law is suggested: "In any class of compounds, the heat of formation is proportional to the number of atomic linkings within the molecule and seems to bear no relation to the masses of the atoms which are combined." *W. D. B.*

Electro-affinity as a basis for the systematization of inorganic compounds. *R. Abegg and G. Bodländer. Am. Chem. Jour.* 28, *220* (*1902*). — A reply to Locke (6, 442). *W. D. B.*

The electro-affinity theory of Abegg and Bodländer. *J. Locke. Am. Chem. Jour.* 28, *403* (*1902*). — A reply to Abegg and Bodländer (preceding review). *W. D. B.*

The teaching of electrochemistry. *S. Cannizzaro. Rend. Accad. Lincei* (*5*) 10, *II., 163* (*1901*). — A paper in which the author expresses his belief that electrochemistry is a branch of chemistry and should be taught by a chemist and not by a physicist or an engineer. *W. D. B.*

A university course in electrochemistry. *J. W. Richards. Trans. Am. Electrochemical Soc.* 1, *41* (*1903*).—An outline of a four-year course in electrochemistry. The author starts with the course in metallurgy as given at Lehigh University and modifies it so as to include the fundamentals of electrical engineering, also adding lectures and laboratory work in specific electrochemical subjects. *W. D. B.*

The theory and practice of continuous flow calorimetry. *H. T. Barnes. Trans. Am. Electrochemical Soc.* 2, *197* (*1902*).—The author describes a simple form of vacuum-jacketed continuous flow calorimeter, the constant for the apparatus being determined from an experiment with water. Unfortunately the method requires one to two liters of liquid. *W. D. B.*

On a means of stirring the liquid in a closed vessel and on a modification of a thermo-calorimeter. *G. Guglielmo. Rend. Accad. Lincei* (*5*) 11, *I., 298* (*1902*).—The author claims that he was the first, in 1892, to use a piece of iron and a magnet as a means of stirring a liquid in a sealed tube. He now points out that efficient stirring can also be obtained by whirling the tube first in one direction and then in the other, provided there be something inside the tube to churn the contents. It is claimed that the bad results of Favre and Silbermann with the mercury calorimeter were due to inefficient stirring, and the author suggests the use of a benzene calorimeter as being more sensitive.

W. D. B.

A novel constant high temperature bath. *C. Baskerville. Jour. Am. Chem. Soc.* 24, *1025* (*1902*).—The bath is porcelain-lined and holds a fusible alloy as liquid. The regulation of the temperature is done by means of a float. No figures are given as to the constancy of temperature attained. *W. D. B.*

One-Component Systems

On the distinction between polymorphism and chemical isomorphism. *G. Bruni. Rend. Accad. Lincei* (*5*) 11, *I., 386* (*1902*).—A discussion of the difference to be drawn between polymorphism (physical isomerism) and chemical isomerism. The conclusion is that we have chemical isomerism if any mixture of the two forms shows any sign characteristic of a two-component system.

W. D. B.

Arsenic pentachloride. *C. Baskerville. Jour. Am. Chem. Soc.* 24, *1070* (*1902*).—Arsenic chloride takes up chlorine at low temperatures, forming the pentachloride which freezes at about −38°. *W. D. B.*

On the specific heats and heat of vaporization of the paraffin and methylene hydrocarbons. *C. F. Mabery and A. H. Goldstein. Am. Chem. Jour.* 28, *66* (*1902*).—The authors have determined the specific heats of a number of pure hydrocarbons and of some crude oils. They have also measured the heat of vaporization of hexane, heptane, octane, hexamethylene, dimethyl pentamethylene, methyl hexamethylene, and dimethyl hexamethylene. *W. D. B.*

On the testing of carbon electrodes. *F. A. J. Fitzgerald. Trans. Am. Electrochemical Soc.* 2, *43* (*1902*).—The porosity is defined as the difference between the real and the apparent densities, divided by the real density. The real density is determined in kerosene, pumping the air out of the electrode. The porosity is greatest at the center of the electrode. In the Acheson graphite electrode studied, the average porosity as defined was 0.26. The real density was 2.19 Special experiments by the Berthelot method showed that the Acheson graphite contains no amorphous carbon. *W. D. B.*

Physico-chemical investigations in the pyridine series. *E. J. Constam and J. White. Am. Chem. Jour.* 29, *1* (*1903*). — The authors studied pyridine, α-picoline and β-picoline. They draw the following conclusions —

1. The regularity in the increase of the heats of combustion between homologues, observed in the aliphatic and aromatic series extends also to the pyridine compounds, being found equal to 156 cal for each CH_2.

2. The heat of formation of pyridine and its homologues can be approximately calculated from the formula,

$$C_nH_{2n-5}N = -51.7 \text{ cal} + 7n \text{ cal}.$$

3. Trouton-Schiff's rule, $MH/T = const$, holds good for the pyridine series also.

4. The affinities of pyridine and the picolines are of approximately the same order as that of *p*-toluidine. *W. D. B.*

On the alleged change of the properties of aluminum. *P. Spica. Gazz. chim. Ital.* 31, *II.*, *67* (*1901*). — Le Bon has claimed that the properties of mercury, magnesium, and aluminum can be modified profoundly by the addition of small quantities of other substances. In the case of aluminum, mercury is the substance to be added. The author shows that the peculiar properties of aluminum amalgam have long been known, that they are not so peculiar as Le Bon has maintained, and that they are easily explicable. *W. D. B.*

Two-Component Systems

On the nature of mercuric iodide in solution. *J. H. Kastle and J. V. Reed. Am. Chem. Jour.* 27, *209* (*1902*). — Supersaturated solutions of mercuric iodide in naphthalene do not crystallize at 100° when the red crystals of mercuric iodide are added to the solution. There is a heavy crystallization when the yellow modification is added. From this the authors conclude that mercuric iodide exists in solution as the yellow form. While no solvent is known which changes the inversion temperature for the red and yellow mercuric iodide, the rate of change varies markedly with the solvent, the viscosity being one of the determining factors. Under vaseline, yellow crystals have been kept for more than a year. *W. D. B.*

A contribution to the electrochemistry of barium compounds. *M. M. Haff. Trans. Am. Electrochemical Soc.* 2, *267* (*1902*). — Tabulated determinations of specific gravity of barium hydroxide solutions at 80° and of solubilities from 0° to 80°. *W. D. B.*

Saturated solutions of salts of analogous series. *C. Rossi. Gazz. chim. Ital.* 31, *II.*, *502* (*1901*). — The author finds that at some temperatures the ratios of the molecular solubilities of some anhydrous analogous salts are whole numbers (Cf. 6, 499). On this he bases speculations. *W. D. B.*

On the relation between solubility and heat of solution. *A. Campetti. Rend. Accad Lincei* (5) 11, *II.*, *99* (*1901*). — The author finds that the van 't Hoff formula for the relation between the change of solubility with the temperature and the heat of solution, holds better in the case of urea and of mannite solutions when the concentrations are expressed in grams per hundred grams of water than when expressed in grams per hundred cubic centimeters.

W. D. B.

On some uncertainties in the application of the periodic law. *N. Tarugi and Q. Checchi. Gazz. chim. Ital.* 31, *II.*, *417* (*1901*). — The author discusses argon, the peroxides, and tellurium; and then shows from experiments of his own that the solubilities of the cinnamates and salicylates of magnesium, calcium, strontium, barium, and mercury appear not to follow any law of periodicity. *W. D. B.*

Cryoscopic experiments with the bromides of arsenic and antimony. *F. Garelli and V. Bassani. Rend. Accad. Lincei* (5) 10, *I.*, *255* (*1901*). — Experiments with benzene, bromoform, iodine, iodide of arsenic point to 194 as the freezing-point constant for $AsBr_3$. Antimony tribromide causes a rise of freezing-point. The authors conclude that the corresponding constant for $SbBr_3$ is 267 as found by Tolloczko, though they criticise some of his conclusions.

W. D. B.

Cryoscopic measurements with methylene iodide. *F. Garelli and V. Bassani. Gazz. chim. Ital* 31, *I.*, *407* (*1901*). — Experiments with ethylene bromide, benzene and iodine pointed to a constant, 140, for methylene iodide. Stannic iodide, arsenic tri-iodide, mercuric iodide, and antimony tri-iodide gave practically normal values. The behavior of sulphur points to a molecular weight of 256, S_8. In all the cases, the apparent molecular weight varies less with the concentration when the concentrations are expressed in grams per 100 cc of solution than when they are expressed in grams per 100 g of solvent. The constant, 140, refers to the second or usual method. *W. D. B.*

Phosphorus oxychloride as cryoscopic solvent. *G. Oddo. Rend. Accad. Lincei* (5) 10, *I.*, *452*; *Gazz. chim. Ital.* 31, *II.*, *138* (*1901*). — From experiments with carbon tetrachloride, toluene, sulphur monochloride, and bromine the author deduces the value 69 for the freezing-point constant of phosphorus oxychloride. Aniline hydrochloride, pyridine hydrochloride, ferric chloride ($FeCl_3$), platinum tetrachloride and gold trichloride give values approximating those to be expected if the molecular weight were half the formula weight.

W. D. B.

Solid solutions and isomorphous mixtures in saturated and unsaturated compounds with open chains. *G Bruni and F. Gorni. Gazz. chim. Ital.* 31, *I.*, *48* (*1901*). — Reviewed (5, 322) from Rend. Accad. Lincei (5) 9, II., 151 (1900).

On the properties of nitrogen peroxide as solvent. *G. Bruni. Gazz. chim. Ital.* 32, *I.*, *187* (*1902*). — A statement of priority as against Frankland and Farmer (6, 519). *W. D. B.*

The lowering of the freezing-point of water produced by concentrated solu-

tions of certain electrolytes, and the conductivity of such solutions. *H. C. Jones and F. H. Getman. Am. Chem. Jour. 27, 433 (1902).* — Preliminary measurements with a large number of electrolytes. In nearly every case, the molecular lowering of the freezing-point passes through a minimum with increasing concentration. The molecular conductivities, on the other hand, decrease regularly with increasing concentration. *W. D. B.*

On the two monochlorides of iodine. *G. Oddo. Rend. Accad. Lincei* (*5*) 10, *II., 54; Gazz. chim. Ital.* 31, *II., 146* (*1901*). — Cryoscopic experiments with ICl_α dissolved in $POCl_3$ showed a molecular weight varying from 161.7 to 168.7. There is therefore no polymerization. It was not possible to keep the β-modification long enough to make any determinations with it. *W. D. B.*

On iodine trichloride. *G. Oddo. Rend. Accad. Lincei* (*5*) 10, *II., 116; Gazz. chim. Ital.* 31, *II., 151* (*1901*). — Iodine trichloride in phosphorus oxychloride gives molecular weights lower than the formula weights. The author accounts for this by assuming electrolytic dissociation into $Cl_2I^\bullet$ and Cl'. It must be stated that there is an enormous experimental error in the author's work, two successive determinations with the same concentration giving *molecular weights of 134 and 165. In water the apparent molecular weight of* iodine trichloride is about 45. The author offers no explanation for this. In water two successive series differ by about ten percent. *W. D. B.*

On sulphuric and disulphuric anhydride. *G. Oddo. Rend. Accad. Lincei* (*5*) 10, *II., 207; Gazz. chim. Ital.* 31, *II., 158* (*1901*). — From freezing-point experiments in phosphorus oxychloride, the author finds that the sulphur trioxide which melts at 14.8° has the formula SO_3, while the so-called solid trioxide has the formula S_2O_6. While sulphuric anhydride chars organic matter at once, this is not the case with the disulphuric anhydride. Neither anhydride reacts with metals or with oxides when perfectly dry. The dimeric form changes into the other with evolution of heat. *W. D. B.*

On compounds of sulphur dioxide with salts. *P. Walden and M. Centnerszwer. Zeit. phys. Chem.* 42, *432* (*1903*). — The melting-point of sulphur dioxide is found to be $-72.7°$. Below 0° a yellow compound, $KI(SO_2)_4$, with a melting-point of $+0.26°$ crystallizes from solutions of KI in SO_2. At lower temperatures ($-60°$) a yellow compound, $KI(SO_2)_{14}$, with a melting-point $-23°$ separates from the solutions. From vapor tension measurements, which are admitted to be somewhat unsatisfactory, the authors argue in favor of the non-existence of the compound of the formula $KI(SO_2)$. The upper limits of the existence of solutions of KI in SO_2 are determined by investigating equilibria at higher temperatures. Cryoscopic determinations indicate that in 0.4 normal solutions in water, the complex compounds of KI with SO_2 and of KCNS with SO_2 are decomposed to a great extent, which was to have been expected from the known affinity of these salts and of SO_2 for water. In concentrated solutions of RbI, $N(CH_3)_4I$, KI, KCNS, KBr, resorcine, and KCl in water, SO_2 is more soluble than in water; the solubility diminishes in the solutions of these compounds in the order named. In aqueous solution of NaCl, SO_2 is less soluble than in water. The authors argue that these complex compounds also exist in the SO_2 solutions of these salts; in other words, they favor the hydrate theory in this case. However, they point out that the combination of the salt with several molecules of the solvent would not change the number of the solute molecules, and so, according to the osmotic theory of solutions, would not influence the boiling- or freezing-point of the solutions. Concerning the abnormally high molecular weights which they have found for KI in SO_2 solutions (395 and 193 when one gram-mol. is contained in 1 liter and 16 liters respectively, in spite of the fact that the solutions are excellent electrolytes) the authors state that they have no explanation, as the assumption that the above-named complex compounds exist in the solutions is unable to clear up the "deviations from the osmotic law". In the final summary, it is stated that polymerization of the salt molecules in the solutions *must* be considered as the main cause of the deviations from the requirements of the osmotic theory.

The reviewer would add that there are no facts whatever upon which to base the assumption of such polymerization, the assumption being made solely to save at all hazards the osmotic theory of solutions and the theory of electrolytic dissociation. The behavior of the SO_2 solutions constitutes a strong argument against these theories; and this behavior is readily explained on the basis of the older view that in solutions the whole of the solvent is bound to the whole of the solute by ties of affinity that are chemical in character. *L. K.*

New studies on solid solutions. *G. Bruni. Rend. Accad. Lincei* (*5*) 11, *II.*, *187* (*1902*).—In dimethyl succinate, as solvent, dimethyl malate, tartrate and racemate give normal values, while hydrobenzoin and isohydrobenzoin form solid solutions. Somewhat too high values are obtained for *p*-tolylhydroxylamine and *p*-cresol in *p*-toluidine and for α-naphthylhydroxylamine in α-naphthylamine. Solid solutions certainly occur with α-naphthol in α-naphthylamine with *s*-tribromaniline in *s*-tribromphenol, and with $C_6H_5CHO.N.C_6H_5$ in azoxybenzene. A number of other cases of solid solutions were studied, the chemical similarity of solvent and solute being always the deciding factor. *W. D. B.*

On the nature and properties of colloidal solutions. *G. Bruni and N. Pappadà. Gazz. chim. Ital.* 31, *I.*, *244* (*1901*).—Colloidal silicic acid, ferric hydroxide, chromic hydroxide, Prussian blue, and egg albumen do not pass through a membrane and do not change the freezing-point of water at all. Dextrine and molybdic acid do diffuse through a membrane, though slowly, and do lower the freezing-point of water. The second group, therefore, form true solutions, the solutes being highly polymerized. Substances of the first group are to be considered as in suspension only, and it is these substances which coagulate. *W. D. B.*

On the formation of mix-crystals by sublimation. *G. Bruni and M. Padoa. Rend. Accad. Lincei* (*5*) 11, *I.*, *565*; *Gazz. chim. Ital.* 32, *II.*, *319* (*1902*).—When azobenzene and stilbene are sublimed together, homogeneous crystals are obtained which contain both components. The same thing occurs when mercuric iodide and bromide are sublimed together. *W. D. B.*

Some new methods for determining the molecular weight of substances in dilute solutions. *G. Guglielmo. Rend. Accad. Lincei* (*5*) 10, *II.*, *232* (*1901*).

—The new methods are modifications of the wet and dry bulb hygrometers. No figures are given to show the accuracy of the methods proposed.

W. D. B.

Determination of molecular weight of volatile substances by the boiling-point method. *G. Oddo. Rend. Accad. Lincei* (*5*) 11, *I.*, *12* (*1902*).—The author has determined the boiling-points of solutions of iodine in benzene and has determined the amount of iodine in the vapor by distilling off some of the solution and analyzing. His results differ markedly from those of Beckmann and Stock. The discrepancy is probably due to the methods of distillation. The author observed no precautions. *W. D. B.*

Determination of molecular weight of volatile substances by the boiling-point method. *G. Oddo. Gazz. chim. Ital.* 31, *II.*, *222* (*1901*); *Rend. Accad. Lincei* (*5*) 11, *I.*, *130* (*1903*).—Even after applying corrections for the volatility of the solute, the author finds abnormally high values for phosphorus oxychloride in carbon tetrachoride and benzene, but normal values in chloroform. Normal values were obtained for phosphorus oxybromide in benzene, thionyl chloride in chloroform, sulphur monochloride in benzene and in carbon tetrachloride. High values were found for phosphorus sulphochloride in benzene. The accuracy of the author's correction for volatility has been disputed by Ciamician, who attributes the apparent polymerization to experimental error. *W. D. B.*

On the polymerization of some inorganic oxychlorides. *G. Ciamician. Rend. Accad. Lincei* (*5*) 10, *II.*, *221* (*1901*); *Gazz. chim. Ital.* 32, *I.*, *254* (*1902*).—Oddo (4, 406) believed that phosphorus oxychloride polymerized in boiling benzene. The author shows that this apparent result is to be ascribed to the volatility of the oxychloride (preceding review). The values are practically normal when a correction is made for the partial pressure of the solute.

W. D. B.

A probable cause of the different colors of iodine solutions. *A. Lachmann. Jour. Am. Chem. Soc.* 25, *50* (*1903*).—Previous investigators have found four sets of colors for iodine solutions: violet, red, red-brown, brown. The author finds that the intermediate shades are due to traces of impurity in the solution. Working with pure solvents, there are only violet or brown solutions. From experiments with sixty-one solvents, the author draws the conclusion that saturated solvents give violet solutions and that brown solutions are formed in solvents which have an unsaturated character. The explanation is offered that addition products are formed to some extent. It is not necessary to assume that all the iodine is present as addition product, since addition of three percent of alcohol to an iodine-chloroform solution gives as dark a brown as can be obtained with pure alcohol. *W. D. B.*

An apparatus for continuous vacuum distillation. *C. F. Mabery. Am. Chem. Jour.* 29, *171* (*1903*).—A description of a form of apparatus which has proved serviceable in the separation of petroleum fractions with high boiling-points. *W. D. B.*

Multi-Component Systems

An investigation of ammonio-silver compounds in solution. *W. R. Whitney and A. C. Melcher. Jour. Am. Chem. Soc.* 25, *69* (*1903*). — From transference experiments, freezing-point determinations, conductivity measurements and solubility tests, the authors conclude that the ammonio-silver compounds contain the complex cation $Ag(NH_3)_2$. *W. D. B.*

On chemical equilibrium between acid salts and sparingly soluble salts. *G. Magnanini. Gazz. chim. Ital.* 31, *II., 542* (*1901*). — The solubility of acid potassium tartrate is increased by the addition of acid potassium sulphate and decreased by the addition of acid potassium oxalate. The solubility of monocalcium phosphate is increased by addition of acid potassium tartrate. The solubility of calcium sulphate is increased by addition of acid potassium tartrate or tartaric acid and is decreased by alcohol. The solubility of calcium tartrate is increased by tartaric acid and decreased by alcohol. *W. D. B.*

On the oxychlorides of mercury. *N. Tarugi. Gazz. chim. Ital.* 31, *II., 313* (*1901*). — The results of the author's investigations seem to be that the compounds $2HgCl_2,HgO$, $HgCl_2,HgO$, $HgCl_2 2HgO$, $HgCl_2 3HgO$, and $HgCl_2 4HgO$ as prepared by other people, are not true compounds, but that the compounds $HgCl_2,HgO$, $HgCl_2 2HgO+$ and $HgCl_2 3HgO$, as prepared by himself, are real compounds. *W. D. B.*

The lowering of the freezing-point of aqueous hydrogen dioxide produced by certain salts and acids. *H. C. Jones and C. G. Carroll. Am. Chem. Jour.* 28, *284* (*1902*). — The lowering of the freezing-point of hydrogen peroxide solutions by the addition of salts is less than when the salts are added to pure water, while the reverse is the case when acids are added. The authors assume that the salts form addition products while the acids are more highly dissociated. *W. D. B.*

On the existence of racemic substances in solution. *G. Bruni and M. Padoa. Rend. Accad. Lincei* (*5*) 11, *I., 212; Gazz. chim. Ital.* 32, *I., 503* (*1902*). — The authors experimented with the dimethyl esters of diacetyl tartrate and racemate in different solvents. With the racemate alone, the result of freezing-point measurements pointed to the existence of tartrates alone in the solution. On addition of an excess of tartrate, the apparent molecular weight rose, indicating a partial formation of racemate in solution. *W. D. B.*

On heterogeneous equilibria in mixed crystals of hydrated isomorphous salts. *G. Bruni ahd W. Meyerhoffer. Rend. Accad. Lincei* (*5*) 11, *I., 185* (*1902*). — A discussion of the equilibria between two salts, each of which forms two or more hydrates, the corresponding hydrates of the two salts being isomorphous. *W. D. B.*

The periodic system and the properties of inorganic compounds, IV. *J. Locke. Am. Chem. Jour.* 27, *455* (*1902*). — The author has determined the solubilities of the double sulphates of the $M_2^IM^{II}(SO_4)_2 6H_2O$ type. He finds in general that the effect of each univalent and each bivalent metal upon the solubility of the salts is a specific one, retained throughout all its compounds in the series, and totally independent of its atomic weight. A quadratic formula was applicable for the "solubility increment". *W. D. B.*

Absorption of gases in organic solvents and in solutions of organic solvents. *M. G. Levi. Gazz. chim. Ital.* 31, *II., 513* (*1901*). — Experiments were made on the solubility of oxygen, methane, and ethylene in methyl alcohol and acetone; also on the solubility of nitrogen in methly alcohol and in methyl alcohol solutions of potassium iodide and of urea of varying concentrations at 5°, 15°, and 25°. The formulas of Jahn applied fairly well to the solubility of nitrogen in the solutions. *W. D. B.*

The quantitative separation of hydrochloric and hydrocyanic acids. *T. W. Richards and S. K. Singer. Am. Chem. Jour.* 27, *205* (*1902*). — Since hydrochloric acid is very much more dissociated than hydrocyanic acid, it was thought that it would be less volatile in dilute solutions. This proved to be the case and the authors distil off all the hydrocyanic acid, leaving all the hydrochloric acid behind. *W. D. B.*

On a method for the determination of very small vapor-tensions in certain circumstances. *L. W. Andrews. Jour. Am. Chem. Soc.* 24, *864* (*1902*). — The author proposes to determine vapor-compositions by bubbling air through a solution, noting the loss in weight and determining the change in concentration. It is assumed that equilibrium conditions are easily reached.

W. D. B.

The equilibrium between urea and ammonium cyanate. *J. Walker. Zeit. phys. Chem.* 42, *207* (*1902*). — Fawsitt (7, 233) found that the equilibrium between ammonium cyanate and urea is displaced with rising temperature, more ammonium cyanate being formed, and he stated that this was contrary to the results of Walker. The author points out that Fawsitt has mis-stated Walker's results and that the two sets of observations are in absolute agreement.

W. D. B.

On the hydrate of sulphuryl chloride and the unchanged solubility in water. *G. Carrara. Gazz. chim. Ital.* 31, *I., 450* (*1901*). — The hydrate of sulphuryl chloride, discovered by Baeyer and Villiger, melts at ordinary temperatures and is therefore not a factor in the rate of decomposition of sulphuryl chloride and water, as studied by the author in 1894. Baeyer and Villiger believe that sulphuryl chloride dissolves in water; but the author shows that this is wrong because in that case the conductivity of water which had been shaken with sulphuryl chloride should change with time, owing to the decomposition of the sulphuryl chloride. No such change can be observed. *W. D. B.*

Contributions to the study of starch-iodide. *L. W. Andrews and H. M. Goettsch. Jour. Am. Chem. Soc.* 24, *865* (*1902*). — A careful study of some of the properties of starch iodide. The theoretical side of the paper is weak and the contention that "starch iodide" is an easily dissociating compound is certainly not proved. *W. D. B.*

A new separation of thorium from cerium, lanthanum, and didymium, and its application to the analysis of monazite. *F. J. Metzger. Jour. Am. Chem. Soc.* 24, *901* (*1902*). —

1. A saturated solution of fumaric acid in 40 percent alcohol precipitates thorium completely from neutral solutions to which 40 percent of their volume of alcohol had been added, while under these condition, the only other metals that give precipitation are zirconium, erbium, silver, and mercury.

2. This precipitation serves as an accurate and rapid separation of thorium from the other earths in monazite, and by its use the thoria can be determined in about one-third the time required by the methods now in use and with equal if not greater accuracy.

3. As the thorium-carbon ratio in thorium fumarate is 1 : 4, thorium and fumaric acid react molecule for molecule.

4. By the aid of a blast-lamp, white vapors were driven off from the thoria left in the boat after the combustion of thorium fumerate in a stream of oxygen (a fact as yet not explained).

5. Rare earth oxalates and thorium thiosulphates are completely converted into the hydroxides by heating to boiling in a strong solution of potassium hydroxide, giving a convenient method for the conversion of those salts into nitrates. *W. D. B.*

Reactions between acid and basic amides in liquid ammonia. *E. C. Franklin and O. F. Stafford. Am. Chem. Jour.* 28, *83* (*1902*). — "The relation borne by the acid amides and the metallic amides towards liquid ammonia as a solvent is strikingly analogous to the well-known relations borne by the ordinary acids and bases to water.

"Metathetic reactions between many acid amides and potassium amide in solution in liquid ammonia take place with all the facility which marks the interaction of ordinary acids and bases in aqueous solution.

"Acid amides in solution in liquid ammonia attack potassium and sodium, and in some cases magnesium, with the evolution of hydrogen and the formation of the metallic derivatives of the acid amides."

Eighteen compounds were prepared by acting on acid amides in liquid ammonia with potassium, sodium, or magnesium amide. *W. D. B.*

A volumetric method for the estimation of sulphuric acid in soluble sulphates. *Y. Nikaido. Jour. Am. Chem. Soc.* 24, *774* (*1902*). — The author titrates sulphates in a 50-60 percent alcohol solution with lead nitrate, using potassium iodide as an indicator. No reference is made to the work of Klein (5, 269). *W. D. B.*

Action of aluminum on salt solutions and on some fused salts. *C. Formenti and M. Levi. Gazz. chim. Ital.* 32, *I.*, *34* (*1902*). — Aluminum precipitates metal from the following solutions: antimony trichloride, bismuth nitrate, bismuth chloride, silver nitrate, copper chloride, copper nitrate, copper sulphate, cobalt chloride, nickel chloride, gold chloride, platinum chloride, palladium chloride, cadmium chloride, lead acetate, lead chloride, lead nitrate, lead chromate, tin chloride, cerium chloride, thorium sulphate, zirconium chloride, zirconium sulphate, thallium chloride, manganese chloride. With the fused chlorides of bismuth, copper, lead, tin, and manganese, and with fused cadmium iodide, aluminum reacts, forming an alloy. Aluminum acts on an aqueous solution of mercuric chloride, forming an amalgam, while hydrogen is set free.

W. D. B.

Esterification by means of inorganic salts. *G. Oddo. Gazz. chim. Ital.* 31, *I., 285* (*1901*). — When alcohol is heated in a sealed tube with such salts as copper sulphate, ferric chloride, tin sulphate, or zinc chloride, ether is formed in amounts varying with the temperature and the nature of the salt. The author has made experiments with a large number of alcohols. He believes that there is an intermediate formation of an alcoholate and a sulphate or chloride, and that these react, forming the ether. Since he obtained no ether by heating alcohol with potassium ethyl sulphate, he believes that Williamson's explanation of the ether formation must be modified.

In the case of benzyl alcohol, the author gives a list of thirty salts which cause esterification, and of twenty salts which do not. Nickel chloride and zinc iodide cause a rapid condensation but with no formation of ether. The salts which cause etherification with one aromatic alcohol do not always have the same effect with another. *W. D. B.*

On the relation between Kolbe's reaction and the cryoscopic behavior of phenols in benzene and other solvents containing no oxygen. *G. Oddo and E. Mameli. Rend. Accad. Lincei* (*5*) 10, *II., 240*; *Gazz. chim. Ital.* 31, *II., 244* (*1901*). — The authors find that Kolbe's reaction takes place most readily with those substances, like naphthol, which lose the CO_2 most readily, in other words, with the substances with which the reaction is most readily reversible. In many cases the cryoscopic behavior of phenols which do not form oxyacids is abnormal and like that of the alcohols. This is not universally true.

W. D. B.

The action of hydrogen on oxygen in presence of water. *A. Marcacci. Rend. Accad. Lincei* (*5*) 11, *I., 324* (*1902*). — The author's experiments seem to show that when hydrogen stands in a gasometer over water containing air, the oxygen disappears, presumably having combined with the hydrogen. When the water contains sodium chloride, the oxygen does not disappear. [This is a most extraordinary result and calls for further tests in which the ratio of oxygen to hydrogen should be increased.] *W. D. B.*

On the cause of the brown color of ammonium sulphide in presence of a nickel salt. *U. Antony and G. Magri. Gazz. chim. Ital.* 33, *II., 265* (*1901*). — The authors bring forward experimental evidence in favor of the view that the brown color observed in ammoniacal nickel sulphide solutions is due to the presence of colloidal NiS_1. *W. D. B.*

Osmotic Pressure and Diffusion

Osmotic studies on Infusoria. *P. Enriques. Rend. Accad. Lincei* (*5*) 11, *I., 340, 392, 440* (*1902*). — The author points out that if animals were necessarily isotonic with the surrounding medium, it would be impossible for them to change from salt-water to fresh water unless they swelled to say ten times their normal value. From this we must conclude that the membranes cannot be impermeable to salts when an animal can live in water of varying concentrations. Experiments with *Infusoria* showed that they first contracted and then expanded on being put in a solution more concentrated than their normal. This was not always easy to observe because the *Infusoria* can only withstand slight changes of concentration and therefore usually die. These successive changes were shown clearly by weighing *Limnaeae* at different times.

W. D. B.

The preparation of cells for the measurement of high osmotic pressures. *H. N. Morse and J. C. W. Frazer. Am. Chem. Jour.* 28, *1* (*1902*). — The authors have succeeded in improving their method for making cells with semipermeable membranes (6, 506) and their cells will now stand thirty-three atmospheres pressure. A preliminary experiment with a *n/2* sugar solution gave a pressure of 13-14 atm, while the osmotic pressure of a normal solution is above 31.4 atm.

W. D B.

New osmotic membranes prepared by the electrolytic process. *H. N. Morse. Am. Chem. Jour.* 29, *173* (*1902*). — A preliminary announcement to the effect that the author has prepared electrolytically diaphragms of the ferrocyanides of zinc, cadmium, manganese, and uranyl; of the phosphates of copper and uranyl; and of the hydroxides of iron and aluminum. It is proposed to study these in detail later.

W. D. B.

Velocities

On the reciprocal effect of two catalytic reactions in the same medium. *A. Coppadoro. Gazz. chim. Ital.* 31, *I.*, *425* (*1901*). — The author has studied the action of hydrochloric acid on sugar solutions and methyl acetate solutions separately and when mixed. If corrections are made for the concentrations of the sugar and the methyl acetate, it is found that each reaction takes place in the mixture independently of the other.

W. D. B.

Rate of hydration of metaphosphoric acid. *C. Montemartini and U. Egidi. Gazz. chim. Ital.* 31, *I.*, *394* (*1901*). — The authors find that the rate of hydration of metaphosphoric acid can be expressed by the formula for monomolecular reaction. They have overlooked the fact that this result was obtained by Sabatier in 1888.

W. D. B.

Rate of hydration of pyrophosphoric acid. *C. Montemartini and U. Egidi. Gazz. chim. Ital.* 32, *I.*, *381* (*1902*). — The reaction between pyrophosphoric acid and water, forming phosphoric acid, was shown to be of the first order.

W. D. B.

Decomposition of bromacetates by different bases in different alcoholic solutions. *A. Schweinberger. Gazz. chim. Ital.* 31, *II.*, *321* (*1901*) — The author studied the decomposition of the bromacetates at 60° in different solvents. The constants are given in the following table:

Solvent	NaOH	KOH	$NaOCH_3$	$NaOC_2H_5$	$NaOC_3H_7$	NH_4OH
Water,	0.82	0.98	—	—	—	2.3
CH_3OH	0.75	0.70	0.32	0.37	0.55	0.75
C_2H_5OH	0.54	0.60	0.59	0.54	0.39	0.33
C_3H_7OH	—	—	1.7	—	—	—

The action of methyl alcohol and of sodium methylate is irregular. The high value for ammonia in water is attributed by the author to the accelerating action of ammonium bromide, though no reason is given why this substance should act in this way.

W. D. B.

The inactivity of lipase towards the salts of certain acid ethers considered in the light of the theory of electrolytic dissociation. *J. H. Kastle. Am. Chem. Jour.* 27, *481* (*1902*). — While lipase accelerates the rate of hydrolysis of di-ethyl succinate by water, it has no effect in the case of sodium ethyl succinate. This was found, on investigation, to be a general phenomenon. No satisfactory explanation could be found. *W. D. B.*

Electromotive Forces

Current electrochemical theories. *L. Kahlenberg. Trans. Am. Electrochemical Soc.* 1, *119* (*1902*). — The point is made that there are fewer variables in the case of the electrolysis of a fused salt than in the case of the electrolysis of a solution of a salt. For that reason it would seem desirable to understand the behavior of the simple case before trying to discuss the effect due to the solvent. This is the more essential since Lorenz has called attention to the unexpected pnenomena attending the electrolysis of fused salts. *W. D. B.*

Differences of potential between metallic cadmium and solutions of cadmium iodide in various solvents. *L. Kahlenberg. Trans. Am. Electrochemical Soc.* 2, *89* (*1902*). — The 'single potential' difference between cadmium and *n*/10 cadmium iodide varies from + 0.479 volt in normal propylamine to — 0.049 volts in lactic acid nitrile. The changes appear to be connected with the chemical affinity between the solvent and solute. *W. D. B.*

The reversible copper oxide plate. *W. McA. Johnson. Trans. Am. Electrochemical Soc.* 1, *187* (*1902*). — From a study of the electromotive force of a copper oxide plate during discharge, the author deduces the existence of the oxides Cu_4O, CuO, Cu_3O_2. *W. D. B.*

Thermodynamical note on the theory of the Edison accumulator. *E. F. Roeber. Trans. Am. Electrochemical Soc.* 1, *195* (*1902*). — A discussion of the theory of the Edison storage battery on the assumption that it is an oxygen-lift cell. As the author has not had an Edison cell with which to experiment, it was impossible for him to check his deductions. *W. D. B.*

A novel concentration cell. *H. S. Carhart. Trans. Am. Electrochemical Soc.* 1, *105* (*1902*). — In the cell $Ni \mid c_1NiSO_4 \mid c_2NiSO_4 \mid Ni$ the current flows in the opposite direction from that predicted by the theory. [This has since been found to be due to the action of the air.] *W. D. B.*

The thermoelectric theory of concentration cells. *H. S. Carhart. Trans. Am. Electrochemical Soc.* 2, *123* (*1902*). — In cases where there is no chemical reaction, the electromotive force of a cell must be given by the temperature coefficient term in Helmholtz's equation and the sum of the thermoelectric forces at the various junctions must be the electromotive force of the cell. Since the potential difference in a concentration cell is a function of the concentrations, it follows that the thermoelectric force at the junctions between metal and electrolyte must change with the concentration. The author finds this to be the case; but, curiously enough, looks upon it as an argument against the osmotic pressure theory of the cell. *W. D. B.*

Voltaic cells with fused electrolytes. *E. A. Byrnes. Trans. Am. Electrochemical Soc.* 2, *113* (*1902*). — Measurements of electromotive force in fused caustic soda. *W. D. B.*

An electrochemical paradox. *C. Hering. Trans. Am. Electrochemical Soc.* 2, *139* (*1902*). — Water was electrolyzed between platinum electrodes placed close together in a glass tube connected with a manometer. The current was kept constant and the voltage dropped from 1.9 volts at one atmosphere to 0.29 volt at 15 atmospheres, remaining practically the same until the tube broke at about 23 atmospheres pressure. The drop in voltage is due to the depolarization at the electrodes. *W. D. B.*

Electrochemical polarisation. *J. W. Langley. Trans. Am. Electrochemical Soc.* 2, *255* (*1902*). — The author defines polarization as "the instantaneous value of the counter-electromotive force existing during the passage of the electrolyzing current." With platinum electrodes in 10 percent aqueous potassium sulphate a maximum counter-electromotive force of 2.45 volts was found. With *n*/5 and *n*/10 H_2SO_4 the value was about 1.8 volts; and with 10 percent potassium chloride, just over 2.0 volts. Using a carbon anode and iron cathode in fused sodium chloride at 900°, 2.0 volts were obtained, and 3.0 volts with fused potassium chloride at 825°. With alumina dissolved in melted cryolite at 1010°, the counter-electromotive force was only 1.2 volts; but this is probably due to the iron becoming passive. *W. D. B.*

The nascent state. *C. J. Reed. Trans. Am. Electrochemical Soc.* 1, *69* (*1902*). — The author objects to the phrase "nascent state". A number of interesting experiments are described with a cell made up of two solutions separated by a porous cup, the anode solution being always hydrochloric acid and the cathode solution a mixture of salts of metal less noble than copper. A copper cathode was used and different metals as anodes. With tin as anode, hydrogen is set free at the cathode; with lead as anode, some metallic tin is precipitated along with the hydrogen; with an anode of cadmium, lead, tin, and hydrogen are set free; with an anode of zinc, cadmium, lead, iron, tin, and hydrogen are deposited; with an anode of sodium or potassium, zinc, cadmium, lead, iron, tin, and hydrogen are precipitated. It is not stated whether the metals precipitate simultaneously or successively; but this would vary with the current density, the relative concentrations and the degree of stirring. The experiments illustrate the fact that a reaction can take place only so long as the potential of the reacting substances is higher than that of the reacting products. *W. D. B.*

A zinc-bromide storage battery. *H. H. Dow. Trans. Am. Electrochemical Soc.* 1, *127* (*1902*). — A cell with zinc and carbon electrodes in bromine water plus bromine is said to give a very constant voltage of 1.7 volts and to be readily reversible. *W. D. B.*

Storage battery invention. *H. Rodman. Trans. Am. Electrochemical Soc.* 2, *177* (*1902*). — A discussion of the relative merits of the lead and the Edison batteries, in which reasons are given for preferring the lead battery. It is stated that a battery better than the ones now in use would control practically all city traffic not on rails. *W. D. B.*

On the effect of electrification on the rate of vaporization. *A. Pochettino. Rend. Accad. Lincei* (*5*) 11, *I.*, *376* (*1902*). — With a cathetometer the author measured the change in vertical diameter of a drop perched on the top of a vertical rod. The effect due to electrification was perceptible and showed itself as a decrease in the rate of vaporization. This is the effect to be predicted from the change of surface tension and of vapor-pressure. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Observations on the electrolytic precipitation of zinc and copper. *E. F. Smith. Jour. Am. Chem. Soc.* 24, *1073* (*1902*). — Zinc can be precipitated from a solution containing sodium acetate if one neutralizes with ammonia when the hydrogen begins to come off in quantity. Zinc in zinc blende and copper in chalcopyrite can easily be determined electrolytically. In the latter case some iron is found in the copper if a platinum dish is used as cathode but none when platinum cylinders are used as beakers. *W. D. B.*

The electrolytic estimation of bismuth and its separation from other metals. *A. L. Kammerer. Jour. Am. Chem. Soc.* 25, *83* (*1903*). — Working at about 50° with a current density of 0.02 amp/qdm, it is possible to precipitate bismuth satisfactorily from a solution containing 1 cc nitric acid (sp. gr. 1.42), 2 cc of sulphuric acid (sp. gr. 1.84), and 1 g potassium sulphate per 150 cc of solution. There is no difficulty in separating bismuth from zinc, cadmium, chromium, nickel,. cobalt, manganese, or uranium; but special precautions must be taken when iron is present. *W. D. B.*

Separation of lead from manganese by electrolysis. *A. F. Linn. Am. Chem. Jour.* 29, *82* (*1903*). — To a solution of lead and manganese nitrates there are added sodium hydrogen phosphate and free phosphoric acid. When electrolyzed with a low current density, lead alone precipitates at the cathode. It takes sixteen to seventeen hours to precipitate 0.1 g lead. *W. D. B.*

The electrical reduction of lead. *P. G. Salom. Trans. Am. Electrochemical Soc.* 1, *87* (*1902*). — A brief description of the process in use at Niagara Falls for preparing spongy lead by the electrolytic reduction of a galena cathode. *W. D. B.*

The manufacture of bisulphide of carbon in the electric furnace. *E. R. Taylor. Trans. Am. Electrochemical Soc.* 1, *115*; 2, *185* (*1902*). — A brief account of the author's process for making carbon bisulphide by heating carbon and sulphur in the electric furnace. The process is a continuous one and the furnaces are 16 feet in diameter and 41 feet high. *W. D. B.*

Continuous electrolysis of solutions of metals. *N. S. Keith. Trans. Am. Electrochemical Soc.* 1, *131* (*1902*). — When one is precipitating a metal, using an insoluble anode, the current density must be decreased as the concentration of the metal becomes less. Instead of doing this by decreasing the current, which involves inefficiency, the author increases the size or number of the electrodes in the tanks to which the dilute solutions are taken for electrolysis.

W. D. B.

A method of electrolytic production of zinc from its ores. *S. S. Sadtler.*

Trans. Am. Electrochemical Soc. 1, *141* (*1902*). — The author proposes leaching zinc out as sodium zincate by means of an electrolytically prepared sodium hypochlorite solution and then precipitating the zinc from the zincate electrolytically. *W. D. B.*

Caustic alkalies and chlorine by the dry electrolytic process. *C. E. Acker. Trans. Am. Electrochemical Soc.* 1, *165* (*1902*). — The electrolyte is fused sodium chloride, the anodes are graphite, and the cathode is molten lead. There are four anodes each carrying 2000 amperes and the voltage is 7 volts. The sodium is constantly removed as fused anhydrous caustic and the circulation kept up by blowing steam through the fused lead in what would be the cathode chamber if there were one. *W. D. B.*

Note on the preparation of metallic lithium. *S. A. Tucker. Jour. Am. Chem. Soc.* 24, *1024* (*1902*). — In this modification of Bunsen and Matthiessen's process there is an asbestos partition in a porcelain crucible. The anode is carbon and the cathode an iron loop with which the molten lithium is fished out of the melt. The lithium cathode is kept fused by a gas jet and a current of 5–7 amperes is used. *W. D. B.*

Note on the Gladstone-Tribe couple. *W. D. Bancroft. Trans. Am. Electrochemical Soc.* 1, *65* (*1902*). — Some of the results obtained by Gladstone and Tribe with their couple have been duplicated by means of a pair of zinc or copper plates and an external current. Potassium chlorate is reduced without evolution of hydrogen and the chlorine is taken out of chloroform. *W. D. B.*

Preparation of *n*-methyl granatanine by electrolytic reduction of *n*-methyl granatonine. *A. Piccinini. Gazz. chim. Ital.* 32, *1 260* (*1902*). — In concentrated sulphuric acid there is no difficulty in reducing *n*-methyl granatonine electrolytically to *n*-methyl granatanine. *W. D. B.*

An electrolytic study of pyroracemic acid. *G. W. Rockwell. Jour. Am. Chem. Soc.* 24, *719* (*1902*). — The following compounds have been detected as a result of the electrolytic oxidation and reduction of pyroracemic acid: acetaldehyde, acetic acid, acetic ester, and lactic acid. It is believed that diacetyl and propionic acid may be formed. Up to 60 percent of the theoretical yield of aldehyde was obtained and up to 28 percent of lactic acid. *W. D. B.*

On the electrolytic reduction of aromatic nitro-compounds to the corresponding amines. *A. Chilesotti. Gazz. chim. Ital.* 31, *II., 567* (*1901*). — Reviewed (6, 206) from Zeit. Elektrochemie, 7, 768 (1901).

The dissolution of soluble metallic anodes. *W. McA. Johnson. Trans. Am. Electrochemical Soc.* 2, *171* (*1902*). — The author points out that the successful 'sliming' of silver in copper anodes depends largely on the formation of an alloy having a lower conductivity, which therefore carries much less of the current and which eventually drops off from the anode. [This explanation would be more plausible in case of electrodes carrying more silver than do the copper anodes in actual use.] The 'sliming' of arsenic and antimony, on the other hand, is undoubtedly due to an oxidation of these metals in the converter, so that they are non-conducting spots in the anode plate. This is one of the great improvements in copper refining since it permits of keeping the solutions pure for an indefinite period. *W. D. B.*

The phenomenon of the formation of metallic dust from cathodes. *F. Haber. Trans. Am. Electrochemical Soc.* **2**, *189* (*1902*). — Reviewed (**6**, 512) from Zeit. Electrochemie, 8, 245 (*1902*).

The equivalent conductivity of the hydrogen ion derived from transference experiments with hydrochloric acid. *A. A. Noyes and G. V. Sammet. Jour. Am. Chem. Soc.* 24, *944* (*1902*). — Experiments with *n*/20 HCl at 10° and 20° gave 0.15882 and 0.16569 for the transference number of chlorine; with *n*/60 HCl at 20° and at 30° the values were 0.16743 and 0.17734. The authors deduce 330 as the most probable migration velocity of the hydrogen at 20°. *W. D. B.*

Measurement of electrolytic diffusion, of transference numbers, and of migration velocities. *P. Straneo. Rend. Accad. Lincei* (*5*) 11, *I.*, *58*, *171* (*1902*). — The author passes the electrolyte between two horizontal electrodes placed close together. The difference of potential is measured while a constant current flows. In making the calculations, the author assumes Nernst's theory of diffusion and his theory of electromotive force. Under these circumstances, it would seem simpler to use the Helmholtz theory at once. *W. D. B.*

On the constitution of certain organic salts of nickel and cobalt as they exist in aqueous solution. *O. F. Tower. Jour. Am. Chem. Soc.* 24, *1012* (*1902*). — "Aqueous solutions of nickel and cobalt salts of dibasic organic acids offer greater resistance to the passage of the electric current than solutions of similar salts of the other metals investigated, notably magnesium, and this resistance is exceptionally great in the case of the tartrates and malates of nickel and cobalt. This abnormal behavior of the last-named salts is also confirmed by the results obtained with the freezing-point method for determining molecular weights." *W. D. B.*

On the basic energy of silver oxide in solution. *M. G. Levi. Gazz. chim. Ital.* 31, *II.*, *1* (*1901*). — By direct analysis the author finds that *1* g Ag_2O dissolves in about 15000 g of water. Conductivity measurements, based on the assumption of AgOH in solution, gave a value $100\,k = 0\ 0115$ at 25°. At a dilution of 7,000 liters, there is only a little over fifty percent dissociation. As a base silver hydroxide stands between trimethyl amine and methyl diethyl amine; it is much stronger than ammonia. *W. D. B.*

Contribution to the knowledge of some inorganic acids. *A. Miolati and E. Mascetti. Gazz. chim. Ital.* 31, *I.*, *93* (*1901*). — When a strong acid is neutralized by a strong base, the conductivity of the solution will pass through a minimum at the moment of neutralization. With a weak acid there will be an increase of conductivity throughout. With a dibasic acid all combinations or intermediate steps are possible. The author has made experiments with sulphurous, selenious, selenic, telluric, chromic, arsenic, phosphorous, arsenious, boric, iodic, and periodic acids. The resulting curves are very interesting though one cannot always agree with the author in his desire to double formulas. *W. D. B.*

A study of the conductivity of certain salts in water, methyl, ethyl, and propyl alcohol, and in mixtures of these solvents. *H. C. Jones and C. F. Lindsay. Am. Chem. Jour.* 28, *329* (*1902*). — With potassium iodide, ammonium bromide, strontium iodide, and lithium nitrate in mixtures of ethyl alcohol or methyl alcohol and water, the conductivity passes through a minimum for about 50 percent alcohol. No minimum was found for cadmium iodide. No minimum was found for any salt in mixtures of methyl and ethyl alcohols.

W. D. B.

Separation of the basic and acid functions in solutions of the amino acids by means of formaldehyde. *U. Schiff. Gazz. chim. Ital.* 32, *I.*, *97* (*1902*). — When formaldehyde is added to a solution of an amino acid, it combines more or less completely with the amino group, changing the electrolyte from an amphoteric one to an acid. The amount of acidity thus produced, depends on the concentration of the amino acid and of the caustic potash used for titration. The author gives the data for a number of amino acids. *W. D. B.*

Separation of basic and acid functions in solutions of albuminoids. *U. Schiff. Gazz. chim. Ital.* 32, *I.*, *115* (*1902*). — Addition of formaldehyde to a neutral solution of egg albumen makes the latter acid (see preceding review).

W. D. B.

The electrolytic rectifier. *C. F. Burgess and C. Hambuechen. Trans. Am. Electrochemical Soc.* 1, *147* (*1902*). — The authors show that the aluminum plate is covered with an oxide film of high resistance, in which there are a number of holes, and that these holes open and shut with the alterations of the current. The leakage in actual practice with an alternating current is much higher than would be expected from experiments with a direct current. By using aluminum and iron as electrodes in fused sodium nitrate, the authors succeeded in getting an energy efficiency of 80 percent. *W. D. B.*

Some phenomena of electrolytic conduction. *C. J. Reed. Trans. Am. Electrochemical Soc.* 2, *235* (*1902*). — If a current be passed through the system Cu | $CuSO_4$ | H_2SO_4 | H_2SO_4 | Pt the volume and concentration of the middle solution will increase, when this solution is separated from the other two by porous diaphragms. The author gives a calculation as to what should happen according to the electrolytic dissociation theory and finds that it does not agree with the facts. He does not take into account, however, the phenomenon of electrical endosmose or the possibility of disturbing factors at the surface between sulphuric acid and copper sulphate. *W. D. B.*

Graphite electrodes in electrometallurgical processes. *C. L. Collins, 2nd. Trans. Am. Electrochemical Soc.* 1, *53* (*1902*). — The author points out the advantages of the Acheson graphite electrodes over other carbon electrodes and calls especial attention to the fact that these can be worked and jointed as though they were wood. *W. D. B.*

Electrolysis by an alternating current. *J. W. Richards. Trans. Am. Electrochemical Soc.* 1, *221* (*1902*). — When an insoluble salt can be formed at the electrodes, there is no reason why there should not be continuous electrolytic decomposition with an alternating current. This is the case, for instance, with cadmium electrodes in a sodium hyposulphite solution, cadmium sulphide being formed. Other instances are cited. *W. D. B.*

On the fusion of quartz in the electric furnace. *R. S. Hutton. Trans. Am. Electrochemical Soc.* 2, *105* (*1902*). — A description of the author's experiments in making quartz tubes by electric heating of sand. The power at the author's disposal, 50 volts and 500 amperes, was not sufficient to permit of very satisfactory results; but attention was called to the many uses for quartz vessels. *W. D. B.*

The efficiency of electric furnaces. *J. W. Richards. Trans. Am. Electrochemical Soc.* 2, *51* (*1902*). — The ratio of the heat not lost in radiation to the total heat supplied is the efficiency of the furnace. Since we do not measure the heat lost in radiation and cannot calculate with any accuracy the amount of heat necessary for the process, the figures for efficiency are only approximate. Since the loss by radiation does not increase as rapidly as the mass, the larger the furnace the more efficient it will be. *W. D. B.*

Pumps and other accessories in electrolytic plants. *D. H. Browne. Trans. Am. Electrochemical Soc.* 2, *219* (*1902*). — A description of pumps, heaters, and evaporators which have and have not been found useful with hot nickel chloride solutions. *W. D. B.*

A unit of electrical quantity for use in electrochemical calculations. *A. H. Cowles. Trans. Am. Electrochemical Soc.* 2, *207* (*1902*). — One hundred ampere-days liberates one cubic meter of hydrogen under standard conditions or one kilocrith. The unit, one hundred ampere-days, is to be known as a kilocrith Col, the Col standing for the monad atom of electricity. Other derived units are the Colad, Cojoule, and Colore. The author believes that it is not a coincidence that one hundred ampere-days set free one cubic meter of hydrogen. *W. D. B.*

Dielectricity and Optics

On the absorption spectra of chloranilic and bromanilic acids, and of their alkali salts. *C. Fiorini. Gazz. chim. Ital.* 31, *I.*, *33* (*1901*). — It was not possible to account for the absorption spectra of chlor- and bromanilic acids and of the potassium and sodium salts on the assumption that the ions alone are colored. As there was no way of determining the amount of color due to the undissociated substance, no quantitative comparison between theory and experiment could be made. *W. D. B.*

On the effect of low temperatures on the change of resistance of selenium caused by light. *A. Pochettino. Rend. Accad. Lincei* (*5*) 11, *II.*, *286* (*1902*). — The resistance of a given selenium cell at + 15° C was 31,000 ohms in the dark and 18,000 ohms in sunlight, photoelectric effect 0.4. At — 185°, the corresponding figures were 2,600 ohms and 1,900 ohms, photoelectric effect 0.3. *W. D. B.*

Chemical action of light. *G. Ciamician and P. Silber. Rend. Accad. Lincei* (*5*) 10, *I.*, *92*, *228* (*1901*); 11, *I.*, *277*; *Gazz. chim. Ital.* 32, *I.*, *218* (*1902*). — Under the influence of light, alcohols react with quinone, forming quinhydrone and an aldehyde or ketone. With mannite, for instance, *d*-mannose is formed. Under the influence of light, aqueous alcohol reacts with nitrobenzene, forming aniline and ethyl aldehyde. This reaction does not run to an end. With absolute alcohol, the chief product is quinaldine, only a little aniline and no aldehyde being formed. *W. D. B.*

Chemical action of light. *G. Ciamician and P. Silber. Rend. Accad. Lincei* (*5*) 11, *II.*, *145*; *Gazz. chim. Ital.* 32, *II.*, *535* (*1902*). — The reaction between quinone and ether, alcohol or glycerol, and the other reactions (preceding review) so far as studied take place readily under the influence of the blue end of the spectrum and very slowly or not at all when the light comes from the red end of the spectrum. *W. D. B.*

Investigations on induced radio-activity. *A. Sella. Rend. Accad. Lincei* (*5*) 11, *I.*, *57*, *242*, *369* (*1902*). — When a plate of metal is connected to one pole of a friction machine and three needles, arranged in a triangle and normal to the plate, are connected with the pole, the plate becomes radio-active whether charged positively or negatively. When charged positively, it is evident that the air has a great deal to do with it. If a smoky flame be brought near, the soot will settle on the plate, forming Kundt's circles which are also circles of radio-activity. *W. D. B.*

Studies on induced radio-activity. *A. Sella. Rend. Accad. Lincei* (*5*) 11, *II.*, *81* (*1902*). — When a metal plate is made radio-active by the author's method (preceding review), the intensity of the radio-activity increases with the time of charge, though not proportionally to it. A plate loses 60 percent of its radio-activity in the first two hours; after that more slowly. Experiments were also made with air which had been exposed for different periods to thorium radiations. *W. D. B.*

THE INFLUENCE OF DISSOLVED GASES ON CONDUCTIVITY FOR A DIRECT CURRENT

BY S. L. BIGELOW

In a previous article,[1] certain facts were described indicating that the strength of a direct current which passes through an electrolytic cell, when the applied electromotive force is small, is closely connected with the amount of gas dissolved in the electrolyte, and much less, if at all, dependent on the concentration of the ions due to the dissociation of sulphuric acid present. These facts were obtained by measurements of residual currents, but each experiment required several days at least, and the number of experiments was correspondingly small. Some results were reached as to the actual size of the residual currents and their dependence on the temperature, but the study of such matters was a means to an end and was not the main issue. The object of the investigation was to make some advance towards a clearer conception of the mechanism of current transference from a solution to an electrode, and to determine whether or not the ions due to electrolytic dissociation are the only possible vehicles of such transference. The study of the same subject was continued, and resulted in the corroboration of the earlier observations and the discovery of some new facts as described below.

Since the publication of the article referred to, an exceptionally interesting and able investigation of residual currents by F. G. Cottrell has appeared,[2] in which it is shown that the strengths of residual currents correspond to those calculated from the laws of diffusion in cases where the electrodes are of a given metal immersed in solutions of salts of the same metal. This is analogous to Salomon's work, and in so far does not bear directly upon the question in hand, as was pointed out in the

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[1] Jour. Phys. Chem. 6, 603 (1902).

[2] Zeit. phys. Chem. 42, 385 (1903).

first article. Cottrell notes and fully recognizes the influence of dissolved gases, stating on page 421 that the current due to them may equal that due to the process he is studying, and on this account he removes the dissolved air from his solutions before beginning his experiments. His theory as to the way in which dissolved oxygen may support a current can be more fitly discussed in a forthcoming article devoted particularly to the subject of decomposition points. He describes also an experiment upon the conductivity of dissolved air, though he does not carry out the corresponding calculations according to his theory. But whether or not these currents due to dissolved air parallel the diffusion phenomena does not immediately affect the problem as to what the carriers are actually discharging at the electrodes. The difference between Cottrell's work and this may be summed up in the statement that he is investigating the rate at which carriers of electrical energy arrive at the electrodes, while this is an investigation as to what carriers, having arrived at the electrodes, are capable of discharging.

Experimental method

It was assumed that the occurrences at the electrodes immediately after the closing of the circuit differ not in kind but only in degree, from those after the current has passed for some time and has reached the proportions and characteristics of a residual current. Therefore the plan was adopted of measuring and comparing the currents which passed after the current had been closed but a short time, thus making it possible to carry out a large number of experiments. All the experiments were done with one cell, the same used for experiment No. 6 of the previous article. It was a small, wide-mouth Jena flask of 125 cc capacity. The electrodes were of platinum 20 × 25 mm, 15 mm apart at the top, and between 17 and 19 mm apart at the bottom, this variation being due to the fact that they were not exactly flat and parallel. Stout platinum wires led from these electrodes to heavy copper rods which passed through the cork of the flask. A short thermometer, graduated in fifths of a degree, was inserted through the cork so that its bulb was in the electrolyte between the electrodes, and the whole cell was immersed in an Ostwald thermostat.

The electrical connections and general method remained the same as those previously employed and illustrated by figure on page 611 of the previous article. A storage battery of large capacity was short-circuited through a gold-plated resistance wire wound on a drum, and any electromotive force desired could be taken off and sent through the experimental cell. A Weston standard laboratory voltmeter, easily readable to 0.002 of a volt, was connected at the poles of the cell all the time, and the electromotive force was one volt (± 0.002) in every experiment. A key switch, when pressed, threw a galvanometer, calibrated as an amperemeter, into the circuit with the cell. The sensitiveness of this galvanometer could be altered at will by means of a resistance box shunt, but to facilitate comparisons the actual deflections and the shunts used are omitted and the results are given as before in terms of micro-amperes.

When everything was ready for an experiment the circuit was closed through the cell by throwing over a whip switch and a stop-watch was started at the same instant. The key throwing in the galvanometer was pressed five to six seconds before a reading was to be made, this time being found ample for the exceptionally dead beat galvanometer to cease vibrating, and just as the stop-watch indicated the time the eye was raised to the telescope and the deflection was noted. The readings were made uniformly ½, 1, 2, 3, 5, 7, 10, and 15 minutes after the closing of the circuit. At the half-minute readings the galvanometer was usually in rather rapid motion, indicating the rapid falling off of the current, and the readings had to be caught as they passed, which makes them somewhat uncertain, but a great deal of practice was had, and it is thought the time error in these observations is probably small and nearly constant.

Depolarization of the electrodes

At the end of each experiment the electrodes were depolarized by heating to a bright red or white heat for half a minute in a Bunsen flame, after which they were allowed to cool for one minute, then immersed in the electrolyte, and the circuit was closed and the stop-watch started just half a minute after this immersion. The copper rods were so heavy they conducted away the heat fast enough to prevent any softening of the solder even during protracted heating of the electrodes. It was considered possible that this treatment did not completely depolarize, and that an alteration in the time of heating, or of cooling, or of the time the electrodes remained in the solution before the current was started, or reversing the electrodes might affect the results. The experiments in Table I. were carried out to determine these points and also the limits within which duplicate experiments might be expected to agree. The variations from the standard treatment of the electrodes described above are stated in the table.

The last line of the table indicates rather unexpectedly that, in spite of the greater time error in the observations, the best agreements may be had in the first measurements, i. e., those at ½, 1, and 2 minutes, a fact which reappears in later experiments. These experiments prove that heating the electrodes to full redness completely destroys previous polarization, and that the length of time they remain in the air after heating and before immersion in the electrolyte, as also the time they remain in the electrolyte before the current is started, up to ten minutes at least, makes very little difference in the results. Therefore this method of depolarization was adhered to in all succeeding experiments.

Experiments 17 to 19 were carried out to determine the effect of using different flasks of the same measured contents and which to all appearance were of the same shape, and the results show a satisfactory agreement. That the values obtained in these three experiments are somewhat higher than those obtained in experiments 1 to 16 is probably due to the fact that the flasks were freshly filled just before the experiments with $n/200\ H_2SO_4$, which had been standing for a number of days in the liter flask in which it was made up, and contained a larger amount of dissolved air than the electrolyte which had been used for experiments 1 to 16.

TABLE I.

Electrolyte $n/200$ molecular H_2SO_4. Electromotive force at electrodes 1.000 (± 0.002) volt. All results are expressed in microamperes.

Effect of altering time electrodes are red hot	No.	Temp.	½ min.	1 min.	2 min.	3 min.	5 min.	7 min.	10 min.
Red hot ½ minute	1	16.7°	583	412	295	243	197	172	156
" " "	2	16.7°	588	412	297	248	199	176	159
" " "	3	17.8°	594	430	312	259	214	194	180
Red hot 2 minutes	4	17.9°	603	439	308	255	210	190	176
Red hot 10 seconds	5	17.9°	601	425	304	255	210	191	177
Just brought to full redness	6	17.9°	588	425	307	258	214	194	180
Barely dull red	7	17.9°	587	423	306	255	210	190	176
Effect of time electrodes are cooled									
Cooled 1 minute	8	13.8°	569	412	297	248	203	181	161
Cooled 5 minutes	9	14.0°	582	418	294	244	197	176	161
Cooled 10 minutes	10	14.1°	581	415	299	248	201	178	161
Cooled 7 seconds, immersed while still hot	11	14.2°	593	420	300	250	208	188	169
Effect of time electrodes are immersed before the current is started.									
Immersed 8 seconds	12	15.1°	588	415	297	248	202	177	161
Immersed ½ minute	13	14.2°	581	411	295	248	202	179	160
Immersed 10 minutes	14	14.9°	582	412	296	248	200	177	160
Effect of reversing electrodes									
Former cathode made the anode	15	14.5°	595	422	304	255	209	188	168
Electrodes in original order once more	16	14.9°	595	418	303	255	208	184	168
Effect of changing flasks									
Flask No. 1	17	18.5°	610	433	312	265	218	197	178
Flask No. 2	18	18.1°	616	440	322	278	225	203	181
Flask No. 3	19	18.3°	610	437	316	267	219	197	179
Highest values in above experiments	—	—	616	440	322	278	225	203	181
Lowest values in above experiments	—	—	569	411	295	243	197	172	156
Difference in percent of smallest values	—	—	8.26	7.06	9.15	14.41	14.21	18.03	16.03

The effect of dissolved air

Two flasks were filled with the electrolyte (always, when not otherwise mentioned, *n*/200 molecular H_2SO_4) and experiment No. 20 was run through at once with one, while the other was attached to a water pump and kept under diminished pressure for several hours, after which it was used for experiment No. 21.[1]

No. 20	18.4°	580	417	299	248	201	175	156
21	15.4°	196	131	91	71	56	47	40

No. 22 is a repetition of No. 20, and No. 23 was carried out with the electrolyte of No. 21, which had been exposed to the air for approximately two hours.

No. 22	19.2°	562	415	302	255	204	181	159
23	—	209	144	98	80	65	56	49

The effect of exhaustion is very apparent and likewise the well-known fact that water exposed to air dissolves it but slowly. It was thought possible to accentuate the effect by taking pains to have complete saturation with air on the one hand and more complete exhaustion on the other. Something was accomplished in each direction though difficulties were encountered.

Saturation with air

A lively current of air was drawn through a fresh sample of the electrolyte in a large wash-bottle for six hours, after which a portion, transferred to the cell, served for experiment No. 24. An hour later, during which time the electrolyte had not been disturbed otherwise than by the removal and replacing of the electrodes, it gave the results under No. 25, and after standing over night the results under No. 26. Air was then drawn through the electrolyte while in the cell for one and a half hours, after which the results under No. 27 were obtained. Fresh electrolyte was put in the flask and air was drawn through

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[1] As the measurements were invariably made at the expiration of ½, 1, 2, 3, 5, 7, and 10 minutes the times are omitted and merely the current strengths in microamperes are given in their proper sequence. It is understood also that the electrodes are always the same, depolarized just before insertion into the flask in which the electrolyte has been made ready.

for about four hours for No. 28, and immediately after this the air was continued for twenty minutes and the results under No. 29 were observed.

No. 24	20.8°	556	386	271	219	170	149	125
25	21.0°	491	353	242	196	151	129	113
26	21.9°	533	383	272	222	174	152	134
27	—	477	350	248	203	157	138	112
28	13.2°	444	320	226	183	137	113	95
29	15.2°	562	399	274	222	170	144	118

The agreement between the above results was not considered satisfactory and much time and a large number of experiments were devoted to an attempt to discover the cause of the variations, but without much success. The differences in temperature will not explain them as may be seen by comparison with the results in Table III. It seemed most probable that they were due to the quality of the air, or rather to the impurities which it contained, and the experiments were repeated with air drawn by means of glass tubes directly from outdoors. Next, the air was passed through a train of wash-bottles containing distilled water, and sodium hydroxide solution, and was filtered through cotton and further purified from CO_2 by passing over soda lime. Finally a gas holder of about six liters capacity was taken to different localities outdoors and filled, and this air was used. Series of experiments were carried out to determine whether the rate at which the air passed through the solution, or the total amount, made any difference. The barometric pressure was also watched. In spite of these efforts the results continued to vary and show sufficient contradictions to prevent any generalizations other than that the variations were probably due to irregularities in diffusion phenomena within the cell. Eventually the plan was adopted of filling the gas holder with outdoor air which had been washed and filtered through cotton, and forcing five liters of this, first through a wash-bottle containing *n*/200 H_2SO_4, and then through the electrolyte in the cell at the rate of about half a liter a minute. The outlet for the air under the surface of the electrolyte was a capillary sufficiently fine to ensure a great number of small bubbles and a thorough stirring. The results given in Table III. were obtained by this method and may be taken as characteristic for *n*/200 H_2SO_4 saturated with air.

Exhaustion

The exhaustion was effected in the experimental cell itself by connecting with a water-pump which held the pressure down to about 17 mm as shown by a manometer in the circuit. When an experiment was to be made, the rubber cork and tube leading to the pump were removed and replaced by the cork holding the previously depolarized electrodes. Table II. contains some of the results.

The electrolyte was probably not completely free from dissolved gases in experiment No. 36, but it is fair to assume that the quantity remaining was decidedly small. The very great reduction in the current strength produced by removal of the gases is sufficiently strikingly demonstrated, and the matter was left at this point to proceed with the investigation of other influences.

The effects of dissolved oxygen, hydrogen, nitrogen, and carbon dioxide

Oxygen as furnished commercially in tanks was used and no precautions were taken to purify it. The six-liter gas holder was simply filled from the tank and the oxygen was then forced through the wash-bottle and electrolyte, the electrodes were put in, and the experiment was carried out immediately.

Fresh *n*/200 H_2SO_4 + air	No. 37	20.0°	539	395	290	244	199
No. 37 + 5 liters O_2 in 10 min.	No. 38	20.1°	1333	1078	837	713	595
No. 38 + 5 liters O_2 in 9 min.	No. 39	20.0°	1484	1183	895	758	627
No. 39 + 5 liters O_2	No. 40	20.0°	[—]	1191	909	772	644

Hydrogen was made from zinc and sulphuric acid in a Kipp apparatus, passed through distilled water into the gas holder, and then forced through the wash-bottle and electrolyte.

Fresh *n*/200 H_2SO_4 + 5 l air 15 min.	No. 41	20.1°	575	418	307	265	216
No. 41 + 5 liters air in 15 min.	No. 42	20.1°	574	417	312	267	232
No. 42 + 5 liters H_2 in 8½ min.	No. 43	20.1°	1111	810	589	520	458
No. 43 + 5 liters H_2 in 10 min.	No. 44	20.0°	1131	824	646	581	539
No. 44 + current of air for 20 min.	No. 45	20.0°	516	376	270	225	190

TABLE II.

	No.	Temp.	½ min.	1 min.	2 min.	3 min.	5 min.	7 min.	10 min.
Fresh electrolyte + 5 hours suction	30	18.1°	207	151	112	93	79	70	62
No. 30 + ¾ hour more suction	31	18.3°	203	150	111	92	77	69	60
Fresh electrolyte + ½ hour suction	32	18.3°	379	281	211	182	151	137	123
No. 32 + 22 hours suction	33	18.5°	27	19.6	14.4	13.1	12.5	(12.5)	(11.7)
Fresh electrolyte + 4 hours suction, warmed occasionally	34	14.0°	163	111	84	74	59	50	41
No. 34 + 18 hours suction	35	12.7°	59	40	29	24	20	17	14.4
No. 35 + 42 hours suction	36	11.5°	28.1	16.4	11.1	9.1	8.5	6.5	5.9

Nitrogen, or rather air with a considerably diminished proportion of oxygen, was obtained by burning a jet of hydrogen in a large bottle until the flame became very voluminous and appeared to be on the point of going out, when it was extinguished to avoid the possibility of having any hydrogen in excess. The nitrogen, with its small remaining content of oxygen, was transferred to the gas holder and forced from this through the electrolyte as usual.

Fresh *n*/200 H_2SO_4 + 21 min. outside air	No. 46	20.0°	542	398	300	252	205
No. 46 + 5 liters nitrogen in 16 min.	No. 47	20.0°	150	111	82	70	57
No. 47 + 4 liters nitrogen in 8 min.	No. 48	20.0°	149	108	80	67	55
No. 48 + 35 min. outside air	No. 49	20.0°	554	397	292	248	206

Carbon dioxide was made from marble and hydrochloric acid in a Kipp apparatus, washed through distilled water and led into the gas holder from which it was forced through the electrolyte.

Fresh *n*/200 H_2SO_4 + 5 liters air in 14 min.	No. 50	20.2°	569	406	295	252	210
No. 50 + 5 liters mixture air and CO_2 (about 33 % CO_2) in 13 min.	No. 51	20.1°	409	295	216	184	151
No. 51 + 5 liters CO_2 in 8½ min.	No. 52	20.0°	—	9.1	5.2	5.0	4.6
No. 52 + 50 min. outside air	No. 53	20.0°	515	378	276	234	195
No. 53 + 5 liters CO_2 in 19 min.	No. 54	20.0°	16.4	9.8	7.1	5.9	4.6
No. 54 + current of air over night	No. 55	20.0°	477	356	261	222	182

It is hardly necessary to call attention to the striking nature of the experimental evidence here presented that the conductivity is increased by the presence of dissolved gases. The largest currents are carried by a solution practically saturated with oxygen (see exp. No. 39) and they are in round numbers three times those carried by the solution saturated with air. The next largest are carried by a solution saturated with hydrogen (see exp. No. 44) where the values are over twice those obtained with a solution saturated with air. That oxygen appears to be more effective than hydrogen is readily explained on the score of its greater solubility, the coefficient of absorption at 20° for oxygen being 0.03103, for hydrogen 0.01819[1]. But quantitative numerical comparison cannot be made on this basis alone, because of the fact that hydrogen diffuses more rapidly than oxygen, and consequently a given amount of it must be more effective. Direct proportionality cannot exist between the current strength and the amount of gas present for the following reason. Assume that 55 microamperes (the current strength at the end of five minutes in experiment No. 48) is due to the nitrogen present, then, when the solution is saturated with air, we should have about four-fifths of this or 44 microamperes current due to the nitrogen. Subtracting this from 216, the largest five-minute value in this series for any experiment saturated with air (Exp. 41), we have 172 microamperes as the current due to the oxygen. When the electrolyte is saturated with pure oxygen there must be about five times as much present as when it is saturated with air, and we should get five times 172 or 860 as a minimum current strength at five minutes. But the observed values are much lower than this. The same calculation for the values at the expiration of one-half minute gives 2279 microamperes for pure oxygen, also much larger than anything observed.[2]

The results with nitrogen are not sufficiently accurate, owing to the crude method of preparing the gas, to justify any conclusions other than the obvious one that dissolved nitrogen is far less efficient than either dissolved oxygen or hydrogen in increasing the conductivity.

The results with carbon dioxide, on the other hand, deserve particular attention, falling as they do below even the lowest

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[1] According to Winkler, Landolt and Börnstein. Tabellen, p. 256.

[2] The values for nitrogen are undoubtedly too large and the substitution of lower values would make the calculated values for oxygen still larger and still more at variance with those observed.

values yet obtained by simple exhaustion (exp. No. 36). Saturating the solution with carbon dioxide must have increased the concentration of both anions and cations and yet the current strength, instead of being increased, is diminished to about one-thirtieth or one-fortieth of its original quantity. This is further experimental evidence that the currents measured here are not dependent solely upon the ions resulting from dissociations. At the same time it is seen that dissolved carbon dioxide is a far worse conductor than either dissolved oxygen or hydrogen, if indeed it can be considered as conducting at all. Of course, if measurements had been made by the Kohlrausch method with alternating currents of comparatively high electromotive force an increase in conductivity would have been observed. The decrease actually noted simply serves to emphasize the difference between the phenomena when the current is continuous and of low electromotive force and when its electromotive force is greater than the decomposition points of the ions present. It is well-known that the quickest and most effectual way to remove a gas completely from a solution is to pass in a current of some other gas, and it may be that the sole function of the carbon dioxide is to remove the dissolved air, and that the results obtained represent closely those characteristic of an air-free solution.

Effect of the concentration of the electrolyte

Experiments were carried out with molecular normal, instead of 1/200 molecular normal sulphuric acid, both to verify the results reported in the previous article, that the quantity of current was not increased even upon greatly increasing the concentration of the electrolyte, and also to demonstrate that the character of the results obtained by measurement of the current during the first few minutes is the same as that obtained by a study of the residual current. Both facts were completely substantiated as sufficiently illustrated by the following experiments:

Fresh normal H_2SO_4 + 20 min. outside air	No. 56	20.0°	342	251	182	153	127
No. 56 + 1¾ hours outside air	No. 57	19.5°	371	267	196	163	133
No. 57 + 3½ hours suction	No. 58	20.0°	176	124	90	76	65

A tube drawn out to a very fine capillary, was put through the stopper connected with the pump and dipped into the electrolyte in such a way that a stream of air, so minute as not to affect materially the diminished pressure, was drawn through the electrolyte when the suction was turned on, thus hastening the removal of the dissolved air.

No. 58 + 10 min. suction	No. 59	20.1°	95	59	40	34	28
No. 59 + 2 hours suction	No. 60	20.0°	25	12	6.5	5.9	5.2

The currents observed are actually less than those obtained with the much more dilute electrolyte, a fact which it will not be attempted to explain at the present time. But the important feature, that the solution saturated with air conducts far better than the same solution without air, remains unchanged, and the equally important fact, that extremely great differences in the number of ions due to ordinary dissociation produce relatively negligible changes in the strength of the current passing, is once more obvious.

Experiments with conductivity water

The constant of the experimental cell was determined in order that the specific conductivity of its contents might be measured by the usual Kohlrausch method without transference to another vessel. The cell was filled with water prepared for conductivity work and the specific conductivity was found to be 1.9×10^{-6}. The electrodes were depolarized and an experiment was run through as usual giving the following results:

No. 61	20.1°	(—)	10.4	9.1	8.5	6.5

The specific conductivity of the water was not measurably altered at the end of this experiment. Suction was applied, accompanied by a very fine stream of air, for 3¼ hours, after which the following values were obtained.

No. 62	19.8°	11 1	8.5	7.1	6.5	4.6

At the end of this experiment the specific conductivity of the water had risen to 2.5×10^{-6}. Five liters of outside air were then run through in 28 minutes before experiment No. 63.

No. 63 19.9° 18.3 15.1 14.4 12.5 10.4

The specific conductivity immediately after this was 4.1×10^{-6}. Suction with the small stream of air, was once more applied and continued for ¾ of an hour.

No. 64 20.3° 13.1 11.1 9.1 7.8 6.5

The specific conductivity sank to 3.3×10^{-6}.

The cell was freshly filled with recently distilled water which showed a specific conductivity of 1.0×10^{-6} and the results under No. 65 were obtained.

No. 65 20.0° 5.2 5.2 4.6 3.9 3.3

Five liters of carbon dioxide were passed through.

No. 66 20.0° 62.1 38.6 26.7 22.9 19.0

The specific conductivity at the conclusion of this experiment was 52.1×10^{-6}.

It appears that water saturated with air does not show anything like the conductivity of the sulphuric acid solutions saturated with air, while it should if the conductivity is dependent wholly on the dissolved gases and not on the ions due to dissociation. It can also be seen that in a general way the conductivity by the Kohlrausch method runs parallel to the conductivity for direct low voltage currents when the electrolyte is nearly pure water.

Water saturated with carbon dioxide appears to conduct better than dilute sulphuric acid saturated with the same gas, an unexpected result which must remain for the present unexplained.

Effect of temperature

In the previous article the high temperature coefficient of the residual current was observed, but at the same time the close connection between that current and the amount of dissolved air was apparent, and the suggestion was made that the increased solubility of gases upon diminution of temperature might just about compensate the decrease in conductivity of a given solution. Table III. contains the results of experiments bearing upon this question. The cell was immersed in a thermostat with the usual automatic regulation and the temperature never varied more than 0.1° and usually was within 0.03° of that given in the table. Before each experiment five liters of air were forced through the wash-bottle containing *n*/200 H_2SO_4 in the thermostat and then through the electrolyte in the flask cell. The rate was such that approximately ten minutes were required for this amount of air to pass, and the experiments themselves serve to show that this treatment saturated the electrolyte satisfactorily for the purpose. Barometer readings were taken and are included in the table.

A comparison of the average values for the different temperatures shows that the connection between current strength and temperature is not a simple one, for the length of time the current has passed must be taken into account. The general trend is towards larger values immediately after the circuit is closed when the temperature is low, and for larger values after some time has elapsed (say ten minutes) when the temperature is higher. For instance, the values at 20° are below those at 15° until the seven-minute reading, those at 25° are below those at 15° until the two-minute reading, and those of 30° are below those at 15° until the one-minute reading. An obvious explanation is that the dissolved gas transports the current and at a low temperature there is more of it in the immediate vicinity of the electrodes than at a higher temperature and the current is correspondingly larger. But this first supply, becoming exhausted, can be replaced only by diffusion, and diffusion takes place the more rapidly the higher the temperature, therefore the current measured after a suitable time interval is larger the higher the temperature in spite of the fact that there are fewer carriers of electrical energy. This resolves itself into further evidence that the dissolved gases are able to effect the transfer of electrical energy from the solution to the electrodes.

A minor point is established by these figures, namely, that the deviation between experiments intended to duplicate each other becomes more pronounced the longer the time the current has passed, yet the time must not be too short either,

TABLE III.

Electrolyte *n*/200 molecular H_2SO_4 saturated with air at the temperature of the experiment. Electromotive force at electrodes 1.000 (± 0.002) volt. All results are expressed in micro amperes

	No.	mm. Hg.	½ min.	1 min.	2 min.	3 min.	5 min.	7 min.	10 min.
Experiments at 15.0°	67	746.5	575	418	307	261	229	195	184
	68	743.6	599	425	314	268	220	194	171
	69	746.7	601	427	308	257	215	210	197
	70	——	597	420	303	253	205	182	166
	71	741.3	595	425	315	269	222	197	179
	72	741.3	584	420	309	261	217	197	182
	73	737.8	595	421	301	250	203	183	159
	74	733.9	584	414	307	259	214	195	182
Average	—	——	591.2	421.2	308.0	259.7	215.6	194.1	177.5
Greatest deviation from average	—	——	16.2	7.2	7.0	9.7	13.4	15.9	19.5
Experiments at 20.0°	75	747.2	584	424	316	277	225	205	206
	76	740.8	556	402	297	248	199	188	165
	77	736.6	562	403	301	255	212	187	177
	78	736.6	530	393	286	242	206	186	173
	79	728.8	539	388	290	246	206	186	172
	80	738.4	555	405	309	271	237	226	215
	81	745.0	551	403	303	263	213	188	176
Average	—	——	553.9	402.6	300.3	257.4	214.7	195.1	183.4
Greatest deviation from average	—	——	30.1	21.4	15.7	19.6	22.3	30.9	31.6
Experiments at 25.0°	82	——	567	[412]	327	286	254	235	212
	83	——	556	412	311	287	238	215	191
	84	——	569	420	321	276	237	220	208
	85	——	—	412	314	278	248	233	203
	86	——	544	401	308	272	223	203	187
	87	742.7	555	406	312	271	233	222	193
	88	742.4	555	412	322	284	253	235	240
	89	741.7	546	404	317	265	226	217	209
Average	—	——	556.0	409.9	316.5	277.4	239.0	222.5	205.4
Greatest deviation from average	—	——	13.0	10.1	10.5	12.4	16.0	19.5	34.6
Experiments at 30.0°	90	738.6	563	425	344	331	337	333	295
	91	738.9	551	420	338	315	315	307	274
	92	739.4	556	432	340	320	318	308	327
Average	—	——	556.7	425.7	340.7	322.0	323.3	316.0	298.7

and the most concordant results may be expected when readings are made at one and at two minutes. It is also advantageous to work at a low temperature.

Decomposition points

It was suggested in the previous article that possibly each electrolyte had its definite decomposition point for any given conditions and that the currents observed in any instance below this point were due to the conduction of dissolved gases. Then the decomposition points should be more marked, and the nicks in the curves showing the relation between electromotive force and current strength should be more pronounced in the absence of dissolved gases. A few experiments in this direction met with moderate success. The same cell which was used for all other experiments was used for these, and thus the conditions were most unfavorable for obtaining any nick in the curve at all, the electrodes being fairly large, rather close together, and equal in size, all of which factors have been proven to be undesirable. At the conclusion of some of the experiments already described, where the electrolyte had been more or less completely exhausted of dissolved air, the electromotive force upon the cell was increased stepwise and the corresponding galvanometer deflections were noted. The method was merely to raise the voltage to the required point by revolving the drum resistance and note the reading of the voltmeter, wait one minute, then press the key and read the galvanometer, then proceed to the next higher voltage and repeat. The observations are given in terms of scale divisions of the galvanometer, which was made less sensitive than it had been in the experiments just finished in order to be able to go up to high voltages.

It will be seen at a glance, without plotting the curves, that a pronounced jump is observable, and consequently a well-marked change in the direction of the curve is obtained in each case, comparing favorably in the matter of distinctness with the results of others obtained by means of specially arranged electrodes and numerous other precautions. That no jump is observed as the electromotive force of the oxygen-hydrogen gas cell is passed, After Expt. No. 33

Volts	1.010	1.020	1.030	1.040	1.050		
Deflection	1.9	1.8	1.9	2.0	2.0		
Volts	1.066	1.078	1.090	1.098	1.106	1.124	1.140
Deflection	1.9	1.9	1.8	1.8	1.9	2.1	2.4
Volts	1.160	1.204	1.300	1.400	1.500	1.600	1.700
Deflection	2.5	2.8	3.5	4.0	5.2	34.2	137.1

After Expt. No. 35

Volts	1.05	1.10	1.15	1.20	1.25	1.30	1.35	
Deflection	2.3	2.6	2.8	2.9	2.9	2.9	3.0	
Volts	1.40	1.45	1.50	—	1.60	1.65	1.70	1.75
Deflection	3.0	3.3	4.1	—	23.0	49.0	93.0	157.0

After Expt. No. 36

Volts	1.05	1.10	1.15	1.20	1.25	1.30	1.35	
Deflection	1.0	1.2	1.4	1.4	1.4	1.5	1.6	
Volts	1.40	1.45	1.50	1.55	1.60	1.65	1.70	1.75
Deflection	1.9	2.4	4.0	9.5	23.9	50.4	94.4	152.2

After an experiment not reported in this article in which *n*/200 H_2SO_4 had been saturated with CO_2

Volts	1.10	1.20	1.30	1.40	1.45	1.50		
Deflection	0.8	1.2	1.6	2.4	3.7	7.8		
Volts	1.55	1.60	1.65	1.70				
Deflection	21.7	45.8	79.8	130.7				

After Expt. No. 60 (molec. norm. H_2SO_4)

Volts	1.10	1.20	1.30	1.40	1.50	1.60		
Deflection	0.9	1.2	1.9	4.0	17.9	64.9		
Volts	1.65	1.70						
Deflection	90.9	152.9						

and that it occurs at or about 1.5 volts is also obvious, but these matters will not be discussed here, as an independent investigation of the decomposition points of solutions, saturated with different gases and gas free, is under way in this laboratory and will be made the subject of another article.

Discussion

The data obtained with solutions saturated with different gases suggests the possibility that oxygen and hydrogen are the only gases which conduct, and this in turn that the conduction by either of these is accompanied by, and accounted for, by the decomposition or formation of water. A decomposition could hardly be furthered by the presence of a large excess of either of the products of the decomposition, and this proposition may be discarded as unlikely. The other alternative, that an equivalent amount of water is formed, demands closer attention. Increased conductivity may be imagined as brought about either by increasing the number of particles conducting or by facilitating the conduction by means of those already present. A dissolved gas, not itself conducting, may be considered as acting in the second way and as facilitating the discharge at the electrodes of hydrogen ions or oxygen (hydroxyl) ions, in other words as a depolarizer.[1] This term 'depolarizer' is indefinite and too often used as a safe and noncommittal term capable of being stretched to fit almost any process. It is desirable to be more precise if possible. Suppose that the hydrogen ions, discharged in transferring the current, unite with dissolved oxygen to form water while the corresponding anions become neutral oxygen at the anode. These ions are replaced by a further dissociation of water and the total amount of oxygen remains undiminished and the current passes more readily than if this oxygen were not present. The same form of reasoning may be applied to the case of a solution containing dissolved hydrogen in place of oxygen. This amounts to the familiar Helmholtz convection current theory, expressed in terms of our present ideas, and substantially as stated on pages 608 and 609 of the first article. It is generally accepted as a satisfactory explanation of the residual currents and may be thought to serve equally well to explain the currents under discussion here. But there is a serious if not insurmountable ob-

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[1] This is the commonly accepted idea. See Cottrell, loc. cit., p. 402, who ascribes the effect of dissolved air to a reduction of the oxygen.

stacle to its application, observed and described in the first investigation and here again more apparent than ever. The experiments show that increasing the concentration of the ions does not increase the strength of the current. If the ions alone transport the current, it is hard to understand why greatly increasing their numbers by substituting normal sulphuric acid for *n*/200 sulphuric acid, neither containing any dissolved gas to speak of, should not be followed by a marked increase in the current. Again, if the ions alone transport the current, but need the presence of something with which one sort at least can react to form water, namely hydrogen or oxygen, it is equally hard to see why a normal solution of sulphuric acid saturated with air does not show a much larger conductivity than an *n*/200 solution of the same acid likewise saturated with air.

Thus the increased conductivity due to dissolved gases does not seem to be satisfactorily explained on the basis that they act merely by facilitating the conduction by means of the ions already present. If they do not act in this way it is logical to presume that they act by increasing the number of particles conducting. It is difficult to see how they can increase the number of particles conducting otherwise than by taking part in the conduction themselves. In other words it is reasonable to assume that dissolved gases conduct. The further hypothesis that they are capable of a differentiation into molecules plus, and others minus, corpuscles or electrons, offers a plausible explanation of how this conduction may be accomplished.

On the other hand the conductivity of distilled water saturated with air is not equal to the conductivity of dilute sulphuric acid similarly saturated, which precludes the possibility of the conduction being due exclusively to dissolved gases. But still, the conductivity of the water saturated with air is greater than that of sulphuric acid solutions without dissolved air, and furthermore solutions of molecular normal and of 1/200 molecular normal sulphuric acid, after being exhausted or after CO_2 has been run through, show practically the same conductivity as distilled water. Therefore the conductivity cannot be due solely to the ions of dissociation either. In this dilemma, which is perfectly recognized, the suggestion is hazarded that the ability of dissolved gases to conduct depends in some way upon the presence of the charged ions, something as we know the passage of an electrical current causes gases to become conductors.

Summary and conclusion

The problem investigated may be stated as follows. What is it which effects the transference of electrical energy from the solution to the electrodes when the electromotive force is constant, in one direction, and smaller than the commonly accepted decomposition point of water? Can dissolved gases transfer the current, and if they can, do they constitute a class of carriers of electrical energy different in some respects from the ions due to dissociation? Occlusion, changes in concentration, diffusion, possible chemical reactions, in fact all the alterations included under the titles of polarization and depolarization, are looked upon as occurring *because carriers of some kind have discharged at the electrodes*, therefore in a sense secondary to the present question, what are these carriers?

In a previous article certain phenomena observed in connection with residual currents were brought to bear upon this question, and now the assumption is made that, so far as this problem is concerned, the same conclusions should be derivable from measurements of a current which has been passing but a short time, and is not a residual current in the usual meaning of the term. This assumption is justified by all the results.

The following facts and conclusions were reached through experiments.

a. Heating platinum electrodes to redness effectually destroys previous polarization in dilute sulphuric acid.

b. It was not possible to find any definite connection between the minor variations in current strength and the impurities which may occur in the air at different times or places. These variations are probably due in the main to irregularities in diffusion processes within the cell.

c. All other conditions being maintained the same and putting the strength of the current passing through the air-free electrolyte as equal to unity, the current passing when the electrolyte is saturated with air is about 15–22, say 19, when saturated with oxygen 53–74, say 63, when saturated with hydrogen 40–64, say 52, when saturated with nitrogen certainly less than 7, when saturated with carbon dioxide less than unity. (Presumably the hydrogen value falls below that of oxygen because of the greater solubility of the latter.)

d. Direct proportionality does not exist between the amount of a dissolved gas and the conductivity, which makes it probable that only a fraction of the whole takes active part in the conduction, a condition analogous to partial dissociation of an electrolyte.

e. Making the electrolyte two hundred times more concentrated, instead of increasing the conductivity diminishes it somewhat, though the values, both when the electrolyte is saturated with air and when it is deprived of dissolved air, are of the same order of magnitude as with the more dilute electrolyte.

f. "Conductivity" water free from dissolved gases gives results lower than sulphuric acid solutions free from dissolved gases though of the same order. But the conductivity of "conductivity" water saturated with air does not equal that of the corresponding sulphuric acid solutions, proving that the conductivity is not wholly independent of the presence of an electrolyte. This gives rise to the suggestion that the charged ions, by their presence, enable the dissolved gas to conduct as a current passing enables a gas to conduct.

g. The strength of the current soon after closing the circuit, is less the higher the temperature, probably owing to the decrease in solubility of gases. The strength of the current after the circuit has been closed a few minutes is greater the higher the temperature, probably owing to the increase in the rate of diffusion.

h. To obtain the so-called decomposition point of an electrolyte it is desirable first to remove dissolved gases as far as possible.

The facts included under (*c*) and (*e*) of this summary are thought to justify the assumption that dissolved gases conduct although their conductivity appears to depend in a manner not yet fully understood upon the presence of an electrolyte which itself takes either but a small part, or no part, in the conduction. The experimental evidence on the whole furnishes support to the hypothesis advanced in the first article that a dissolved gas is capable of furnishing carriers of both plus and minus charges, though this ability appears at present to be confined to oxygen and hydrogen.

No more plausible hypothesis to account for this conduction has occurred to the writer than that based on an application of Thomson's corpuscular or electron theory as first suggested, but it is not supposed that the evidence here presented is sufficient to prove that this is the best possible hypothesis. It is thought that the experimental facts obtained are of some little interest in themselves, whatever the explanation for them eventually adopted, and it is only hoped that enough interest in the subject may be awakened to induce some other investigator to verify these results and extend them in the numerous directions which are so plainly open. Once more it must be said that these currents are small in comparison with those passing when visible electrolysis has begun, and the conclusions reached are not to be considered as in opposition to the dissociation theory nor to the customary consequences drawn from it. They apply merely to a different group of facts which are not conveniently explained by existing theories.

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Ann Arbor, Mich.,
March, 1903.

POTENTIAL DIFFERENCES WITH SATURATED SOLUTIONS

BY D. MCINTOSH

In a paper published a number of years ago, Luther[1] offered a thermodynamic proof that changing the solvent at one electrode should have no effect on the electromotive force in a two solution cell if the solutions were already saturated with respect to the electrolyte. This view was disputed by Bucherer[2] and by Miller[3] for the case of a hydrated salt and Luther[4] yielded this point after a brief discussion.[5] The objection urged was that addition of alcohol to a saturated solution of copper sulphate would cause dehydration of the salt and therefore must affect the electromotive force. Both Bucherer and Miller admit that there is a radical difference between cells with a hydrated salt as solid phase and cells with an anhydrous salt as solid phase. Luther's proof, therefore, still stands with regard to the latter cells, and we are asked to consider it as proved that the electromotive force is zero in the combination,[6]

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2, KCl}, \text{ water} \mid \text{alcohol}, \mathrm{KCl, Hg_2Cl_2} \mid \mathrm{Hg}.$$

If it were not for the thermodynamical proof, no one would care whether this combination did or did not give an electromotive force; but any general proof must be tested carefully to see whether some tacit assumption may not vitiate it. Luther's proof is based on the assumption that the two solutions are non-miscible. This does not apply in the case under consideration. The two solutions will diffuse until homogeneous and the question arises whether this diffusion has any effect on the electro-

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[1] Zeit. phys. Chem. **19**, 529 (1896).
[2] Ibid. **20**, 328 (1896); **22**, 590 (1897).
[3] Jour. phys. Chem. **1**, 521 (1897).
[4] Zeit. phys. Chem. **22**, 85 (1897).
[5] Ibid. **26**, 170 (1898).
[6] Cf. Luther. Zeit. Elektrochemie, **8**, 403 (1902).

motive force or not. There are several possibilities. If the cation is hydrated, a current flowing through the solution from the water to the alcohol would dilute the aqueous alcohol and would therefore tend to restore equilibrium. Since alcohol would precipitate potassium chloride from the aqueous solution, and since more potassium chloride would dissolve in the alcoholic solution as the alcohol diffused out, it is not unreasonable to suppose that an electrolytic transfer of potassium chloride from the aqueous to the alcoholic solution would hasten diffusion. If water moves with the positive current, as a sort of electrical endosmose, this would dilute the alcoholic solution and bring about equilibrium. These are three hypotheses, any one of which calls for the existence of an electromotive force with the aqueous solution the anodic one. Other hypotheses could be formulated; but it seemed better to determine the facts. A number of experiments have therefore been made and the apparatus used will now be described and the results given.

Apparatus, etc.

The cells were made up in tubes of various kinds, depending on the substance used. In the case of those containing mercury, platinum wires were fused into the bottoms of the tubes, and connections between the cells made by means of narrow siphons or moistened yarn. The other cells were simple test-tubes, in which the electrodes of silver or lead were placed.

The measurements were made by the well-known Poggendorff compensation method, using either a Rowland-D'Arsonval galvanometer or a Lippmann capillary electrometer as a zero instrument. An accumulator served as a working element, and was compared with a standard Clark cell during each series of measurements. With this apparatus results could be obtained to 0.5 millivolt, an accuracy quite sufficient for the purpose, since cells of the same composition measured at different times often differed by several millivolts.

Materials used

Ethyl alcohol, dehydrated by copper sulphate and distilled, at 78° C under 75.8 cm pressure.

Methyl alcohol, dehydrated by baryta and distilled, at 65° C under 75.1 cm pressure.

Potassium chloride, precipitated from a saturated solution of potassium chloride by hydrochloric acid, washed, and fused. Mercurous chloride, obtained from the commercial calomel by sublimation.

The laboratory silver nitrate, recrystallized lead chloride, and Merck's C. P. cadmium chloride were also used.

In order to have some knowledge of the concentrations, the solubility of potassium chloride in the various solutions at 25° C was determined. The results are given in Table I. and refer to solutions containing no mercurous chloride.

TABLE I.

Solubility of KCl in gram-mol. per liter. Water-alcohol solution

Ethyl	Percent alcohol by weight	Methyl
4.18	0	4.18
3.21	10	3.27
2.40	20	2.46
1.78	30	1.81
1.26	40	1.28
0.84	50	0.83
0.56	60	0.53
0.305	70	0.303
0.125	80	0.134
0.042	90	0.087
0.011	100	0.052

It has long been known that concentrated solutions of potassium chloride act on calomel with the formation of small amounts of mercuric chloride and mercury. Solutions freshly made up and ones saturated with mercurous chloride by long standing were examined and the results are given in Tables II. and III. In these and the following tables the current flows through the solutions in the direction of the arrow. In all cases, the aqueous solution is the anodic, and the alcoholic solution the cathodic.

TABLE II.

Mercury electrodes ; solutions saturated with mercurous and potassium chlorides

Ethyl alcohol			
		Electromotive force	
Percent of alcohol	Percent of alcohol	Fresh solution	Saturated with Hg_2Cl_2
100	0	0.024	0.029
100	10	0.020	0.023
100	20	0.018	0.019
100	30	0.016	0.017
100	40	0.012	0.016
100	50	0.009	0.013
100	60	0.008	0.010
100	70	0.004	0.007
100	90	0.003	0.002
	←——	——	
0	100	0.024	0.026
0	90	0.020	0.017
0	80	0.017	0.012
0	70	0.015	0.007
0	60	0.012	0.006
0	50	0.010	0.006
0	40	0.007	0.005
0	30	0.006	0.004
0	20	0.004	0.003
0	10	0.002	0.002
	——	——→	

Richards and Archibald have shown[1] that solutions of cadmium chloride have no action on mercurous chloride. A few experiments were therefore made with cadmium chloride instead of potassium chloride and the results are given in Table IV.

Cells in which the water and alcohol were saturated with lead chloride were also tried, using, of course, lead electrodes. The measurements gave 0.002 volt as the result in the case of the water, against both ethyl and methyl alcohol.

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[1] Zeit. phys. Chem. 40, 385 (1902).

TABLE III.

Mercury electrodes; solutions saturated with mercurous and potassium chlorides

Methyl alcohol

		Electromotive force	
Percent of alcohol	Percent of alcohol	Fresh solution	Saturated with Hg_2Cl_2
100	0	0.031	0.032
100	10	0.029	0.027
100	20	0.026	0.025
100	30	0.022	0.021
100	40	0.017	0.018
100	50	0.014	0.017
100	60	0.010	0.014
100	80	0.006	0.007
100	90	0.004	0.003
	<————		
0	100	0.031	0.032
0	90	0.017	0.021
0	80	0.014	0.015
0	70	0.007	0.014
0	50	0.006	0.012
0	40	0.005	0.009
0	30	0.004	0.006
0	20	0.003	0.004
0	10	0.002	0.003
	————>		

In Table V. are given some results obtained by using saturated solutions of silver nitrate and silver electrodes.

While it is clear that Luther's conclusions in regard to these cells are unsound, it is important to see exactly where the flaw in his reasoning came in. It is to be found in one of the so-called fundamental laws of energetics:[1] "If two systems are in equilibrium with a third, they are in equilibrium with each other." This statement is not universally true, and Luther has

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[1] Zeit. phys. Chem. 19, 533 (1896).

TABLE IV.

Mercury electrodes; solutions saturated with mercurous and cadmium chlorides

		Electromotive force	
Percent of alcohol	Percent of alcohol	Ethyl alcohol	Methyl alcohol
100	0	0.025	0.017
100	20	0.023	0.014
100	40	0.017	0.006
100	80	0.012	0.002
	⟵		
0	100	0.023	0.017
0	80	0.017	0.012
0	60	0.013	0.010
0	20	0.013	0.002
	⟶		

TABLE V.

Silver electrodes; solutions saturated with silver nitrate

		Electromotive force	
Percent of alcohol	Percent of alcohol	Ethyl alcohol	Methyl alcohol
100	0	0.005	0.005
100	20	0.003	0.004
100	40	0.002	0.002
100	60	0.002	0.001
100	80	0.001	0.001
	⟵		
0	100	0.005	0.005
0	80	0.003	0.003
0	60	0.003	0.003
0	40	0.002	0.001
0	20	0.001	——
	⟶		

been so unfortunate as to make use of it in a case where it does not hold. If we take a saturated alcoholic solution of salt and a saturated aqueous solution of salt, the two solutions are each in equilibrium with solid salt but they are not in equilibrium with each other. This law of Ostwald's is true only for non-miscible phases. Luther makes use of it two pages later in a way which is wrong. He inverts the statement of Konowalow and of Nernst, saying: "Two solutions of the same substance are in distribution equilibrium when the partial pressure of the solute in the vapor phase is the same", or "saturated solutions of the same substance are in distribution equilibrium". Neither of these statements is true even for partially miscible liquids. A saturated solution of succinic acid in ether is not in equilibrium with a saturated solution of succinic acid in water. When brought together there will be a passage of ether to the water solution, of water to the ether solution, and a change both in the relative and absolute concentrations of succinic acid in the two phases.

In the present state of our knowledge, it does not seem possible to offer a satisfactory explanation for the direction of the current. While the possibility of hydrated ions cannot be denied, it seems improbable that this should be an important factor in the case of potassium chloride. Nothing is known as to solubility and dissociation of mercurous chloride in the mixed solvents. While the general direction of the current is what might be expected if the relative solubilities of potassium chloride were the decisive factor, the behavior of the cells when methyl alcohol is substituted for ethyl alcohol does not confirm this because then the potential difference of water against methyl alcohol should always be less than those against ethyl alcohol. Another argument against this view is that the current flows in the same direction with mercury, silver, and lead electrodes. The effect of the current is to dilute the anodic solution of potassium chloride and the cathodic solutions of silver nitrate and of lead chloride.

There remains the question of electrical endosmose. It is known that water does move with the positive current through porous diaphragms, but it is rather a long step from this to the case of water diffusing into an alcoholic solution. While there may be an analogy, there are no experiments which would justify such a conclusion.

The conclusions to be drawn from this work are:—

(1) In cells of this type, the electromotive force is not zero.

(2) The electromotive force is due to the saturated solutions not being in equilibrium.

(3) It is not possible to predict the sign or the value of the electromotive force from any property of the components.

It is my pleasant duty to express my indebtedness to Professor Bancroft — at whose suggestion these experiments were made — for his kindness during their progress.

McGill University, Montreal,
February, 1903

THE RATES OF THE REACTIONS IN SOLUTIONS CONTAINING FERROUS SULPHATE, POTASSIUM IODIDE, AND CHROMIC ACID

BY CLARA C. BENSON

In this paper, which may be regarded as a sequel to my experiments on the rate of oxidation of ferrous salts by chromic acid,[1] and to those of Mr. R. E. DeLury[2] on the oxidation of potassium iodide by the same substance, I have determined the effect of the concentrations of the reagents on the rate of oxidation of ferrous sulphate and of potassium iodide in solutions containing both.

After describing the method of working, and arranging the results of the measurements, I have made use of them to discuss the various theories put forward (in advance of rate measurements) to account for the great acceleration often exerted by iron salts on reactions involving oxidation.

Of these the favorite is the "Peroxide Theory", according to which the primary product of the oxidation of iron is a peroxide, which subsequently breaks down into ordinary ferric salts, transferring part of its oxygen to other chemicals ("acceptors") in the process. I have not been able to reconcile the results of my measurements with the consequences of this theory.

Finally, without expressing an opinion on the custom of "explaining" the kinetics of chemical systems by inventing reactions where the formulas are related to the rates by certain rules, I have endeavored to comply with the fashion of the day by setting up a theory of my own — the "Ferroiodion Theory" — which can be brought into accord with the main results of the rate measurements.

The experiments of the present paper have all been carried out at zero; a few at higher temperatures, which show that

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

[2] Ibid. 7, 239 (1903).

the rate of liberation of iodine is decreased by raising the temperature, will be published separately.

Method of working

The method of carrying out the experiments was much the same as that employed in my measurements of the rate of oxidation of ferrous sulphate. When the standardized solutions had been cooled to 0° in wash-bottles clamped in the thermostat, the amounts necessary for an experiment (100 to 200 cc acid, 100 to 300 cc bichromate, 50 cc oxidation product, 5 to 30 cc potassium iodide), were blown into measuring flasks or pipetted out, and mixed with the proper quantity of water in a beaker suspended in the bath.[1] The whole was well stirred, the ferrous sulphate (measured in a 1 cc pipette divided into 1/100 cc, and diluted with 100 cc water in a Nessler tube) was poured in, and a stop-watch was set in motion by pressing on a pedal.

At the expiration of the desired interval, 10 cc of a half-saturated solution of ammonium bicarbonate was poured in from a test-tube, 5 cc of a filtered 1 pct starch solution was added, and the iodine was determined by *n*/100 sodium arsenite dropping slowly from a burette (1 cc per minute); a Witt stirrer kept the contents of the beaker well mixed.

By adding alternate drops of *n*/100 iodine and arsenite solutions, the end-point could be determined within 0.05 cc. Duplicates however often differed more,[2] although the probable error in individual experiments does not exceed 5 percent. This includes the uncertainty in the end-point, and the errors in the four burette readings and in measuring out the requisite volumes of water and of five reagents; the extreme variation in the temperature of the reacting mixture never reached 0.5° C.

Owing to the small amount of iodine liberated, an uncertainty of two or three drops of arsenite represents a greater per-

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[1] The potassium iodide was diluted with 100 cc water, and added last, just before the ferrous sulphate

[2] For instance, *Cr*, 20 cc; *Ac*, 10 cc; *KI*, 20 cc; *F*, 1.0 cc; θ, 4; *As* found :—4.27, 4.22, 4.26, 4.35, 4.25, 4.20, 4.25, 4.35, 4.20, 4.29, in a number of experiments carried out at intervals of weeks.

centage error than is at all desirable; any large increase in the concentrations of the reagents, however, was impossible, owing to the rapidity of the oxidation; while the advantages consequent on working with excess of all the reagents save one could not be dispensed with.

When the volume much exceeded 700 cc the end-point was more difficult of determination, and the readings were subject to a correction for the iodine necessary to give a color. A similar correction of 0.10 cc *As* was necessary when the amount of the potassium iodide used was less than 20 cc. (Expts. 14, 15, 16, 17.) The scope of the investigation was further limited by the fact that some of the iodine disappears on adding ammonium bicarbonate, if more than 5 cc of *n*/20 ferrous sulphate remain to be oxidized in the 700 cc of reacting mixture; owing to this circumstance I have not carried out any measurements with ferrous sulphate in excess.

I have assured myself, however, that within the limits to which I have restricted myself, the method of analysis described above yields reliable results.

As iodine is liberated (though very slowly) by the action of chromic acid and of ferric salts on potassium iodide in the absence of ferrous sulphate, it was necessary to undertake a number of blank experiments (in which no ferrous sulphate was added). The duration of these, in minutes, is given after "*Blanks*" at the foot of the tables; a small circle to the right of the number indicates that no free iodine could be detected, an asterisk, liberation of iodine equivalent to one drop (0.05 cc) of *n*/100 arsenite; two asterisks, two drops.

On account of the importance of accurate determinations of the total iodine liberated during the oxidation of a given quantity of iron (y_∞), the time of oxidation has been extended in certain cases to one or two hours. In these instances the amount of iodine liberated in the blank experiment is very considerable — it is given with the others at the foot of the Tables, and the amount there stated has been subtracted from the result of the titration to give the figures entered under "*As*" after $\theta = 60$, 120, etc., in the body of the Tables.

Solutions

Solutions of sulphuric acid ($0.059F$[1] = $0.1181n$), potassium bichromate ($0.0083F = 0.05n$), potassium iodide ($0.0479F$), and ferrous sulphate[2] ($0.5n$), were prepared in quantities sufficient to serve for the whole series of measurements; the acid, bichromate and iron were standardized as described in the former paper,[3] and the iodide gravimetrically with silver. Before using, the acid, bichromate, and ferrous sulphate were each diluted to ten times the original volume.

The volumetric solution of iodine was compared with the ferrous sulphate by means of permanganate, and was also standardized independently against freshly sublimed iodine.

The "oxidation product" was prepared by making up 200 cc acid, 600 cc bichromate, and 20 cc ferrous sulphate (the undiluted solutions were used) to 2 liters. 50 cc of this contained the product of oxidation of 5 cc $F/20$ ferrous sulphate, and in addition 10 cc $F/120$ bichromate unreduced. This excess of bichromate was taken into consideration in expressing the initial composition of the solutions in the various experiments. A fresh supply of the "oxidation product" was prepared every five or six days.

RESULTS OF THE MEASUREMENTS

Explanation of the Tables

At the head of each table is given the total volume of the reacting mixture and its initial composition, in the following units. *Ac* 10 represents 10 cc of $0.059F$ sulphuric acid; *Cr* 10, 10 cc of $0.0083F$ potassium bichromate, including unreduced bichromate in the oxidation product; *KI* 10, 10 cc of $0.0479F$ potassium iodide; F 1.0, 1 cc of $0.05F$ ferrous sulphate; *Ox* 5, the product of oxidation of 5 cc of $0.05F$ ferrous sulphate. Thus the headings give very closely the number of equivalents of the various reagents, one formula weight of bichromate being

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[1] One gram formula weight H_2SO_4 in 17.04 liters.

[2] Free from ferric salt. Jour. Phys. Chem. 7, 5, (1903) footnote.

[3] Ibid. 7, 5 (1903).

equivalent to seven of sulphuric acid and to six of ferrous sulphate or of potassium iodide.

Under θ is entered the interval in minutes between the addition of the ferrous sulphate and that of the ammonium bicarbonate; under *As* the number of cc of $n/100$ sodium arsenite equivalent to the iodine liberated. Under "*Cr* 20" or "*Ac* 15" the number of minutes in which the same amount of iodine was liberated in other experiments where the concentration of the bichromate, or acid, was "20" or "15" instead of that given at the head of the Table; these numbers were obtained by graphic interpolation from the results of the experiments in question. Under θ/T is entered the quotient of the two times. "*Calc. 4th, 5.1*," indicates that if the rate were proportional to the fourth power of the concentration of the reagent named at the head of the column, the quotient would be 5.1.

Ry is a contraction for $dy/d\theta$, the rate of liberation of iodine; and *Rx* for $dx/d\theta$, the rate of formation of ferric salt, in the units defined above; $As = 5y$.

Influence of the acid on the rate *Ry*

By comparing Expts. 1, 3, 7; 2, 4, 8; 5, 11, 9; 12, 10; the influence of the concentration of the acid on the rate of liberation of iodine may be determined in the presence of three different quantities of potassium bichromate; in all cases the rate is very nearly proportional to the fourth power of the concentration of the acid. In this respect the reaction under consideration differs markedly from the reaction of chromic acid on either ferrous sulphate or potassium iodide alone; and, so far as I am aware, affords the first example on record where the rate is proportional to so high a power of the concentration of one of the reagents. Except in the polymerization of cyanic acid,[1] the highest power hitherto met with has been the second. As the rate is not changed by the addition of potassium sulphate, Expt. 28, the effect must be ascribed to the hydrogen ion.

Influence of the potassium bichromate on the rate *Ry*

Reducing the amount of chromate present from thirty to

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[1] J. H. van 't Hoff. Études de Dynamique Chimique, page 94 (1884).

twenty equivalents, multiplies the time required for the liberation of a given quantity of iodine by 1.8 (Expts. 12, 5), while reduction from twenty to ten multiplies the time by 2.2 or 3 (Expts. 5, 1; 6, 2; 9, 7). If the rate is to be expressed as some power of the concentration of the bichromate, the first experiments would gives

$$Ry = \text{const.} \times (\text{conc. bichromate})^{1.5}$$

and the others

$$Ry = \text{const.} \times (\text{conc. bichromate})^{1.3 \text{ to } 1.6}.$$

Mr. DeLury has found that when potassium iodide is oxidized by chromic acid in the absence of ferrous sulphate, the rate is proportional to the first power of the concentration of the bichromate, while Expts. 34 and 35 of the present paper, and Tables III, VI, and VII of my article on the oxidation of ferrous sulphate show that in the absence of potassium iodide the rate of oxidation of ferrous sulphate varies between the first and the 1.8th power of the concentration of the bichromate.

Influence of the potassium iodide on the rate Ry.

Increasing the amount of potassium iodide present from 5 to 10 units (Expts. 14, 16; 15, 17) multiplies the rate by about 1.8, a second doubling of the concentration (10 to 20 units) (Expts. 16, 5; 17, 6) again multiplies the rate by about 1.7, while further increase from 20 to 30 units (Expts. 18, 5; 19, 6) multiplies the rate by 1.5. The effect produced by increasing the concentration of the potassium iodide is thus greatest when the concentration of the potassium iodide itself is greatest; rising to proportionality when KI = 20 to 30. The regular increase in the quotient θ/T in the experiments compared, (Expts. 14, 15, 16) is too great to be ascribed to the change in the ratio between the concentrations of the iodide produced by the progress of the reaction. It is not due to difference in the rate of oxidation of the iron (Table XVII), it is too general to be accidental, and I have assured myself that it is not due to systematic errors in the analysis.

Influence of the ferrous salt on the rate *Ry*

Comparing the experiments in which the initial concentrations of the iron was 1.0 with those in which it was 0.5, it will be seen that the time corresponding to a given value of *As* in the former is half or little less than half that in the latter. A few experiments with other quantities of iron (Table X) give the same result.

When y is small, $\Delta y/\Delta\theta$ is approximately equal to $dy/d\theta$, the rate of liberation of iodine. In Table XI the smallest values of *As* have been collected from the previous tables; doubling F approximately doubles *As*.

The rate of liberation of iodine is therefore quite closely proportional to the concentration of the ferrous salt in the solution.

Influence of the products of oxidation on the rate *Ry*

To illustrate the great retarding effect of the products of oxidation on the rate of liberation of iodine, I have set side by side in Table XII the results of five experiments in which the initial concentration of the oxidation product (see page 359) was 0, 2.5, 3.3, 5.0, and 10.0, respectively.

The order of magnitude of the retardation is the same as in the oxidation of ferrous sulphate in the absence of iodides; and, as in the latter case, is due almost exclusively to the ferric salt —see Expts. 28, 29, 30, Table XIII.

In the absence of ferrous sulphate, ferric salts exert a decided accelerating action on the oxidation of potassium iodide by chromic acid. This is well shown by the experiments in Table XIV, for which I am indebted to Mr. R. E. DeLury. The ferric salt used was a fresh solution of iron alum; the amount taken is given in 10^{-5} gram-atoms of iron. The third and fourth experiments of the series prove that the difference between the first and the second is not altogether due to the ferrous salt produced by reduction of the iron alum; it must be ascribed in part to direct acceleration by the ferric salt.

If the product of oxidation, made up as described on page 359, be allowed to stand for a week, it gradually deposits a yellow-brown precipitate, and its retarding power is lessened; an illustration is given in Table XV, in which the time in days elapsed since the preparation of the oxidation product is given after "Age".

As in such dilute solutions the hydrolysis of the ferric sulphate must have been instantaneous,[1] this slow decrease in the power of retarding oxidation must be ascribed to changes in the colloidal hydrate, and might prove a means of throwing light on the latter.

Influence of certain other compounds of iron on the rate *Ry*

The influence exerted by ferric salts has been dealt with in the preceding section.

In Table XIII are given the results of experiments in which the power of Haemoglobin (from chickens' blood, 0.25 pct Fe), of Ferrosomatose (Baeyer and Co., Elberfeld, 0.26 pct Fe), and of Potassium Ferrocyanide, to accelerate the oxidation of potassium iodide, was tested. In no case was any liberation of iodine observed. In the "*Blanks*" an amount of the standard ferrous solution equivalent to the total iron in the substance tested was added instead.

The great acceleration observed with ferrous sulphate is therefore due to the presence of the ferrous ion only.

In preliminary experiments on the oxidation of ferrous sulphate[2] I observed that sodium tartrate could not altogether stop the liberation of iodine in solutions containing ferrous salt; ferrous tartrate, therefore, acts as an accelerator, and if proper allowance were made for the effect of the tartrate on the $\overset{+}{\mathrm{H}}$-concentration, similar experiments might serve to determine the dissociation of this and other complex ferrous compounds.

The rate of oxidation of the ferrous salt, *Rx*

In the absence of any other feasible method of determining ferrous salts in the presence of ferric salt, chromic acid, etc., I have been forced to fall back on its power of accelerating the

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[1] Zeit. phys. Chem. 21, 1 (1896).

[2] Jour. Phys. Chem. 7, 3 (1903).

oxidation of potassium iodide, and have already described a method of analysis based on that principle.[1]

In order to obtain data for the calculation, a number of mixtures were made up with different initial quantities of iron, the concentrations of the other reagents being the same as in Expts. 5, 16, 14, 1, 9, and 23 respectively, and the amount of iodine liberated in 30 (or 60) minutes[2] was determined. The results are given in Table XVI.

In each of the Expts. 1, 2, 5, 6, 9, 14, 15, 16, 17, and 23, the numbers under *As* were subtracted from the value of *As* for 30 (or 60) minutes — in the case of Expt. 5, Table XVII, these differences are tabulated under "*Diff.*" — thus obtaining the amount of iodine liberated in from 22 to 30 (or 52 to 60) minutes in solutions containing initially $F-x$ units of ferrous sulphate; curves drawn from the data of Table XVI served to determine $F-x$. The values so obtained are given in Table XVII.

In this calculation there are two inaccuracies: — When $\theta = 8$, the difference *As* ($\theta = 8$) *minus* *As* ($\theta = 30$) gives the amount of iodine liberated in 22 minutes, while the curves were drawn for 30 minutes; $F-x$ for $\theta = 8$, however, is so small, and the reaction between $\theta = 8$ and $\theta = 30$ is so slow, that no serious error is introduced. Secondly, no account has been taken of the decrease in concentrations of the acid, bichromate, and iodide due to the progress of the reaction; this also is allowable, because as may be seen from Table XVIII, although the "total iodine" liberated during the oxidation of a given quantity of iron is not independent of the concentrations of the various reagents, yet the influence of small changes may safely be neglected. In the experiments for which $F-x$ was calculated the iodine liberated in 30 or 60 minutes respectively was practically identical with the "total iodine".

By means of the values of $F-x$ so obtained, the effect on Rx caused by changing the concentrations of the reagents may be ascertained.

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

[2] In Expt. 1, 90 minutes.

Doubling the concentration of the acid multiplies the rate of oxidation of the iron by 8 to 12 (between the 3d and 4th power of 2); Expts. 5 and 9, Table XVII.

Doubling the concentration of the bichromate doubles it (first power); Expts. 1 and 5, 2 and 6.

Increasing the concentration of the ferric salt greatly reduces the rate, the effect on Rx and on Ry being about the same; Expts. 23 and 5, Table XVII.

Increasing the concentration of the iodide first lowers the rate of oxidation of the iron (KI = 0 to KI = 5.0, Expts. 19, 14), then increases it again (KI = 5.0 to KI = 20.0, Expts. 14, 16, 5; 15, 17, 6).

With regard to the influence exerted by the concentration of the ferrous salt on the rate of its own oxidation, comparison of Expts. 5, 16, 14, 1 ($F = 1.0$) with Expts. 6, 17, 15, 25 ($F = 0.5$) shows that the time corresponding to a given value of x in the former is half that in the latter; *i. e.*, that doubling F doubles Rx (first power). In the absence of iodides, doubling F quadruples the rate (second power).

In order to make a direct comparison between Rx in the presence and in the absence of potassium iodide, the experiments of Table XIX were carried out with the same quantities of the other reagents as Expts. 1, 5, and 7, but without potassium iodide; $F-x$ was determined by means of Tables XIX,*b*, as already described.[1] From these experiments it appears, in accordance with the results of my former work, that in the absence of potassium iodide, doubling the acid (KI = 0) multiplies the rate by 4 (second power), and that doubling the bichromate (KI = 0) multiplies it by 2.8 (1.4th power).

Summary of the results of the measurements

The rate of liberation of iodine in the absence of ferrous salts (DeLury) is very nearly proportional to the concentration of the bichromate, and to the square of that of the acid. The relation between the rate and the concentration of the iodide can

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[1] Jour. Phys. Chem. 7, 3 (1903).

be expressed by an equation of the form $Ry = mC + nC^2$. The oxidation is accelerated by ferric salts.

The rate of oxidation of ferrous sulphate in the absence of iodides is proportional to the second power of the concentration of the ferrous salt, and to the second power of that of the acid. The order of the reaction with respect to the bichromate is variable (1.4th to 1.8th). The oxidation is much retarded by ferric salts.

In presence of ferrous salts, the rate of liberation of iodine is proportional to the 1.3d to 1.6th power of the concentration of the bichromate, to the fourth power of that of the acid, to the first power of that of the ferrous salt, and to the first (or a less) power of that of the iodide. The oxidation is much retarded by ferric salts.

In presence of iodides, the rate of oxidation of ferrous sulphate is proportional to the first power of the concentration of the ferrous salt, to the third or fourth power of that of the acid, and to the first power of the concentration of the bichromate. Increase in the concentration of the iodide first decreases, then increases the rate.

The total iodine, y_∞, *liberated during the oxidation of a given quantity of ferrous sulphate* (F) depends on the concentrations of the reagents and is only roughly proportional to the quantity of ferrous sulphate, y_∞/F increasing as F decreases.

Having ascertained the facts with regard to the kinetics of the system: chromic acid, ferrous salt, iodide, it remains to compare them with certain theories which have been put forward to explain this and similar cases of catalysis. Of these the most prominent are, the Catalytic theory, the Active Oxygen theory, and the Peroxide theory, to which I have added a fourth, the Ferroiodion theory.

The catalytic theory

In certain cases the rate of a reaction is changed by the presence of a foreign substance — platinum, for instance, to quote a classical example — and since Berzelius' day it has been customary to ascribe the effect to "Catalysis" by the substance in question. In the oxidation of potassium iodide by chromic acid, however, it is obvious that much more than the rate is affected by the presence of ferrous sulphate; — the influence of the concentrations of the reagents on the rate is profoundly modified; so that the analogy with cases of simple catalysis is very slight.

The active oxygen theory

A number of instances of "induced oxidation" can be satisfactorily accounted for by the supposition that for every atom of oxygen taken up by the "inductor" — the ferrous salt in the present case — one, or some other whole number of atoms of oxygen become "active" and attack substances otherwise incapable of oxidation under the conditions of the experiment.

In the case under consideration the amount of iodine liberated during the oxidation of one atom of iron does not represent a whole number of atoms, and is not independent of the concentrations of the reagents; so that, in its simple form, the active oxygen theory is not applicable. When further developed, this theory passes into the

Peroxide theory,

according to which the primary product of the oxidation of the ferrous salt is a peroxide which afterwards reacts with the iodide and with the residual ferrous sulphate, forming ferric salts and liberating iodine.

This theory has found an able champion in Manchot, who is of the opinion[1] that "In every process of oxidation there is formed a *primary oxide*, which in general has the character of a peroxide." My own experiments which show that the rate of oxidation of ferrous sulphate is proportional to the square of the concentration of the ferrous salt, and to the first or a higher power of that of the bichromate, might fairly be quoted in support of this view; the molecular interpretation being that two molecules of ferrous sulphate enter into reaction "primarily" with one or

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[1] Liebig's Ann. 325, 95 (1902).

more of the bichromate. The ratio 2 : 1 (2 : 1.8 fits the facts better) corresponds to the formula Fe_2O_5, for which Manchot argues (see below).

In a paper entitled "Ueber Peroxydbildung beim Eisen"[1] this author has published determinations of the "total iodine". liberated during the oxidation of certain quantities of ferrous sulphate by chromic acid in the presence of potassium iodide' Recalculated for a volume of 700 cc, and with the concentrations expressed in the units employed throughout this paper, these measurements are reproduced in Table XX. As will be noted, numbers iv, v, and vi were carried out under the same conditions; in viii and ix hydrochloric acid was used instead of sulphuric acid; the temperature in all cases was 0.2°–0.6° C.

In his experiments, Manchot let 10–15 cc *F*/10 ferrous sulphate flow into the mixture of the other reagents with the water; the addition of the iron took 1½ to 2 minutes, during which the reacting mixture was well stirred. He draws the following conclusions: — "The experiments show that for one Fe two equivalents of iodine are set free, so that the ferrous salt consumes three equivalents of oxygen. This quantity is independent of the concentration of the chromic acid, of which in all the experiments (particularly No. ii and No. x) a residue remains.

"In the small variations in the amount of thiosulphate [*As*, Table XX] the secondary action of the peroxide on the ferrous salt is disclosed, as naturally it is not possible to add the ferrous salt in every case with exact uniformity. If this secondary reaction be favored, by pouring the chromic acid into the ferrous salt, so that the latter is in excess (particularly when more of it is used), much less iodine is liberated for one Fe oxidized, which furnishes the proof that the secondary reaction in question really takes place.

"The primary ferric peroxide is certainly not higher than Fe_2O_5. For a considerable increase of the Acceptor [iodide] causes only an *in*considerable increase in the amount of thiosulphate [*As*]. The latter remains always a little below that

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[1] Liebig's Ann. 325, 105 (1902).

corresponding to two equivalents of oxygen. This also speaks for the formula Fe_2O_5; because, other experiments with Acceptors show that it is not possible to prevent altogether this secondary reaction between ferrous oxide and peroxide."

In my own experiments (Table XVIII) y_∞/F falls as low as 1.2 or 1.4 and changes with the concentrations much more than in those of Manchot. The same is true of y/x in the experiments of Table XVII. The explanation is to be found, not in "want of uniformity" in adding the ferrous sulphate — the mixing was complete and a homogeneous solution formed before the liberation of more than a trace of iodine — but in the data of Table XVIII itself, which show that increase in the concentrations of the reagents increases y_∞/F. In Manchot's experments the concentrations were much greater than in mine; his results approach more nearly to what is evidently the limiting ratio, viz: 2.

So far as I am aware, the peroxide theory has not yet been applied to explain in detail any particular case of catalysis where the rates have been measured, although it has become customary to assume the existence of "primary" peroxides in advancing qualitative explanations for incompletely studied reactions. In the succeeding paragraphs, therefore, I have developed the consequences of the theory for this particular case, and compared them with the results of the measurements.

The theory assumes the occurrence of three different reactions in the solution: formation of the peroxide, action of the peroxide on the iodide, and action of the peroxide on the residual ferrous salts. Of these, the first may be regarded as the reaction whose rate is measured, and the others as following quickly after it, otherwise the peroxide would accumulate in the solution; moreover, the slow disappearance of the ferrous salt has been established by direct experiments with potassium ferrocyanide.

Representing by p the quantity of the peroxide which contains one atom of iron ($\frac{1}{2}Fe_2O_5$ if Manchot's formula be adopted), and by n the number of molecules of potassium iodide or ferrous sulphate with which that quantity of peroxide reacts ($n = 2$, according to Manchot) the last two reactions may be represented by the following chemical equations: —

$$p + n\overset{-}{\mathrm{I}} = \overset{+++}{\mathrm{Fe}} + n\overset{\circ}{\mathrm{I}} \ldots\ldots\ldots\ldots\ldots\ldots (i)$$

and

$$p + n\overset{++}{\mathrm{Fe}} = (n+1)\overset{+++}{\mathrm{Fe}} \ldots\ldots\ldots\ldots\ldots (ii)$$

Writing dp for $\partial p/\partial\theta \cdot d\theta$, the amount of peroxide formed in a unit of time, d_1p for the amount entering into reaction *i*, and d_2p for the amount entering into reaction *ii*, also in a unit of time, the assumption that the peroxide is destroyed as soon as it is formed may be expressed by the equation

$$dp = d_1p + d_2p.$$

The amount of iodine liberated, dy, if expressed in equivalents, is obviously equal to nd_1p, while the ferric salt formed,

$$dx = d_1x + d_2x = d_1p + (n+1)d_2p.$$

The rates of the two reactions *i* and *ii* above, must, in general, depend on the concentrations of the iodide and ferrous salt; adopting the form most in harmony with the prevalent practice in chemical kinetics, the ratio of the two rates may be set proportional to the quotient of some powers of the concentrations.[1]

$$d_2p/d_1p = k(F-x)^s/(C-y)^t \ldots\ldots\ldots\ldots\ldots (1)$$

and the rate of formation of peroxide to the r-th power of the concentration of the ferrous salt

$$dp/d\theta = K(F-x)^r \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

From these equations the following expressions for the rate of liberation of iodine,

$$\left.\begin{aligned} Ry &= \frac{dy}{d\theta} = \frac{dy}{dp}\cdot\frac{dp}{d\theta} = \frac{nd_1p}{d_1p + d_2p}\cdot\frac{dp}{d\theta} \\ &= \frac{Kn(C-y)^t(F-x)^r}{(C-y)^t + k(F-x)^s} \end{aligned}\right\} \ldots\ldots\ldots (3)$$

and for the "total iodine"

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[1] *C* represents the initial concentration of the iodide, and *F* that of the ferrous salt. *K* in Equation 2 is a function of the concentrations of the acid and bichromate.

$$y_\infty = \int_{x=0}^{x=F} dy = \int_0^F \frac{n(C-y)^t}{(C-y)^t + k(n+1)(F-x)^s} dx \ldots\ldots\ldots (4)$$

may be obtained.

I have integrated the latter expression for three particular cases, viz: (*i*) $t = s = 1$; (*ii*) $s = 2$, $t = 1$; (*iii*) $s = t = 2$; introduced experimentally determined values for y_∞, solved for n and k, and then by means of Equation (3) computed the relative rates for different concentrations of potassium iodide. The results are tabulated for comparison with the experiments. Finally, I have shown that no other assumptions as to the values of s and t would bring the results of the calculations into better agreement with the experimental numbers.

Case i. $s = t = 1$. — Substituting, and integrating (treating $C-y$ as constant, and equal to C) the expression for the "total iodine" becomes

$$y_\infty = \frac{nC}{k(n+1)} \cdot \log \text{nat} \frac{C + kF(n+1)}{C} \ldots\ldots\ldots (5)$$

Making use of the results of Expt. 5: $F = 1.0$, $C = 20$, $y_\infty = 1.56$, and Expt. 14: $F = 1.0$, $C = 5$, $y_\infty = 1.20$, numerical values for n and k may be obtained. As, in Expt. 14, $C - y$ falls from 5.0 to 3.9, while the integral was obtained under the assumption that $C - y = C$, I have obtained limits for n and k by setting $C = 5$ in one calculation, and $C = 4$ in a second.

The values are,

$$n = 1.77 \text{ and } 1.71 \qquad k = 1.91 \text{ and } 1.44 \ldots\ldots\ldots (6)$$

and by introducing them into Equation (3), and at the same time setting $s = t = 1$, $x = 0$, and $F = 1$, the (initial) rates of liberation of iodine in the presence of different concentrations of the iodide were calculated.

The results, multiplied by an arbitrary constant, are given in Table XXI; Ry for $C = 5$ has been set 100 to facilitate comparison.

Increase in the concentration of the iodide from 5 to 30 adds but

30 percent to the rate; the experiments show that 300 percent is added.

Calculating backwards, setting $Ry(C=20) = 2.4 \times Ry(C=5)$ — see Expts. 5 and 14 — there follows, $k = 17.5$; whence, assuming $n = 2$ (Manchot)

$$y_\infty(C=5) = 0.46\ ;\ \textit{obs.}\ 1.20$$

$$y_\infty(C=20) = 0.87\ ;\ \textit{obs.}\ 1.56$$

Case ii. $s = 2$, $t = 1$. — Substituting in Equations (3) and (4), setting $C - y = C$, and carrying out the integration in Equation (4) there results:

$$Ry = dy/d\theta = \frac{KnC(F-x)^r}{C+k(F-x)^2} \ldots\ldots\ldots\ldots\ldots (7)$$

and

$$y_\infty = \frac{n\sqrt{C}}{\sqrt{k(n+1)}} \cdot \tan^{-1} \frac{\sqrt{K(n+1)} \cdot F}{\sqrt{C}} \ldots\ldots\ldots (8)$$

Introducing the same pair of values as in Case *i*, and solving for n and k,

$$n = 1.82 \qquad k = 3.78 \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

(Only the upper limit for k — the more favorable — being computed.) Initial values of Ry, $(x = 0)$, (Table XXII) have been calculated from (7) and (9), setting $Ry(C=5)$ 100, as before. The results are much the same as in case *i*; widely different from the experiments.

Case iii. $s = t = 2$.

$$Ry = \frac{KnC^2(F-x)^r}{C^2+k(F-x)^2} \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

and

$$y_\infty = \frac{Cn}{\sqrt{k(n+1)}} \cdot \tan^{-1} \frac{\sqrt{k(n+1)} \cdot F}{C} \ldots\ldots\ldots (11)$$

whence $n = 1.80$, $k = 72.3$, and the numbers under "initial Ry $(F = 1.0)$" in Table XXIII.

The results of the calculation are in better agreement with the experiments than those of *i* and *ii*; although in the Table the first increment of C has more effect than the last, while in reality the reverse is the case. The agreement, such as it is, however, is due to the circumstance that F has been set equal to unity, and x to zero in making the computation. If F be set 0.5, and $x = 0$, no value of r can be found that will make Ry half what it is when $F = 1.0$; this is evident on inspecting Equation (10); to show how wide the discrepancy may be in particular cases, Ry has been calculated for $r = 1$ and $r = 2$, and the results entered in Table XXIII.

Similar want of success must necessarily attend the substitution of other values for s and t; Equation (3) can be brought into partial accordance with the experiments only if $t = 1$, and k is large enough to annihilate the term $(C-y)^t/k$ in the denominator[1]. This would make y_∞ proportional to C, and less than F, neither of which is supported by the observations.

The calculations of the preceding paragraphs show that the Peroxide Theory cannot reconcile the results of the experiments on the rate of liberation of iodine with those on the "total iodine". This however is not the only respect in which it fails. Three others may be mentioned briefly.

First, the influence of the iodide on the rate of oxidation of the ferrous salt. If the liberation of iodine be the result of a secondary reaction between peroxide and iodide, increase in the concentration of the iodide can cause increase in the rate of liberation of iodine only by causing a corresponding increase in the "total iodine" and decrease in the rate at which ferric salt is formed. The measurements show that doubling the concentration of the iodide almost doubles Ry, and slightly *increases* Rx.

Second, the influence of the iodide on the rate of liberation of iodine. According to the theory, each successive increment of the iodide should have less effect than the preceding, until finally, when $y_\infty = 2F$, further addition of iodide should leave the rate unchanged. According to the experiments, the influence of the iodide increases with its concentration.

Finally, it has been established in the experimental part of this paper, that in the absence of iodides, doubling the concentrations of either the acid or the ferrous salt quadruples the rate

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[1] After dividing both numerator and denominator by k.

at which the iron is oxidized; while in their presence doubling the concentration of the acid multiples it by eight or twelve, and doubling that of the iron, by two. It is hard to see how these facts can be accounted for by a theory which assumes that the "primary reaction" is the same in both cases.

In short, the "Peroxide Theory" was set up before the rate measurements were made, and in attempting to explain them it breaks down.

The ferroiodion theory

If it be assumed that the iodide takes part in the reaction whose rate is measured, many of the difficulties met with in the previous paragraphs may be avoided. The chromic acid may be represented, for instance, as acting on ferrous iodide, forming ferric salt and iodine:

$$K_2Cr_2O_7 + 2FeI_2 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 2I_2 + 7H_2O.$$

In view of the results of the rate measurements, the "primary reaction" may be considered to take place between the ions

$$\overset{--}{Cr_2O_7},\ \overset{+}{FeI},\ \overset{-}{I}\ \text{and}\ 4\overset{+}{H} \ldots\ldots\ldots\ldots\ldots (i)$$

and the fact that, in general, less than two atoms of iodine are liberated for each atom of iron oxidized may be accounted for by assuming simultaneous direct action of the chromic acid on the ferroion.

This theory offers an explanation for all the principal results of the experimental investigation.

By introducing a new reaction (Equation *i*) in solutions containing both ferrous salts and iodides, it accounts for the fundamental differences between the oxidation of ferrous sulphate or potassium iodide alone, and in solutions containing both.

By including potassium iodide in the primary reaction, it is able to account for proportionality between *Ry* and the concentration of that reagent, while avoiding the difficulties raised by the Peroxide Theory. The decrease in *Rx* consequent on the first addition of potassium iodide can be ascribed to diminution in the number of $\overset{++}{\text{Fe}}$ ions (formation of $\overset{+}{\text{FeI}}$, Ferroiodion), while the subsequent increase is due to increase in the rate of reaction (*i*) brought about by increase in the concentration of the iodide.

Finally, by admitting direct action between chromic acid and ferrous sulphate, the Ferroiodion Theory explains the variations in the "total iodine" liberated during the oxidation of a given quantity of iron. Increasing the concentration of the acid or of the iodide increases the rate of the main reaction over that of the other, and thus causes y_∞ to approach more nearly its limiting value, $2F$; while the diminution in y_∞/F as F increases is caused by the rate of oxidation of ferrous sulphate being proportional to the square of its concentration, while the rate of formation of ferric salt by reaction (*i*) is proportional to the first power only.

This theory, however, like the Peroxide Theory, affords no explanation of the variable "order" of the reaction with respect to the bichromate, and it exaggerates somewhat the influence of the iodide. Doubling the concentration of the potassium iodide ought to double the rate of liberation of iodine; Expts. 5, 14, and 16 show that this condition is complied with only when $C = 20$ or larger; between $C = 5$ and $C = 20$, doubling C multiplies the rate by 1.7 or 1.8 only.

A simple calculation reveals a similar discrepancy in dy/dx. The reactions assumed are,

$$(i) \text{ between } \overset{--}{\text{Cr}_2\text{O}_7},\quad \overset{+}{\text{FeI}},\quad \overset{-}{\text{I}},\quad \text{and}\quad 4\overset{+}{\text{H}}$$

and

$$(ii) \text{ between } \overset{--}{\text{Cr}_2\text{O}_7},\quad 2\overset{++}{\text{Fe}},\quad \text{and}\quad 2\overset{+}{\text{H}}$$

If A, B, C, and F be the quantities of acid, bichromate, iodide, and ferrous salts (in equivalents) initially present, x and y the ferric salt and free iodine already formed, d_1x, and d_2x the ferric salt formed in unit time by reactions *i* and *ii* respectively, and a the fraction of the residual ferrous salt uncombined with iodine; the rates of the two reactions at the beginning of an experiment, before x and y are large enough to be taken into consideration ("initial rates") may be written

$$R_1 = d_1x/d\theta = \tfrac{1}{2}dy/d\theta = k_1A^4BCF(1-\alpha) \quad \ldots\ldots\ldots (12)$$

$$R_2 = d_2x/d\theta = k_2A^2BF^2\alpha^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

and the initial ratio,[1]

$$\frac{dy}{ax} = \frac{2kA^2C(1-\alpha)}{kA^2C(1-\alpha)+\alpha^2F} \quad \ldots\ldots\ldots\ldots (14)$$

in which $k = k_1/k_2$.

As y/x changes but slowly in the experiments for which x has been calculated, it is possible to obtain the initial value of dy/dx from the Tables with a fair degree of approximation. In Expt. 5 (A, 10; B, 20; C, 20; F, 1.0) it is 1.3. Introducing this value in Equation (14), there follows

$\alpha^2/k(1-\alpha) = 1077$; and $dy/dx = 0.63$ for $C = 10$,
obs. 0.9 (Expt. 16),

the observed change being less than that called for by the theory.[2]

To bring the Ferroiodion Theory into still better accord with the experimental results, it must evidently be modified in some manner which, while leaving the main features of the theory intact, will lessen the influence of the iodide a little, especially when the concentration of that reagent is low. As the principal reaction (oxidation of $\overset{+}{\mathrm{FeI}}$) can hardly be interfered with without sacrificing the main points of agreement with the experiments, the remedy must be sought in introducing a third or fourth simultaneous reaction, or in modifying the subsidiary reaction already admitted, viz., the direct oxidation of ferrous salt.

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[1] By introducing x and y, and integrating between the limits $x = 0$ and $x = F$, an expression for y_x may be obtained; it is not however of a convenient form for computations.

[2] In computing dy/dx by Equation 14 it must be noted that $\alpha^2/(1-\alpha)$ is a function of C; they are connected by the equation of equilibrium

$$C\alpha = \text{Const} \times (1-\alpha),$$

corresponding to the reaction

$$\overset{-}{\mathrm{I}} + \overset{++}{\mathrm{Fe}} = \overset{+}{\mathrm{FeI}}.$$

If α is large, $(1-\alpha)/\alpha^2$ is proportional to C; this assumption — the most favorable one — has been made in computing dy/dx for $C = 10$ above.

If it be supposed that the "primary" product is a peroxide — the evidence of the rate measurements (oxidation of $FeSO_4$, page 367) in favor of this hypothesis remains, although, as has been shown, that drawn from the liberation of iodine will not bear examination — increase in the concentration of the iodide, while increasing the rate of the main reaction, will lessen the rate of the "direct" oxidation, by converting $\overset{++}{\mathrm{Fe}}$ ions into $\overset{+}{\mathrm{Fe}}\mathrm{I}$, and may thus diminish the supply of iodine arising from secondary decomposition of the peroxide. The rate of liberation of iodine will thus be less than proportional to the concentration of the iodide, until the latter is great enough to dispose of all of the Fe ions. From then on, *Ry* will be proportional to *C*.

In conclusion, I wish to express my thanks to Prof. W. Lash Miller for the interest he has displayed in this research.

The University of Toronto,
April, 1903.

TABLE I.

Ac, 10; Cr, 10; KI, 20; Ox, 5; V, 700

Expt. 1. F = 1.0						Expt. 2. F = 0.5					
θ	As	Cr 20	θ/T	Ac 15	θ/T	θ	As	Cr 20	θ/T	Ac 15	θ/T
1	0.80	0.35	2.9	0.25	4.0	2	0.75	0.80	2.5	0.5	4.0
2	1.40	0.7	2.9	0.5	4.0	4	1.40	1.55	2.6	1.0	4.0
4	2.40	1.35	2.9	0.90	4.4	8	2.15	2.90	2.8	1.7	4.7
8	3.50	2.6	3.0	1.60	5.0	20	3.60	—	—	—	—
16	4.95	—	—	—	—	30	3.80	—	—	—	—
25	5.55	—	—	—	—	90	4.00	—	—	—	—
30	5.65	—	—	—	—	—	—	—	—	—	—
60	6.85	—	—	—	—	—	—	—	—	—	—
90	7.15	—	—	—	—	—	—	—	—	—	—
120	7.10	—	—	—	—	—	—	—	—	—	—

Calc: 1st, 2.0; 4th, 5.1 1st, 2.0; 4th, 5.1

Blanks: 22°; 28*; 42, As = 0.2; 60, As = 0.35; 90, As = 0.50; 120, As = 0.75

TABLE II.

Ac, 15; Cr, 10; KI, 20; Ox, 5; V, 700

Expt. 3. F = 1.0						Expt. 4. F = 0.5			
θ	As	Cr 20	θ/T	Ac 20	θ/T	θ	As	Ac 20	/T
0.5	1.55	0.25	2.0	0.18	2.9	0.5	0.80	0.17	3.0
1	2.55	0.40	2.5	0.30	3.3	1	1.45	0.35	3.0
2	4.15	0.80	2.5	0.70	2.9	2	2.45	0.7	3.0
4	5.55	1.60	2.5	1.30	3.1	4	3.45	1.5	2.7
8	6.90	3.10	2.6	2.20	3.6	25	4.35	—	—
25	8.35	—	—	—	—	—	—	—	—

Calc: 1st, 2.0; 4th, 3.2 4th, 3.2

Blanks: 25°; 29*; 39**

TABLE III.

Ac, 10; Cr, 20; KI, 20; Ox, 5; V, 700

	Expt. 5. F = 1.0							Expt. 6. F = 0.5				
θ	As	Cr 30	θ/T	Ac 15	θ/T	KI 30	θ/T	As	Cr 20	θ/T	KI 30	θ/T
0.5	1.05	0.25	2.0	0.1	5	0.3	1.7	0.40[1]	0.2	2.5	0.3	1.7
1	1.90	0.55	1.8	0.2	5	0.7	1.4	1.00	0.50	2.0	0.8	1.3
2	3.10	1.05	1.9	0.5	4	1.4	1.4	1.75	1.20	1.7	1.7	1.2
4	4.30	2.10	1.9	0.9	4.4	2.7	1.5	2.50	2.0	2.0	3.0	1.3
8	5.60	4.40	1.8	1.6	5	5.5	1.5	3.30	4.0	2.0	5.0	1.6
20	7.10	—	—	—	—	—	—	4.05	—	—	—	—
30	7.70	—	—	—	—	—	—	4.20	—	—	—	—
120	7.85	—	—	—	—	—	—	—	—	—	—	—

Calc: 1st, 1.5; 4th, 5.1 1st, 1.5 1st, 1.5 1st, 1.5

Blanks: 20°; 28*; 120, As = 0.65

TABLE IV.

Ac, 20; Cr, 10; KI, 20; Ox, 5; V, 700

Expt. 7. F = 1.0				Expt. 8 F = 0.5	
θ	As	Cr 20	θ/T	θ	As
0.25	2.15	0.1	2.5	0.25	1.15
0.5	3.50	0.2	2.5	0.5	2.10
1	4.75	0.35	3.0	1	2.95
2	6.70	0.82	2.5	2	3.90
4	7.80	1.6	2.5	4	4.65
8	8.55	3.6	2.2	25	4.90
30	8.80	—	—	—	—

Calc: 1st, 2.0

Blanks: 20°; 32*

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[1] Probably too low; does not fall on curve.

TABLE V.

KI, 20; Ox, 5; F, 1.0; V, 700

Expt. 9 Ac, 20; Cr, 20		Expt. 10 Ac, 15; Cr, 30		Expt. 11. Ac, 15; Cr, 20					
θ	As	θ	As	θ	As	Ac 20	θ/T	Cr 30	θ/T
0.25	4.05	0.5	4.45	0.5	3.00	0.15	3.3	0.22	2.2
0.5	5.75	1	5.90	1	4.60	0.30	3.3	0.55	1.9
1	7.15	2	7.15	2	6.00	0.60	3.3	1.05	1.9
2	8.00	4	8.00	4	7.50	1.30	3.1	2.50	1.6
8	8.60	20	8.35	30	8.35	—	—	—	—
20	8.80	—	—	—	—	—	—	—	—
30	8.75	—	—	—	—	—	—	—	—
120	8.50	—	—	—	—	—	—	—	—

Calc: 4th, 3.1 1st, 1.5

Blanks (Expt. 9): 27°; 32*; 75, As = 0.50; 120, As = 0.70

Blanks (Expt. 10): 27°; 38*; 48**

Blanks (Expt. 11): 26°; 40*

TABLE VI.

Ac, 10; Cr, 30; KI, 20; Ox, 5; V, 700

Expt. 12. F = 1.0				Expt. 13 F = 0.5	
θ	As	Ac 15	θ/T	θ	As
0.5	1.75	0.08	6.2	0.5	0.90
1	2.95	0.15	6.6	1	1.55
2	4.15	0.4	5	2	2.45
4	5.30	0.8	5	4	3.30
25	7.75	—	—	30	4.55
30	7.55	—	—	—	—

Calc: 4th, 5.1

Blanks: 27°; 38*; 48**

TABLE VII.

Ac, 10; Cr, 20; KI, 5; Ox, 5; V, 700

Expt. 14. F = 1.0				Expt. 15. F = 0.5			
θ	As	KI 10	θ/T	θ	As	KI 10	θ/T
1	0.95	0.6	1.7	2	0.90	1.30	1.5
2	1.55	1.1	1.8	4	1.35	2.1	1.9
4	2.40	2.3	1.8	8	2.05	3.9	1.8
8	3.40	4.2	1.9	60	3.60	—	—
60	5.65	—	—	—	—	—	—
120	5.75	—	—	—	—	—	—
180	6.00	—	—	—	—	—	—

Calc: 1st, 2.0 1st, 2.0

Blanks: 60°; 180*

TABLE VIII.

Ac, 10; Cr, 20; KI, 10; Ox, 5; V, 700

Expt. 16. F = 1.0				Expt. 17. F = 0.5			
θ	As	KI 20	θ/T	θ	As	KI 20	θ/T
1	1.40	0.7	1.4	1	0.65	0.7	1.4
2	2.20	1.2	1.7	2	1.30	1.4	1.4
4	3.30	2.3	1.8	4	2.05	2.7	1.5
8	4.30	4.0	2.0	8	2.95	5.5	1.4
60	6.80	—	—	60	4.20	—	—
120	7.00	—	—	—	—	—	—

Calc: 1st, 2.0 1st, 2.0

Blanks: 60°; 120, As = 0.10

TABLE IX.

Ac, 10; Cr, 20; KI, 30;
Ox, 5; V, 700

Expt. 18 F = 1.0		Expt. 19 F = 0.5	
θ	As	θ	As
0.5	1.50	0.5	0.60
1	2.40	1	1.10
2	3.70	2	1.85
4	5.10	4	2.95
20	7.75	20	4.55
105	7.80	—	—

Blanks: 16°; 21*; 105, As = 1.40

TABLE X.

Expt. 20. Ac, 10; Cr, 20; KI, 20; Ox, 5; F, 2.0; V, 700

θ	As	F 1.5	θ/T	F 1.0	θ/T	F 0.5	θ/T
0.25	1.40	0.36	0.7	0.7	0.36	1.5	0.17
	Calc:	1st, 0.75		1st, 0.5		1st, 0.25	

Expt. 21. Ac, 10; Cr, 20; KI, 20; Ox, 5; F, 1.5; V, 700

θ	As	F 1.0	θ/T	F 0.5	θ/T
0.25	0.95	0.45	0.55	1.0	0.25
0.5	1.90	1.0	0.50	2.3	0.13
	Calc:	1st, 0.67		1st, 0.33	

Expt. 22. Ac, 20; Cr, 10; KI, 20; Ox, 5; F, 0.25; V, 700

θ	As	F 0.5	θ/T	F 1.0	θ/T
0.5	1.00	0.2	2.5	0.1	5
	Calc:	1st, 2.0		1st, 4.0	

TABLE XI.

θ	As (F = 1.0)	As (F = 0.5)	Expt. (F = 1.0)	Expt. (F = 0.5)
2.0	1.40	0.75	1	2
0.5	1.55	0.80	3	4
0.5	1.05	0.40[1]	5	6
0.25	2.15	1.15	7	8
0.5	1.75	0.90	12	13
2.0	1.55	0.90	14	15
1.0	1.40	0.65	16	17
0.5	1.50	0.60	18	19

TABLE XII.

Ac, 10; Cr, 20; KI, 20; F, 1.0; V, 700

Expt. 23 Ox, 0		Expt. 24 Ox, 2.5		Expt. 25 Ox, 3.3		Expt. 26 Ox, 5.0		Expt. 27 Ox, 10.0	
θ	As	θ	As	θ	As	θ	As	θ	As
0.5	3.95	0.5	1.50	1	2.25	0.5	1.05	1	1.40
1	5.00	1	2.40	2	3.40	1	1.90	2	2.25
2	5.85	2	4.80	4	4.80	2	3.10	4	3.55
4	6.30	—	—	-	—	4	4.30	8	4.85
20	7.20	—	—	-	—	8	5.60	16	6.50
43	7.40	—	—	-	—	20	7.10	—	—
—	—	—	—	-	—	30	7.75	—	—
—	—	—	—	-	—	120	7.85	—	—

---

[1] See footnote Table III. In Table XI. "As (F = 1.0)" signifies the reading at time θ when F = 1.0; "Expt. (F = 1.0)" is the number of the experiment from which the data were taken. Similarly with "As (F = 0.5)" and "Expt. (F = 0.5)."

TABLE XIII.

KI, 20; V. 700

Expt.	Addition	Ac	Cr	Ox	F	θ	As	Blank
28	20 cc F/40 K_2SO_4	10	20	0	1.0	1	4.90	5.00
29	5 cc F/20 $Cr_2(SO^4)_3$[1]	10	20	0	1.0	1	4.90	5.00
30	10 cc *n*/100 Iodine	10	20	5	1.0	8	5.55	5.60
31	0.1 g Haemoglobin	20	10	5	0	5	0.00	0.80
32	1.0 g Ferrosomatose	10	20	0	0	15	0.00	7.00
33	0.2 g $K_4Fe(CN)_6$	10	20	0	0	20	0.00	7.20

TABLE XIV.

KI, etc. in gram-mols × 10^{-5}; Temp. 30° C; V, 100 cc

Expt.	KI	H_2SO_4	$K_2Cr_2O_7$	Fe'''	Fe''	θ	Thio.
i	142	240	1.968	0	0	5	0.90
ii	142	240	1.968	25	0	5	13.60
iii	142	240	0	25	0	5	4.07
iv	142	240	1.968	0	4.07	5	8.61

TABLE XV.

Ac, 10; Cr, 20; KI, 20; F, 1.0; V, 700; $\theta = 4$

Age	5	11	21	22	140
As	3.73	4.63	4.73	4.72	5.70

TABLE XVI.

F	Expt. 5B $\theta = 30$	Expt. 16B $\theta = 60$	Expt. 14B $\theta = 60$	Expt. 1B $\theta = 90$	Expt. 9B $\theta = 30$	Expt. 23B $\theta = 30$
0	0.00	0.00	0.00	0.00	0.00	0.00
0.2	1.85	1.85	1.70	1.80	2.05	1.75
0.4	3.50	3.50	3.00	3.25	3.80	3.15
0.6	5.00	4.85	3.90	4.45	5.50	4.40
0.8	6.85	5.85	4.50	6.20	7.00	—
1.0	7.70	6.80	5.65	7.10	8.75	7.30

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[1] Chrome alum was used.

Table XVII.

Expts. 5 and 6. Ac, 10; Cr, 20; KI, 20; Ox, 5; V, 700;
Expt. 5, F = 1.0; Expt. 6, F = 0.5.
Expts. 16 and 17. Ac, 10; Cr, 20; KI, 10; Ox, 5; V, 700;
Expt. 16, F = 1.0; Expt. 17, F = 0.5.
Expts. 14 and 15. Ac, 10; Cr, 20; KI, 5; Ox, 5; V, 700;
Expt. 14, F = 1.0; Expt. 15, F = 0.5.
Expt. 35. Ac, 10; Cr, 20; KI, none; Ox, 5; F = 1.0; V, 700.
Expts. 1 and 2. Ac, 10; Cr, 10; KI, 20; Ox, 5; V, 700;
Expt. 1, F = 1.0; Expt. 2, F = 0.5.
Expt. 9. Ac, 20; Cr, 20; KI, 20; Ox, 5; F = 1.0; V, 700.
Expt. 23. Ac, 10; Cr, 20; KI, 20; Ox, none; F = 1.0; V, 700.

	Expt. 5			Expt. 16	Expt. 14	Expt. 35	Expt. 1	Expt. 9	Expt. 23
θ	As	Diff.	$F - x$	$F - x$	$F - x$	$F - x$	$F - x$	$F - x$	$F - x$
0.25	—	—	—	—	—	—	—	0.50	—
0.5	1.05	6.65	0 85	—	—	0.82	—	0.30	0.44
1	1.90	5.80	0.72	0.62	0.80	0.70	0.84	0.14	0.33
2	3.10	4.60	0.54	0.55	0.66	0.54	0.75	0.07	0.18
4	4.30	3.40	0.38	0.40	0.47	0.34	0.60	—	0.12
8	5.60	2.15	0.24	0.26	0.37	—	0.44	0.02	—
30	7.70	—	—	—	—	—	—	—	—

	Expt. 6	Expt. 17	Expt. 15	Expt. 2
θ	$F - x$	$F - x$	$F - x$	$F - x$
0.5	0.44	—	—	—
1	0.36	0.39	—	—
2	0.27	0.30	0.34	0.40
4	0.18	0.21	0.26	0.32
8	0.08	0.12	0.18	0.20

TABLE XVIII.

Ox. 5; F, 1.0; Vol. 700 cc

Expt.	Ac	Cr	KI	θ	As
1	10	10	20	120	7.10
3	15	10	20	25	8.35
7	20	10	20	30	8.80
5	10	20	20	120	7.85
11	15	20	20	30	8.35
9	20	20	20	30	8.75
12	10	30	20	25	7.75
10	15	30	20	20	8.35
14	10	20	5	180	6.00
16	10	20	10	120	7.00
5	10	20	20	120	7.85
18	10	20	30	105	7.80

TABLE XIX.

KI, none; Ox. 5; F, 1.0; V, 700

	Expt. 34 Ac, 10; Cr, 10			Expt. 35 Ac, 10; Cr, 20			Expt. 36 Ac, 20; Cr, 10		
θ	As	$1-x$	k_2[1]	As	$1-x$	k_2	As	$1-x$	k_2
0.0	4.45	1.0	—	4.45	1.0	—	6.70	1.0	—
0.5	3.65	0.90	0.22	3.65	0.82	0.44	5.18	0.78	0.56
1.0	3.10	0.85	0.17	3.10	0.70	0.43	4.08	0.61	0.64
2.0	2.75	0.75	0.16	2.40	0.54	0.43	3.07	0.45	0.61
4.0	2.25	0.62	0.16	1.50	0.34	0.48	2.15	0.32	0.62

TABLE XIX.*b*

$FeSO_4$	1.0	0.8	0.7	0.6	0.4	0.3	0.25	0.0
As (Expt. 34)	4.45	—	2.62	—	1.57	—	—	0.0
As (Expt. 35)	4.42	3.55	—	2.85	1.90	—	1.20	0.0
As (Expt. 36)	6.70	—	4.70	—	2.90	2.17	—	0.0

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[1] $k_2 = \frac{1}{\theta} \cdot \frac{x}{1-x}$.

TABLE XX.

No.	Ac	Cr	KI	F	As	As calc. (2 equiv.)
i	230	16	26	5.16	47.2	51.8
ii	230	21	26	5.15	47.3	51.7
iii	440	16	47	5.02	47.8	50.4
iv	225	16	48	5.11	47.3	51.3
v	225	16	48	5.11	48.2	51.3
vi	225	16	48	5.11	47.9	51.3
vii	225	16	48	5.11	47.8	51.3
viii	225	16	48	5.11	48.7	51.3
ix	440	16	47	5.14	48.6	51.6
x	230	20	48	5.15	50.0	51.7

TABLE XXI.

C	Initial *Ry* (calc.)		Initial *Ry*
	k = 1.91	*k* = 1.44	Obs.
5	100	100	100
10	116	113	170
20	126	119	280
30	131	127	405

TABLE XXII.

C	Initial *Ry*	
	Calc.	Obs.
5	100	100
10	116	170
20	126	280
30	131	405

TABLE XXIII.

C	Initial *Ry* (calc.)				
		F = 0.5 $r = 1$		F = 0.5 $r = 2$	
	F = 1.0	*Ry*	Ratio	*Ry*	Ratio
5	100	112.8	1.13	56.4	0.56
10	227	164.8	0.73	82.4	0.36
20	331	186.2	0.56	93.1	0.28
30	363	190.8	0.53	95.4	0.26
Obs.	—	—	0.5	—	0.5

CONTENTS

NEW BOOKS

Oeuvres completes de J. C. Galissard de Marignac. *Publiées par E. Ador. Hors-série des Mémoires de la Société de Physique et d'Histoire naturelle de Genève. Tome I. Notice biographique; travaux divers, 1840-1860; pp. lv + 701. Tome II. Mémoires et critiques, 1860-1887; pp. 840. 19 × 28 cm. Genève, Ch. Eggimann et Cie; Paris, Masson et Cie; Berlin, R. Friedlaender und Sohn. 1902. Price: both volumes, paper, 30 francs.* — The two large volumes here before us contain the life work of one of the most exact and patient chemical workers the world has ever known. Marignac's name is most familiar in connection with the determination of atomic weights; but in the field of the double salts he has left an enduring name, and he was one of the pioneers among the rare earths.

His career as to dates and places is as follows: — Born in 1817, he received his early training in the École Polytechnique and the École des Mines between the years 1835 and 1839. His inclination towards mathematical studies was very marked at this time, and it is not surprising to find that when his interests turned later to chemistry he selected that branch of it for his own in which exact work and exact thought counted for most. In 1840 he went to Liebig in Giessen, and under his influence carried out a couple of researches in organic chemistry, the only ones he ever undertook.

Although the young chemist was gradually making a name for himself in Paris, he accepted a call in 1841 to the Academy at Geneva, his birthplace, willingly abandoning the idea of any such larger career as his natural gifts might have led him into, in order to return to his old home; here he lived for the remainder of his years.

In 1873 the Academy became the University of Geneva, and Marignac became one of its professors; but this place he did not long retain. His son Edward, a young man of great promise, had died two years earlier, and from this blow Marignac never completely recovered; his teaching too was always difficult to him, though those who heard his lectures found them of extraordinary clearness. In 1878 he gave up teaching and retired to his laboratory; sickness attacked him not long after, and he became so enfeebled as to be incapable of carrying on experimental work; in this condition he lingered on for several years until in 1894 he died.

Marignac's gift was absolute scientific candor, and a very rare clear-sightedness. He was never willing to take the word for the idea. While he was not a genius of the first rank, yet his contribution to the progress of chemistry was a very substantial one. His interests ran mainly in two directions, stoichiometric and crystallographic; his apparent digressions into other fields, as for example in the research on the specific heat of solutions, were really to find new points of view for considering stoichiometric relations. His endless patience and a very great intelligence in selecting appropriate methods of work qualified him in the highest degree for atomic weight determinations. Ostwald says of his determinations that "though carried on with great care they were performed with much less expenditure of material and labor than those of Stas. Nevertheless they led to exactly the same result; not in one case only, but in every case where the same element was investigated by both; a brilliant proof of the exactness attained with relatively slight means by Marignac". And the confirmation of this is before us in the table appended to the second of these volumes, where Marignac's values are placed side by side with the "international" values for 1903; the showing is that out of the twenty-nine elements determined by him not more than half a dozen and these the least important show any material variation from the figures current to-day.

Although he made no great contribution to chemical theory, his discussion of theoretical matters is always very clear and definite, and he was ever in the forefront of progress. He was one of the first French chemists (1865) to adopt the new atomic weights; and oxygen was always his standard; first as 100, following Berzelius; and later as 16. In an article published in 1883 he states in the most convincing way the advantages of this basis.

Outside of the exact determination of atomic weights and the analysis of compounds, Marignac's keenest interest was in the crystallographic forms of naturally occurring minerals and of laboratory products. These volumes contain hundreds of such crystallographic determinations, both for simple salts and for a host of double and complex salts, many of which he prepared for the first time; notably among the fluotungstates, fluosilicates, silicotungstates, and the like. He was also actively interested in the rarer elements, such as niobium and tantalum, as well as cerium, lanthanum, erbium, and others of the rare earth's group, to the knowledge of which he made contributions of great value. Out of the hundred and odd papers included in these volumes, only a few are brief critical notices; the vast majority give the results of Marignac's own constant and painstaking labors. A lengthy biographical notice by his son in-law serves for introduction.

The publication is sumptuous in apperance, but a little examination shows a good many typographical errors; there is no alphabetical index. Except for such slight imperfections, it is a splendid and fitting monument to a great man.

A. P. Saunders

Quantitative Classification of Igneous Rocks. *Based on chemical and mineral characters, with a systematic nomenclature. By Whitman Cross, Joseph P. Iddings, Louis V. Pirsson, and Henry S. Washington. With an introductory review of the development of systematic petrography in the 19th century, By Whitman Cross. Chicago: University of Chicago Press.*—This book of nearly 300 pages is chiefly a reprint of certain essays which appeared in the tenth volume of the *Journal of Geology*. The introductory review by Cross gives an excellent summary of the progress of systematic petrography to date.

The main portion of the book—pp. 96 to 235—is devoted to a new scheme for the classification and nomenclature of igneous rocks. The nature of the magma from which such a rock is derived is considered its most fundamental characteristic. Its chemical composition—determined either by actual analysis or by estimation from the kinds and amounts of the component minerals—is cast according to certain definite rules into terms of "standard minerals". These are, as nearly as is consistent with convenience in calculation, the minerals which would actually crystallize under ordinary conditions from the given magma. The five principal sub-divisions of rocks, called *Classes*, are based on the ratio of quartz, feldspar, etc., to the ferro-magnesium silicates and allied minerals. The ratios chosen are (*a*) more than 7 : 1, (*b*) between 7 : 1 and 5 : 3, (*c*) between 5 : 3 and 3 : 5, (*d*) between 3 : 5 and 1 : 7, and (*e*) less than 1 : 7. These same ratios are employed in the more minute classification. The classes are divided into *Orders* on the basis of the ratio of quartz to feldspar, etc., and the further sub-divisions, *Rang* and *Grad*, are made in accordance with the relative amounts of the bases occurring in the predominant or subordinate group of minerals. Provision is made for more minute classification by the use of *sub-classes*, sub-orders, etc.

The proposed scheme, though somewhat involved, may be characterized as a vast improvement on the present systems, or rather *lack* of system, in that each rock name has a definite quantitative meaning and expresses one or more important ratios between the various constituents.

On the other hand, there are a number of considerations which render doubtful the desirability of adopting the new classification. For instance, the micas, aluminous pyroxenes and aluminous hornblendes, which are so important as components of rocks, find no place among the "standard minerals" on account of the difficulty of formulating rules for their computation. Again, the decision as to whether a given mineral should be classed with quartz and feldspar or with the ferro-magnesian silicates must often be entirely arbitrary. For example, rutile (TiO_2), is placed in the latter group. Finally, since the proposed names of rock types express only the chemical composition, or, rather only certain chemical ratios which can be computed from the chemical composition, it is questionable whether such a complicated system and nomenclature will be found as serviceable as some simpler method. The reviewer has found very satisfactory a plan of indicating the general composition of a magma by a number. Thus the number 5721075, by the convention adopted, indicates by each digit the amount of one constituent. These are arranged in the order of their abundance in the earth's exterior portion. So the above number signifies a magma whose SiO_2 content is graded as 5 on a scale of 0 to 9, that is, between 55 % and 60 %. Grade 7 for Al_2O_3 was placed at 18-20 %. The "2" indicates 2½-4 % of iron oxides, and so on; — 1 to 2 % CaO, less than 1 % MgO, 9 to 11 % Na_2O and 5 to 6.5 % K_2O. Such a number shows at a glance the approximate ratio between the percentages of any two constituents, and can readily be filed on a card with proper reference to the literature.

Returning from this diversion to the book under consideration, it should be stated that the tables for computation and glossary at the end will be found very helpful to any who has occasion to use the new system. *A. C. Gill*

Lois générales de l'Action des Diastases. *By Victor Henri. 16 × 25 cm; pp. xi + 129. Paris: A. Hermann, 1903.* — The author adopts Ostwald's classification of catalytic actions: Catalysis, pure and simple; autocatalysis; catalysis with rapid formation of intermediate substances; catalysis with slow formation of intermediate substances; catalysis of a series of successive reactions. Since each of these cases has its own typical reaction velocity curve, it is comparatively easy to determine the class into which any particular catalytic reaction falls.

The rate of inversion of sugar by invertine is more rapid than it should be if the reaction were a case of catalysis pure and simple. The ferment itself is unchanged at the end of the reaction; but the rate of inversion is decreased by the presence of one of the decomposition products, levulose. The whole course of the reaction can be accounted for on the assumption that invertine forms compounds with sugar and with levulose, there being a reversible equilibrium between the two.

The rate of hydrolysis of salicine by emulsine appears at first to follow a different law because the rate is less than that of a case with catalysis pure and simple. A more careful investigation shows that the reaction is similar in nature to the preceding, the apparent difference being due to the different relative amounts of the two compounds. *Wilder D. Bancroft*

Die chemisch-physikalische Beschaffenheit der Heilquellen. *Vortrag, gehalten auf der 74. Versammlung Deutscher Naturforscher und Aerzte zu Karlsbad. By W. Meyerhoffer. 16 × 24 cm; pp. 32. Hamburg: Leopold Voss, 1902. Price: paper, 1 mark.* — The author explains about ions and osmotic pressure, and points out the arbitrariness of giving analyses in terms of salts instead of ions. If a reference to salts must be made it should be based on the salts which actually crystallize when the solution is evaporated to dryness at some constant temperature.

One of the springs at Gastein is known as the Poison Spring, although nothing poisonous has ever been found in it. The author shows that the conductivity of this water is very low, and he therefore attributes its unpleasant effect to its purity, it producing turgidity of the membranes lining the stomach. For the same reason he deprecates the use of distilled water for drinking purposes. The evil effect of very pure water can hardly be worth considering, however, unless one takes large quantities on an empty stomach.

There is a short discussion on the relative effects of Apollinaris, Vichy, and Hunyadi Janos, based on the freezing-points of these waters and on the nature of the dissolved salts. While interesting enough, it is not clear that we know anything more about these waters than we did before. From the physical-chemical point of view, as expounded by Meyerhoffer, the chief object in drinking Apollinaris is to dilute the wine which has already been drunk.

In the last few pages, the author takes up the question of natural versus artificial mineral waters. He is rather inclined to accept the belief that a natural mineral water is really different from an artificial water having apparently the same composition. He suggests the existence of minute quantities of some catalytic agent as a possible cause of the alleged difference.

Wilder D. Bancroft

Vorlesungen über theoretische und physikalische Chemie. *By J. H. van 't Hoff. Zweite Auflage. Part II: Chemical Statics. 15 × 23 cm; pp.*

xx + 148. Braunschweig: F. Vieweg und Sohn, 1903. — When a play is given for the first time in a German theatre, it is announced as "Zum ersten Mal". The second performance is often announced as "Zum ersten Mal wiederholt". This is a custom which might well be adopted in some cases by publishers. In this new edition of van 't Hoff's lectures, about two and one-half pages have been added and one page has been cut out. The new matter deals with the experiments of Bruni and Adriani, p. 106; of Keiser, p. 115; of Pope and Peachy, p. 117; of Wedekind, p. 118; of Pope, p. 119; of Rinne, p. 141. A reference to Schiff's work, p. 122, has been omitted. If there are other changes, they have escaped the notice of the reviewer. *Wilder D. Bancroft*

Zur Verwertung speziell der Wiedergewinnung des Zinns von Weissblechabfällen. *By Hans Menicke. (Sammlung Chemischer und chemisch-technischer Vorträge. VII. Band. 11. Heft.) 16 × 25 cm; pp. 377 to 444. Stuttgart: Ferdinand Enke, 1902. Price: paper, 1.20 marks.* — A discussion of the electrolytic methods of recovering tin from tin scrap. The general conclusion is that caustic soda is the only electrolyte which can be used with profit, and that the addition of any chloride to it is a mistake. There seems to be no reason to believe that any process using an acid solution will be a success. For professional reasons, practically no actual data are given and the monograph is valuable because it calls attention to many of the experimental difficulties and not because it tells how to avoid them. The author maintains that much of the commercial tin runs as low as 95-98 pct Sn and that it is therefore unreasonable to discriminate against electrolytic tin because it does not reach a standard of 99.8 percent pure. He thinks that 98.5 percent Sn would not be an unreasonable standard, especially when the tin is to be used in an alloy.

Wilder D. Bancroft

Elektromagnetische Aufbereitung. *By F. Langguth. (Handbuch der Elektrochemie.) 17 × 26 cm; pp. 64. Halle: Wilhelm Knapp, 1903. Price: paper, 3 marks.* — The author discusses the development and importance of electromagnetic concentration, the principles involved, the machinery in use, and the efficiency thereof. The work is really of more interest to the engineer than to the chemist. *Wilder D. Bancroft*

Einführung in die Elektrochemie. *Nach der elektrolytischen Dissociationstheorie. By Peter Gerdes. 14 × 21 cm; pp. viii + 123. Halle: Wilhelm Knapp, 1902. Price: paper, 4 marks.* — The author discusses chemical units, arrangement of cells, osmotic pressure, electrolysis, polarization, the properties of acids and bases, primary batteries, storage cells, thermopiles and dynamos, Faraday's law, electrolytic refining, and electroplating within the space of somewhat more than one hundred small pages. The treatment is therefore necessarily superficial and is often inaccurate. Two instances will suffice to illustrate this: the decomposition voltage for water is not two volts and that is no evidence that zinc is diatomic. The arrangement of the material is very bad, voltameters being discussed on p. 59 and Faraday's law on p. 104. The book cannot be recommended to anybody. *Wilder D. Bancroft*

Chemisches praktikum. *By A. Wolfrum. I. Teil: Analytische Uebungen. 12 × 19 cm; pp. 562 + xvii. Leipzig: Wilhelm Engelmann, 1902. Price: bound, 10 marks.* — The object of the book is to prepare students for technical work by giving them practice in the kinds of analysis and preparation work which they are likely to meet later in life. The first part of the book deals with qualitative analysis, including qualitative organic analysis; the second part with quantitative analysis, including gas analysis and toxicology; the third part with technical analysis. Under technical analysis come water, fuels, ores, heavy chemicals, raw materials and mineral colors, fertilizers, clays and cement, sugar, fats, oils, and aniline products. *Wilder D. Bancroft*

Kalender für Elektrochemiker sowie technische Chemiker und Physiker, *für das Jahr 1903. VII. Jahrgang. Mit einer Beilage. By A. Neuburger. 10 × 15 cm; pp. xxxi + 583. Berlin: M. Krayn. Price: bound, 4 marks.*— This little book contains a large number of useful tables and should prove valuable as a pocket reference. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

On the phase rule. *R. Wegscheider. Zeit. phys. Chem.* 43, *93* (*1903*). — The author discusses the appearance of the two forms of sodium chlorate from solution and defines them as thermodynamically identical phases. A simpler way of putting it is that the equilibrium depends on the pressure, temperature, and concentrations. If two forms are identical in respect to these conditions, they will be stable simultaneously. The two forms of the sodium chlorate do not exist in solution. The author calls attention to the statement by Gibbs that stable equilibrium with $n + 3$ phases is improbable. Under certain conditions which are apparently fulfilled with sodium chlorate such a state of things is possible. *W. D. B.*

On the conception of independent components. *R. Wegscheider. Zeit. phys. Chem.* 43, *89* (*1903*). — The author objects to all the customary definitions of independent components and then gives a definition which implies that one can name the independent components in all cases, whereas one can tell the number from the experiments while the actual selection of the components is not always possible. The author states that his definition does away with some limitations of the phase rule noted by Roozeboom. What Roozeboom actually said was that the number of components varies if we introduce certain limitations, which is an entirely different thing. *W. D. B.*

On the proof of the phase rule. *W. Nernst. Zeit. phys. Chem.* 43, *113* (*1903*). — A reply to Wegscheider's article on independent components (preceding review). *W. D. B.*

The absolute zero of the centigrade thermometer. *J. A. Groshans. Zeit. phys. Chem.* 42, *626* (*1903*). — The author outlines a method for calculating the absolute zero from the relations between the boiling-points or freezing-points of compounds and the absolute temperature. *W. D. B.*

Investigations on the formation of organic sulphur compounds. *M. Berthelot. Ann. Chim. Phys.* (*7*) 22, *322* (*1901*). — Reviewed (5, 406) from Comptes rendus, 132, 55 (1901).

New investigations on the isomerism of sulphocyanic ethers. *M. Berthelot. Ann. Chim. Phys.* (*7*) 22, *327* (*1901*). — Reviewed (5, 406) from Comptes rendus, 132, 57 (1901).

The formation of hydrocarbons from the metallic carbides. *M. Berthelot.*

Ann. Chim. Phys. (7) 22, *464* (*1901*). — A discussion of the heat effects when different carbides are acted on by water and dilute acids. *W. D. B.*

Description of a new oxy-hydrogen furnace. *H. Moissan. Ann. Chim. Phys.* (7) 24, *289* (*1901*). — The author has used a furnace in which a carbon crucible is set in a lime case and heated with an oxy-hydrogen flame. A temperature of 1800° can be reached. It is absolutely essential that there shall be no iron in the line and that the flame shall not come in direct contact with the carbon crucible. *W. D. B.*

One-Component Systems

Determination of the boiling-points of copper and of zinc. *C. Féry. Ann. Chim. Phys.* (7) 28, *428* (*1903*). — Zinc and copper were distilled in the electric furnace and the temperatures determined by means of the optical pyrometer. The apparent boiling-point of zinc is 1040° and of copper 2100°. Owing to superheating, the value for zinc is about 100° too high. When brass is distilled, the zinc volatilizes almost immediately, leaving practically pure copper behind. *W. D. B.*

The boiling-point of liquid hydrogen determined by hydrogen and helium gas thermometers. *J. Dewar. Ann. Chim. Phys.* (7) 23, *417* (*1901*). — Reviewed (6, 431) from Am. Jour. Sci (4) 11, 290 (1901).

Study of the hydrides of the metalloids of the second group. *R. de Forcrand and Fonzes-Diacon. Ann. Chim. Phys.* (7) 26, *247* (*1902*). — Reviewed (6, 347) from Comptes rendus, 134, 171, 229, 281 (1902).

Study of the heats of vaporization of aniline, orthotoluidine and other organic substances. *W. Louguinine. Ann. Chim. Phys.* (7) 27, *105* (*1902*). — The author has determined, for a number of substances, the specific heats, the variation of the boiling-points with the pressure, the heats of vaporization, and the vapor-densities. From an application of Trouton's law it appears that aniline, monomethyl aniline, dimethyl aniline, orthotoluidine, and dimethyl orthotoluidine are not polymerized as liquids. Dichloracetic and propionic acids are polymerized to some extent as vapors.

The author deprecates Kahlenberg's use (5, 225) of the Regnault-Pfaundler formula, believing it to be inapplicable. *W. D. B.*

Correction of the values for the specific heats and heats of vaporization of some high-boiling organic compounds. *W. Louginine. Ann. Chim. Phys.* (7) 26, *228* (*1902*). — The author finds that the use of a zinc chloride bath for heating substances preliminary to putting them in the calorimeter has introduced a source of error into his own measurements and those of Reuss. He has now perfected his movable stove so that he can work at higher temperatures than before and has redetermined some of his data for the higher boiling organic compounds. *W. D. B.*

On the heat of vaporization of mercury. *W. Kurbatoff. Zeit. phys. Chem.* 43, *104* (*1903*). — The author finds 67.8 cal for the heat of vaporization of mercury as against 62 cal found by Person. This makes the Trouton constant 21.5.

The vapor density at the boiling-point corresponds to a molecular weight of 200.6. *W. D. B.*

Relation between molecular heat of fusion and boiling-point. *R. de Forcrand. Ann. Chim. Phys.* (7) 28, *384, 531* (*1903*). — Reviewed (5, 407; 6, 348) from Comptes rendus, 132, 879 (1901); 134, 708, 743, 768 (1902).

Red and yellow mercuric oxides and the mercuric oxychlorides. *E. P. Schoch. Am. Chem. Jour.* 29, *319* (*1903*). — The oxides of mercury were made by the various methods and the differences between the two forms examined especially in regard to the vapor pressure, density and crystal form. The writer disagrees with other workers in refusing to accept the color of the masses as a criterion of the degree of change. Of the oxy compounds the trimercurdioxychloride, the tetramercurtrioxychloride, and the pentamercurtetroxychloride each had three isomeric forms; the conditions for obtaining the interconversion of the forms are not given.

The attempt to produce definite compounds by fusion of the oxide and the chloride resulted in failure since an absolutely accurate method of identifying the solid phase was lacking. *H. R. C.*

Allotropic forms of silver. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *307* (*1901*). — Reviewed (5, 409) from Comptes rendus, 132, 234 (1901).

Determination of the specific heats of tungsten and molybdenum. *E. Defacqz and M. Guichard. Ann. Chim. Phys.* (7) 24, *139* (*1901*). — Between 93° and 444° the specific heat of molybdenum is practically constant, the value being 0.072. The specific heat of tungsten on the other hand is 0.0340 at 93°, 0.0366 at 258°, and 0.0375 at 423°. It should be noted that the specific heat of molybdenum varies in different experiments from 0.070 to 0.076, but the variation is irregular. *W. D. B.*

On Boyle's law at very low pressures. *A. Battelli. Ann. Chim. Phys.* (7) 25, *365* (*1902*). — Reviewed (5, 320) from Nuovo Cimento (5) 1, 5 (1901).

Experiments to determine the limits of olfactory sensitiveness. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *460* (*1901*). — Experiments showed that the odor of iodoform could be detected with 1×10^{-8} milligrams in 40 cc of air. When only one cubic centimeter of this mixture was taken, no odor could be detected. It is believed that musk could be detected at about one-thousandth this concentration. *W. D. B.*

Experimental study of the propagation of heat by convection in a cylinder of water with a vertical axis, heated or cooled from the sides; application to a determination of the maximum density of water and of aqueous solutions. *L. C. de Coppet. Ann. Chim. Phys.* (7) 28, *145* (*1903*). — When water in a vertical copper cylinder is heated or cooled uniformly through the sides of the cylinder only, the water separates into two equal parts in which there are general movements in opposite directions. "One of these parts has the shape of a solid cylinder whose axis is the axis of the copper cylinder. I shall call this the 'internal mass'. The other half of the liquid, the 'external mass', has the form of a hollow cylinder. It fills the space between the internal mass and the walls of the copper cylinder. I have proved that the readings, at any moment are practically the same for thermometers whose bulbs are placed at the same horizontal level in the internal mass and the distance from the axis has no effect. On the other hand, in the external mass, a greater or lesser distance from the metallic walls (the source of heating or cooling) has a marked effect upon the readings of thermometers whose bulbs are at the same horizontal level. But when two thermometers are placed at the same level in the external mass and exactly the same distance from the walls, the readings at any moment will be the same, provided, of course, that the copper vessel is a true cylinder, and that the thermometers themselves are alike."

The temperature of the maximum density of pure water, under a pressure of one atmosphere, as found by the author's method is 3.98° on the hydrogen thermometer, or 4.005° on the mercury thermometer. While this value may not be exact, it is as accurate as it can be made by any method of measurement now known. *W. D. B.*

Study of the fluorides and oxyfluorides of sulphur. *H. Moissan and P. Lebeau. Ann. Chim. Phys.* (7) **26**, *145* (*1902*).—The authors have prepared, and studied the compounds, SF_6, SO_2F_2, and SOF_2, all of which are fairly stable. *W. D. B.*

Study of a new silicon hydride. *H. Moissan and S. Smiles. Ann. Chim. Phys.* (7) **27**, *5* (*1902*).—Reviewed (**6**, 347) from Comptes rendus, **134**, 569 (1902).

The arsenides of the alkaline earths. *P. Lebeau. Ann. Chim. Phys.* (7) **25**, *470* (*1902*).—Reviewed (**4**, 405) from Comptes rendus, **129**, 47 (1899).

Some properties of fused lime. *H. Moissan. Ann. Chim. Phys.* (7) **26**, *280* (*1902*).—Reviewed (**6**, 350) from Comptes rendus, **134**, 136 (1902).

Two-Component Systems

Compounds of the lithium halides with ammonia. *J. Bonnefoi. Ann. Chim. Phys.* (7) **23**, *317* (*1901*).—A study of the dissociation pressures of the compounds of the lithium halides with ammonia and with substituted ammonias. The guiding principle was the application of Clapeyron's law. In the course of the work the author has determined a number of thermochemical data for the substituted ammonias. *W. D. B.*

Note on the application of the phase rule to the fusing-point of copper, silver, and gold. *T. W. Richards. Zeit. phys. Chem.* **42**, *617* (*1903*).—Reviewed (**6**, 432) from Am. Jour. Sci. (4) **13**, 377 (1902).

On the connection between constitution and cryoscopic behavior of solvents. *K. Auwers. Zeit. phys. Chem.* **42**, *513* (*1903*).—The author has studied the effect of substituting different groups in toluene. If we arrange these groups in the following order,

CH_3, Cl, Br, I, NO_2, CO_2R, CN, CHO, NH_2, CO_2H, OH,

we find that each succeeding group increases the abnormal behavior of the solute and decreases the abnormal behavior of the solvent. *W. D. B.*

Cryoscopic notes. *K. Auwers. Zeit. phys. Chem.* 42, *629* (*1903*). — Experiments on the α- and β-naphthols dissolved in *p*-dibrombenzene showed that a nitrogroup in the ortho position has practically no effect while a nitro group in the para position increases the abnormality. It was found impossible to get satisfactory results with *p*-azoxyanisol as solvent.

W. D. B.

On saponine froth. *J. v. Zawidski. Zeit. phys. Chem.* 42, *612* (*1903*). — By means of an optical analysis, the author shows that there is more saponine in the froth than in the solution, a result which is in accord with what is to be expected from the surface tension relations, saponine lowering the surface tension of water.

W. D. B.

On the solution of solid metals in mercury and other melted metals. *M. Berthelot. Ann. Chim. Phys.* (*7*) 22, *320* (*1901*). — The author believes that the action of mercury on metals is not to form a solution but something more nearly corresponding to an emulsion.

W. D. B.

Studies on chemical equilibria. *O. Boudouard. Ann. Chim. Phys.* (*7*) 24, *5* (*1901*). — Reviewed (4, 224, 230, 409) from Comptes rendus, 128, 98, 307, 822, 824, 1522, 1524 (1899); 130, 132 (1900).

Silver and hydrogen. *M. Berthelot. Ann. Chim. Phys.* (*7*) 22, *305* (*1901*). — When silver and hydrogen are heated together at 500°, there is a slight disintegration of silver. When sodium bicarbonate is heated in a silver crucible to a temperature below 800°, an alloy of silver and sodium is formed.

W. D. B.

Combination of silver with oxygen. *M. Berthelot. Ann. Chim. Phys.* (*7*) 22, *289* (*1901*). — When silver is heated with oxygen at about 500°, there is marked disintegration of the silver and some suboxide is formed. When silver is heated to 500° in an atmosphere of nitrogen, water vapor, or carbon dioxide, there is no visible change. The reaction between silver and oxygen is not to be detected at 100° ; but was observed at 200° after forty-four hours.

W. D. B.

Boiling-point determinations with volatile solutes. *G. Oddo. Gazz. chim. Ital.* 32, *II.*, *97*, *107*, *123*, *494* (*1902*). — A polemic against Ciamician.

W. D. B.

On the depolymerization of some inorganic oxychlorides. *G. Ciamician. Gazz. chim. Ital.* 32, *II.*, *369* (*1902*). — A polemic against Oddo. *W. D. B.*

On the maximum density of aqueous solutions of some organic compounds. *W. Müller. Zeit. phys. Chem.* 43, *109* (*1903*). — The experiments were made with de Coppet's apparatus and led to the following conclusions : —

1. The molecular lowering of the temperature of the maximum density of water is very different for organic substances of different constitution.

2. The lowering of the temperature of the maximum density is approximately proportional, except in the case of alcohol, to the concentration, just as it is with inorganic substances. The increase of the molecular lowering with increasing concentration is too marked in many cases to be due to experimental error and is probably due to a partial association between solvent and solute.

3. The change in the position of the maximum density caused by dissolving an organic substance is not a function solely of the molecular weight of the solute.

4. The chemical constitution of the organic solute has a marked effect.

5. The molecular lowering increases with increasing number of hydroxyl groups in the solute.

6. The three dioxy-benzenes have practically the same effect in dilute solution, though not in concentrated solution. The conclusion to be drawn from this is that isomers have the same effect provided there is no polymerization.

W. D. B.

Study of some salts of uranium. *Oechsner de Coninck. Ann. Chim. Phys.* (7) 28, *5* (*1903*). — Reviewed (5, 412) from Comptes rendus, 132, 90, 204 (1901).

The form of the actual isotherms in gas mixtures. *F. Caubet. Zeit. phys. Chem.* 43, *115* (*1903*). — Kuenen (6, 435) had criticized two isotherms found by Caubet (6, 278), saying that they were theoretically impossible. Caubet finds that, owing to a misprint, these isotherms were drawn improperly and that the actual isotherms are in agreement with Kuenen's conclusions. *W. D. B.*

The compounds of silver with mercury. *M. Berthelot. Ann. Chim. Phys.* (7) 317, (*1901*). — Reviewed (5, 412) from Comptes rendus, 132, 241 (1901).

Investigations on calcium silicide. *H. Moissan and W. Dilthey. Ann. Chim. Phys.* (7) 26, *289* (*1902*). — Reviewed (6, 353) from Comptes rendus, 134, 503 (1902).

Preparation and properties of potassium and sodium hydrides. *H. Moissan. Ann. Chim. Phys.* (7) 27, *339* (*1902*). — Reviewed (6, 352) from Comptes rendus, 134, 18, 71 (1902).

On the state of silicon in cast iron. *P. Lebeau. Ann. Chim. Phys.* (7) 26, *5* (*1902*). — Reviewed (6, 351) from Comptes rendus, 133, 1008 (1901).

On the silicides of cobalt. *P. Lebeau. Ann. Chim. Phys.* (7) 27, *271* (*1902*). — Reviewed (7, 139) from Comptes rendus, 135, 475 (1902).

The silicides of vanadium. *H. Moissan and Holt. Ann. Chim. Phys.* (7) 27, *277* (*1902*). — Reviewed (7, 139) from Comptes rendus, 135, 78, 493 (1902).

On the heat of combustion of aluminum. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *479* (*1901*). — When mixed with aluminum carbide it was found possible to burn aluminum completely. The heat of formation of Al_2O_3 is 380.2 cal.

W. D. B.

Multi-Component Systems

On the maxima and minima in the decomposition curves for hydrated mix-crystals. *R. Hollman. Zeit. phys. Chem.* 42, *597* (*1903*). — The author eliminates one case from his previous paper (6, 503), of a maximum or minimum with the ratio of the salts the same in the mix-crystals but different in the solutions. When all three ratios are different, a maximum or minimum is still possible, and an instance of this is to be found in the system, manganese sulphate, copper sulphate, and water, studied by Stortenbeker. *W. D. B.*

Action of hydrides on sulphides and selenides. *H. Pélabon. Ann. Chim. Phys.* (7) 25, *365* (*1902*). — Reviewed (4, 410; 5, 149, 203, 412, 413; 6, 200) from Comptes rendus, 130, 576, 911; 131, 416 (1900); 132, 78, 774, 1411 (1901)

On changes of solubility caused by inorganic salts. *W. Biltz. Zeit. phys. Chem.* 43, *41* (*1903*). — The solubility of phenyl sulphocyanate in water is decreased by sodium perchlorate, sodium chlorate, potassium bromide, potassium chloride, and sodium chloride in that order, sodium chloride having the greatest effect. Sodium iodide and potassium iodide increase the solubility.

W. D. B.

On the solubility of silver chloride in presence of mercury salts. *B. Finzi. Gazz. chim. Ital.* 32, *II.*, *324* (*1902*). — The author gives figures illustrating the solubility of silver chloride in solutions of mercuric salts. *W. D. B.*

On the conditions for forming orthoclase and albite. *E. Bauer. Zeit. phys. Chem.* 42, *567* (*1903*). — The preparation of quartz or feldspar from anhydrous melts is impossible because a vitreous mass is obtained instead of a crystalline one. From aqueous solutions it is possible to obtain quartz, orthoclase, and albite. The author discusses the question of fields and then describes the results of some experiments made under pressure at 520°. After this comes a statement of the relative stability of quartz and orthoclase depending on the conditions of crystallization. There can be no question but that an application of the phase rule to geological problems is bound to lead to important results.

W. D. B.

On the solubility of sodium acetate in aqueous alcohol. *G. Schiavon. Gazz. chim. Ital.* 32, *II.*, *532* (*1902*). — Some experiments showing the solubility of sodium acetate in aqueous alcohol at different concentrations and in pure water.

W. D. B.

On the existence of colloidal tungstic acid. *N. Pappadà. Gazz. chim. Ital.* 32, *II.*, *22* (*1902*). — Tungstic acid dissolves in sodium tungstate solution as a colloid. *W. D. B.*

Studies on zinc oxide. *R. de Forcrand. Ann. Chim. Phys.* (7) 27, *26* (*1902*). — Reviewed (6, 356; 7, 139, 141) from Comptes rendus, 134, 601; 135, 36, 133 (1902).

Silver and carbon monoxide. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *300* (*1901*). — When silver and carbon monoxide are heated together at about 500°, there is disintegration of the silver and precipitation of carbon. The author believes that this carbon is not formed according to the equation

$$2CO = CO_2 + C,$$

but that there is an intermediate formation of a gaseous suboxide according to the equation

$$3CO = C_2O + CO_2.$$

W. D. B.

Action of different metals on carbon monoxide. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *303* (*1901*). — Different metals were heated with carbon monoxide in sealed tubes at 550° for several hours. With mercury, tin, aluminum, cobalt, antimony, selenium, and tellurium, carbon dioxide is formed and no free carbon. With lead, copper, zinc, cadmium, iron, and nickel, there is formation both of carbon dioxide and of free carbon. *W. D. B.*

On the action of cuprous salts on hydrocarbons and carbon monoxide. *M. Berthelot. Ann. Chim. Phys.* (7) 23, *32* (*1901*).—The absorption of carbon monoxide, acetylene, and ethylene by acid cuprous chloride solution is not complete and varies with the temperature and pressure. The absorption of propylene and trimethylene appears not to be reversible, other compounds being formed. Cuprous chloride changes trimethylene into propylene. *W. D. B.*

On the theory of the action of the halogens on alkalies. *F. Foerster and E. Müller. Zeit. Elektrochemie,* 8, *921* (*1902*).—The authors discuss the mass law relations on the assumptions that chlorine acts on water to form hypochlorous acid and that chlorate, except in alkaline or hot solutions, is formed by the action of hypochlorous acid on hypochlorite. It is shown that even with our present unsatisfactory knowledge of the equilibrium constants, there are a number of interesting and apparently contradictory data which can easily be explained. *W. D. B.*

The action of iodine on alkalies. *F. Foerster and K. Gyr. Zeit. Elektrochemie,* 9, *1* (*1903*).—When iodine is added to an alkaline solution, there is first a reversible formation of hypo-iodic acid. In presence of an excess of alkali, hypo-iodite is formed, though there is always some free hypo-iodic acid due to hydrolysis. Hypo-iodic acid and hypo-iodite react to form iodate and iodide, the reaction being analogous to, but more rapid than, the corresponding one of the formation of chlorate. When neutral oxidizing agents act upon potassium iodide solutions, there are always formed iodine, alkali, and hypo-iodic acid. *W. D. B.*

Action of a metallic oxide or hydroxide on solutions of salts of other metals. *A. Mailhe. Ann. Chim. Phys.* (7) 27, *362* (*1902*).—Reviewed (6, 357) from Comptes rendus, 133, 226 (1901); 134, 42, 233 (1902).

Chemical equilibria. *M. Berthelot. Ann. Chim. Phys.* (7) 25, *145, 153, 164, 176* (*1902*).—Reviewed (6, 201, 356) from Comptes rendus, 132, 1277, 1449, 1517; 133, 5 (1901).

Studies on the dissociation of salts of the heavy metals. *H. Ley and K. Schaefer. Zeit. phys. Chem.* 42, *690* (*1903*).—A study of nitrogen salts of mercury, especially the succinimide, with reference to acids and mercury salts of inorganic acids. Mercury cyanide differs radically in its behavior from the imides, and the authors conclude that the mercury is attached to carbon and not to nitrogen. *W. D. B.*

The equilibrium $CO_2 + H_2 = CO + H_2O$. *O. Hahn. Zeit. phys. Chem.* 42, *705* (*1903*).—A preliminary report on the behavior of water gas. Using platinum as a catalytic agent, the author has determined the equilibrium at temperatures between 700° and 1400°. The displacement of the equilibrium with the temperature is given by van 't Hoff's formula very satisfactorily between 786° and 1086°. At 1200° and 1400° there is no agreement between the values calculated and those found. The reason for this is not yet clear. Quartz vessels are attacked by water gas at the higher temperatures. *W. D. B.*

Investigations on the action of hydrogen peroxide on silver oxide. *M. Berthelot. Ann. Chim. Phys.* (7) 23, *52* (*1901*). — Reviewed (5, 413) from Comptes rendus, 132, 897 (1901).

New series of experiments on the action of hydrogen peroxide on silver peroxide. *M. Berthelot. Ann. Chim. Phys.* (7) 24, *78* (*1902*). — Reviewed (6, 356) from Comptes rendus, 133, 555 (1901).

The reduction with calcium carbide. *B. Neumann. Zeit. Elektrochemie*, 8, *939* (*1902*). — A reply to v. Kügelgen (7, 141). *W. D. B.*

On the slow alteration of copper alloys in contact with air and alkali chlorides. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *457* (*1901*). — A piece of brass was left in a bottle containing a sodium chloride solution for two years. At the end of that time, the zinc was entirely dissolved and the copper had been changed very largely into cuprous oxide. *W. D. B.*

Distinction between physical and chemical supersaturation with gases. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *433* (*1901*). — Hydrogen peroxide acts on a permanganate solution, decolorizing it and setting free oxygen. By careful manipulation, it is possible to avoid the evolution of oxygen. The question arose whether there was a supersaturated solution of oxygen formed or an instable compound. Since oxygen dissolves with an evolution of heat, and the evolution of oxygen from this solution is accompanied by an evolution of heat, some compound must have been formed which decomposed readily. Since the experiment was made with a solution containing a slight excess of permanganate, the evolution of heat could not have been due to hydrogen peroxide. *W. D. B.*

On the heat evolved in the action of free oxygen on potassium pyrogallate. *M. Berthelot. Ann. Chim. Phys.* (7) 25, *75* (*1902*). — The heat of reaction, referred to 16 g of oxygen is about 60.2 cal; but varies with the amount of oxygen already absorbed. The development of heat is gradual and not instantaneous. *W. D. B.*

Osmotic Pressure and Diffusion

On the osmotic pressure of a solution with a distinctly variable density. *M. Planck. Zeit. phys. Chem.* 42, *584* (*1903*). — For the osmotic pressure of a solution when the solvent is under the pressure of its saturated vapor, the author deduces the formula

$$s dp_c = v_1 d\pi + dc \int_{p_c}^{p_0 + \pi} \frac{\partial v}{\partial c} dp.$$

In this equation p_0 is the vapor pressure of the pure solvent, p_1 is the pressure on the solution, and $p_1 - p_0 = \pi$ the osmotic pressure. The concentration is represented by c; s is the change in volume when 1 g solvent is distilled from a large quantity of solution of the concentration c at constant temperature under the constant vapor pressure p_c of the solution. *W. D. B.*

Studies on diffusion. *J. Thovert. Ann. Chim. Phys.* (7) 26, *366* (*1902*). — Reviewed (6, 506) from Comptes rendus, 134, 826 (1902).

Velocities

On the change of the rate of crystallization with the temperature for substances having a low rate of crystallization. *W. Borodowsky. Zeit. phys. Chem.* 43, *75* (*1903*). — The author draws the following conclusions: —

1. The curve for the change of the rate of crystallization with the temperature has a maximum for substances having a low rate of crystallization: to 15°-20° below the melting-point, the rate of crystallization increases approximately proportionally to the supercooling, passing through a maximum and then falling off.

2. This maximum occurs at about 15°-20° supercooling when the rate of crystallization is measured in tubes of about the same diameter. Modification 1 of salipyrin is an exception to this rule.

3. Direct observation of the crystallization and of the form of the meniscus shows that a portion of the supercooled melt remains as such between the crystals before the maximum rate of crystallization is reached. After this maximum is reached, the melt crystallizes practically completely.

4. Impurities decrease the rate of crystallization, the effect being more marked on the ascending than on the descending portion of the curve.

5. Decreasing the radius of the tube decreases the effect of the heat of fusion on the rate of crystallization and displaces the maximum rate towards higher temperatures.

6. If the heat of fusion could be withdrawn instantaneously and isothermally from the melt, the rate of crystallization would decrease linearly with falling temperature. *W. D. B.*

Reaction between phosphorous acid and mercuric chloride. *C. Montemartini and U. Egidi. Gazz. chim. Ital.* 32, *II.*, *182* (*1902*). — The authors have studied the rate at which mercuric chloride reacts with phosphorous acid according to the equation,

$$2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + 2HCl + H_3PO_4.$$

When the initial molecular ratio of mercuric chloride to phosphorous acid is two, and when there is present an excess of mercurous chloride, the reaction is thought to be of the third order. The evidence for this conclusion is not overwhelming. *W. D. B.*

A periodic contact catalysis. *G. Bredig and J. Weinmayr. Zeit. phys. Chem.* 42, *601* (*1903*). — When a 10-11 pct solution of hydrogen peroxide is placed over a mercury surface, the latter becomes covered with a shining bronze-colored film and there is an evolution of oxygen gas which ceases periodically, there being 1-20 periods per minute, depending on the conditions. Traces of electrolytes have a very disturbing effect on the phenomenon, as do ether and olive oil, while alcohol does not prevent it. Electrical measurements against the calomel electrode showed an electromotive force of ca. 0.254 volt when the mercury was catalytically active and of ca. 0.322 volt when the mercury was catalytically inactive, the hydrogen peroxide electrode being cathode in both cases. *W. D. B.*

Electromotive Forces

On the passivity of iron and on periodic phenomena with iron electrodes. *C.*

Fredenhagen. Zeit. phys. Chem. 43, *1* (*1903*). — If passive iron is a metallic modification, it should be formed at a definite potential which would be independent of the nature of the electrolyte. The formation of an oxide should depend on the concentration of the oxygen set free at the electrode. Neither of these conditions is satisfied experimentally. The author shows that all the phenomena connected with passive iron can be accounted for satisfactorily on the assumption of a surface layer of oxygen. In sulphate solutions, the passivity disappears very rapidly. In nitric acid, there is a greater tendency to form an oxide film and this complicates matters to some extent. In concentrated alkaline cyanide solutions iron also becomes passive, but not in dilute or acid solutions.

The author also discusses the periodic phenomena which have been observed for instance with iron and silver in nitric acid. *W. D. B.*

Comment on the paper of Mr. H. C. Bijl on cadmium cells. *W. Jaeger. Zeit. phys. Chem.* 42, *632* (*1903*). — The author supplements Bijl's paper (7, 224) by stating that experiments at the Reichsanstalt have shown the reliability of Weston cells with a 12-13 percent cadmium amalgam. *W. D. B.*

Electrochemical relations of allotropic states. *M. Berthelot. Ann. Chim. Phys.* (7) 23, *49* (*1901*). — Reviewed (5, 418) from Comptes rendus, 132, 732 (1901).

Studies of cells with two salt solutions. *M. Berthelot. Ann. Chim Phys.* (7) 27, *145*, *158*, *192*, *208*, *219*, *260*, *289*, *328* (*1902*). — Reviewed (6, 360, 441; 7, 143) from Comptes rendus, 134, 793, 835, 873; 933, 1009; 135, 5, 129, 485 (1902).

Thermo-electromotive forces. *A. Abt. Ann. Chim. Phys.* (7) 22, *145* (*1901*). — Reviewed (5, 620) from Drude's Ann, 2, 266 (1900).

The measurement of potential differences by means of the telephone. *F. Fischer. Zeit. Electrochemie*, 9, *18* (*1903*). — The author hopes to see the telephone become "the universal instrument for making all electrical measurements needed in electrochemical work." In this paper he describes the measurement of potential differences. The essential feature of the arrangement is the varying the sensitiveness of the telephone by varying the resistance in series with it. *W. D. B.*

On the conditions for chemical activity with the silent discharge. *M. Berthelot. Ann. Chim. Phys.* (7) 22, *445* (*1901*). — Ozone requires a very low potential for its formation, the formation of nitric acid a higher potential, and the reaction between hydrogen and oxygen a still higher one. The author discusses the fall of potential in the air under ordinary circumstances and shows how the silent discharge due to this has a marked effect on the growth of vegetation. This is all preliminary to the conclusion that there will be a difference of potential and a silent discharge between two adjacent masses of gas, provided they are at very different temperatures. The author then concludes that the phenomena of the hot-cold tube are due to the silent discharge and not to an alleged displacement of equilibrium. *W. D. B.*

Practical method for electrical analysis of gases. *M. Berthelot. Ann. Chim. Phys.* (7) 23, *433* (*1901*).—A description of methods for recognizing gases, depending on their behavior when exposed to the spark discharge.

W. D. B.

On the modification of metallic surfaces by light. *H. Buisson. Ann. Chim. Phys.* (7) 24, *320* (*1901*).—Reviewed (5, 418) from Comptes rendus, 130, 1298 (1900).

Electrolysis and Electrolytic Dissociation

On the electrolysis of formic acid, oxalic acid, and potassium carbonate. *F. Salzer. Zeit. Elektrochemie*, 8, *893* (*1902*).—When formic acid in sulphuric acid solution is electrolyzed between platinized electrodes, the potential difference starts low and rises steadily. With a smooth anode, the potential difference starts over 0.6 volt higher and gradually decreases with the time, approaching as lower limit the value towards which the platinized electrodes were tending as upper limit. In a solution containing no sulphuric acid there was a continuous rise of potential with a smooth anode, but the increase is not as great as would be caused by the change in resistance of the solution, so the anode potential must have fallen. In alkaline formate solution there is a steady rise of potential and a steady decrease in percentage oxidation, this decrease being greater with the smooth anode than with the platinized.

When oxalic acid is electrolyzed in sulphuric acid solution, the potential remains fairly constant if the current density is low. If the current density be 2 amp/qdm, there comes a point when the potential rises suddenly, then becoming approximately constant at the new level. At this point the percentage oxidation falls off from nearly 100 pct to just over 10 pct.

Experiments on the electrolysis of potassium carbonate showed that percarbonate was formed most readily in neutral solutions, an excess of alkali or of carbonic acid being detrimental. Platinizing the anode also has a bad effect. When potassium bicarbonate is electrolyzed between smooth electrodes, the voltage drops steadily from 3.5 V at the end of the first half hour to 3.12 V at the end of eight and one-half hours. Most of the percarbonate experiments were made with an anode density of 3.6 amp/qdm. *W. D. B.*

Another note on eliminating cathodic depolarization by means of potassium chromate. *E. Müller. Zeit. Elektrochemie*, 8, *909* (*1902*).—Measurements on the change of current density with absolute cathode potential for a mixture of potassium iodate and chromate shows that iodate begins to be reduced at about −0.2 V; chromate begins to reduce at +0.2 V, and the diaphragm is formed at +0.4 V. After it is once formed, the diaphragm is effective at lower voltages. It lasts quite a while even when no current is flowing. Periodates destroy the diaphragm. The reduction of chromates with mercury cathode is made possible by the continual breaking up of the diaphragm by the moving surface of the electrode. *W. D. B.*

On the electrolytic analysis of mercury. *F. Glaser. Zeit. Elektrochemie*, 9, *11* (*1903*).—When mercury is precipitated from cyanide solution, the deficit is due chiefly to the platinum cathode dissolving. The solubility of the platinum becomes quite serious as the temperature rises. Potassium or sodium amalgam accelerates the dissolving of the platinum, which takes place with evolution of hydrogen and even when no oxygen is present. Under the same condition, gold and silver are not attacked. *W. D. B.*

On the communication of Mr. Arndt on the preparation of metallic calcium. *W. Borchers and L. Stockem. Zeit. Elektrochemie,* 8, *938* (*1902*). — A reply to Arndt (7, 144). *W. D. B.*

On the electrolysis of fused caustic soda. *M. LeBlanc and J. Brode. Zeit. Elektrochemie,* 8, *939* (*1902*)*;* 9 *230* (*1903*). — Rejoinders to Lorenz (7, 143, and next review). *W. D. B.*

On the electrolysis of fused caustic soda. *R. Lorenz. Zeit. Elektrochemie,* 9, *155, 333* (*1903*). — Rejoinders to Le Blanc and Brode (preceding review).

Saturated gypsum solutions as conductivity standards. *G. A. Hulett. Zeit. phys. Chem.* 42, *577* (*1903*). — In order to avoid the necessity of standardizing flasks, the author recommends the use of a saturated gypsum solution as a normal for conductivity determinations. To avoid the effect due to the size of the solid particles, solutions should be made from large clear crystals. Data are given for the conductivity of these solutions for every degree from 10°–30°. Measurements are also given for the change of the conductivity with the concentration at 18° and 25°. Attention is called to the fact, so often overlooked, that the apparent conductivity varies with varying position of the electrodes in the glass vessels.

Starting with a copper retort holding 60 liters and with a tin condenser, the author has been able to get 40 liters of water having a conductivity not exceeding 10^{-6}. *W. D. B.*

On the variation of the electrolytic conductivity with the temperature below 0°. *J. Kunz. Zeit. phys. Chem.* 42, *591* (*1903*). — Unsuccessful attempts were made at measuring the conductivity of supercooled solutions, and the author therefore studied the conductivity of sulphuric acid solutions below 0°. By extrapolation from Déguisne's results, Kohlrausch obtained the apparent result that the conductivity of dilute solutions becomes zero at −39°. The author's experiments make it certain that this is due to extrapolation over too wide a range. He has followed some solutions to −74°. In all cases, the conductivity drops off rapidly at first, and then less rapidly. The author inclines to the view that if the solution did not solidify, the conductivity would become zero at the absolute zero. He shares Kohlrausch's opinion that the temperature variation is due largely to an increased viscosity of the solvent with respect to the ions. *W. D. B.*

On the temperature coefficient of the electrical conductivity in aqueous and organic solutions. *G. Carrara and M. G. Levi. Gazz. chim. Ital.* 32, *II., 36* (*1902*). — Conductivity measurements every degree or oftener have been made from 0° to 10° or 20° with potassium iodide in methyl alcohol, ethyl alcohol, pyridine, formic acid and water; and with potassium chloride, sodium nitrate, cadmium iodide, acetic acid, monochlor acetic acid, and propionic acid in water. With nearly all the aqueous solutions, there is an irregularity in the temperature coefficient at about the temperature of the maximum density of the solution. *W. D. B.*

On the strength of halogen-substituted oxy-benzoic acids with reference to their constitution. *A. Coppadoro. Gazz. chim. Ital.* 32, *I.*, *537* (*1902*). — The author has determined the conductivity and conductivity constant for a number of halogen-substituted oxy-benzoic acids. Measurements were also made with the methyl and ethyl esters of some of these acids; but the platinized platinum electrodes seemed to act on the solutions, possibly causing hydrolysis.

W. D. B.

Spectrophotometric study of some dissolved electrolytes. *P. Vaillant. Ann. Chim. Phys.* (*7*) 28, *213* (*1903*). — Color measurements made with a Gouy spectrophotometer. The following conclusions were drawn:

1. The ion, as defined by conductivity measurements, has a characteristic color, independent of the molecule from which it is formed and of other molecules which may be present.

2. The addition of a colorless electrolyte to a solution containing a colored electrolyte changes the color of the latter by changing its degree of dissociation and of hydration. The two effects are independent, the first depending chiefly on the amount of electrolyte added and very little on its nature, while the second depends largely on the tendency of the second electrolyte to form hydrates.

3. In pure organic solvents, the molecule is in a definite state of hydration, which is usually less than that in aqueous solutions.

The organic solvent has a dehydrating effect on the electrolyte, similar to that of another electrolyte. In a mixture of water and organic solvent, the degree of hydration is determined by the dehydrating power of the solvent and by the ratio of the solubilities of the electrolyte in water and in the organic solvent.

"It is clear that these conclusions apply only to those salts which have been studied. These are too few in number to permit of generalization from the results. These results would not apply to electrolytes which formed definite compounds, that could be isolated, either with the other electrolyte or with the organic solvent.

"It is possible, however, to draw one conclusion from these experiments in regard to the electrolytic dissociation theory. In the first place, when the addition of a colorless substance causes a change of color in the solution, it is not safe to deduce the formation of a compound between that substance and the colored substance in solution. One must first make sure that it is not possible to get the same color by adding a certain amount of water to a solution of the colored substance in an organic solvent.

"Since the electrolytic dissociation and the hydration change independently, the first cannot be a result of a change in the hydration of the molecule, or, in other words, the hydrate theory cannot alone account for the observed facts.

"The green hydrate of copper sulphate has the formula $CuSO_4.H_2O$ and not $CuSO_4.4H_2O$, as has been erroneously assumed. The absorption constant for solutions in methyl alcohol is therefore to be attributed to the dilution of the solutions examined and not to a very slight difference between the blue and the green hydrates." *W. D. B.*

ADHERENCE OF ELECTROLYTIC METAL DEPOSITS

BY C. F. BURGESS AND CARL HAMBUECHEN

A study of the conditions which determine the adherence of one metal electrolytically deposited upon another is an interesting and promising field of research from the scientific standpoint, as well as of importance from the technical standpoint. It is not the purpose of this paper to present instructions as to how adherent deposits may be attained, but rather to call attention to some of the problems which are worthy of scientific investigation and the solution of which will have a bearing upon practical applications.

The value of an electro-deposited metal is determined by its degree of adherence to the surface upon which it is deposited, and upon the physical conditions or structures that the molecules assume during the process of deposition.

The adherence is governed by various factors, some of which are well understood and others of which offer promising lines for research. The metal surface which is to receive the deposit should have, in the greatest degree, that property which Wesley has defined as "next to godliness". The surface should be clean; not only apparently, but actually free from all foreign materials. Surfaces which may pass inspection of the eye, may not meet the tests of the electroplating tank, and appearances alone are here, as in many other cases, frequently deceptive. Everything on the metal surface, whether it be visible oxide, grease and scale, or invisible and transparent layers of oil, hydroxides, or other chemical compounds, and even films of gas, may be considered as dirt in accordance with that definition which defines it as " matter in the wrong place ". The cleaning of the surface is an operation requiring the utmost care of the operator, and the work thereby involved constitutes the largest item of expense in the operation of an electroplating plant.

The scientist may be inclined to regard this problem of cleaning as belonging to the kitchen and work-shop rather than to the scientific laboratory, but further progress, for which there is much room, requires more attention than has previously been given this matter.

The methods of preparing the surface may be, for convenience, divided into the mechanical, physical, chemical and electrolytic methods. The mechanical means include grinding, scouring, and the use of abrasives and sand blast. The physical methods include burning, and dissolving by means of solvents, such as gasoline, alcohol, and the like. The chemical methods make use of the acids, alkalies, cyanides, and various other materials which act chemically upon the materials to be removed, making them soluble or changing the nature of them in such a manner that they may be readily removed by mechanical means.

Disadvantages which are attendant upon chemical methods in common use are due to the deleterious action of the acids upon the metal to be plated, to the penetration of the acid into the pores of the metal with the consequent difficulty of complete removal, and to the liberation of hydrogen and other gases which may be absorbed by the metal. The acid dip which is almost invariably used where steel is to be plated upon, in some instances affects the physical property of the steel to such an extent that certain grades of steel sheet and wire cannot be plated. The finest grades of steel wire are so seriously affected by the chemical treatment, commonly deemed necessary in preparation for plating, that its strength and elasticity are greatly reduced. To just what this "rotting" is due is perhaps not definitely known. It cannot be ascribed entirely to the removal of a thin layer of the surface metal, or to the penetration of the acid into the metal, and the absorption of hydrogen is assumed by some to be the cause of the deterioration.

A simple experiment to show the harmful action of hydrogen may be performed as follows: A piece of flexible steel piano wire is immersed in a dilute solution of sulphuric acid, and after the liberation of hydrogen has proceeded for a few minutes, the steel may be found to have become so brittle that it cannot be bent without breaking, whereas previously, it could have been bent at a sharp angle. If the ends of a piece of steel wire about one foot long, are held in such a position that the wire assumes a semi-circular form, after the liberation of gas has proceeded for a few minutes, the wire will become so brittle that it will snap in two even before any relatively large amount of metal has been removed by the dissolving action of the acid. These experiments show the marked influence of gases which may be absorbed by a metal. Iron, which has absorbed hydrogen, may be restored to its original condition by an annealing process. Experiments which we have performed, show that such iron may be partially annealed electrolytically by using the iron as an anode in a solution from which oxygen is liberated upon it.

Electrolytic methods of preparing the surface consist in the utilization of various phenomena which may take place in the electrolytic cell and, in some cases, with decided advantage over other methods. The oxidation or corroding action at the anode may be utilized in dissolving certain substances from the metal surface constituting the anode without the disadvantage of a simultaneous evolution of hydrogen. The articles to be prepared may also, under other conditions, be used as the cathode, and the reducing action there taking place may be utilized in the reduction of reducible oxides and similar compounds. An investigation which might be of interest would be the determination of what compounds are capable of electrolytic reduction, and the rapidity and efficiency of the operation. The oxides of copper and lead may be reduced very quickly. Certain oxides of iron may be reduced after a long subjection to the cathode action, and other oxides seem to undergo little or no reducing action. The determination of the relative amounts of hydrogen absorbed by a metal in contact with an acid and at the cathode, might also be of interest.

In addition to the chemical effects of the electric current, the physical action of the liberated gases may also play a useful part in the removal of materials from the surface preparatory to plating. If a metal upon which there is a layer of varnish, paint, or enamel, be used as cathode in a solution from which hydrogen is liberated, the hydrogen bubbles will gradually work their way under the layer of material and loosen it up to such an extent that it may readily be removed. An experiment which we performed to show this effect was the following: A piece of bicycle tubing was coated with enamel and subjected to a thorough baking process. By using it as the cathode in a dilute solution of sodium hydroxide, the coating of enamel was almost completely removed in about an hour's time.

After the surface has been cleaned by one of the foregoing methods, it is necessary to place it in the plating solution without allowing it to be exposed to the air for any considerable length of time. With some metals an instantaneous exposure to the atmosphere causes oxidation to take place, thus necessitating very rapid handling. This is especially so with aluminum. Other metals, such as copper, may be exposed for some time without harming the surface.

A peculiarity, the reason for which does not seem to have been explained, is that a metal, by contact with the plating electrolyte itself, may change the character of its surface to such an extent that a coating subsequently deposited will not adhere firmly to it. We have observed during an investigation on the electro-deposition of iron, that if the iron cathodes are allowed to remain for a few hours in the solution without the flow of current, a subsequent deposition of iron will take place, but the layer thus deposited may be readily separated from the previous layer. This gives rise to a laminated structure in the metal cathodes and a cross section of the cathode will show the times at which the current has been interrupted. This same phenomenon has previously been pointed out in the electrolytic separation of nickel.

Aside from the proper preparation of the surface, the degree of adherence of one metal upon another depends upon a certain relation between the metals themselves. It is claimed by some, that the adherence is due to an actual alloying of the two metals at their surface of contact, while others hold the view that the cohesion of the metal particles in intimate contact is sufficient to account for the adherence of the coating. It is quite likely that each of these views is correct to a certain extent.

It is a matter of common observation that certain combinations of metals present conditions for better adherence than do others, and on the supposition of a true alloying, this fact would be explained by the chemical affinity existing between different metals. That iron and nickel do not readily form alloys is cited as an explanation of the difficulty which has been encountered in producing an adherent nickel coating upon iron. This does not seem entirely warranted, however, inasmuch as almost all of the nickel plating in this country is done directly upon iron without the intervention of a layer of copper which was at one time supposed to be necessary for the best results. This better adherence of nickel has been accomplished by a more careful preparation of the iron surface, and a study of the alloying of the metals during electrolytic deposition is made difficult on account of this question of preparation of the surface. If the adherence depends solely upon the alloying property, it would naturally be expected that it would become better after considerable length of time, inasmuch as the process of alloying proceeds indefinitely. It is a matter of common observation, however, that many deposited coatings become non-adherent after a lapse of time. A striking experiment to illustrate the fact that one metal may be absorbed by another metal, under suitable conditions, may be performed by depositing a thin layer of gold upon a zinc surface. The gold will be absorbed by the zinc to such an extent that in a few weeks time the gold will have entirely disappeared from view. The alloying effect of metals was also pointed out by Dr. Haber in the Proceedings of the American Electrochemical Society, Vol. II., pages 189–196, and similar instances were also cited by Drs. Carhart and Kahlenberg and Mr. Reed in a discussion of the same paper.

There is little doubt, however, that a considerable degree of adherence may be produced without any alloying effect whatever, and to produce such adherence, requires an intimate contact of a large number of particles of metal. If the surface to receive the deposit is absolutely smooth, it is evident that a smaller number of particles of the deposited metal can cohere with it than if the surface is somewhat roughened. This explains the reason for the common practice of dipping aluminum and certain other metals which have previously been polished, into an acid or other chemical bath to give a rough or dull surface, and thereby virtually increasing the amount of surface upon which the deposition takes place. To obtain the best results, requires that every particle of this surface thus exposed shall receive a particle of the deposited metal and to attain this condition in the highest degree, the character of the electrolyte itself plays an important part.

It is a well-known fact that a metal deposited from one solution may be more adherent than the same metal deposited from another solution, although the exact cause for such difference is not thoroughly understood. While the chemical nature of the solution may be the influencing factor, its physical properties undoubtedly play a certain part. Certain observations which we have made, tend to show that phenomena such as the viscosity, surface tension, and capillarity, exert an influence. In some cases the addition of a small amount of alcohol or other similar chemical inert agent may materially improve the quality of adherence.

The readiness with which a solution will "wet" the surface to be plated upon determines, to a considerable degree, the adherence. If there is little attraction between the metal and the solution, the liquid will not work its way into the cavities and interstices of microscopic size on the surface, and it is only the more elevated points that actually make contact with the solution. The result is that it is only such elevated points that receive a deposit, and the intervening spaces are bridged over by the metal coating without actually making contact with the entire underlying metal surface. The natural result will be that, while we may have a continuous metal layer deposited, such layer does not make intimate metal contact with the entire metal surface receiving the deposit. Investigations, such as have been carried out by Herzen (Archives des Sciences, p. 232, 1902), on the surface tension of liquids, and the relation of such property to the quality of adherence might lead to some interesting results and conclusions, and indicate principles to be followed in the composition of plating solutions for attaining the most satisfactory results.

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1903.

CHEMICAL POTENTIAL AND ELECTROMOTIVE FORCE[1]

BY WILDER D. BANCROFT

In the paper by Gibbs on the *Equilibrium of Heterogeneous Substances* there are a few pages on the modification of the conditions of equilibrium by electromotive force, in which the electromotive force of certain cells is expressed in terms of the chemical potentials of the cation or anion at the two electrodes. The results thus obtained have received little attention, and the object of this paper is to point out the relation between the Gibbs formulas and those deduced within the past few years by Nernst, Ostwald, and others. After showing that the conditions of equilibrium, which had been found without reference to electrical considerations, will apply to an electrolytic fluid and its independently variable components, Gibbs proceeds to seek the remaining conditions of equilibrium, which relate to the possibility of electrolytic conduction.[2]

"For simplicity, we shall suppose that the fluid is without internal surfaces of discontinuity (and therefore homogeneous except so far as it may be slightly affected by gravity), and that it meets metallic conductors (*electrodes*) in different parts of its surface, being otherwise bounded by non-conductors. The only electrical currents which it is necessary to consider are those which enter the electrolyte at one electrode and leave it at the other.

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[1] The first draft of this paper was written early in 1899 and was submitted to Professor Gibbs, who made a number of suggestions. I have withheld the paper from publication in the vain hope that Professor Gibbs would himself some day show the relation between his formula and the osmotic pressure theory of voltaic cell. The paper as published is based on the first draft and on Professor Gibbs's letter, chiefly on the latter. The original outline was mine; but the bulk of the paper is a more or less literal transcript from Professor Gibbs's letter.

[2] Trans. Conn. Acad. 3, 502 (1878).

"If all the conditions of equilibrium are fulfilled in a given state of the system, except those which relate to changes involving a flux of electricity, and we imagine the state of the system to be varied by the passage from one electrode to another of the quantity of electricity ∂e accompanied by the quantity ∂m_a of the component specified, without any flux of the other components or any variation in the total entropy, the total variation of energy in the system will be represented by the expression,

$$(V'' - V')\partial e + (\mu''_a \mu'_a)\partial m_a + (\Upsilon' - \Upsilon'')\partial m_a,$$

in which V', V'', denote the electrical potentials in pieces of the same kind of metal connected with the two electrodes, Υ', Υ'', the gravitational potential at the two electrodes, and μ'_a, μ''_a, the intrinsic potentials for the substance specified. The first term represents the increment of the potential energy of electricity, the second the increment of the intrinsic energy of the ponderable matter, and the third the increment of the energy due to gravitation.[1] But by (682) $\partial m_a = a_a \partial e$. It is therefore necessary for equilibrium that

$$(V'' - V') + a_a(\mu'' - \mu' - \Upsilon'' + \Upsilon') = 0. \qquad (684)$$

"When the effect of gravity may be neglected, and there are but two electrodes as in a galvanic or electrolytic cell, we have for any cation

$$V'' - V' = a_a(\mu'_a - \mu''_a), \qquad (687)$$

and for any anion

$$V'' - V' = a_g(\mu''_g - \mu'_g), \qquad (688)$$

where $V'' - V'$ denotes the electromotive force of the combination. That is:—

When all the conditions of equilibrium are fulfilled in a galvanic or electrolytic cell, the electromotive force is equal to the difference in the values for the potential for any ion or apparent ion at the surfaces of the electrode multiplied by the electro-

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[1] It is here supposed that the gravitational potential may be regarded as constant for each electrode. When this is not the case, the expression may be applied to small parts of the electrodes taken separately.

chemical equivalent of that ion, the greater potential of an anion being at the same electrode as the greater electrical potential and the reverse being true of any cation."

The limitation that there shall be only one solution makes the formulas (687) and (688) apply in their present shape only to cells with concentration electrodes, in other words, to amalgam or gas cells. To apply the formulas deduced by Gibbs, we must be able to evaluate the (intrinsic or chemical) potentials involved. If we are considering the case of a dilute solution and if we make the assumption that Avogadro's law holds for the solute, we may write

$$\mu_a = \mathrm{B} + \frac{\mathrm{RT}}{\mathrm{M}_a} \log \gamma_a \qquad (1)$$

or

$$\gamma_a d\mu_a = \frac{\mathrm{RT}}{\mathrm{M}_a} d\gamma_a \qquad (2)$$

For small values of γ_a,

where γ_a is the density of a component (in this case, mass of the solute divided by the volume of the electrode), M_a its molecular weight, A the constant of Avogadro's law $\left(\frac{pv}{m\mathrm{T}} = \frac{\mathrm{A}}{\mathrm{M}}\right)$, and B a quantity which depends on the solvent and the solutions, as well as the temperature, but which may be regarded as independent of γ_a so long as this is small, and which is practically independent of the pressure in ordinary cases. We may avoid 'hedging' in regard to B by using the differential equation (2). We may simply say that this equation holds for changes produced by varying the quantity of (*a*) when γ_a is small. It is not limited to changes in which T is constant, for the change in μ_a due to T appearing in (1) (both explicitly and implicitly in B) becomes negligible when multiplied by the small quantity γ_a. We can then write

$$\mathrm{V}'' - \mathrm{V}' = a_a(\mu'_a - \mu''_a) = a_a \frac{\mathrm{AT}}{\mathrm{M}_a} \log \frac{\gamma'_a}{\gamma''_a},$$

γ'_a and γ''_a being the densities supposed small of the cation (*a*) in the two electrodes, which are supposed identical, except for the dissolved (*a*). Here a_a has reference to the solution and M_a to the electrode. It may be more convenient to divide a_a into the factors $E_a a_H$, where a_H is the weight of hydrogen, which carries the unit of electricity, and E_a the weight of (a) which carries the same quantity of electricity as the unit of weight of hydrogen. In other words, E_a is Faraday's 'electrochemical equivalent' and a_a is Maxwell's 'electrochemical equivalent'. This gives

$$V'' - V' = a_H A T \frac{E_a}{M_a} \log \frac{\gamma'_a}{\gamma''_a};$$

now γ'_a and γ''_a, as defined, are volume concentrations, and

$$a_H A \frac{E_a}{M_a} = \frac{R}{F n_1 n_2},$$

where R is the gas constant, F the number of coulombs per equivalent weight, n_1 the degree of polymerization of the cation in the electrode (assumed to be the same in both electrodes), and n_2 the valency of the cation in the solution. We may therefore write

$$V'' - V' = \frac{RT}{F n_1 n_2} \log \frac{C_1}{C_2},$$

which is the equation for concentration electrodes as deduced on the basis of the osmotic pressure theory of the voltaic cell.[1] This formula, as deduced, involves the assumption that the gas law holds. If this is not the case, either that molecular weight must be used for which the solute follows the gas law, the apparent molecular weight, or a correction must be introduced as was done by Cady when he took the heat of dilution into account.[2]

Gibbs worked out the formula for the electromotive force only for the one case of concentration cells; but there were several reasons why the matter of electrolysis was not discussed

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[1] V. Turin. Zeit. phys. Chem. 5, 340 (1890); 7, 221 (1891); Meyer. Wied. Ann. 40, 244 (1890); Zeit. phys. Chem. 7, 477 (1891); Schaller. Zeit. Elektrochemie, 5, 259 (1898); Richards and Lewis. Proc. Am. Acad. 34, 87 (1898); Cady. Jour. Phys. Chem. 2, 551 (1898); Bancroft. Ibid. 3, 107 (1899).

[2] Jour. Phys. Chem. 2, 561 (1898).

more fully in the paper on the Equilibrium of Heterogeneous Systems. "In the first place, cases of true equilibrium (even for open circuit) are quite exceptional. Thus the simple case of unequal concentration of the electrolyte cannot be one of equilibrium since the process of diffusion cannot be stopped. Cases in which equilibrium does not subsist were formally excluded and indeed could not be satisfactorily treated without the introduction of new ideas quite foreign to those necessary for the treatment of equilibrium.

"Again the consideration of electrical potential in the electrolyte, and especially the consideration of difference of potential in electrolyte and electrode involves the consideration of quantities of which we have no apparent means of physical measurement, while the difference of potential in "pieces of metal of the same kind, attached to the electrodes" is exactly one of the things which we can and do measure. Nevertheless, with some hedging in regard to the definition of the electrical potential, we may apply

$$V'' - V' = a_a(\mu'_a - \mu''_a)$$

to points in electrolyte (′) and electrode (″). This gives

$$V'' - V' = a_a\left(B + \frac{AT}{M_a}\log\gamma_a - \mu''_a\right) \qquad (3)$$

or

$$V'' - V' = \frac{a_a AT}{M_a}\log\frac{\gamma_a}{G}\,.\text{''} \qquad (4)$$

This is the Nernst formula for the potential difference between a metal and a solution of one of its salts, Gibbs using log G where Nernst uses log P. This method of deducing this formula has perhaps one advantage over that adopted by Nernst. It brings out the fact that the so called solution pressure P is a function of at least three variables, the nature of the metal electrode, the nature of the solvent, and the temperature. The specific effect of the solvent, if any, is contained in the term B. Since we know that the chemical potential of a dissolved substance varies with the solvent,[1] it is reasonably certain *a priori*

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[1] Miller. Jour. Phys. Chem. 1, 636 (1897).

that B does not have the same value for different solvents.[1] This differs from the case of the cells with concentration electrodes, in which no terms for the solvent appears, and in which, experimentally, the nature of the solvent is immaterial.

Ostwald[2] has shown that the Nernst formula applies even when an insoluble or complex salt is formed, but that, with such a system as Ag | AgCl KCl, it is easier to measure the concentration of chlorine as ion than it is to measure that of silver as ion. The relation between the concentration of chlorine as ion and silver as ion, which was deduced by Ostwald, can also be obtained from the Gibbs formulas by making the same assumptions. For the case of silver chloride dissociated into silver as ion and chlorine as ion we have the three equations

$$\mu_{Ag} = B_1 + \frac{AT}{M_1} \log \gamma_1,$$

$$\mu_{Cl} = B_2 + \frac{AT}{M_2} \log \gamma_2,$$

$$\mu_{AgCl} = B_3 + \frac{AT}{M_3} \log \gamma_3.$$

The three potentials are also connected by the relation

$$M_1\mu_1 + M_2\mu_2 = M_3\mu_3.$$

If we postulate that the potential of undissociated chloride is constant when there is solid silver chloride present, we have

$$\mu_{Ag} = \frac{S}{M_1} - \frac{M_2}{M_1}\mu_{Cl}.$$

Substituting in equation (4) we have

$$V'' - V' = a_a\left(\frac{S - M_2B_2}{M_1} - \frac{AT}{M_1}\log \gamma_2 - \mu''_a\right),$$

making

$$\frac{S - M_2B_2}{M_1} - \mu''_a = \frac{AT}{M_a} \log G',$$

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[1] Since this was first written the experiments of Kablenberg have demonstrated this fact conclusively.

[2] Lehrbuch, 2, I., 877.

and remembering that $M_1 = M_a$, we have

$$V'' - V' = \frac{a_a AT}{M_a} \log \frac{G'}{\gamma_2}.$$

"The case of unequal concentration, or in general cases in which the electrolyte is not homogeneous, can be treated as follows:[1]

Supposing, for convenience, that the cell is in the form of a rectangular parallelopiped with edge parallel to axis of x and cross-section of unit area. The electrolyte is supposed homogeneous in planes parallel to the ends, which are formed by the electrodes.

Of course we should get equilibrium if proper forces could be applied to prevent the migration of the ions, and also of the part of the solution which is not dissociated. What would these forces be? For the molecules[2] (12) which are not dissociated, the force per unit of mass would be $\frac{d\mu}{dx}$ 12. (The problem is practically the same as that discussed on pp. 203 *ff*, E. H. S.) If the unit of mass of the cation has the charge c_1, the force necessary to prevent its migration would be

$$\frac{d\mu_1}{dx} + c_1 \frac{dV}{dx}.$$

For an anion (2) the force would be

$$\frac{d\mu_2}{dx} - c_2 \frac{dV}{dx}.$$

Now we may suppose that the same ion in different parts of a dilute solution will have velocities proportional to the forces which would be required to prevent its motion. We may therefore write for the velocity of the cation (1)

$$-\frac{k_1}{c_1}\left(\frac{d\mu_1}{dx} + c_1 \frac{dV}{dx}\right),$$

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[1] Since the rest of the paper, with the exception of the last paragraph, is practically a single quotation, it has seemed simpler to omit the quotation marks.

[2] In the succeeding pages the cation is referred to as (1), the anion as (2), and the undissociated molecule as (12).

and for the flux of the cation (1)

$$\phi_1 = -\frac{k_1}{c_1}\gamma_1\left(\frac{\partial\mu_1}{\partial x}+c_1\frac{dV}{dx}\right) = -AT\frac{k_1}{c_1M_1}\frac{d\gamma_1}{dx} - k_1\frac{dV}{dx}\gamma_1, \quad (5)$$

and for the flux of the anion (2)

$$\phi_2 = -\frac{k_2}{c_2}\gamma_2\left(\frac{d\mu_2}{dx}-c_2\frac{dV}{dx}\right) = -AT\frac{k_2}{c_2M_2}\frac{d\gamma_2}{dx}+k_2\frac{dV}{dx}\gamma_2, \quad (6)$$

where k_1, k_2 are constants (migration velocities) depending on the solvent, the temperature, and the ion. Now whatever the number of ions the flux of electricity is given by the equation

$$\phi + \Sigma \pm c_1\phi_1,$$

where the upper sign is for cations and the lower for anions, and the summation for all ions.

This gives

$$\phi = AT\Sigma \mp \frac{k_1}{M_1}\frac{d\gamma_1}{dx} - \frac{dV}{dx}\; c_1k_1\gamma_1.$$

That is,

$$\phi\frac{dx}{\Sigma c_1k_1\gamma_1} = AT\frac{\Sigma\mp\frac{k_1}{M_1}d\gamma_1}{\Sigma c_1k_1\gamma_1} - dV.$$

The form of this equation shows that since ϕ is the current, $\frac{dx}{\Sigma c_1k_1\gamma_1}$ is the 'resistance' of an elementary slice of the cell, and the next term the (internal) electromotive force of that slice.

Integrating from one point to another in the electrolyte

$$\phi\int\frac{dx}{\Sigma c_1M_1\gamma_1} = AT\int\frac{\Sigma\mp\frac{k_1}{M_1}d\gamma_1}{\Sigma c_1k_1\gamma_1} + V' - V''.$$

The evaluation of these integrals which denote the resistance and electromotive force for a finite part of the electrolyte depends on the distribution of the ions in the cell.

For one salt with varying concentration

$$\phi \frac{dx}{c_1k_1\gamma_1 + c_2k_2\gamma_2} = \mathrm{AT}\,\frac{-\frac{k_1}{\mathrm{M}_1}\,d\gamma_1 + \frac{k_2}{\mathrm{M}_2}\,d\gamma_2}{c_1k_1\gamma_1 + c_2k_2\gamma_2} - d\mathrm{V},$$

or, since,

$$c_1\gamma_1 = c_2\gamma_2, \text{ and } c_1d\gamma_1 = c_2d\gamma_2,$$

$$\phi \frac{dx}{c_1k_1\gamma_1 + c_2k_2\gamma_2} = \mathrm{AT}\,\frac{-\frac{k_1}{c_1\mathrm{M}_1} + \frac{k_2}{c_2\mathrm{M}_2}}{k_1 + k_2} \cdot \frac{d\gamma_1}{\gamma_1} - d\mathrm{V}$$

$$\phi \int \frac{dx}{c_1k_1\gamma_1 + c_2k_2\gamma_2} = \mathrm{AT}\,\frac{-\frac{k_1}{c_1\mathrm{M}_1} + \frac{k_2}{c_2\mathrm{M}_2}}{k_1 + k_2} \log \frac{\gamma_1''}{\gamma_1'} + \mathrm{V}' - \mathrm{V}''.$$

The resistance depends on the concentration throughout the part of the cell considered, but the electromotive force depends only on the concentration at the terminal points (′ and ″). For $c_1\mathrm{M}_1$ and $c_2\mathrm{M}_2$ we may write $\frac{v_1}{a_H}$ and $\frac{v_2}{a_H}$, where v_1 and v_2 are the 'valencies' of the molecules. This gives

$$\mathrm{V}'' - \mathrm{V}' = a_H\mathrm{AT}\,\frac{\frac{k_1}{v_1} - \frac{k_2}{v_2}}{k_1 + k_2} \log \frac{\gamma_1'}{\gamma_2''} \text{ for } \phi = 0 \text{ (circuit open).} \quad (7)$$

When the two ions have the same valency this is identical with Nernst's equation[1] for the potential difference between two concentrations of the same electrolyte, the k_1 and k_2 of the Gibbs equation being the u and v of the Nernst formula. The general formula for the potential difference between two concentrations of the same electrolyte has not hitherto been obtained, Planck's formulation being limited explicitly to cases in which the cation and anion have the same valence,[2] while Lovén[3] considers the simplified case in which there are two different electrolytes having the same osmotic pressure.

The case in which there are two electrolytes and no concentration difference is a less simple problem. We may regard

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[1] Zeit. phys. Chem. 4, 137 (1889).

[2] Wied. Ann. 40, 576 (1890).

[3] Zeit. phys. Chem. 20, 593 (1896).

it as relating to a tube connecting two great reservoirs filled with different electrolytes of the same concentration, *i. e.*,

$$\Sigma_0 c_0 \gamma_0' = \Sigma_0 c_0 \gamma_0''.$$

We use $(_o)$ for any ion, $(_,)$ for any cation, $(_\bullet)$ for any anion. The tube is supposed to have reached a stationary state and dissociation is complete. The number of ions is immaterial, but they all must have the same valency *v*. Now by Equations (5) and (6), since $c_o M_o = v/a_{11}$

$$\phi_0 = -\frac{a\mathrm{AT}}{v} k_0 \frac{d\gamma_0}{dx} \mp k_0 \frac{d\mathrm{V}}{dx} \gamma_0,$$

or, writing N for the constant $\frac{a\mathrm{AT}}{v}$,

$$\phi_0 = -\mathrm{N} k_0 \frac{d\gamma_0}{dx} \mp k_0 \gamma_0 \frac{d\mathrm{V}}{dx}$$

$$\frac{c_0 \phi_0}{k_0} = -\mathrm{N} c_0 \frac{d\gamma_0}{dx} \mp c_0 \gamma_0 \frac{d\mathrm{V}}{dx},$$

$$\Sigma_0 \frac{c_0 \phi_0}{k_0} = -\mathrm{N} \Sigma_0 \frac{c_0 d\gamma_0}{dx}, \text{ and } \Sigma_0 \pm \frac{c_0 \phi_0}{k_0} = -\frac{d\mathrm{V}}{dx} \Sigma_0 c_0 \gamma_0.$$

The first equation makes $\frac{d\Sigma_0 c_0 \gamma_0}{dx}$ constant throughout the tube, and since $\Sigma_o c_o \gamma_o'' = \Sigma_o c_o \gamma_o$, $\Sigma c_o \gamma_o$ must be constant throughout the tube. The second equation thus makes $\frac{d\mathrm{V}}{dx}$ constant, throughout the tube. Let $\mathrm{X} = -\frac{d\mathrm{V}}{dx}$. Our original equation is

$$\phi_0 = -\mathrm{N} k_0 \frac{d\gamma_0}{dx} \pm \mathrm{X} k_0 \gamma_0.$$

Now with X constant, this is easily integrated.

$$\frac{\phi_0}{\mathrm{X}k} = -\frac{\mathrm{N}}{\mathrm{X}} \frac{d\gamma_0}{dx} \pm \gamma_0,$$

$$\pm \frac{\mathrm{N}}{\mathrm{X}} \frac{d\gamma_0}{dx} = \gamma_0 \mp \frac{\phi_0}{\mathrm{X}k_0},$$

$$\frac{d\gamma_0}{\gamma_0 \mp \frac{\phi_0}{\mathrm{X}k_0}} = \pm \frac{\mathrm{X}}{\mathrm{N}} dx,$$

$$\log\left(\gamma \mp \frac{\phi_0}{Xk_0}\right) = \pm\frac{X}{N}x + \log H_0,$$

$$\gamma_0 \mp \frac{\phi_0}{Xk_0} = H_0\sigma^{\pm\frac{X}{N}x}.$$

To determine H_0 we have

$$\gamma_0'' - \gamma_0' = H_0(\sigma^{\pm\frac{X}{N}x''} - \sigma^{\pm\frac{X}{N}x'}).$$

If we put the origin of coordinates in the middle of the tube, we have $x' = -x''$. Let $P = \sigma^{\frac{X}{N}x''}$,

$$\gamma_0'' - \gamma_0' = \pm H_0(P - P^{-1}). \quad \text{Let } \Delta_0 = \gamma_0'' - \gamma_0',$$

$$\gamma_0 \mp \frac{\phi_0}{Xk_0} = \pm\Delta_0\frac{\sigma^{\pm\frac{X}{N}x}}{(P - P^{-1})},$$

$$c_0k_0\gamma_0 \mp \frac{c_0\phi_0}{X} = \pm c_0k_0\Delta_0\frac{\sigma^{\pm\frac{X}{N}x}}{P - P^{-1}}.$$

The condition of no electric current gives

$$\Sigma_0c_0k_0\gamma_0 = \Sigma_0 \pm c_0k_0\Delta_0\frac{\sigma^{\pm\frac{X}{N}x}}{P - P^{-1}}.$$

Apply to both ends and add

$$\Sigma_0c_0k_0\gamma_0'' + \Sigma_0c_0k_0\gamma_0' = \Sigma_0 \pm c_0k_0\Delta_0\frac{\sigma^{\pm\frac{X}{N}x''} + \sigma^{\pm\frac{X}{N}x'}}{P - P^{-1}}$$

$$= \Sigma_0 \pm c_0k_0\Delta_0\frac{P + P^{-1}}{P - P^{-1}}.$$

If we set, to abridge

$$k_1' = \Sigma_1c_1k_1\gamma_1' \qquad k_1'' = \Sigma_1c_1k_1\gamma_1''$$
$$k_2' = \Sigma_2c_2k_2\gamma_2' \quad . \qquad k_2'' = \Sigma_2c_2k_2\gamma_2''$$

where the summations are for cations or anions *separately*, the last equation may be written

$$k_1'' + k_2'' + k_1' + k_2' = \frac{P + P^{-1}}{P - P^{-1}}(k_1'' - k_1' - k_2'' + k_2'),$$

which gives

$$P^2 = \frac{k_1'' + k_2'}{k_1' + k_2''}.$$

$$\text{Now } \log P = \frac{X}{N}x'' = \frac{-X}{N}x' \quad 2\log P = \frac{X(x'' - x')}{N} = \frac{V' - V''}{N}$$

$$\frac{V' - V''}{N} = \log\frac{k_1'' + k_2'}{k_1' + k_2''}; \;\; V'' - V' = \frac{A\alpha T}{v}\log\frac{k_1' + k_2''}{k_1'' + k_2'};$$

k_1' is the part of the conductivity of the first electrolyte which is due to the cations. If the first electrolyte contains only one cation (1) and one anion (2) and the second only one cation (3) and one anion (4) we have

$$V'' - V' = \frac{A\alpha T}{v}\log\frac{c_1k_1\gamma_1' + c_4k_4\gamma_4''}{c_3k_3\gamma_3'' + c_2k_2\gamma_2'},$$

or since

$$c_1\gamma_1' = c_2\gamma_2'' = c_3\gamma_3'' = c_4\gamma_4''$$

$$V'' - V = \frac{A\alpha T}{v}\log\frac{k_1 + k_4}{k_3 + k_2}, \tag{8}$$

which is the Planck formula.[1]

It is thus clear that the Gibbs conception of the electromotive force as a measure of the chemical potential leads to the results actually discovered by Nernst and Planck. While the original equation of Gibbs is absolutely accurate, this is not the case for Equations (1–8) which contain the same explicit assumptions which were made first by Nernst and afterwards by Planck.

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[1] Wied. Ann. 40, 574 (1890).

ELECTROCHEMICAL ANALYSIS AND THE VOLTAIC SERIES

BY J. E. ROOT

When two platinum electrodes are dipped into an electrolytic solution and a difference of potential is created by means of an external electromotive force, only a small current flows when the potential difference is small. This current is known as the residual current, and its magnitude depends on the amount of air dissolved in the electrolyte, on the size of the electrodes, and on the distance between them. While the theory of the residual current is still a matter of discussion,[1] the current itself is of no importance in regard to analytical determinations, because no measurable change in the electrolyte is produced by it. As the potential difference between the electrodes is increased, the residual current increases, though not rapidly. Above a certain value, which is not clearly marked, the current increases much more rapidly with increasing potential difference than before and the electrolyte undergoes measurable decomposition.[2] The counter-electromotive force of polarization at the moment when this change occurs is known as the decomposition voltage of the solution. The difference of potential as measured on a voltmeter is the decomposition voltage plus the fall of potential in the solution, and therefore depends on the size and distance apart of the electrodes. The decomposition voltage depends on the nature, concentration, and temperature of the solution. The decomposition voltage increases with increasing dilution, but this change is not very large and would rarely exceed 0.1 volt for complete precipitation in most of the solutions used in electrochemical analysis. In general, the decomposition voltages for different solutions vary with the nature of the acid radical and of the basic radical, though the metals which are

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[1] Bigelow. Jour. Phys. Chem. 7, 327 (1903).

[2] Le Blanc. Zeit. phys. Chem. 8, 299 (1891).

instable in presence of water and certain acids form apparent exceptions. It is obviously possible to arrange the salts of the different metals with the same acid radical in the order of decreasing decomposition voltages, each successive metal precipitating at a lower voltage than the one immediately preceding it in the series. Such an arrangement is known as an electrochemical or a voltaic series. It is found experimentally that the order of the metals is not independent of the acid radical. Thus tin stands above copper in the electrochemical series when chlorides are in question and below it in cyanide solutions.

This difference of decomposition voltage is what makes the electrolytic separation of two metals possible. If two metals precipitate from a given solution as two phases, each phase consisting of one of the metals pure, then we can separate these two metals electrolytically by electrolyzing under a difference of potential sufficient to precipitate one metal and not to precipitate the other. This is feasible practically only when there is a difference of at least 0.2–0.3 volt between the decomposition voltages of the two salts. When there is only a very slight difference between the decomposition voltages, no separation can be made. When the difference of decomposition voltage is at least 0.3 volt, a separation is possible unless the metals can precipitate as a single phase. This is a contingency which must always be kept in mind. In concentrated cyanide solutions, the decomposition voltage for silver is nearly 1 volt higher than that for mercury, but some silver precipitates as amalgam when a mixture of the mercury and silver salts is subjected to electrolysis.

When the decomposition voltages are markedly different and when the two metals cannot separate as a single phase, a separation is always possible; but there are two ways of carrying this out which may be called the constant voltage and the constant current methods. In constant voltage separations, the voltage is kept constant at a value just below that at which the second metal can precipitate. The initial current is then relatively high and decreases as the first metal precipitates, reaching the value of the residual current when the first metal has entirely precipitated. This method has several distinct advantages. It is of universal application. Since the second metal cannot precipitate, by hypothesis, the current can be allowed to run for an indefinite period if desired. From the magnitude of the current, some information can be obtained as to the amount of metal which is yet to be precipitated. The constant voltage separation was first introduced as a general method by Freudenberg.[1] It is not, however, in general use. The theory of electrochemical analysis is of comparatively recent development, and the practice proceeded along lines which were simpler experimentally though not theoretically.

Ever since the time of Faraday the chemist has been familiar with the voltameter. The measurement of current by means of the voltameter is a chemical measurement and the current is the only one of the three electrical units, volt, ampere, ohm, which can be measured readily with the appliances to be found in every chemical laboratory. Since the current measurement was the only one that the chemist could make easily, it was natural for him to hold the current constant, or approximately constant, and thus to develop the constant current methods of separation. We shall therefore find that practically all the standard methods of separation are constant current methods and we must consider what conditions are essential for a separation with constant current. The initial current must be higher than the residual current, otherwise there would be no precipitation at all. Since it would not be practical to break the circuit at the very moment when the first metal was completely precipitated, some device must be found which will permit the passage of a current higher than the residual current, which shall prevent the second metal from precipitating, and which shall not alter the weight of the deposit. At first it seems impossible to satisfy such requirements; but this is easily done if the ion that is discharged is either volatile or soluble in the solution. If the decomposition voltage of hydrogen lies be-

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[1] Zeit. phys. Chem. 12, 97 (1893).

tween that of the two metals, hydrogen will be set free instead of the second metal. This is the usual way in which the difficulty is solved, but it is not the only way in which it might be overcome. Suppose we wish to separate copper from iron, both metals being present as sulphates. We can either make the solution so acid that the iron cannot precipitate under the conditions of the experiment, or we can change the iron into the ferric state and no precipitation of iron will occur until the current has changed the ferric salt back into ferrous salt. This latter method, while theoretically sound, is less generally applicable than the other and need not be considered further. The essential condition, then, for a constant current separation is that the decomposition voltage for hydrogen shall lie below that of the second metal. While one object to be obtained in selecting one solution for a given separation rather than another is to have the decomposition voltages for the two metals as different as possible, the second very important object is to obtain a solution in which the decomposition voltage for hydrogen lies below that of one of the metals. In any given solution, the metals, whose decomposition voltages lie below that of hydrogen, can be separated from each other only by a constant voltage method, while any metal of this group can be separated from any of the other metals by a constant current method except in so far as the possible precipitation of the two metals as one phase may affect the situation.

This distinction between constant voltage and constant current separations was seen clearly by Freudenburg,[1] who first discusses the analogy between the precipitation of metals by the current and by hydrogen sulphide and then goes on:

"The behavior of the metals with reference to the potentials of hydrogen in different solutions is what has made the simplest separations possible and the earlier methods depend on it almost exclusively. Since it is not necessary in those cases to maintain a definite potential difference, it was very easy for the importance of this to be completely overlooked. Up to now

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[1] Zeit. phys. Chem. 12, 103 (1893).

people have used the same potential difference for all precipitations and, by means of resistances, have varied the current density in such a way as to keep the evolution of gas from affecting the precipitate." This same distinction is recognized less clearly by Neumann:[1] "The separation of certain metals from others may be effected by the addition of strong mineral acids to their salt solutions. In this way the deposition of iron, cobalt, nickel, cadmium, and zinc is prevented. Since those metals are in all cases first separated for which the least electromotive force is required, it will be the noble metals, gold, silver, copper, and mercury that are first deposited; while if a considerable excess of acid be present, the remainder of the series of metals given on p. 35 will not be deposited, a liberation of the hydrogen of the acid being produced instead." The significance of the constant current separation is here recognized only for the case of acid solutions, and there is no clear appreciation of the importance of a general classification based on the intermediate evolution of hydrogen. The other text-books on electrochemical analysis are still more vague in regard to the principles on which the separations depend. At the time I began this work there were no data which would enable one to make a proper classification for many of the solutions ordinarily used in electrochemical separations.

While a determination of the decomposition voltages in different solutions would in itself have given the necessary data for such a classification, it would have given nothing more. Instead of making a series of such determinations, it was therefore thought best to measure the potential differences and currents under the conditions of actual analytical work, with the platinum electrodes actually employed. While the potential differences at which the metals precipitate differ from the true decomposition voltages by the fall of potential through the liquid, these values are the limiting values which must not be exceeded in a constant voltage separation. In this way data are obtained as to the order of magnitude of the residual current.

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[1] Electrolytic Methods of Analysis, p. 166.

In the following experiments, the same anode and the same cathode were always used, and they were always the same distance apart. The concentrations and temperatures are given in each case so that the conditions are all clearly defined and can easily be reproduced. The cathode was a Classen platinum dish 9.4 cm in diameter and 4.7 cm deep. The wetted surface was approximately 145 cm^2 when there were 200 cc of solution in the dish and 121 cm^2 when there were 150 cc. The anode was a perforated Classen disc 4.5 cm in diameter. The distance between the anode and cathode was 1 cm and was measured as follows. The anode was placed on the bottom of the dish and then raised vertically 1 cm and clamped in position. A mark on the stem of the electrode made it possible to adjust the electrode anew. A sheet of asbestos board on a tripod was placed beneath the dish and so arranged as to permit of the easy heating of the electrolyte by means of a Bunsen burner. All measurements were made either at 20° or at 60°. Since the value of the residual current is a function of the time, all readings were made three minutes after closing the circuit. The current was obtained from storage cells and the difference of potential between the anode and the cathode was regulated by means of a variable resistance placed in series. The current was measured with a Weston milli-ammeter and the potential difference with a Weston voltmeter, the current readings being taken only while the voltmeter circuit was open. The chemicals for the experiments were taken from the laboratory stock and were not purified further.

The following stock solutions were prepared, each containing 0.2 g metal per 50 cc: copper sulphate, lead nitrate, nickel sulphate, cadmium sulphate, zinc sulphate, mercuric chloride, silver nitrate. The bismuth nitrate solution contained about 0.2 g Bi per 12 cc and enough free nitric acid to prevent precipitation. The antimony trichloride solution was approximately 25 g $SbCl_3$ and 250 cc dilute HCl per liter, or about 0.2 g Sb per 16 cc. The ammonium oxalate solution was saturated at 20°. The Na_2HPO_4 solution contained 90 g crystallized sodium phosphate per liter and had a specific gravity of 1.025 at 20°. The phosphoric acid solution was made by diluting 125 g glacial acid to one liter and its specific gravity was 1.3. The ammonia solution had a specific gravity of 0.92 at 20° and the sodium hydroxide solution one of 1.28. The potassium cyanide solution contained 260.4 g KCN per liter (4*N*) and was kept in a tightly-stoppered bottle away from the air.

In Tables I-XXXIX are given the experiments with cyanide, oxalate, and phosphate solutions. Lead cyanide is insoluble in hot and cold cyanide solutions. At 60° a precipitate occurs in the alkaline citrate cyanide solution of bismuth. Silver oxalate does not dissolve in an excess of ammonium oxalate.

TABLE I.

Solution : N/4 KCN
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	—	2.45	22
0.58	0.05	2.74	44[1]
0.81	0.1	3.0	87
1.0	0.21	3.36	185
1.32	1.4	3.65	350[2]
1.5	2.3	3.9	530
1.8	4.3	4.3	850
2.0	5.5	4.51	1050

[1] Slight bubbles at cathode.
[2] Solution turns yellow round the anode, probably owing to presence of paracyanogen.

TABLE II.

Solution : N/4 KCN + 0.2 g Ag as $AgNO_3$
Vol. 200 cc. Temperature 20°

Volts	Milli-amperes	Volts	Milli-amperes
0.8	0.2	2.83	70[2]
1.05	0.4	3.14	145
1.4	1.85	3.55	385
1.7	6.1	3.77	500
2.04	15[1]	4.0	770
2.48	25	4.28	1000

[1] Deposit of silver.
[2] Few bubbles at anode. Solution slightly yellow at end of run.

Table III.

Solution : N/4 KCN + 0.2 g Hg as $HgCl_2$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.3	1.3	3.6	120[2]
1.8	18	4.0	225
2.2	30[1]	4.2	350
2.5	35	4.55	600
2.7	60	4.75	800
3.2	70	5.15	1150

[1] Slight deposit of mercury at cathode; few bubbles at anode.
[2] Bubbles at both electrodes.

Table IV.

Solution : N/4 KCN + 0.2 g Bi as $Bi(NO_3)_3$ + 4 g cryst. citric acid
+ NaOH in slight excess
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.22	1.1	2.75	35[3]
1.5	1.8	3.25	90
2.0	8.5[1]	3.66	410
2.5	25[2]	3.9	475

[1] Anode turns brown.
[2] Bubbles at anode ; cathode turns black.
[3] Heavy deposit of metal at cathode, no bubbles. Metal black and does not adhere well.

Table V.

Solution : N/4 KCN + 0.2 g Cd as $CdSO_4$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.6	3.0	4.0	175[3]
2.1	10	4.5	375
2.5	20	4.96	650
2.8	55[1]	5.1	750
3.35	85[2]	5.3	950
3.75	120	6.0	1500

[1] Slight deposit of metal.
[2] Appearance of bubbles at anode.
[3] Bubbles at both electrodes.

TABLE VI.

Solution : N/4 KCN + 0.2 g Zn as $ZnSO_4$

Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.25	1.0	3.1	135
1.55	2.5	3.6	305
2.0	6.5	3.85	475
2.4	20	4.0	570
2.85	70	4.5	900

---

[1] No zinc was deposited. In this run, as in some of the others, no record was kept of the voltage at which hydrogen appeared.

TABLE VII.

Solution : N/4 KCN + 0.2 g Ni as $NiSO_4$

Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.0	2.1	2.8	350
1.58	10	3.1	455
1.69	11	3.43	650
2.08	80	3.8	820
2.35	170[1]	4.2	1050[2]

---

[1] Traces of bubbles at cathode.

[2] No nickel deposited.

TABLE VIII.

Solution : N/4 KCN + 0.2 g Cu as $CuSO_4$

Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
0.74	0.5	2.28	390
1.0	2.4	2.5	520
1.3	10	2.85	680
1.6	60	3.35	770
1.75	145[1]	4.0	850
2.0	265	4.4	1000[2]

---

[1] Bubbles appear.

[2] No copper deposited.

TABLE IX.

Solution : N/4 KCN
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	0.0	2.5	75[1]
0.48	0.1	2.82	165
0.66	0.2	3.12	293
1.0	1.25	3.4	560
1.23	4.0	3.67	760
1.7	10	3.9	1010
1.94	15	4.15	1280
2.2	28		

---

[1] Slight bubbles at cathode.

TABLE X.

Solution : N/4 KCN + 0.2 g Ag as $AgNO_3$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.1	1.4	2.7	135[3]
1.4	5.5	3.05	240
1.8	17[1]	3.34	465
2.14	65[2]	3.5	620
2.4	115	3.8	1020

---

[1] Slight deposit of silver.
[2] Heavy deposit of silver.
[3] Bubbles at anode.

TABLE XI.

Solution : N/4 KCN + 0.2 g Hg as $HgCl_2$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.76	1.0	2.85	125[2]
1.1	1.6	3.05	140
1.46	6.3	3.4	240
1.75	15	3.7	380
2.0	60[1]	4.0	650
2.35	110	4.4	1000

---

[1] Slight deposit of metal.
[2] Bubbles seen at anode.

TABLE XII.

Solution : N/4 KCN + 0.2 g Cd as $CdSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.15	2.5	3.15	185
1.55	7.5	3.7	200
1.8	10	3.9	250
2.1	13	4.2	375
2.5	55	4.5	680
2.82	125[1]	4.65	850

---

[1] Deposit of metal ; bubbles at anode.

TABLE XIII.

Solution : N/4 KCN + 0.2 g Ni as $NiSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.9	2.8	2.2	190
1.15	4.3	2.57	468
1.5	7.3	2.8	870
2.0	90[1]	3.5	1250

---

[1] Bubbles.
No nickel is deposited.

TABLE XIV.

Solution : N/4 KCN + 0.2 g Zn as $ZnSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.25	4.1	2.8	90[2]
1.7	7.8	3.27	250
2.0	12	3.95	500
2.39	25[1]	4.1	1100

---

[1] A few bubbles at anode.
[2] More bubbles.
No zinc is deposited.

TABLE XV.

Solution : N/4 KCN + 0.2 g Cu as $CuSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.74	1.55	2.2	550
0.93	3.1	2.6	840[3]
1.26	23	3.0	1050[4]
1.55	110[1]	3.27	1300
1.9	300[2]	3.5	1600

---

[1] Few bubbles at anode.

[2] Bubbles at both electrodes.

[3] Slight deposit of copper, which rapidly dissolves if current is broken.

[4] Heavy deposit of copper dissolving when circuit is broken, with marked counter-electromotive force.

TABLE XVI.

Solution : 150 cc sat. ammonium oxalate
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	1	1.25	40
0.4	6	1.45	125[1]
0.85	10	1.8	460

---

[1] Bubbles at both electrodes.

TABLE XVII.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Hg as $HgCl_2$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	2	1.22	48
0.4	15	1.5	70
0.65	40[1]	1.85	220[3]
0.9	45[2]	2.15	500

---

[1] Slight deposit of metal; no bubbles at anode.

[2] Bubbles at anode.

[3] Bubbles at cathode.

Mercuric oxalate is also soluble at 20° in an excess of ammonium oxalate.

TABLE XVIII.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Cu as $CuSO_4$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	4	1.8	350[2]
1.0	110[1]	2.15	920
1.45	150	2.9	1900

---

[1] Slight deposit of metal ; bubbles at anode.
[2] Some bubbles at cathode.
Copper oxalate is also soluble at 20°.

TABLE XIX.

Solution : 170 cc sat. ammonium oxalate + 0.1 g Bi as $Bi(NO_3)_3$
Vol. 176 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	0.9	1.15	60[1]
0.4	3.5	1.5	160
0.8	20	1.8	370[2]

---

[1] Deposit of metal ; bubbles at anode.
[2] Bubbles at cathode.
Bismuth oxalate does not dissolve at 20°.

TABLE XX.

Solution : 170 cc sat. ammonium oxalate + 0.1 g Sb as $SbCl_3$
Vol. 178 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	0.9	1.2	65[1]
0.4	7	1.7	210
0.8	15	2.0	400

---

[1] Deposit of metal ; bubbles at anode.
A good deposit is obtained at the highest current.
Antimony oxalate is soluble at 20°.

TABLE XXI.

Solution : 150 cc sat. ammonium oxalate + 1 g Pb as $Pb(NO_3)_2$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.8	11	1.8	125
1.25	30	2.0	175
1.55	80[1]	2.3	375[2]

[1] Deposit of metal ; bubbles at anode.
[2] Bubbles at cathode.
Lead oxalate does not dissolve at 20°.

TABLE XXII.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Cd as $CdSO_4$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.5	1.8	115[1]
0.88	6.5	2.0	175
1.27	12	3.5	350

[1] Deposit of metal ; bubbles at anode.
Cadmium oxalate does not dissolve at 20°.

TABLE XXIII.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Ni as $NiSO_4$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.0	12	1.9	400[3]
1.3	60	2.35	750
1.4	100[1]	2.75	900
1.6	200[2]	3.3	1600

[1] Bubbles at anode.
[2] Bubbles at cathode.
[3] Deposit of metal.
Nickel oxalate is soluble at 20°.

TABLE XXIV.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Co as $CoSO_4$
Vol. 179 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	6.9	1.4	158[1]
1.0	15	1.65	250
1.2	55	1.9	425[2]

---

[1] Bubbles at both electrodes.
[2] Slight deposit of metal which dissolves rapidly on breaking the circuit. Cobalt oxalate is soluble at 20°.

TABLE XXV.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Fe as $FeSO_4$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.25	40	1.6	255
1.45	135[1]	1.9	450[2]

---

[1] Bubbles at both electrodes.
[2] Slight deposit of metal; dissolving rapidly when circuit is broken. Iron oxalate is soluble at 20°.

TABLE XXVI.

Solution : 150 cc sat. ammonium oxalate + 0.1 g Sn as $SnCl_2$
Vol. 175 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	12	1.6	200
0.8	18	2.0	500
1.3	120[1]	2.1	600[2]

---

[1] Bubbles at both electrodes.
[2] Slight deposit of metal.
Tin oxalate does not dissolve at 20°.

TABLE XXVII.

Solution: 150 cc sat. ammonium oxalate + 0.1 g Zn as $ZnSO_4$
Vol. 175 cc. Temp. 60°. Cathode copper-plated

Volts	Milli-amperes	Volts	Milli-amperes
0.2	Reverse current	1.6	75[1]
0.4	0	1.85	210
0.8	3.5	2.1	525
1.25	18	2.6	1400[2]

---

[1] Bubbles at anode.
[2] Deposit of metal.
Zinc oxalate is soluble at 20°.

TABLE XXVIII.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.1	1.5	13
0.8	0.4	1.9	75[1]
1.2	6.5	2.2	240
1.3	10	2.5	475

---

[1] Bubbles at both electrodes.

TABLE XXIX.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Ag as $AgNO_3$
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.2	1.2	45[1]
0.8	0.4	1.9	70

---

[1] Deposit of metal; bubbles at anode.
Silver phosphate is readily soluble at 20° in the amount of phosphoric acid added.

TABLE XXX.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Hg as $HgCl_2$

Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.1	1.3	45[1]
0.8	0.3	1.4	60
1.2	18	1.7	65

---

[1] Deposit of metal; bubbles at anode. Current decreases rapidly as metal precipitates. Deposit is black and powdery; not very adherent. The mercury phosphate redissolves in the sodium phosphate before the phosphoric acid is added.

TABLE XXXI.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Cu as $CuSO_4$

Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.15	1.75	115[1]
0.8	0.4	2.15	165
1.4	12	2.55	500

---

[1] Deposit of metal; bubbles at anode.

TABLE XXXII.

Solution: 50 cc Na_2HPO_4 + 20 cc H_3PO_4 + 0.1 g Bi as $Bi(NO_3)_3$

Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.1	1.9	100[1]
0.8	0.15	2.15	275
1.4	11	2.3	475

---

[1] Deposit of metal; bubbles at anode.

20 cc H_3PO_4 are necessary to redissolve the precipitate. The coating of metal is good and adherent.

TABLE XXXIII.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Sb as $SbCl_3$
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.3	11	2.0	90[1]
1.8	15	2.4	375

---

[1] Deposit of metal; bubbles at anode.

Antimony phosphate is soluble in the amount of phosphoric acid added at 20°. The coating of metal is good.

TABLE XXXIV.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Pb as $Pb(NO_3)_2$
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.8	0.13	2.25	55
1.25	3.5	2.45	160
1.75	15	2.85	425[2]
2.0	35[1]	3.2	600[3]

---

[1] Bubbles at both electrodes.

[2] Traces of metal.

[3] More metal.

Lead phosphate is soluble in the amount of phosphoric acid added at 20°.

TABLE XXXV.

Solution: 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Cd as $CdSO_4$
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.47	12	2.4	275
1.85	20	2.8	600
2.1	140[1]	2.9	700[2]

---

[1] Bubbles at both electrodes.

[2] Traces of metal.

Cadmium phosphate is soluble in the amount of phosphoric acid added at 20°.

TABLE XXXVI.

Solution : 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Zn as $ZnSO_4$
Vol. 150 cc. Temp. 60°. Cathode copper-plated

Volts	Milli-amperes	Volts	Milli-amperes
0.2	Reverse current	2.0	30[1]
0.4	0	2.2	90
0.85	0.3	2.4	170
1.2	1.0	2.75	425[2]
1.5	10	3.15	500[3]

---

[1] Bubbles at anode.
[2] Bubbles at cathode.
[3] Excellent deposit of metal.
Zinc phosphate is soluble in the amount of phosphoric acid added at 20°.

TABLE XXXVII.

Solution : 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Co as $CoSO_4$
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.7	15	2.7	650
1.95	135[1]	2.9	1000
2.3	360	3.5	1750[2]

---

[1] Bubbles at both electrodes.
[2] No deposit of metal.
Cobalt phosphate is soluble in the amount of phosphoric acid added at 20°.

TABLE XXXVIII.

Solution : 50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Ni as $NiSO_4$
Vol. 150 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.25	6.5	2.65	700
1.75	20	2.9	1000
1.9	75[1]	3.3	1300
2.3	400	3.5	1650[2]

---

[1] Bubbles at both electrodes.
[2] No deposit of metal.
Nickel phosphate is soluble in the amount of phosphoric acid added at 20°.

TABLE XXXIX.

Solution: 50 cc. Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g Sn as $SnCl_2$
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.6	12	2.5	525
2.0	90[1]	2.95	850
2.2	225	3.3	1000[2]

---

[1] Bubbles at both electrodes.
[2] No deposit of metal.
Tin phosphate is insoluble at 20°.

Since it is not clear from any published experiments what part the sodium phosphate plays in the phosphate separations, it was thought best to make some measurements with and without sodium phosphate. These are given in Tables XL–XLVIII. It also seemed desirable to decrease the amount of free phosphoric acid.

TABLE XL.

Solution A: 6 cc H_3PO_4 + 0.1 g Ag as $AgNO_3$
Solution B: A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.05	0.8	0.15
0.8	0.15	1.3	40
1.3	60[1]	1.35	50[1]

---

[1] Deposit of metal; bubbles at anode.

TABLE XLI.

Solution A: 6 cc H_3PO_4 + 0.1 g Hg as $HgCl_2$
Solution B: A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	**Milli-amperes**	**Volts**	**Milli-amperes**
0.4	0.05	0.8	1.0
0.84	0.6	1.2	35
1.3	45[1]	1.3	50[1]

[1] Deposit of metal; bubbles at anode.

TABLE XLII.

Solution A: 6 cc H_3PO_4 + 0.1 g Cu as $CuSO_4$
Solution B: A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	**Milli-amperes**	**Volts**	**Milli-amperes**
0.9	0.1	1.3	7
1.35	12	1.5	50
1.55	40[1]	1.6	60[1]
2.1	125[2]	1.8	100

[1] Good deposit of metal; bubbles at anode.
[2] Bubbles at both electrodes.

TABLE XLIII.

Solution A: 6 cc H_3PO_4 + 0.1 g Bi as $Bi(NO_3)_3$
Solution B: A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	**Milli-amperes**	**Volts**	**Milli-amperes**
0.8	0.4	1.4	12
1.4	7.0	1.9	60[1]
1.9	60[1]	2.4	300

[1] Good deposit of metal; bubbles at anode.

TABLE XLIV.

Solution A : 6 cc H_3PO_4 + 0.1 g Sb as $SbCl_3$
Solution B : A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	Milli-amperes	Volts	Milli-amperes
1.4	3	1.4	4
1.9	12	2.0	60[1]
2.2	100[1]	2.2	100
2.6	550		

[1] Deposit of metal ; bubbles at anode.
Metal powdery and not very adherent.

TABLE XLV.

Solution A : 6 cc H_3PO_4 + 0.1 g Pb as $Pb(NO_3)_2$
Solution B : A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	Milli-amperes	Volts	Milli-amperes
1.3	12	1.3	8
2.1	60[1]	2.0	15
2.5	160[2]	2.2	40[3]
2.7	275	2.5	100

[1] Bubbles at electrodes.
[2] Deposit of metal.
[3] Bubbles at anode; metal at cathode; traces of peroxide at anode.

TABLE XLVI.

Solution A : 6 cc H_3PO_4 + 0.1 Co as $CoSO_4$
Solution B : A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	Milli-amperes	Volts	Milli-amperes
1.6	12	1.7	15
2.1	150[1]	2.1	150[1]
2.5	400	2.5	300
2.8	550	2.9	550[2]
3.4	650[3]	3.5	650

---

[1] Bubbles at both electrodes.
[2] Traces of metal.
[3] No deposit of metal.

TABLE XLVII.

Solution A : 6 cc H_3PO_4 + 0.1 g Ni as $NiSO_4$
Solution B : A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	Milli-amperes	Volts	Milli-amperes
1.7	20	2.1	75
2.0	40	2.3	150[1]
2.4	120[1]	2.7	325
2.8	580	3.1	500
3.4	800[2]	3.5	700

---

[1] Bubbles at both electrodes.
[2] No deposit of metal.

TABLE XLVIII.

Solution A : 6 cc H_3PO_4 + 0.1 g Sn as $SnCl_2$
Solution B : A + 50 cc Na_2HPO_4
Vol. A 130 cc, B 170 cc. Temp. 60°

A		B	
Volts	Milli-amperes	Volts	Milli-amperes
1.4	12	0.85	2
2.1	150[1]	1.4	3
2.3	240	1.9	60[1]
2.7	450	2.3	225
3.15	600[2]	3.1	600[2]

[1] Bubbles at both electrodes.
[2] No deposit of metal.

From these experiments, it is certain that the sodium phosphate is of no importance in making complex salts and changing the relative order of precipitation. Since the deposit is equally good from a phosphoric acid solution, it seems probable that the addition of sodium phosphate is an unnecessary complication. Professor Edgar F. Smith, of the University of Pennsylvania, says that they have already made determinations in his laboratory without using sodium phosphate. It is also by no means certain that the amount of free phosphoric acid now prescribed is at all necessary. The general conclusion to be drawn from my measurements is that all the phosphate separations need revision.

Since a number of separations have been made in tartrate solutions, some measurements have been made with these solutions. In each case the tartrate solution contained 7.5 g crystallized tartaric acid and 35 cc aqueous ammonia sp. gr. 0.92. The results are given in Tables XLIX–LIX.

Table XLIX.

Solution : amm. tartrate
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.2	1.0	1.85	75
0.4	4.5	1.9	85[1]
0.8	10	2.0	125[2]
1.3	18	2.35	450
1.7	45		

[1] Bubbles at cathode.
[2] Bubbles at anode.

Table L.

Solution : amm. tartrate + 0.1 g Ag as $AgNO_3$
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.4	0.8	1.0	75[1]
0.8	60	1.5	75

[1] Deposit of metal ; bubbles at anode.

Table LI.

Solution : amm. tartrate + 0.1 g Hg as $HgCl_2$
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.9	35	1.6	65
1.2	65[1]	2.1	150

[1] Deposit of metal ; bubbles at anode.

TABLE LII.

Solution : amm. tartrate + 0.1 g Pb as $Pb(NO_3)_2$

Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.8	12	1.4	50[2]
1.3	40[1]	1.9	80[3]

[1] Deposit of metal.

[2] No bubbles at anode.

[3] Bubbles at both electrodes.

Some peroxide deposits at anode. Deposit at cathode good and adherent.

TABLE LIII.

Solution : amm. tartrate + 0.1 g Bi as $Bi(NO_3)_3$

Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.8	11	1.7	40
1.25	35	2.0	65
1.35	40[1]	2.3	225[2]

[1] Deposit of metal ; no bubbles at either electrode.

[2] Bubbles at both electrodes.

Very good deposit of metal at cathode.

TABLE LIV.

Solution : amm. tartrate + 0.1 g Cu as $CuSO_4$

Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.25	80	1.75	160
1.4	90	2.0	250[2]
1.65	160[1]	2.3	550

[1] Traces of copper.

[2] Bubbles at both electrodes.

Copper deposit not good.

TABLE LV.

Solution: amm. tartrate + 0.1 g Co as $CoSO_4$
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.9	6	1.8	60
1.35	15	2.0	150[1]

[1] Bubbles at both electrodes; metal at cathode; deposit good.

TABLE LVI.

Solution: amm. tartrate + 0.1 g Cd as $CdSO_4$
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.7	22	2.2	125
2.1	80[1]	2.3	125

[1] Deposit of metal; bubbles at anode. Deposit is good if voltage is kept low.

TABLE LVII.

Solution: amm. tartrate + 0.1 g Zn as $ZnSO_4$
Vol. 170 cc. Temp. 60°. Cathode copper-plated

Volts	Milli-amperes	Volts	Milli-amperes
0.2	Reverse current	1.7	15
0.4	0.1	2.2	22
0.8	1.8	2.3	70[1]
1.3	10	2.5	160

[1] Deposit of metal; bubbles at anode.

TABLE LVIII.

Solution: amm. tartrate + 0.1 g Ni as $NiSO_4$
Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.85	10	1.85	125[1]
1.35	15	2.3	600[2]

[1] Bubbles at cathode; none at anode.
[2] Deposit of metal and bubbles at each electrode.

TABLE LIX.

Solution : amm. tartrate + 0.1 g Sn as $SnCl_2$

Vol. 170 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.65	25	2.5	375
1.9	75[1]	3.0	650
2.25	130	3.5	1200[2]

[1] Bubbles at both electrodes.

[2] No deposit of metal.

From Neumann's measurements of the electromotive force,[1] we know the voltaic series in chloride, nitrate, and sulphate solutions. His experiments on hydrogen refer to a normal acid, and it seemed desirable to have the data on file showing that zinc precipitates before hydrogen in a neutral solution. Experiments were therefore made with zinc sulphate, magnesium sulphate, and sodium sulphate, the first giving metal, the second hydrogen and a sparingly soluble base, and the third hydrogen and a soluble base. All these series were made with a coppered cathode so that they might be comparable.

TABLE LX.

Solution : 1 mol $ZnSO_4$ per liter

Vol. 200 cc. Temp. 20°. Cathode copper-plated

Volts	Milli-amperes	Volts	Milli-amperes
0.8	0.1	2.3	12
1.4	1.0	2.5	15
1.7	2.0	2.75	125[1]

[1] Metal at cathode ; bubbles at anode.

---

[1] Zeit. phys. Chem. 14, 229 (1897).

TABLE LXI.

Solution: 1 mol $MgSO_4$ per liter

Vol. 200 cc. Temp. 20°. Cathode copper-plated

Volts	Milli-amperes	Volts	Milli-amperes
1.3	0.4	2.75	40[1]
1.7	10	3.1	160[2]
2.5	12	3.5	410

[1] Bubbles at anode.
[2] Bubbles at cathode.

TABLE LXII.

Solution: 1 mol Na_2SO_4 per liter

Vol. 200 cc. Temp. 20°. Cathode copper-plated

Volts	Milli-amperes	Volts	Milli-amperes
1.7	2.0	3.0	100[1]
2.5	10	3.35	350[2]
2.75	15	3.5	525

[1] Bubbles at anode.
[2] Bubbles at cathode.

A convenient method for determining nickel is the one using a solution of ammonium sulphate and ammonia. Since cadmium can be separated from nickel in a solution containing ammonium sulphate and sulphuric acid, it seemed necessary to make some measurements with cadmium and nickel in ammonium sulphate solutions to which ammonia or sulphuric acid had been added. The results obtained are given in Tables LVIII–LXXI.

TABLE LXIII.

Solution: 10 g $(NH_4)_2SO_4$ + 30 cc NH_4OH (0.92) + 0.2 g Ni as $NiSO_4$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
0.76	0.6	2.35	600[2]
1.15	3.0	2.75	1000
1.5	3.8	2.95	1250[3]
1.85	75[1]	3.25	1570
2.15	365	3.5	2080

[1] Bubbles at anode.
[2] Bubbles at both electrodes.
[3] Deposit of metal.

TABLE LXIV.

Solution: 10 g $(NH_4)_2SO_4$ + 30 cc NH_4OH (0.92) + 0.2 g Ni as $NiSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.85	2.4	2.0	325[1]
1.15	10	2.1	550
1.6	18	2.4	900

[1] Deposit of metal; bubbles at anode.

TABLE LXV.

Solution: 10 g $(NH_4)_2SO_4$ + 30 cc NH_4OH (0.92) + 0.2 g Cd as $CdSO_4$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.2	2.5	2.4	85[2]
1.7	3.7	2.85	185
2.1	25[1]	3.25	650

[1] Bubbles at anode.
[2] Heavy deposit of metal.

TABLE LXVI.

Solution: 10 g $(NH_4)_2SO_4$ + 30 cc NH_4OH (0.92) + 0.2 g Cd as $CdSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.45	0.2	1.8	15
0.9	1.5	2.3	175[1]
1.45	12	2.64	410

---

[1] Heavy deposit of metal; bubbles at anode.

TABLE LXVII.

Solution: 10 g $(NH_4)_2SO_4$ + 4 cc H_2SO_4 (1.09) + 0.2 g Ni as $NiSO_4$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
0.76	0.15	2.7	420[2]
1.0	1.5	3.05	680
1.4	2.4	3.4	1050
2.0	85[1]	3.65	1300
2.35	160	4.4	2750

---

[1] Bubbles at both electrodes.
[2] Very slight deposit of metal.

TABLE LXVIII.

Solution: 10 g $(NH_4)_2SO_4$ + 4 cc H_2SO_4 (1.09) + 0.2 g Ni as $NiSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
1.2	1.9	2.6	800
1.95	75[1]	2.8	1250[3]
2.2	265[2]	3.1	2000

---

[1] Slight bubbles at anode.
[2] Bubbles at both electrodes.
[3] Traces of metal.

TABLE LXIX.

Solution: 10 g $(NH_4)_2SO_4$ + 4 cc H_2SO_4 (1.09) + 0.2 g Cd as $CdSO_4$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
1.12	2.9	2.4	75[1]
1.65	3.9	2.8	275[2]
2.15	18	3.5	800

---

[1] Traces of bubbles at anode.
[2] Deposit of metal.

TABLE LXX.

Solution: 10 g $(NH_4)_2SO_4$ + 4 cc H_2SO_4 (1.09) + 0.2 g Cd as $CdSO_4$
Vol. 200 cc. Temp. 60°

Volts	Milli-amperes	Volts	Milli-amperes
0.8	0.5	2.0	35
1.26	5	2.32	185[1]
1.7	12	2.75	525[2]

---

[1] Slight deposit of metal; bubbles at anode.
[2] Good deposit of metal.

TABLE LXXI.

Solution: 10 g $(NH_4)_2SO_4$ + 8 cc H_2SO_4 (1.09) + 0.2 g Ni as $NiSO_4$
Vol. 200 cc. Temp. 20°

Volts	Milli-amperes	Volts	Milli-amperes
0.76	0.1	2.5	650
1.15	1.1	2.85	1050
1.65	3.5	3.1	1250
2.2	215[1]	3.7	2150[2]

---

[1] Bubbles at both electrodes.
[2] Slight deposit of metal.

From these experiments it seems improbable that a satisfactory separation of cadmium from nickel can be obtained when only 4 cc H_2SO_4 are added. The addition of more acid raises the voltage at which nickel precipitates and has little effect on cadmium, so that a separation is then possible. One curious phenomenon comes out even more clearly here than in the previous experiments, the effect of cadmium sulphate on the evolution of hydrogen. In Table LXVII there is visible evolution of hydrogen under a potential difference of 2.0 volts. In Table LXIX there is no perceptible evolution of hydrogen at 2.8 volts. The first solution contains 0.2 g Ni as $NiSO_4$, the second 0.2 g Cd as $CdSO_4$; otherwise there is no difference between them.

From the tables given in this paper and from some that have not been published, I have compiled tables showing the voltaic series for each solution and the approximate voltage at which each metal appears under the conditions of the experiments. The values for zinc are not strictly comparable with those for the other metals because they were made with a copper cathode, and the potential difference Cu–Pt should be added. In cases where no precipitation of metal was obtained, the value is said to be higher than the highest voltage actually measured.

For the sake of completeness, the voltaic series for normal solutions of the metals as ions is given in Table LXXII. This is taken from Neumann's experiments[1] and, barring insoluble salts, holds for chlorides, nitrates and sulphates. It must be remembered that electromotive force measurements and electrolysis measurements will give the same order only in case the reaction at the electrode is strictly reversible, which is possibly not true for nickel.

TABLE LXXII.
Voltaic series in normal solutions

Ag
Hg
Cu
Sb
Bi
H(H_2SO_4)
Pb
Sn
Co
Ni
Fe
Cd
Zn
H(NaOH)

---

[1] Zeit. phys. Chem. 14, 223 (1894).

TABLE LXXIII.

Voltaic series in N/4 KCN + 0.2 g metal per 200 cc

Temp. 20°		Temp. 60°	
Ag	2.04	Ag	1.8
Hg	2.2	Hg	2.0
Bi	2.5	H	2.5
H	2.74	Cu	2.6
Cd	2.8	Cd	2.8
Zn	>4.5	Zn	>4.1
Ni	>4.2	Ni	>3.5
Cu	>4.4		

TABLE LXXIV.

Voltaic series in 2N/1 KCN + 0.2 g metal per 200 cc

Temp. 20°		Temp. 60°	
Hg	1.98	Ag	1.67
H	2.3	Hg	1.87
Cd	2.5	Cd	2.3
Ag	2.9	H	2.65[1]
Cu	>3.3	Cu	>3.3
Zn	>3.3	Zn	>3.3
Ni	>3.5	Ni	>3.5

---

[1] This determination was made with an old solution and is probably wrong. As the value is of no interest, it was not redetermined.

TABLE LXXV.

Voltaic series in oxalate solution + 0.1 g metal per 175 cc

Temp. 60°		Temp. 60°	
Hg	0.65	Cd	1.8
Cu	1.0	Ni	1.9
Bi	1.15	Co	1.9
Sb	1.2	Fe	1.9
H	1.45	Sn	2.1
Pb	1.55	Zn	2.6 (copper)

TABLE LXXVI.

Voltaic series in acid sodium phosphate solutions

50 cc Na_2HPO_4 + 15 cc H_3PO_4 + 0.1 g metal per 150 cc

Temp. 60°		Temp. 60°	
Ag	1.2	Pb	2.85
Hg	1.3	Cd	2.9
Cu	1.75	Zn	3.15 (copper)
Bi	1.9	Co	>3.5
H	1.9	Ni	>3.5
Sb	2.0	Sn	>3.3

TABLE LXXVII.

Voltaic series in phosphate solutions

6 cc H_3PO_4 + 0.1 g metal per 130 cc

Temp. 60°		Temp. 60°	
Ag	1.3	H	2.25
Hg	1.3	Cd	2.4
Cu	1.6	Zn	2.7 (copper)
Bi	1.9	Zn	3.4 (platinum)
Sb	2.1	Co	2.9
Pb	2.2	Ni	>3.5
		Sn	>3.5

TABLE XXVIII.

Voltaic series in ammoniacal tartrate + 0.1 g metal per 170 cc

Temp. 60°		Temp. 60°	
Ag	1.0	Co	2.0
Hg	1.2	Cd	2.1
Pb	1.3	Zn	2.3 (copper)
Bi	1.30	Ni	2.3
Cu	1.65	Sn	>4.8
H	1.9		

TABLE LXXIX.

Voltaic series in alkaline tartrate solution

5 g cryst. sodium potassium tartrate + 25 cc NaOH (sp. gr. 1.28 at 20°) + 0.1 g metal per 150 cc

Temp. 20°		Temp. 20°	
Zn	1.7 (platinum)	Bi	2.0
Cu	1.75	Sb	2.0
Co	1.75	Sn	>3.0
Pb	2.0	Ni	>2.8
H	2.0		

These tables point to the possibility of several new separations, but we will only consider two at the present moment. From Table LXXIV it appears that the decomposition voltage for silver is nearly a volt higher than that for mercury in a double normal potassium cyanide solution at 20°. A series of runs showed, however, that silver was always precipitated with the mercury. This is not especially surprising since mercury precipitates as a liquid and silver and mercury are known to form compounds. When the decomposition voltages of two metals are practically the same, no separation is possible. The converse is not necessarily true that a separation can be made when the decomposition voltages are very different. This is true only when neither of the metals affects the decomposition voltage of the other, a condition which does not hold experimentally in this case.

From Tables LXXIX it appears that nickel does not precipitate from an alkaline tartrate solution while cobalt does. This points to the possibility of precipitating cobalt at the cathode free from nickel and is the method actually proposed by Vortmann.[1] Some preliminary experiments indicate that this separation is more satisfactory than has hitherto been supposed.

The main object of this investigation was to obtain the data necessary for a classification of the methods of analysis now in use. In Tables LXXX–LXXXV are given most of the important separations for silver, mercury, copper, bismuth, lead,

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[1] Monatshefte für Chemie, 14, 536 (1893).

TABLE LXXX.

Silver or mercury from			
Cu	Nitric acid	V	V
	Cyanide	C	C
Bi	Nitric acid	V	V
Pb	Excess nitric acid	C	C
Sn	Sulphide (Ag_2S insoluble)		
Fe	Nitric acid	C	C
	Cyanide	C	C
Ni	Acid	C	C
	Cyanide	C	C
Cd	Nitric acid	C	C
	Cyanide	V?	C
Zn	Cyanide	C	C

TABLE LXXXI.

Copper from			
Bi	Cyanide + citrate bismuth precipitates	C	C
Pb	Excess nitric acid	C	C
Sn	NH_3 + tartrate	C	C
Fe	Acid, phosphate, or oxalate	C	C
Ni	Acid, phosphate	C	C
	Oxalate	V?	C
Cd	Acid	V?	C
	Phosphate	C	C
	Cyanide, cadmium precipitates	C	C
Zn	Acid, phosphate	C	C

TABLE LXXXII.

Bismuth from			
Pb	None		
Sn	NH_3 + tartrate	C	C
Fe	Acid sulphate	C	C
Ni	Acid sulphate	C	C
Cd	Acid	C	C
Zn	Acid	C	C

TABLE LXXXIII.

Iron from			
Ni	None		
Cd	Alkaline cyanide cadmium precipitates	C	C
	Acid $(NH_4)_2SO_4$, cadmium precipitates	C	C
	Phosphate, cadmium precipitates	C	C
Zn	Alkaline cyanide, zinc precipitates	C	C

TABLE LXXXIV.

Nickel from			
Cd	Alkaline cyanide cadmium precipitates	C	C
	Acid $(NH_4)_2SO_4$, cadmium precipitates	C	C
Zn	NaOH + tartrate, zinc precipitates	C	C

TABLE LXXXV.

Cadmium from			
Zn	Sulphate	C	C
	Cyanide	C	C
	Phosphate	C	C
	Oxalate	C	V?

tin, nickel, iron, cadmium, and zinc. The first column gives the metal and the second the solution. In the third column C means that a constant current separation is used and V a voltage separation. In the fourth column the same letters refer to the method of separation as predicted from measurements of decomposition voltage. The third column thus refers to practice, and the fourth to theory. Obviously the two should agree.

As was to have been expected, practically all the determinations are constant current separations, and the few which are not are of minor importance. There are only a few cases in which there is a discrepancy between the analytical method and the results of decomposition measurements. The separation of cadmium from zinc in oxalate solutions becomes intelligible in view of the experimental fact already referred to, that cadmium precipitates before hydrogen, though at a higher voltage. This may also account for the separation of silver from cadmium in cyanide solution; but I think not. It seems more probable that the behavior of silver and cadmium in cyanide solutions, of copper and nickel in oxalate solution, and of copper and cadmium in acid solution should be referred to the formation of an alloy. It is known that the decomposition voltage is changed under these circumstances.[1] On the other hand, it is also possible that it is merely a result of insufficient stirring just as Smith[2] found that copper carries down iron when precipitated on a platinum dish, but does not when precipitated on a vertical cathode.

Some experiments were made on the rate of deposition when the solution was stirred vigorously. I succeeded in getting copper completely precipitated inside of twenty minutes, when the paper of Gooch and Medway[3] appeared, in which a more efficient stirring had given still better results in point of time.

In this paper are given the data necessary for a systematic classification of most of the analytical methods with the exception of the sulphide solutions. The work was undertaken at the suggestion of Professor Bancroft, and has been carried under his direction.

Cornell University.

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[1] Coehn. Zeit. phys. Chem. 38, 609 (1901).

[2] Jour. Am. Chem. Soc. 24, 1073 (1902).

[3] Am. Jour. Sci. (4) 15, 320 (1903).

NEW BOOKS

The Sub-Mechanics of the Universe. *By Osborne Reynolds. Published for the Royal Society of London. 18 × 26 cm; pp. xvii + 251. Cambridge: The University Press, 1903.* — In the author's statement, the theory presented in this publication was arrived at through the following series of preliminary steps. First, a mechanical explanation of the sudden change in the rate of flow of the gas in the tube of a boiler when the velocity reaches a certain limit (1874). Second, the discovery of the thermal transpiration of gases, together with the analytical proof of the dimensional properties of matter (1879). Third, the discovery of the criterion of the two manners of motion of fluids (1883). Fourth, the discovery of "dilatancy" as the ruling property of all granular media (1885). Fifth, the effecting of the analysis for viscous fluids, and the determination of the criterion (1895); which led to recognition of the possibility of the analytical separation of the general motion of a fluid into mean varying motion, displacing momentum, and relative motion. This suggested the view that the medium of space is granular, the grains being in relative motion and at the same time subject to varying mean motion. The present research shows that this view affords a purely mechanical explanation of the physical phenomena of the universe. The method employed is that of the general equations of a conservative system.

The medium of space is taken to be an indefinitely extended system of uniform spherical grains of changeless shape and size, generally in normal piling, and so close together that the grains cannot change their neighbors, although they are assumed to be continually in motion relative to one another. It thus constitutes, to a first approximation, an elastic medium with six symmetrically placed axes of elasticity. When strained, such a medium must expand — exhibit " dilatancy."

In spaces in which there are local inequalities in the medium about local centers, owing to an *absence* of some of the grains necessary for normal piling, such local inequalities are permanent. They are necessarily attended by displacements and strains, extending indefinitely throughout the medium and causing dilatation equal everywhere to the volume of the missing grains.

When the arrangement of the grains about the centers is that of a nucleus of grains in normal piling, on which grains in the strained normal piling rest, the nucleus cannot gear with the surrounding grains in strained normal piling: there must be a singular surface of misfit between the two. This singular surface is free to maintain its motion through the medium, in any direction, by a species of propagation, a number of grains entering the surface on one side and an equal number leaving it on the other. During this motion the grains forming the nucleus remain stationary. The inequalities in question correspond to molecules of matter. Matter is accordingly regarded as a strain, which is propagated through the medium.

Certain components of the dilatation are due to the variation of those components of the inward strain that cause curvature in the normal piling of the medium. These components, taken to a first approximation only, give rise to efforts tending to cause two inequalities at finite distances to approach each other. These efforts are proportional to the inverse square of the distance, and correspond to gravitation. The terms not taken into account in this approximation involve the inverse distance to the sixth power, and so have a very short range. They correspond to surface tensions, and to cohesion between the surfaces of the inequalities.

In the foregoing only *negative* inequalities, those due to a deficiency of grains, have been considered. If *positive* inequalities existed, the efforts acting between them would be reversed, dispersing them through space. This circumstance is in accord with the lack of evidence of such inequalities.

A *complex* inequality would result from the removal of a number of grains in the otherwise uniform medium to another position. It consists of two equal inequalities, one positive and one negative, and corresponds to electricity. Calculation is made of the effort of the tendency to revert to the state of normal piling. This is found to be enormously greater than the effort corresponding to gravitation. Disruptive reversion of complex inequalities gives rise to transverse undulations in the medium, i. e., to waves of light.

Thus far the theory maintains a quantitative character, and the constants of the postulated medium are determined in such wise that the results of the theory accord with experimental data. Among the quantities whose numerical values are found are the diameter, the mean velocity, and the mean path of the grains. These quantities completely define the state of the medium in spaces where the piling is normal. They also determine its mean density, which is found to be ten thousand times that of water. Other values determined are those of the mean pressure in the medium, the coefficient of the transverse elasticity resulting from the gearing of the grains where the piling is normal, and the rates of propagation and of degradation of the transverse and normal waves. Further analytical examination of the behavior of the postulated medium shows that the periods of vibration of the molecules must coincide with the periods of the waves; and it accounts for the absorption, refraction, dispersion, polarization, metallic reflection, and aberration of light. The author claims, in conclusion, to have shown that there is one, and indeed only this one, conceivable purely mechanical system capable of accounting for "all the physical evidence, as we know it, in the universe."

The simple nature, the quantitative character, and above all the surprising scope of this remarkable speculation constitute serious claims to attention. If the theory should prove of real service in the solution of such problems as the search for the forms of the characteristic equations of fluids, for the forms of the specific heats of substances, for the relation between the combining weights of the chemical elements, or for the relationship between the series of spectrum lines of the elements, it will have justified itself, which is more important than any attempt to justify its pretentious metaphysical title. *J. E. Trevor*

Lehrbuch der kosmischen Physik. *By Svante August Arrhenius. 15 × 23 cm. Erster Teil, pp. viii + 472; Zweiter Teil, viii + 473 to 1026. Leipzig: S. Hirzel, 1903. Price: paper, 38; bound, 40 marks.* — Most of us who knew

Arrhenius only from the chemical side, were startled some time ago to find him the author of a vast cosmical speculation, in which the nature of comets, nebulae, protuberances, faculae, zodiacal light, *Gegenschein*, and, furthermore, the variations of barometric pressure, of terrestrial magnetism, etc., were systematically interpreted. A part of the theory has since been modified by the investigation of Schwarzschild, though it at once gave new impetus to all questions relating to light pressure and cosmical dust. The book before us, with its two large octavo volumes of about five hundred pages each, shows why Arrhenius was led to this line of research; and it likewise contains his most recent revisions of his theory.

The first volume deals with astronomical and geological phenomena; and the chapters on the stars recall much of Newcomb's more recent work, so far as subject-matter is concerned. In the geologic portions it is refreshing to read appreciative accounts of the work done under the supervision of Dutton, Becker, Gilbert, Hague, and others, whence it follows that of the tons of scientific literature which issue from the Departments in Washington, a few, at least, will not escape the recording angel, wherefore let us be thankful. In addition to the solar dust theory ingrained throughout the volume, the book contains *many original features, a discussion of which would carry us beyond the purposes* of this Journal; suffice it to say that the fixed stars, the solar system, the sun, the nebular hypothesis, are first treated in turn, after which the earth with its lands and seas makes up the subject-matter of the remaining half of the book. An account is given of original researches, always with a citation of the author and frequently of the year of publication; but full references are not offered.

The chemically interesting feature of the first volume is the discussion of solar heat. Arrhenius looks with small favor on Helmholtz's and Kelvin's theories, as being incompatible with geological evidence; and actually has the hardihood to propose a return to chemical theories. He is aware, of course, that the latter have been almost universally rejected. They seem hopelessly insufficient to account for the tremendous outpour of heat observed. But he argues that in the redistribution of chemical equilibria at very high temperatures, the *exchanges of energy are enormously greater than at lower* temperatures, and that for this reason computations made with ordinary laboratory data, such as those following from the combustion of carbon, for instance, have no bearing on the problem. To the reviewer it also seems plausible, in view of the recently discovered heat manifestations of radium, that a definite chemical theory of solar heat may be looked for in the near future.

The second volume is an exhaustive treatise on meteorology, beginning with a detailed account of Aitken's researches on atmospheric dust. The reviewer notes with interest the larger order of Aitken's dust numbers and their probable maxima in summer, in comparison with the smaller numbers and winter maxima obtained for nuclei when observed by measuring the coronas of cloudy condensation. It seems probable that different bodies are observed in the two cases, and that from the coronas the mere dust effect is eliminated. The earlier chapters of the book deal with those subjects which only a born meteorologist can find patience to worthily peruse, such as the variation of atmospheric pressure, heat absorption, temperature, hygrometry, clouds, winds, cyclones, storms, etc., notwithstanding their undeniable terrestrial or even cosmic importance. In treating atmospheric circulation, in relation to which Ferrel's great theory seems no longer to be adequate, a full reivew is given of the clear-cut presentation of the subject due to Bjerknes and Sandström, which will be welcomed as a valuable feature of this part of the book.

The concluding chapters on meteorological accoustics, optics, atmospheric electricity, and terrestrial magnetism, will be found interesting reading even by those who are not specially interested in meteorology; and it is here that Arrhenius finds abundant occasion for citing evidence showing the resources of his theory.

The book is full of statistical information, abounding in tables, charts, and figures, and in many instances Arrhenius has obviously endeavored to get at the arithmetic of the case from computations of his own. The information is throughout specific. As a whole the work will take rank beside the great contributions of Mohn, Guldberg (who it will be noted, shared with Arrhenius this double allegiance to chemistry and geophysics), and others, who have made meteorology a debtor to the thinkers of the North. *C. Barus*

Principles of Inorganic Chemistry. *By Harry C. Jones. 14 × 21 cm; pp. xx + 521. New York: The Macmillan Company, 1903. Price: bound, $4.00.* — The present book of Dr. Jones is a welcome addition to the slowly growing class of larger texts in which chemistry is approached from a modern standpoint. There is hardly a doubt that the teaching of elementary chemistry must sooner or later make large use of the broadened view gained from physical chemistry. The older texts which have tried to make themselves modern by adding a chapter on physical chemistry at the end of the book, have not gained much thereby. If the newer ideas are to count for anything, they must be incorporated, taken into the body of the subject. The large and admirable text of Ostwald is well known, in which the theory of electrolytic dissociation is used with great freedom, and the study of chemical substances made as far as possible a study of the ions. The same general system is followed here, though it is not necessary to accuse Dr. Jones of having borrowed from Ostwald; indeed in one respect at least — in the freer use of the periodic system in classification — the present volume as a teaching manual has to the reviewer's mind a decided advantage over that of Ostwald.

But a fundamental question is suggested anew by the appearance of this book, — Is not the theory of electrolytic dissociation made too prominent in these new texts, to the exclusion or neglect of other generalizations of physical chemistry; generalizations which may prove in the end of far more value in making of this branch an exact science? Would it not be worth while for some one to write us a textbook of inorganic chemistry in which the phase rule, mass action, etc., should come more nearly to their rights?

The book before us bears abundant evidence of the painstaking work which has been put upon it, and the more of such books we can have, the better. In its main outlines too it is excellent; though there are several matters of general arrangement that could perhaps have been bettered, there are also many points of detail where inaccuracies of one kind and another have crept in, and very many turns in the presentation of the subject which invite discussion. The main fault of the book is the very common one that it can hardly be said to appeal to any one class of students; there is too much elementary material for the advanced worker, and on the other hand the material is both too difficult and too incompletely worked out for the beginner, who would surely be swamped before he had weathered a hundred pages of it.

The treatment of the whole subject betrays the habit of mind of one accustomed to deal with much maturer students than college freshmen. But if in this way it loses its simplicity, there is an offsetting gain in completeness, and there are many passages, notably some in which the practical applications of chemistry are set forth, which are admirable.

Minor errors in the text are regrettably numerous. Thus, to mention only some of them: On p. v. we are told that the theory of electrolytic dissociation was "discovered" by van 't Hoff and Arrhenius; on p. 10, Proust is spoken of as an Englishman; on p. 63, it is stated that "the alcohols dissolve in water in all proportions"; on p. 206, ammonia is said to be "a good refrigerating agent on account of its high specific heat"; on p. 288, ether is spoken of as an oxidation product of alcohol, and on p. 225 nitric oxide is said to have the power "of giving up some of the oxygen which it already possesses—of being a reducing agent"; on p. 284, Mendeleeff is accused of having termed the critical temperature "the absolute boiling-point of the gas"; on p. 289, it is said that a salt M_2CS_3 is a salt of thiocarbonic acid, and three lines below such salts are called trithiocarbonates; on the same page carbon disulphide is described as a "liquid melting at −113°; on p. 337, in speaking of the purification of potassium hydroxide by alcohol, it is said that the alcoholic solution after filtering from carbonate is "evaporated away from all traces of carbon dioxide". With regard to the properties of water some strange statements appear. Thus on page 58 we find "the tension of water vapor is as we would expect, greatest when the water is in the form of vapor, less when the water is liquid, and least when the water is in the solid state". The reviewer is unable to say whether this statement is correct or not, being unable to understand what it means; hardly less difficult is this from p. 47,—"while water exists in the atmosphere in the form of vapor, it takes up many kinds of impurities". But there can be no doubt that the statement on p. 55, "since water expands from 4° to 0° ice is lighter than water", is logically defective.

Of misprints or slips of the pen a few may be noted: "Tyndal", on p. 56; "ammonia" for "mercury", p. 207, l.24; "nitrates" for "nitrites", p. 226, l.5; "hyponitrate" for "hyponitrite", p. 228, l.17; "H_4SiF_4" for "H_4SiO_4", p. 300, l.29; "ammonium gas", p. 357; we find "hydrolyzed" usually so spelled throughout, but on p. 424, and again on p. 430, it appears as "hydrolized".

Peculiarities of usage appear now and again; one does not need to be a purist to take exception to the use in an elementary text of $\frac{1}{2}H_2O$, and $1\frac{1}{2}H_2O$ in formulæ on p. 367; and at the discovery of the term "septahydrate" on p. 326, or elsewhere, one looks to see whether P_2O_5 is called "quinquoxide".

Instances of this kind might perhaps be multiplied indefinitely if one read the book through for the sole purpose of collecting them. The reviewer has read most of it, but for the better reason that the text is really interesting; the author's own interest in his subject never flags— the style has even at times a kind of fervor most rare in a textbook —and the energy so stored up is set free again as warmth in the reader.

It must be said however that beyond minor errors such as those cited above, the book surely has grave faults as a manual for elementary instruction, particularly in the want of a natural development of the subject at the beginning. The first chapter, after the time-worn paragraph on the relation between physics and chemistry, takes up the subject of elements and compounds, giving a complete list of the known elements with their symbols; the derivation of the symbols is not given except in the cases of copper and iron, and indeed there appears to be no mention anywhere in the volume of the origin of the symbols for tin, antimony, mercury, and the others that are apt to puzzle the beginner. In the next section (p. 6), occurs a chemical equation $H_2 + O = H_2O$, which is useless if the student does not understand it, and wrong if he does.

The second chapter is on generalizations and introduces us to the laws of the conservation of mass, of constant proportion, multiple proportion, combining weights; the atomic theory and the conservation of energy. After this follows a chapter on oxygen and ozone in which chemical formulæ are used with freedom and the gas laws are introduced. Chapter IV treats of hydrogen; Chapter V of water and hydrogen dioxide, and incidentally introduces the phase rule; Chapters VI, VII, and VIII, including forty-six pages, are devoted entirely to theoretical matters, and embrace the determination of atomic and molecular weights, Avogadro's hypothesis, the law of Dulong and Petit, isomorphism, abnormal vapor densities, law of mass action, freezing-point and boiling-point methods, osmotic pressure and its theory, the theory of electrolytic dissociation, and the conductivity method. After this is done with, the arrangement of the material becomes more logical, and of the rest of the text there is nothing to be said but that it is in the main very good.

As mentioned above, the subject is treated throughout from the standpoint of the electrolytic dissociation theory. Facts which go to support this theory are made the most of, and their bearing is clearly pointed out, while those which do not so well accord with it, if mentioned at all, are left to tell their own tale. This is not from any desire on the part of the author to mislead, but doubtless because he believes that in the end all things must be brought into agreement with this theory. Whatever the future may reveal, he has great faith who can now write (p. V), "we know to-day that nearly all inorganic reactions are reactions between ions, molecules and atoms as such having nothing to do with the reactions." Dr. Jones even goes so far as to think that phosphoric acid ions are the most important constituent of commercial fertilizer (p. 372). Indeed one comes away from reading the book with the feeling that the ion has been rather overworked.

But with all its faults—and most of them can easily be corrected—the book is surely an advance on any other elementary text written in English, and it can be recommended without hesitation, if not without qualification, to the attention of all teachers and advanced students. That the beginner can use it with profit remains to be proved. *A. P. Saunders*

The Rôle of Diffusion and Osmotic Pressure in Plants. *By Burton Edward*

Livingston. The Decennial Publications of the University of Chicago. Second Series, Volume VIII. 14 X 22 cm; pp. xiii + 144. Chicago: University of Chicago Press, 1903. Price: bound, $1.50 net. — The first part of the book contains a brief sketch of the theory of solutions; the second consists of the application of the general principles to plant physiology. The chapters in the second part are: turgidity; absorption, and transmission of water; absorption and transmission of solutes; influence of the osmotic pressure of the surrounding medium upon the organisms. Under turgidity we find the subheads: protoplasm and its limiting membranes; plasmolysis; the permeability of the protoplasmic layers; action of the protoplasmic membrane; the nature of the osmotically active solutes; the maintenance of turgidity in spite of permeability to certain solutes; the relation of turgidity to vital activity.

This is a very interesting book and can be commended to physical chemists. There are three stages in the history of any two branches of science. At first the two are entirely independent and neither profits by the other. Then each takes something from the other, but takes it on authority. Lastly, a worker in either science avails himself of principles discovered in the other; but with a full knowledge of the limitations. We have passed through the first stage with regard to botany and physical chemistry, and are now in the second.

The development along the line of least resistance is as marked in botany as it is in physical chemistry. When anything unexpected occurs in the domain of the latter science, we attribute it to "variations from the gas laws." In botany it is sufficient to say "change in the protoplasmic membrane."

Wilder D. Bancroft

Lectures on the History of the Development of Chemistry since the Time of Lavoisier. *By A. Ladenburg. Translated from the second German edition by Leonard Dobbin. 13 X 18 cm; pp. xv + 371. Chicago: The University of Chicago Press, 1902. Price: bound, $1.75, net.* — A translation of Dr. Ladenburg's familiar lectures on the history of chemistry could not fail to be a most welcome addition to chemical literature. For the present edition moreover the author has written a supplementary lecture covering in outline the recent developments in physical chemistry, stereochemistry, the new gases of the air, and a few other topics.

Compared with the work of E. von Meyer the present has the great advantage of being readable as well as instructive, and one only regrets that conciseness has been pushed to an extreme and that one page often has to do the work of ten. But references to the literature are numerous, and if the book is used as an outline merely — as it is meant — it gives what is necessary. It would be most desirable that this very weak department of chemistry should some day be enriched by a larger work from the same hand; in the meantime it will be an advantage to all who teach chemical history that this work has been improved and made more available.

Of errors in text there are few, mostly typographical; the statement that Horstmann, Gibbs, van der Waals, and van 't Hoff have devoted themselves exclusively to physical chemistry is, let us hope, due to a slip in translation. On the whole, the translator has preserved to a surprising degree the charm of the original text, if the expression is not too strong; at any rate the book is hard to put down when once taken up. In type and general make-up it is all that it needs to be, and it is most heartily commended to the attention of all students.

A. P. Saunders

Elektro-Metallurgie des Nickels. (*Monographien über angewandte Elektrochemie, Band VI.*) *By W. Borchers. 16 × 24 cm; pp. 35. Halle: Wilhelm Knapp. Price: paper, 1.50 marks.*—The title of this monograph is somewhat misleading. There is very little attempt made to discuss the actual technical electrochemistry of nickel. Stress is laid on what is to be done in the future, as a result of experiments made in the author's laboratory by Günther. While it is quite possible that nickel may be deposited at the cathode and lead peroxide formed at the anode, this is not yet a commercial success and is therefore of relatively less interest than the processes which are actually in use to-day. Thus there is no reference to the separation of nickel and copper by D. H. Browne of Cleveland, although information in regard to this is not difficult to obtain. This pamphlet may give an accurate sketch of conditions as they exist in Germany; but it is not up to date as regards American practice.

Wilder D. Bancroft

Das neue Institüt für Metallhüttenwesen und Elektrometallurgie an der königlichen technischen Hochschule zu Aachen. *By Wilhelm Borchers. Abschnitt: Elektrische Massinstrumente; bearbeitet von H. Danneel. 20 × 29 cm; pp. 61. Halle: Wilhelm Knapp, 1903. Price: paper, 6 marks.* — A description of the new electrochemical laboratory at Aachen, with a statement of the equipment, a sketch of the scientific work which has already been done there, and an outline of what is to be attempted. The laboratory can draw up to 20 H. P. from the city lighting circuit and has its own gas-generating plant which will give 50-60 H. P. and can easily be enlarged to a capacity of 100 H. P. The scientific investigations include: the non-electrical preparation of calcium carbide; the manufacture of graphite; the electrolytic deposition of zinc with anode production of lead peroxide; the treatment of nickel copper matte; the treatment of certain zinc ores; the electrolytic preparation of sodium, calcium, and strontium from fused chlorides; the electrolytic extraction of the cerium metals; the extraction of copper sulphide ores with ferric sulphate; the treatment of titaniferous ores.

The future work of the laboratory will be along the two great lines of precipitation of metals from aqueous solutions and from fused salts. It is recognized as essential that the equipment must permit of experiments being made on a large scale. The new laboratory makes this possible.

Wilder D. Bancroft

Die Elektrochemie und die Metallurgie der für die Elektrochemie wichtigen Metalle auf der Industrie- und Gewerbe-Ausstellung in Düsseldorf, 1902. *By H. Danneel. 20 × 29 cm; pp. 80. Halle: Wilhelm Knapp, 1903. Price: paper, 6 marks.* — The greater part of this sketch has already appeared in the *Zeitschrift für Elektrochemie.* The author describes the exhibits of the Aachen laboratory and of Hartmann and Braun; devotes several pages to the new Heraeus platinum foil furnaces, and three more to gas generators and gas engines. There is a section on machinery for treating ore and one on the annual production of metals. The deposition of copper and the manufacture of accumulators are treated at some length. Goldschmidt's thermite process receives nine pages, and three are given to Heraeus's autogenous welding of aluminum, while the last few pages are devoted to arc and incandescent lamps. Considering everything, the price of the pamphlet seems high. *Wilder D. Bancroft*

Ueber den Einfluss der Kernsubstitution auf die Reaktionsfähigkeit aromatischer Verbindungen. *By Julius Schmidt. (Sammlung Chemischer und chemisch-technisher Vorträge. VII. Band. 9/10 Heft.) 16 × 25 cm; pp. 283 to 376. Stuttgart: Ferdinand Enke, 1902. Price: paper, 1.20 marks.* — The subject is discussed under the following heads: reactions affected by a group in the ortho position to the reacting group; reactions affected by a group in the para position to the reacting group; reactions affected by a group in the meta position to the reacting group; regularities in connection with the introduction of NO_2 and NH_2 groups into the benzene nucleus and with the oxidation and reduction of quinones and hydroquinones; effect of different substitutions on the behavior of pyridine, quinoline, and their derivatives. There is a great deal of interesting information in the pamphlet and it is well arranged.

Wilder D. Bancroft

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Tenth annual report of the committee on atomic weights. *F. W. Clarke. Jour. Am. Chem. Soc.* 25, *223* (*1903*). — The determinations of Ladenburg and of Scott point to a value for iodine of about 126.97. For calcium, Richards finds 40.126 and Hinrichsen 40.138. Meyer gets 79.21 for selenium and Cleve 173.1 for ytterbium. Two determinations of tellurium have been made, Gutbier finding 127.51 and Scott 127.74. Brauner makes the atomic weight of lanthanum 139.04, while Jones confirms Brauner's earlier results, getting 138.77. Richards and Merigold obtain 238.52 for uranium, and Mme. Curie reports 225 for radium. *W. D. B.*

Revision of the atomic weight of cerium. *B. Brauner. Zeit. anorg. Chem.* 34, *103*, *207* (*1903*). — The atomic weight of cerium is 140.25 with a slight uncertainty in the second decimal. Pure cerium tetroxide is not white but slightly yellowish. Cerium tetroxide which contains silica or silver oxide is pure white. The author criticises at length the experiments of Wyrouboff and Verneuil.
W. D. B.

Note on the probable atomic weight of tellurium and on atomic weights in general. *P. Köthner. Zeit. anorg. Chem.* 34, *393* (*1903*). — A criticism of Seubert's method of calculating from atomic weight determinations from which decimal places have been dropped. By changing back and forth from the oxygen to the hydrogen standard, Seubert calculates both 126.6 and 126.7 for tellurium for the same data (hydrogen standard). After a discussion of all the atomic weight determinations of tellurium, the author decides on 126.71 as the most probable value ($H = 1$). *W. D. B.*

On the conception of independent components. *R. Wegscheider. Zeit. phys. Chem.* 43, *376* (*1903*). — A reply to Nernst (7, 395). The author persists in speaking of limitations of the phase rule when he means limitations of the experimental conditions. *W. D. B.*

An attempt at a physical explanation of the periodic regularity of the chemical elements. *A. J. Batschinski. Zeit. phys. Chem.* 43, *372* (*1903*). — The author makes the following hypothesis: "The atoms are in a state of vibration: the period of vibration determines the properties of the element; the periods of vibration of allied elements stand in simple relations one to another." The author then postulates that the period of vibration T is given by the formula

$$T = \pi\sqrt{\frac{m}{g}},$$

where m is the atomic weight and g is the coefficient of a constant attracting force. To account for the numerical values of T not coming out quite as they should, the author decides that g is probably not quite constant. *W. D. B.*

The problem of the systematic classification of inorganic compounds. *J. Locke. Zeit. anorg. Chem.* 33, *58* (*1902*). — Essentially a German adaptation of a previous paper (6, 442). *W. D. B.*

The problem of the systematic classification of inorganic compounds. *R. Abegg and G. Bodländer. Zeit. anorg. Chem.* 34, *180* (*1903*). — A reply to Locke (6, 442 and preceding review). *W. D. B.*

Note concerning the calculation of thermochemical results. *T. W. Richards. Jour. Am. Chem. Soc.* 25, *209* (*1903*). — Since the heat capacities of a system are apt to change during a reaction, the question arises what capacities are we to take in a thermochemical measurement involving a change of temperature. The author points out that the heat capacity of the reacting substances should be taken if the results are to be referred to a final temperature and the heat capacity of the products if the results are to be referred to the initial temperature. *W. D. B.*

On F. W. Clarke's new thermochemical constant. *W. v. Loeben. Zeit. anorg. Chem.* 34, *174* (*1903*). — The author gives his reasons for believing that Clarke's formula (7, 307) does not represent the facts. *W. D. B.*

F. W. Clarke's new thermochemical law. *J. Thomsen. Zeit. phys. Chem.* 34, *487* (*1903*). — The author gives his reasons for believing that Clarke's new formula (7, 307) does not represent the facts. He claims that his own formula, deduced years ago, is still the best both from a theoretical and an experimental point of view. *W. D. B.*

The prevention of bumping. *H. Scudder. Jour. Am. Chem. Soc.* 25, *163* (*1903*). — When a capillary sealed at one end and filled with air is placed open end down at the bottom of a flask, almost any liquid can be distilled without bumping. It is always desirable and often essential that the capillary tube shall be completely immersed. *W. D. B.*

One-Component Systems

Physical and natural equilibrium between the modifications of acetaldehyde, I. *R. Hollman. Zeit. phys. Chem.* 43, *129* (*1903*). — Pure paraldehyde melts at 12.55°, while the natural melting-point or stable triple point is at 6.75°, the melt containing 88.3 molecular percents of paraldehyde. Pure acetaldehyde melts at – 118.45°. The author has determined the freezing-point curve for paraldehyde and acetaldehyde, the boiling-point curve under one atmosphere pressure, and the critical curve. The stable boiling-point is at 41.6°, the liquid containing 53.4 molecular percents of paraldehyde. The equilibrium curve for the melt is thus displaced from 88.3 percent at 6.75° to 53.4 percent at 41.6°. The natural critical point is at 218° with 11 molecular percents of paraldehyde. Metaldehyde appears to show a stable triple point at about 167°. Further experiments with metaldehyde are to be given in a later paper, and it is to be hoped that the author will also study the aldol condensation. *W. D. B.*

Boiling-point, freezing-point, and vapor tension of pure nitrogen at low pressures. *K. T. Fischer and H. Alt. Drude's Ann.* 9, *1149* (*1902*). — Pure nitrogen gas, prepared from sal-ammoniac, potassium bichromate, and sodium nitrite, was condensed by means of liquid air, and found to be free from oxygen. All the temperature measurements were made with a copper-constantan couple, and a hydrogen thermometer. It is found that the solidification point as well as the boiling-point is well defined. The solid nitrogen, being denser than the liquid, sinks to the bottom when formed. By the hydrogen thermometer the boiling-point is found to be — 195.67° for standard pressure, and solidification point — 210.52° at a pressure of 86 mm. A comparison of the values obtained by Baly is made. From the measurements of the vapor tension the author tests Dühring's boiling-point equation, and the formula of Ramsay and Young very satisfactorily. The heat of vaporization is calculated to be 48.9 calories for standard pressure. Considering liquid air to be a solution of oxygen in nitrogen, the raising of the boiling-point of nitrogen with different percentages of oxygen is calculated by the van 't Hoff formula. At sufficiently low temperatures nitrogen is separated out from liquid air very completely, and hence a method of separating the two gases is suggested. *H. T. B.*

The heat of vaporization of fluids. *G. Bakker. Drude's Ann.* 9, *1128* (*1902*). — In a previous paper the author put forward the law that the heat of vaporization is proportional to the difference between the specific gravity of fluid and vapor for cases where the molecules in the two states are equal in form. In the present paper the law is discussed with reference to the condition equation of van der Waals. The paper is of the nature of a reply to critics, who have discussed the law in relation to the van der Waals equation.
H. T. B.

On the relation between the heat of vaporization and the critical constants. *A. J. Batschinski. Zeit. phys. Chem.* 43, *369* (*1903*). — The author writes the formula of Bakker in the following form:

$$Mr = 2T + 6.5\frac{T_k^2}{T}\,\frac{1}{\dfrac{v}{v_k} + 0.44}.$$

Here M is the molecular weight, v the volume of the liquid at the absolute temperature T, while T_k, p_k, and v_k are the critical constants. The formula holds only for 'normal' substances. *W. D. B.*

The physical properties of the elements from the standpoint of the van der Waals equation. *J. Traube. Zeit. anorg. Chem.* 34, *413* (*1903*). — For elements which follow Dulong and Petit's law, the author calculates that the co-volume increases by 1/273 per degree. After a discussion of other properties, the author comes to the conclusion that the van der Waals equation applies to solids. It must be kept in mind that the equations of Richards, of which the author makes use, are not correct. *W. D. B.*

On the specific heat of water vapor. *M. Thiesen. Drude's Ann.* 9, *80* (*1902*). — In order to deduce a more reliable value for the specific heat of water vapor a study is made of the work of Regnault and others. The most probable value is obtained, and tables constructed showing the variation with temperature. The following formula is found to hold with some accuracy :

$$C_0 = 0.4610 - 0.095 \frac{t}{80} + 0.044 \left(\frac{t}{80}\right)^2.$$

No additional experimental work has been done, but the great need of a careful series of measurements is pointed out. *H. T. B.*

The influence of temperature on the elasticity of the elements. *C. Schaefer. Drude's Ann.* 9, *665* (*1902*). — The present paper is a continuation of previous work. It is found from these experiments that the temperature coefficient of the modulus of elasticity as well as the coefficient of expansion and temperature of fusion are periodic functions of the atomic weights. A reply is offered to the criticism of Sutherland of the author's first paper, and it is pointed out that his theoretical formula does not accord with the experimental facts. *H. T. B.*

Two-Component Systems

Mix-crystals of mercuric and silver iodides. *A. Steger. Zeit. phys. Chem.* 43, *595* (*1903*). — A detailed account of some work, a summary of which was reported to the Amsterdam Academy by Roozeboom in 1900. Mercuric iodide and silver iodide form two series of solid solutions, the first containing 0–5 pct AgI and the second 20–100 pct AgI. The presence of the other component changes the temperature at which each component changes into another modification. At 158° as a maximum temperature, there is a formation from the mix-crystals of the double salt $HgI_2 2AgI$. At 118° there is a new series of solid solutions, and at 45°–50° the double salt changes from red to yellow. *W. D. B.*

Solubilities and transition points of lithium nitrate and its hydrates. *F. G. Donnan and B. C. Burt. Jour. Chem. Soc.* 83, *335* (*1902*). — The concentration temperature curve shows two hydrates, $LiNO_3 3H_2O$, and $LiNO_3 0.5H_2O$. Cryohydric temperature, −19.8° ; melting-point of the trihydrate, 29.88°; transition temperature tri- and semihydrates, 29.6° ; transition temperature semihydrate and anhydrous salt, 61.1°. *H. R. C.*

Redetermination of the inversion temperature of sodium sulphate with reference to the international scale. *T. W. Richards and R. C. Wells. Proc. Am. Acad.* 38, *481* (*1902*) ; *Zeit. phys. Chem.* 43, *465* (*1903*). — As a final value the authors find the inversion temperature of sodium sulphate at 32.383° ± 0.001 on the hydrogen scale. It is believed that this fixed point is quite as trustworthy as the standard ones of 0° and 100°. As it is nearer the ordinary temperature than either of the others, and as it is practically independent of the barometer, it may prove more serviceable than the other two. *W. D. B.*

On the supposed inversion point of cadmium sulphate. *H. v. Steinwehr. Drude's Ann.* 9, *1046* (*1902*). — The present paper is another of a series of papers from the Reichsanstalt. The author repeats the solubility experiments of Kohnstamm and Cohen, and finds no break in the curve corresponding to their observations and attributed by them to a change in the hydrate. Additional evidence is therefore obtained to show that the irregularity in the Weston cell is due to a change in the amalgam. *H. T. B.*

Experimental test of the relation between the heat of solution and the change of the solubility with the temperature in the case of dissociated substances. *A. A. Noyes and G. V. Sammet. Zeit. phys. Chem.* 43, *513* (*1903*). — The authors have determined the change of solubility with the temperature for potassium perchlorate and for *o*-nitrobenzoic acid. From these data they have calculated the heats of solution at 20° and have compared the results thus obtained with their own direct measurements. In the case of the potassium perchlorate, the calculated heat of solution differed from that actually measured by 1.1 pct. In the case of the *o*-nitrobenzoic acid, there is a discrepancy of 7.6 pct, which disappears if we assume a 20 pct polymerization of the undissociated acid. *W. D. B.*

The solubility of the chloride, the bromide, and the iodide of lead in water at temperatures from 0° upwards. *D. M. Lichty. Jour. Am. Chem. Soc.* 25, *469* (*1903*). — The solubility curves for lead bromide and chloride intersect at about 35° when the concentrations are expressed in grams, and at about 88.5° when expressed in mols. Lead iodide is very much less soluble than either the bromide or the chloride. *W. D. B.*

On the inversion of polymorphous substances. *J. Meyer. Zeit. anorg. Chem.* 33, *140* (*1902*). — The author has determined the solubilities of monoclinic and rhombic sulphur in chloroform, benzene, and ether. At each temperature the ratio of the solubilities appears to be independent of the solvent. From the data, the author attempts to calculate the heat effect for the change of monoclinic sulphur into the rhombic. The experimental error is relatively so large that the calculation is an absolute failure. Toluene would have been a better solvent than any that he has tried. *W. D. B.*

A differential method for determining small freezing-point depressions. *H. Hausrath. Drude's Ann.* 9, *522* (*1902*). — A thermocouple was used for measuring the depression in preference to a mercury thermometer. In each experiment the freezing-point of the solution was compared with that of pure water under exactly similar conditions. Determinations were made to the hundred thousandth of a degree. It was found that urea follows Raoult's law to the lowest concentration. Cane sugar shows too high a depression, and alcohol too low a value. For the heavy metals the freezing-point curve of the hydrolyzed salt at low concentration approaches that for the non-hydrolyzed. In the case of dilute solutions of strong electrolytes a low value was obtained, which was found to be anomalous. The reverse was the case for strong solutions. *H. T. B.*

The freezing-points of dilute solutions. *T. W. Richards. Jour. Am. Chem.*

Soc. **25**, *291* (*1903*). —The author analyzes the solution which is in equilibrium at a given temperature with a large mass of ice. In this way the percentage dissociation of potassium chloride is found to be 84, 87, 89, and 93 for concentrations, 0.1258 *n*, 0.09442 *n*, 0.0378 *n*, and 0.0309 *n*, respectively. Whetham's conductivity measurements at 0° indicated a 93 percent dissociation for the last solution. *W. D. B.*

The determination of molecular weights. *H. C. Biddle. Am. Chem. Jour.* **29**, *341* (*1903*). — In this paper is described a tensimeter method for the determination of the differences in the vapor pressures of solvent and solution, from which the molecular weight of the solute may be calculated. Since the author recommends the method only for cases where the solvent has a high vapor pressure, the effect of air and other impurities is neglected. The results of the method having indicated that the iodine molecule was diatomic, osmotic pressure measurements were made. The results of both methods agree.

H. R. C.

Studies on supersaturated solutions. *G. Jaffé. Zeit. phys. Chem.* **43**, *566* (*1903*). — Experiments with potassium nitrate solutions cooled rapidly to 20° and held there, showed that some form of nucleus was present which caused crystallization, which could not be removed by heating, but which could be removed by repeated filtering. In this way it was possible to increase the time before supersaturated solutions crystallize. The results were so irregular that it is not possible to say whether there is a definite limit of concentrations for any temperature inside of which a supersaturated solution will not crystallize spontaneously, while beyond the limit it will. When the potassium nitrate solutions have been freed from the unknown nuclei by repeated filtration, it is almost invariably an instable modification which finally crystallizes. Some solubility determinations were made with this instable form.

Experiments were also made with slow cooling, observing the temperature at which crystals first appear. It was found that this temperature fell gradually with each heating and cooling, no lower limit being found.

The behavior of potassium chlorate, potassium chloride, and ammonium chloride shows that marked supersaturation is not confined to hydrated salts.

W. D. B.

On the relation of the alloys to the law of Wiedemann and Franz. *F. A. Schulze. Drude's Ann.* **9**, *555* (*1902*). —Alloys of bismuth and lead as well as bismuth and tin are found to follow the law of Wiedemann and Franz as closely as pure bismuth. The metals have been divided by Matthiessen into two groups showing their relation to their conducting power for electricity. The alloys of the first group possess a conductivity which may be calculated from the relation of the volumes of the constituents, but alloys of the second group do not show this relation. From a study of the relation between electrical and thermal conductivity the author finds a similar grouping possible for thermal conductivity. The groups are: Group *1*: Zinc, tin, lead, cadmium: Group 2: All other metals. *H. T. B.*

Liquid baths for melting-point determinations. *H. Scudder. Jour. Am. Chem. Soc.* **25**, *161* (*1903*). — A bath made by heating together seven parts by weight of sulphuric acid (1.84) and three parts of potassium sulphate is liquid at ordinary temperatures and does not boil at 325°. When the proportions are six and four, instead of seven and three, the bath is mushy at ordinary temperatures and boils above 365°. The vapor is only slightly acid. For higher temperatures the author recommends fused zinc chloride. *W. D. B.*

Multi-Component Systems

Equilibria in the system, succinonitrile, silver nitrate, and water. *W. Middelberg. Zeit. phys. Chem.* 43, *305* (*1903*). — The system succinonitrile, silver nitrate, and water is especially interesting because there are three anhydrous binary compounds, $C_2H_4(CN)_2 4AgNO_3$, $C_2H_4(CN)_2 2AgNO_3$, $C_2H_4(CN)_2 AgNO_3$, a ternary compound, $2C_2H_4(CN)_2.AgNO_3.H_2O$, and one with a probable composition of $4[2C_2H_4(CN)_2\ AgNO_3]H_2O$. When we add to all this the complication of two liquid phases, we get a system which would be a hopeless tangle without the phase rule as a guiding principle. As it is, the author clears up the situation in the admirable manner characteristic of the Leiden laboratory.

W. D. B.

On tetragenic double salts with special reference to Kainite. *W. Meyerhoffer. Zeit. anorg. Chem.* 34, *145* (*1903*). — By tetragenic the author means a double salt containing four ions exclusive of water. The aqueous solution is therefore a four-component system. Such a double salt may have two or three temperatures of formation. Two are known for kainite, $MgSO_4KCl3H_2O$, one at 76° and one at 85°. The author discusses the equilibrium relations for kainite with varying temperature, "polytherm," and shows that there must be other temperatures of formation.

One chapter is devoted to the "characteristics" of the solutions, meaning thereby the limiting conditions determining the number of components. This is followed by a discussion as to the best way of writing the formula for kainite. The conclusion reached is that $MgSO_4KCl3H_2O$ represents the facts better than any other.

In the last part of the paper, the author discusses some of the patents in regard to the working up of kainite from the point of view of the solubility curves and equilibrium relations. *W. D. B.*

Equilibria between the iron oxides, carbon monoxide, and carbon dioxide. *E. Bauer and A. Glaessner. Zeit. phys. Chem.* 43, *354* (*1903*). — With FeO and Fe_3O_4 as solid phases, the ratio of carbon dioxide to monoxide passes through a minimum at 490°. With Fe and FeO as solid phases, this ratio passes through a maximum at 690°. Under atmospheric pressure, FeO, Fe_3O_4, and C can coexist as solid phases at 647°, while Fe, FeO, and C coexist at 685°. In all cases there is an increased amount of carbon monoxide in the vapor, the higher the temperature. The reduction of the ferro-ferric oxide to iron takes place in two stages:

$$Fe_3O_4 + CO = 3FeO + CO_2,$$
$$FeO + CO = Fe + CO_2.$$

In addition there is also to be considered the equilibrium

$$C + CO_2 = 2CO.$$

At 490°, under constant pressure, the heat of formation of the ferro-ferric oxide is 267,380 cal, while that of ferrous oxide at 680° is 67,350 cal. *W. D. B.*

On gaps in the crystallization series for isomorphous substances. *W. Stortenbeker. Zeit. phys. Chem.* 43, *629* (*1903*). — The author defends the very plausible hypothesis that isomorphous substances always form a continuous series of solid solutions. Since thallium nitrate and potassium nitrate do not form a continuous series, it was necessary to show that they were not isomorphous. The proof offered for this is that a crystal of thallium nitrate does not cause a supersaturated solution of potassium nitrate to crystallize. This is satisfactory, but then the author starts off unfortunately on the question whether mix-crystals are or are not to be considered as solid solutions. This difficulty does not arise if one defines a solution as a phase of continuously varying composition. *W. D. B.*

The precipitation of mixed bromide and sulphocyanate solutions by silver. *F. W. Küster and A. Thiel. Zeit. anorg. Chem.* 33, *129* (*1902*). — Silver bromide and silver sulphocyanate form two series of solid solutions, the first containing 0–3 mol percent AgBr, and the second 90–100 mol percent AgBr. When silver nitrate is added to a solution containing potassium bromide and potassium sulphocyanate, both silver bromide and silver sulphocyanate are precipitated. The solubility of silver sulphocyanate is 1.08×10^{-6} at 25°. *W. D. B.*

A lecture experiment on mass action. *A. v. Dieterich and L. Wöhler. Zeit. anorg. Chem.* 34, *194* (*1903*). — Experiments are described illustrating the reaction between mercurous chloride and caustic potash, using phenolphthaleine as indicator. *W. D. B.*

Lowering of the freezing-point by non-electrolytes in concentrated aqueous solutions. *W. A. Roth. Zeit. phys. Chem.* 43, *539* (*1903*). — With increasing concentration there is decreasing molecular lowering of the freezing-point with acetic acid, glycerol, and thio-urea, while the reverse is true for chloral hydrate and glucose. If we are to account for these peculiarities by association and by mutual action, we have to assume that the mutual action varies very much with the temperature. In no case were the most concentrated solutions much more than normal. *W. D. B.*

Note on the solubility of boric acid in acids. *W. Herz. Zeit. anorg. Chem.* 34, *205* (*1903*). — The solubility of boric acid decreases rapidly with increasing addition of sulphuric, nitric, or acetic acid, but increases with addition of tartaric acid. *W. D. B.*

The corrosion of iron. *W. R. Whitney. Jour. Am. Chem. Soc.* 25, *394* (*1903*). — It is shown that iron will dissolve in pure air-free water, precipitating as hydroxide when air is admitted. The author shows that, in a steam-heating plant, the action of carbonic acid may easily become a cyclic one and therefore produce an amount of corrosion entirely out of proportion to the absolute concentration of the carbonic acid. *W. D. B.*

A study of magnesium and manganous hydroxides and of barium sulphate with respect to the phenomena of adhesion and of solution. *H. E. Patten.*

Jour. Am. Chem. Soc. 25, *186* (*1903*). — When caustic potash is added to a solution of magnesium chloride and potassium sulphate, neither chloride nor sulphate is carried down by the precipitated magnesia. Barium sulphate does not carry down magnesium oxide or magnesium chloride. On the other hand sulphate is carried down when manganese, iron, or chromium salts are precipitated. When precipitated barium sulphate is boiled with the chloride of iron, manganese, or chromium, some of the metal passes into the precipitate. A colloidal solution of chromium hydroxide coagulates readily when a soluble sulphate is added, but does not do so when a chloride or nitrate is added.

W. D. B.

On the molecular state of borax in solution. *H. S. Shelton. Zeit. phys. Chem.* 43, *494* (*1903*). — The author confirms the results of Kahlenberg and Schreiner that the hydrolysis of borax in aqueous solution forms boric acid and a sodium borate in which the ratio of sodium to boron is unity. He thinks it possible however that the formula for this borate may be $NaBO_2$ instead of NaH_2BO_3. One reason for this belief is that silver nitrate precipitates $AgBO_2$ from the solution. *W. D. B.*

Method of preparing the previously hypothetical carbon monosulphide. *J. Thomsen. Zeit. anorg. Chem.* 34, *187* (*1903*). — Carbon bisulphide, diluted with nitrogen is passed over heated copper, forming the hitherto unknown monosulphide CS. The new compound was not isolated. *W. D. B.*

The action of hydrogen sulphide on arsenic trioxide in aqueous solution. *F. W. Küster and G. Dahmer. Zeit. anorg. Chem.* 33, *105* (*1902*); 34, *410* (*1903*). — It seemed improbable that the action of hydrogen sulphide on an aqueous solution of arsenic trioxide should really carry the whole of the arsenic into the form of arsenic trisulphide. Special experiments on the amount of free hydrogen sulphide showed, however, a quantitative formation of the trisulphide. The colloidal sulphide is precipitated rapidly when shaken very vigorously with finely-powdered barium sulphate, copper oxide, or marble.

W. D. B.

Note on colloidal copper acetylide. *F. Küppert. Zeit. anorg. Chem.* 34, *453* (*1903*). — When ammoniacal cuprous chloride is added to an aqueous solution of acetylene, there is formed a colloidal copper acetylide which however soon coagulates. Presence of more than 0.2 pct of gelatine checks the coagulation. *W. D. B.*

Hydrosulphurous acid. *J. Meyer. Zeit. anorg. Chem.* 34, *43* (*1903*). — The author confirms Moissan's results (7, 140) as to the formula of the sodium salt of hydrosulphurous acid, $NaHSO_2$. The salt acts towards salts of the nobler metals much as hydrazine does, forming colloidal solutions. The rate of decomposition of sodium hydrosulphite is proportional to the concentration of the salt and of the decomposition product. *W. D. B.*

The formation of bleaching powder. *F. Winteler. Zeit. anorg. Chem.* 33, *161* (*1902*). —

1. Dry chlorine does not react with dry calcium hydroxide.

2. Chlorine water is an intermediate product in the reaction between chlorine and slaked lime.

3. Chlorine water is a mixture of chlorine, hypochlorous acid, hydrochloric acid, and water in reversible equilibrium.

4. Chloride of lime has no definite formula and is a mixture of CaOHCl, CaOHOCl, $CaCl_2$, $Ca(OCl)_2$, HClO, HCl, and free lime, the relative amounts depending on the conditions of preparation.

5. In chloride of lime there is always to be found basic calcium chloride, and also basic calcium hypochlorite.

6. The decomposition of bleaching powder into chloride and oxygen takes place in a too alkaline solution.

7. The decomposition of bleaching powder into chlorate and chloride takes place in acid solutions.

8. Good commercial bleaching powder can be made from chlorine containing as much as 6 pct carbon dioxide. *W. D. B.*

On the cause of the cementing value of rock powders and the plasticity of clays. *A. S. Cushman. Jour. Am. Chem. Soc.* 25, *451* (*1903*). — The author concludes "that the cementing power of rock powders is a property similar to the plasticity of clays and that all rock powders that have cementing powers show the same peculiar relation to water that is shown by substances that possess an amorphous colloid structure, i. e., they can be dehydrated and rehydrated until, by prolonged high heating, the structure is destroyed."

It is not claimed that the gelatinous mass in which silicic acid separates from a dilute solution is in any way comparable to a plastic clay mass. The question is purely one of the condition of the particles which go to make up the mass of plastic rock-powder or clay. It is the amorphous particles which, by reason of their characteristic structure, are able to absorb water and assume the condition which causes them to exhibit that coherence which in the mass we denote plasticity. There seems to be no reason to suppose that particles which are entirely crystalline in their nature have anything to do with plasticity except to act as a diluent. *W. D. B.*

The state of some peracids and their salts in solution. *L. Pissarjewsky. Zeit. phys. Chem.* 43, *160* (*1903*). — The author draws the following conclusions:

1. The compound Na_4UO_8 is a salt of the weak acid, $UO(OH).(O_2H)_3$, and has the formula $Na_4(O_2)_3UO_2$. In aqueous solution there is an equilibrium between the undecomposed salt and its products of hydrolysis, NaOH and H_2O_2. On standing, the sparingly soluble acid, $UO(OH)_3O_2H$, separates from a solution of $Na_4(O_2)_3UO_2$.

2. Besides the pertungstic acid, $WO_2(OH)(O_2H)$, there also exists in solution a pertungstic acid, $WO_2(O_2H)_2$, and possibly at low temperatures the acids $WO(OH)(O_2H)_3$ and $WO(O_2H)_4$.

3. The pertungstic acids, $WO_2OH(O_2H)$ and $WO_2(O_2H)_2$, are hydrolyzed in aqueous solution, H_2O_2 being formed.

4. The results of conductivity measurements with KVO_4 and $K_8V_5O_{20}$ show that the first is a salt of the monobasic acid, while the second is a double

compound of the tetrabasic pyropervanadic acid with the salt of the monobasic metapervanadic acid.

5. In a solution of sodium perborate at 25°, there is to be found sodium borate, sodium hydroxide, sodium peroxide, boric acid, hydrogen peroxide, and perhaps a trace of sodium perborate. With falling temperature the amount of sodium perborate increases until, at 0°, the solution contains chiefly $NaBO_3$.
W. D. B.

Pervanadic acid. *L. Pissarjewsky. Zeit. phys. Chem.* 43, *173* (*1903*). — When vanadium pentoxide is dissolved in aqueous, chemically pure hydrogen peroxide, the monobasic pervanadic acid, $H(O_2)VO_2$, is formed. On standing, this solution decomposes with evolution of oxygen and formation of the vanadic acids (meta, tetra, or hexavanadic acids); these vanadic acids are formed by the action of aqueous hydrogen peroxide on an excess of V_2O_5. These vanadic acids are changed to the pervanadic acid, $H(O_2)VO_2$, by the action of hydrogen peroxide. *W. D. B.*

Velocities

Studies on inversion. *C. Kullgren. Zeit. phys. Chem.* 41, *407* (*1902*). — When sugar solutions are inverted at 100° by pure water or by salt solutions, the first order "constant" rises as the experiment proceeds. This is due to the formation of an acid, which can be determined alkalimetrically.

The amount of acid formed is greater in the presence of salts; it is not proportional to the yellowness of the solution.

The results of the rate measurements may be expressed by the formula

$$dx/dt = kx(A-x),$$

which states that the rate is proportional to the concentration of the sugar and to that of the products of hydrolysis.

Measurements of the rate near the beginning of the experiments give a figure for the dissociation of water at 100°, which is in accord with the calculations of Kohlrausch. *W. L. M.*

A study of the dynamic isomerism of thiourea and ammonium thiocyanate. *J. E. Reynolds and E. A. Werner. Jour. Chem. Soc.* 83, *1* (*1903*). — One kg of carefully dried ammonium thiocyanate was melted and rapidly heated to the desired temperature; samples were removed at intervals, quickly chilled, and analyzed — the thiourea being determined by iodine, using a method described in the paper.

The reaction is reversible, equilibrium being reached from either side (in 45 minutes at 170°) when the fused mass consists of one part thiourea to three of thiocyanate. Above 182° both isomers are decomposed.

The melting-points of mixtures of the two isomers were determined; when the ratio is 1 : 3 as above, the melting-point is lowest.

Crystals of the compositions $CSN_2H_4.NH_4CNS$, and $CSN_2H_4.NH_4CNS$, were obtained by treating the previously fused mass with acetone or alcohol respectively. *W. L. M.*

Action of metallic magnesium upon aqueous solutions. *L. Kahlenberg. Jour. Am. Chem. Soc.* 25, *380* (*1903*). — Magnesium acts very slowly on caustic potash solutions, relatively slowly on solutions of the chlorides of calcium, strontium, and barium, fairly rapidly on solutions of magnesium salts including solutions in alcohol. This result is not what one would have expected from the dissociation theory, and the author explains it as due to the chemical affinity between magnesium and the solution. While this explanation is correct so far as it goes, it does not really get us anywhere because we do not know why the affinity between magnesium and magnesium chloride solution, for instance, should be greater than between magnesium and calcium chloride solution, for instance. *W. D. B.*

Electromotive Forces

Ozone as oxidizing agent. *R. Luther and J. K. H. Inglis. Zeit. phys. Chem.* 43, *203 (1903).* — "Dissolved ozone gives the electromotive force of a strong oxidizing agent. With smooth platinum electrodes which have previously been properly treated, ozone gives an electromotive force depending on the temperature, the concentration of hydrogen as ion, and the concentration of ozone. The measurements can be duplicated to within one millivolt.

"An ozone electrode changes to an oxygen electrode, because charging with oxygen lowers and charging with hydrogen raises the oxidation potential of an ozone electrode. A platinum electrode can be made practically free from hydrogen or oxygen by bathing it in an acidified ferro-ferric salt solution. In this way the effect of the 'previous history' of the electrode can be eliminated.

"The change of the electromotive force of a platinum ozone electrode with the concentration of hydrogen as ion and of ozone is given by the formula :

$$\pi(\mathrm{Pt},\ O_3) - \pi\,(\text{solution}) = \pi_0 + \frac{RT}{F} \log C_{O_3} \times C_H .$$

"The electromotive force of an ozone-hydrogen cell at + 1° is given by the formula (C in mols per liter) :

$$\pi(\mathrm{Pt},\ O_3) - \pi\,(\mathrm{Pt},\ H_2) = 1.861 = 0.054 \log_{10} C_{O_3} \text{ volt.}$$

"Ozone is possibly the anhydride of a (weak) acid, whose possible composition is H_2O_7 or H_2O_5.

"By the action of ozone in acid solution on potassium iodide in neutral solution, three equivalents of iodine are set free per molecule of ozone.

"By the action of ozone in neutral solution on potassium iodide, two equivalents are set free per molecule of ozone. By the action in acid solution of ozone on ferrous salt, two molecules of ferrous salt is oxidized to ferric salt for one of ozone." *W. D. B.*

Contributions to our knowledge of hydrogen peroxide. *K. Bornemann. Zeit. anorg. Chem.* 34, *1 (1903).* — A platinum electrode charged with oxygen has a much greater catalytic action in forming and decomposing hydrogen peroxide than an electrode free from oxygen. If the oxygen is removed gradually by cathodic polarization, the catalytic action of the platinum decreases at the same time. With such polarized electrodes, it was possible to obtain a quantitative cathodic yield of hydrogen peroxide at potentials between 0 and −0.77 volt (the hydrogen electrode being taken at zero). At potentials between −0.78 and −1.08 the highest concentration of hydrogen peroxide becomes less and less, approximating zero at the oxygen potential.

When a mixture of hydrogen and oxygen is decomposed by platinum, it is possible under certain circumstances to show an immediate formation of hydrogen peroxide. The two characteristic potentials for hydrogen peroxide are − 0.8 and − 1.4 volts.

The unknown oxidizing agent discovered by Bose (6, 155) was shown not to be hydrogen peroxide because it does not give the reaction with titanic acid.
W. D. B.

The residual current accompanying galvanic polarization treated as a problem of diffusion. *F. G. Cottrell. Zeit. phys. Chem.* 42, *385* (*1903*). — The author includes under the term residual all currents which pass through electrolytic cells when low electromotive forces are applied to the electrodes. In the majority of his experiments the electromotive force was small, from 0.1 to 0.8 volt. A mathematical consideration of an hypothetical cell, cylindrical in shape, the two ends closed by parallel electrodes, only one of which is capable of polarization, on the basis of Fick's law, Nernst's logarithmic formula for the electromotive force, and the assumptions that dissociation is complete and diffusion is uniform, leads to a number of conclusions. A few of those which appear to the reviewer as of greatest interest are the following. (*a*) The applied electromotive force determines the concentration in the immediate neighborhood of the electrode capable of polarization, and the current passing is a measure of the amount of dissolved substance which reaches the electrode through diffusion in unit time. This involves the assumption that the electrochemical reaction is instantaneous, or at least too rapid to measure, an assumption which is found to be justified by much of the experimental evidence, but not in all cases. (*b*) From the formula which is deduced, it appears that when the electromotive force is 0.15 volt any monovalent ion is very nearly completely removed from the solution at once upon the arrival at the electrode; for a similar removal of a divalent ion only half this electromotive force, or 0.075 volt is needed. (*c*) Curves constructed in accordance with the formula offer an explanation for the familiar nicks in the current strength — electromotive force curves observed when the voltage is gradually increased, and which are usually construed as indicating the existence of a 'decomposition point' and that *ions have 'intensities of fixation'*. (*d*) *It appears that the value* $I\sqrt{t}$ must remain constant when I denotes the current strength and t the time, expressed in amperes and minutes or any other convenient units. (*e*) The current strength must be independent of the electromotive force applied. (*f*) Since all of the substance is removed immediately that it reaches one electrode, the concentration in the layer of electrolyte next that electrode must be 0. At the other electrode the concentration remains at its original value, and thus the arrangement is perfectly analogous to that with which Stefan studied the velocity of diffusion, excepting that here the current strength is the direct measure of the amount of material diffusing. Stefan's formulæ are therefore utilized.

Some of these conclusions are tested experimentally and the apparatus used is ingenious and well adapted to the purpose, though too complicated for detailed description within the limits of a review. An experiment with 1/100 *n* $ZnSO_4$ in an almost saturated solution of K_2SO_4 between amalgamated zinc plates, with an applied electromotive force of 0.1 volt, showed a satisfactory constancy of the value $i\sqrt{t}$. Dissolved air cannot be considered as removed immediately upon arrival at the electrode, because the current strength is obviously not independent of the applied electromotive force. Rather, the electrochemical process is to be looked upon as proceeding more slowly than substance is furnished by diffusion. This should make itself evident by a flattening of the curve representing current strength as a function of the time, and the curve should be almost horizontal as long as the electrochemical process predominates, corresponding to an almost constant current strength. When the diffusion processes catch up with the electrochemical there should be a drop and a gradual approximation to the so-called normal curve. The figures presented as an illustration of this are measurements after two intervals only, the first after nine, the second after twenty-five minutes. When platinized platinum electrodes were used, precisely the reverse phenomena was observed, the current strength dropping from the start even faster than required by the normal curve. This behavior is ascribed to the 'electrolytic capacity' of the electrode itself. This 'capacity' is due to occlusion and diffusion of the gas within the electrode, and the suggestion is made that we thus have one diffusion phenomena superimposed on another and the resultant should be expressible by formulation similar to that for the simpler case if Fick's law holds for a gas within a metal.

Owing to the difficulty in applying corrections for dissolved gases, air was carefully removed from the solutions before the experiment in which metals deposited were undertaken. To save the long wait for occluded gases to diffuse out of an ordinary electrode, thin layers of platinum were made on glass by means of the cathode discharge, and these were used as electrodes. An experiment on the effect of dissolved air was carried out in a cell consisting of a tube 15 cm long by 1 cm in diameter. The cathode was a platinum film so thin that the glass looked as though slightly smoked; the anode (in a comparatively distant part of the apparatus) was a negative accumulator plate; the electrolyte was 1/10 *n* H_2SO_4 containing dissolved air. This combination should have an electromotive force of its own of 1.5 volts, but only 1.1 volts were observed. The interval between 1.1 and 1.5 volts is considered as a region of hysteresis. The measurements showed that the current was still diminishing at the end of 46 hours and 49 minutes. Experiments with amalgamated copper electrodes and $CuSO_4$ solutions in H_2SO_4 are said to conform to the theory, but the numerical results are not given. The probable cause of Caspari's excess potential (Ueberspannung) is discussed briefly, and a possible explanation is offered.

The hope was entertained that liquid amalgams would furnish constant electrodes, but their behavior led to the conclusion that they too have "electrolytic capacities", due to diffusion and possibly chemical reactions within them. Experiments with a zinc amalgam anode and an amalgamated zinc cathode, in a solution of $ZnSO_4$ in K_2SO_4 solution as electrolyte, and 0.8 volt applied electromotive force gave results showing approximately constant values for $i\sqrt{t}$. The same cell was used with an electromotive force of 0.4 volt and the values for $i\sqrt{t}$ fell about 20 percent lower, whereas they should have been the same if it be true that the current quantity is independent of the electromotive force. This variation is not considered as excessive however.

After sufficient time has elapsed a 'stationary' condition should be reached when the current strength becomes a minimum and remains constant, corresponding to a linear fall in the concentration of the electrolyte from the anode to the cathode. A mathematical development of the subject leads to a verification of Salomon's formula for such cases. Cottrell calculates that if the distance between the electrodes be 1 cm the stationary condition should be reached in 2/3 of a day, if it be in 1/2 cm in 4 hours, if 1 mm in 10 minutes. Amalgamated zinc electrodes were fixed with paraffin and wax on the ends of sections of glass tube 16 mm in diameter and 5.5 mm long and 1.5 mm long. These cells contained 1/100 *n* $ZnSO_4$ in saturated K_2SO_4 solution and 1.5 volts were applied. Practically stationary conditions were realized within the calculated time limits, though certain variations were observed. Experiments were made with a cell of similar dimensions, but with a platinum cathode and a mercury anode, electrolyte Hg_2SO_4 and H_2SO_4, electromotive forces 0.3 and 0.4 volt. Again, approximately stationary conditions were reached, and these conditions were considered to be nearly enough the same at the two voltages to further substantiate the theory.

The article contains much new and valuable information, both theoretical and experimental, and a short summary or review cannot do it justice. It deserves close study by any one interested in the numerous problems concerning electrolysis. Some of the conclusions require more experimental evidence and may or may not be accepted finally, but the whole investigation marks a distinct advance in our knowledge of the subject. It is to be hoped that the author will fulfil his promise, once or twice expressed, to continue this work, and another article from him will be awaited with expectation. *S. L. B.*

The vacuum thermocouple as a radiometer. *P. Lebedew. Drude's Ann.* 9, *209* (*1902*). — It is pointed out that the thermocouple becomes much more sensitive to radiant heat when enclosed in a vacuum jacket. Quantitative tests show that the sensitiveness remains unaltered for a range of pressures from 1 atm to 5 mm, but from 5 mm to 0.01 mm it rises rapidly and becomes for polished platinum 25 times as sensitive. Pressures under 0.01 mm change the sensitiveness so little that it may be said to be a practical limit. The author's results confirm what has already been known in regard to the efficacy of a vacuum jacket as a thermal shield. *H. T. B.*

Electrolysis and Electrolytic Dissociation

Anodic oxidation of metals and electrolytic evolution of oxygen. *A. Coehn and Y. Osaka. Zeit. anorg. Chem.* 34, *86* (*1903*). — When different anodes are used, the break at — 1.1 volts (measured against hydrogen in the same solution) is reversible and is independent of the nature of the anode. The second break is not reversible, depends on the nature of the anode metal and varies between — 1.28 and — 1.75 volts. With a nickel anode in caustic potash solution, no ozone is formed even at potentials above 3 volts, while there is marked formation of ozone under the same circumstances with a platinum anode. With a pulverulent nickel anode, visible electrolysis takes place at 1.57 volts. A pulverulent nickel electrode makes an oxygen electrode which reaches equilibrium rapidly. *W. D. B.*

The equivalent conductivity of the hydrogen ion derived from transference experiments with hydrochloric acid. *A. A. Noyes and G. V. Sammet. Zeit. phys. Chem.* 43, *49* (*1903*). — Reviewed (7, 323) from Jour. Am. Chem. Soc. 24, 944 (1902).

The equivalent conductivity of the hydrogen ion derived from transference experiment with hydrochloric acid. *A. A. Noyes. Jour. Am. Chem. Soc.* 25, *165* (*1903*). — As it had been suggested that the discrepancy between the author's results (7, 323) and the calculations of Kohlrausch and of Ostwald might be due to the concentration (*n*/60) used, new experiments have been made with a more dilute acid (*n*/180). The new results are 0.1671 at 20° as against 0.16743 for the more concentrated solutions. The difference is less than the possible experimental error. *W. D. B.*

The action of diaphragms in the electrolysis of salt solutions. *W. Hittorf. Zeit. phys. Chem.* 43, *239* (*1903*). — The transference numbers for $CdCl_2$, $ZnCl_2$, and CdI_2, given in the previous paper (6, 443) are wrong owing to an error in the calculation. The corrected values agree well with those found by the author nearly fifty years ago. Further experiments with different membranes gave the following results. Earthenware, and agar-agar cause endosmose so that the unchanged solution moves in the direction of the positive electricity. With an animal membrane, with parchment paper, or with membranes made out of albuminous materials, many salt solutions appear to change into a more concentrated and a more dilute solution, the former moving against the positive electricity and the latter with it. This is most marked with the salts of the heavy metals, though the effect disappears when the concentration becomes sufficiently high. This phenomenon is not to be observed with the salts of the alkali metals. The author finds himself unable to predict these facts from any theory of electrical endosmose. *W. D. B.*

Transference experiments to determine the constitution of salts. *R. Kremann. Zeit. anorg. Chem.* 33, *87* (*1902*); 35, *48* (*1903*). — According to Werner's view, the luteo-, purpureo-, and praseo-salts have the cobalt as part of the cation, while the cobalt is part of the anion in the diamine cobalt potassium nitrite. Transference experiments showed that the colored layer moved to the cathode in the first three cases and to the anode in the last. Experiments with methyl orange showed that the colored layer remained stationary in strongly acid solutions and moved to the anode in alkaline or slightly acid solutions. From this, the author concludes that methyl orange is not to be considered as an amphoteric electrolyte. From experiments with potassium zincate, he concludes that it is not a colloidal solution. Bredig (next review) takes issue with him on both these conclusions, and the second paper is a reply to the criticisms of Bredig. *W. D. B.*

Determinations of constitution by qualitative transference measurements. *G. Bredig. Zeit. anorg. Chem.* 34, *202* (*1903*). — A criticism of Kremann (preceding review) on the ground that his conclusions rest on qualitative experiments only and are subject to error. *W. D. B.*

On the conductivity and internal friction of solutions. *G. Rudorf. Zeit. phys. Chem.* 43, *257* (*1903*).—The author has measured the conductivity and internal friction of a number of binary and ternary solutions. The general result is that there is no quantitative relation between the two, though the author believes firmly that there is one and that it is masked by disturbing factors varying from case to case. *W. D. B.*

On the nature of conduction in electrolytic glowing bodies. *E. Bose. Drude's Ann.* 9, *164* (*1902*).—The study has to do with conduction in metallic oxides of high melting-point, with particular reference to the type of conduction in the Nernst lamp. It is shown that the large decrease in resistance that takes place in the filament, on the passage of a direct current, is due to the deposition of metal from the cathode towards the anode with a corresponding setting free of oxygen. The gas returns to the cathode partly by diffusion in the filament itself, and partly through the outer layers.

In a vacuum a characteristic blue light surrounds the glowing filament, not shown when an alternating current is used. Curves are drawn showing the increase in resistance when the current is changed from a direct to an alternating, and vice-versa. With the lamp permanently attached to a mercury pump so as to keep up the vacuum more metal was deposited the longer the filament was burnt, and the conduction approached more and more to a pure metallic conduction. When air was allowed to enter the metal returned to oxide again. *H. T. B.*

Gas discharge from electrolytic bodies in vacuum. *E. Bose. Drude's Ann.* 9, *1061* (*1902*).—The author continues his experiments on gas discharge from glowing electrolytic bodies. He points out that the blue light observed in the space around the filament in a Nernst lamp, which he at first thought to be of the same origin as the blue of the heavens, does not show any polarization. It is suggested that the glow may be due to metallic vapor, which becomes a good conductor at the high temperature. The blue light is not obtained with alternating currents. A part of the paper is devoted to the description of some observations on the production of cathode rays from electrolytic cathodes. It is found that rays are produced from the metalloids as well as from electrolytic substances, having a low vapor tension. What he calls an anion-maker in its electrochemical properties such as PbO_2 does not produce cathode rays when made the cathode in a discharge tube with aluminum electrodes, although on reversing the current cathode rays are produced from the aluminum. *H. T. B.*

On the electrical conductivity of compressed powders. *F. Streintz. Drude's Ann.* 9, *854* (*1902*).—This is a continuation of the author's previous paper (5, 422). He investigates a large number of compounds, and shows that conduction similar to electrolytic conduction does not exist as he first suggested. Several important improvements in the apparatus which he had previously used were made. Pressures from 10,000 to 13,000 atms were used. The effect of temperature on the conductivity was studied down to the temperature of liquid air. It is stated that the powder from a conductor forms a good coherent column of metallic luster and hardness, while that from a non-conductor possesses neither metallic luster nor cohesion. Some interesting results are given for metallic oxides and sulphides. *H. T. B.*

Studies in neutralization. *M. Berthelot. Ann. Chim. Phys.* (*7*) 24, *39, 53* (*1902*). — Reviewed (6, 208) from Comptes rendus, 132, 1377 (1901).

Dielectricity and Optics

A determination of the dielectric constant of crystals with electric waves. *W. Schmidt. Drude's Ann.* 9, *919* (*1902*). — Drude's method, somewhat modified as described by Starke and Loewe, is used for the present measurements. It is found that Maxwell's relation between dielectric constant and refractive index holds only for sulphur. It is shown that the difference in dielectric constant for crystals in different directions is often very great, amounting in some cases to nearly 50 percent. *H. T. B.*

On the formation of ozone by the point discharge in oxygen. *E. Warburg. Drude's Ann.* 9, *781* (*1902*). — It is found that the maximum amount of ozone produced by the negative point discharge, is three times as much as that produced by the positive discharge. On reverting to the positive discharge from the negative, the amount falls to that corresponding to the former. The influence of temperature is approximately the same for both positive and negative discharge. *H. T. B.*

Negative electrification by falling water drops. *A. Schmauss. Drude's Ann.* 9, *224* (*1902*). — A stream of water impinging on a metal plate becomes positively electrified, imparting a negative charge to the plate. This phenomenon, the "Lenard Effect," is the basis of study of the present paper. It is found that the stream removes the ions in air ionized by Röntgen rays, and it is suggested that rain passing through the upper atmosphere conveys the negative ions to the earth in addition to the method of transport suggested by the theory of C. T. R. Wilson. An atmosphere of CO_2 was tried, which gave a smaller result than for air. Streams of ammonia and carbon disulphide show similar results. *H. T. B.*

Determination of the rotatory power of sugar. *H. Pellat. Ann. Chim. Phys.* (*7*) 23, *291* (*1901*). — This investigation was carried out for a Government Commission which was to report on methods for analyzing alcohols and sugars. At 20° a solution containing 16.75 g pure sugar per 100 cc will cause a rotation of 21.67° in a tube 20 cm long when the source of light is the D line of sodium. The effect of a changing temperature is given by the formula

$$R_{20} = R[1 + 0.00037\,(t - 20)].$$

The effect of the wave-length of light is given by the formula

$$R_\lambda = R_D\left(\frac{A}{\lambda^2} + \frac{B}{\lambda^4}\right),$$

where $A = 0.325483$ and $B = 0.00757003$. *W. D. B.*

ELECTROLYTIC COPPER REFINING

BY F. J. SCHWAB AND I. BAUM

In determining the best conditions for the electrolytic refining of copper, we must consider: the cost of the power necessary to precipitate a tank full of copper under different current densities and at different temperatures; the cost of heating the tank; the deterioration of the electrolyte; the interest charge on the copper in the tank; the cost of pumping; and the quality of the copper deposited. Good adherent copper can be obtained at almost any current density provided the rate of circulation be sufficient. The question of the cost of pumping has not been taken up by us and is supposed to remain constant while the conditions are varied. The watt hours necessary to precipitate a gram of copper increase with increasing current density and decrease with rising temperature. The cost of heating increases with rising temperature and the interest charge on the copper in the tank decreases with increasing current density. With increasing current density we have to strike a balance between the increasing power and the decreasing interest charge. With rising temperature we have to strike a balance between the decreasing cost of power and the increasing cost of heating. The object of this paper is to furnish data bearing on these points. We have therefore determined the relation between voltage, current density and temperatures for pure copper plates set a definite distance apart in four solutions. By expressing the voltages in terms of the voltage at 20° we eliminate the effect of the distance between the plates and the percentage variations hold for any set of plates in the same solutions. We have determined the relation between current efficiency, current density and temperature for pure copper plates in four different solutions. These experiments were necessary because Foerster and Seidel[1] had found a marked falling off of the current efficiency above 50°.

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[1] Zeit. anorg. Chem. 14, 138 (1897).

These runs also give us the degree of neutralization of the acid by copper. Incidentally we have made some experiments on the effect of iron salts. We have determined the cost of heating of tanks similar to those used by the Baltimore Copper Co., and we have calculated the variation of the cost with varying conditions of temperature and current density for the case of all power costing at the rate of twenty dollars per horse-power year, and for the case in which steam heating costs only one-thirtieth of electrical heating.

TEST NO. 1

The object of this test was to determine the variation of voltage with variation of temperature, current density and solution. In commercial copper refining, two standard solutions are used, each solution containing 16 percent copper sulphate crystals. The refineries using the Hayden system make up their electrolytic solutions to contain also 6 percent concentrated sulphuric acid, while the plants operating with the multiple system use a 9 percent acid solution. It has been claimed that the addition of a small quantity of sodium chloride produces a more coherent form of copper when precipitating at the higher current densities.

It was our intention to investigate the relative merits of operating a plant with these various electrolytes. Accordingly, we made up the following solutions:

Solution A

16 percent copper sulphate and 9 percent sulphuric acid

Solution B

16 percent copper sulphate and 6 percent sulphuric acid

Solution C

Solution A + sodium chloride (1 : 2,000,000 of solution)

Solution D

Solution B + sodium chloride (1 : 2,000,000 of solution)

Electrolytic or pure copper plates were used as electrodes. These electrodes, three in number (one cathode and two anodes), were held together by means of gutta-percha tops, in which three grooves were cut, one centimeter apart. In order to maintain this distance throughout the length of the plates, gutta-percha clamps were put on the bottom of the electrodes. The tops also performed the duty of holding up the plates. Some difficulty was at first experienced in keeping the plates immersed at constant depth for, at the higher temperatures, the gutta-percha became soft and the grooves widened, causing the plates to drop. This obstacle was overcome by driving holes through the plates about four centimeters from the ends with an ordinary ten-penny nail. By this means, the metal was forced outward, giving a firm support and preventing the slipping of the plates.

As before stated, two anodes and one cathode were used, copper being precipitated from the anodes at both sides of the cathode. The plates were five centimeters wide and were immersed in the solution to the depth of ten centimeters, thus giving one square decimeter of cathode surface.

To maintain a uniformity of solution throughout the run, stirring rods were provided for each cell. This was quite an important feature and was the most difficult part of the apparatus to design and construct. Owing to the small amount of space between the electrodes and the sides of the glass beakers, it was absolutely essential that the stirring rod shafts should run perfectly true. All fittings had to be made of glass. The bearings of the stirring rods were mounted on iron brackets at a sufficient distance above the tops of the supports to enable the easy removal of the beakers. As the stirring rods were made in the form of propellers, and as they fitted through circular holes in the gutta-percha tops, they had to be constructed in two sections and coupled together. Pulleys were mounted on the tops of each of the stirring-rod shafts. They were belted to a main driving pulley on whose shaft a cone pulley was also fitted. The object of this latter pulley was to give variable speeds at which to run the stirring rods. The power was supplied by a small four-volt motor which was belted to the cone pulley.

The four beakers were fitted into a wooden top, on which, as we have heretofore stated, the brackets were fastened.

As the temperature of the electrolytes had to be varied between 20° C and 90° C, it was necessary that this be done by a water-bath. An agate-ware vessel was used for this purpose. The wooden top was placed upon this vessel, thus allowing the beakers to be immersed in the water.

Each beaker was provided with a thermometer passing through a hole in the gutta-percha tops, and thereby enabling us to make accurate readings of the temperature in each beaker.

To make good contact all connections were soldered, the electrodes having a small wire fastened to their upper corners. The four cells were run in series. Current was supplied by a battery of storage cells.

As the reading of the potential difference between the plates of each cell was an essential part of this run, it was necessary to devise some means by which this could be readily done. Accordingly, a switchboard was designed and constructed in such a manner that by simply closing a certain switch, the voltage for the corresponding cell could be read. A diagram of this switchboard and all the connections is shown in Fig. 1.

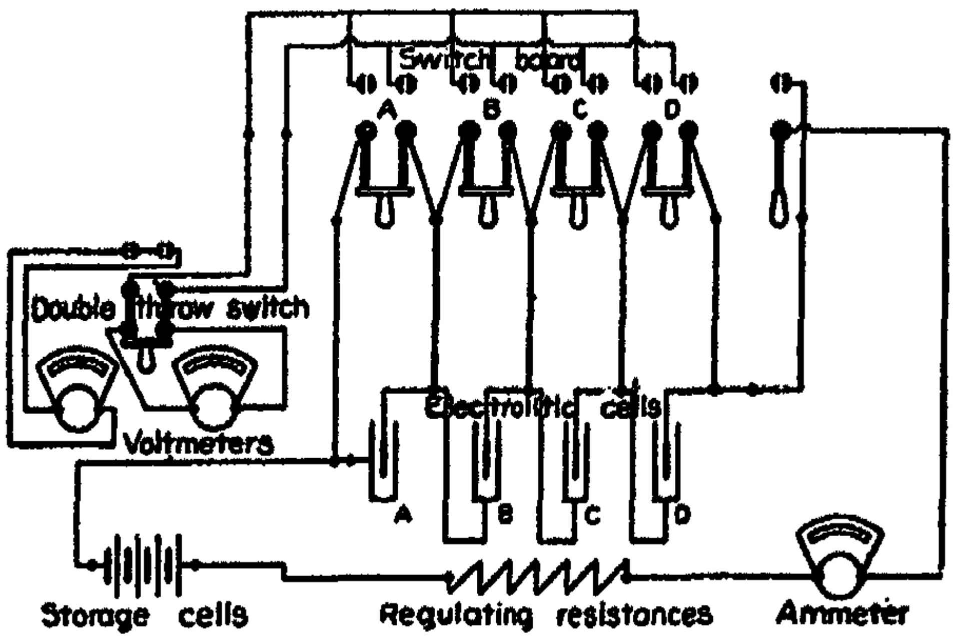

Fig. 1

Two voltmeters were used; one reading up to 0.3 volt, the other up to 1.5 volts. The latter voltmeter was used for voltages above 0.3 volt.

The run was started by placing the electrolytes in their respective beakers, inserting the electrodes in the gutta-percha tops, and immersing them in the solution, coupling the stirring rods together, rigging up the belting on the various pulleys, and making all the electric connections as shown in the diagram. The driving motor was then started and kept going throughout the run. By means of the water-bath, under which a flame was applied, the solutions in the beakers were heated up and kept practically constant at 20° C. A current of one ampere per square decimeter was then turned on and the potential difference between the plates in each cell was then read by simply throwing up the proper switches, readings at the same time being taken of the temperature of the electrolytes in each cell. The quality of the copper precipitated was then investigated, after which the current density was increased to 1.5 amperes per

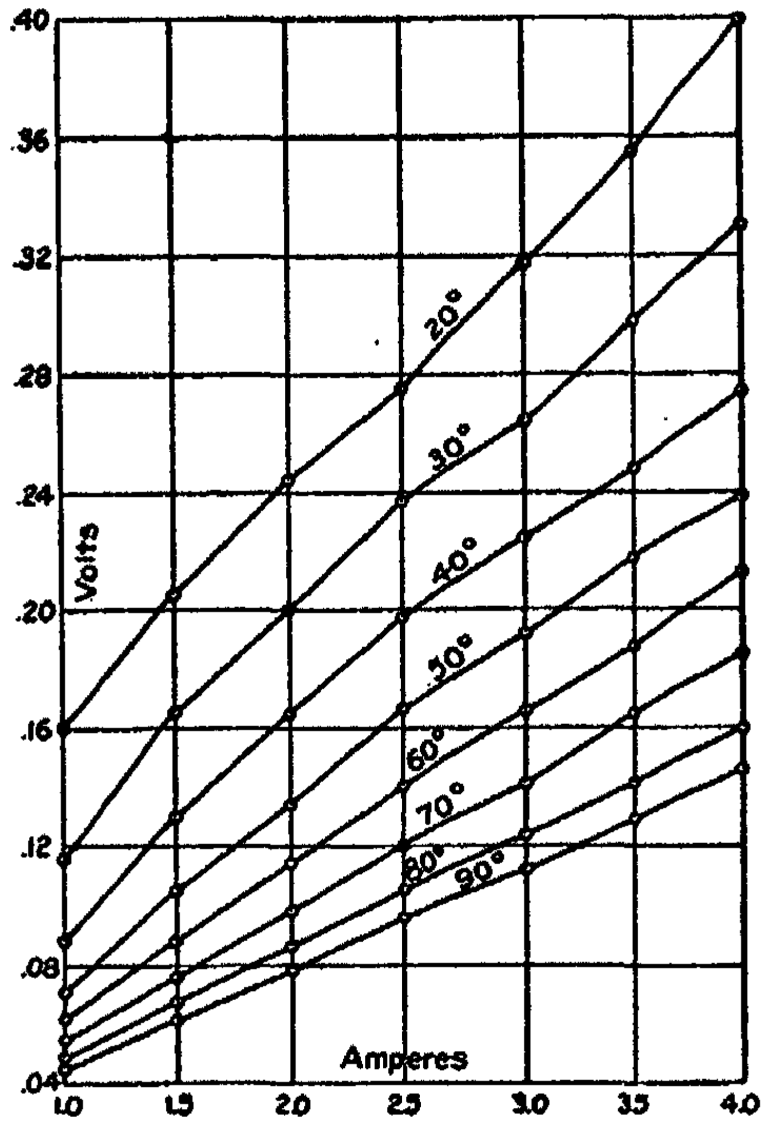

Fig. 2

square decimeter and the same process repeated. Similar readings were made for current densities up to 4 amperes per square decimeter, varying by 0.5 ampere steps. At the end of these runs the temperature of the electrolytes was increased to 30° C and the same readings taken as for the 20° run. This was continued by 10° steps up to 90°. As a check upon our results and to note if any change had taken place in the electrolytes, the runs were repeated from 90° to 20° by decreasing increments of 10°.

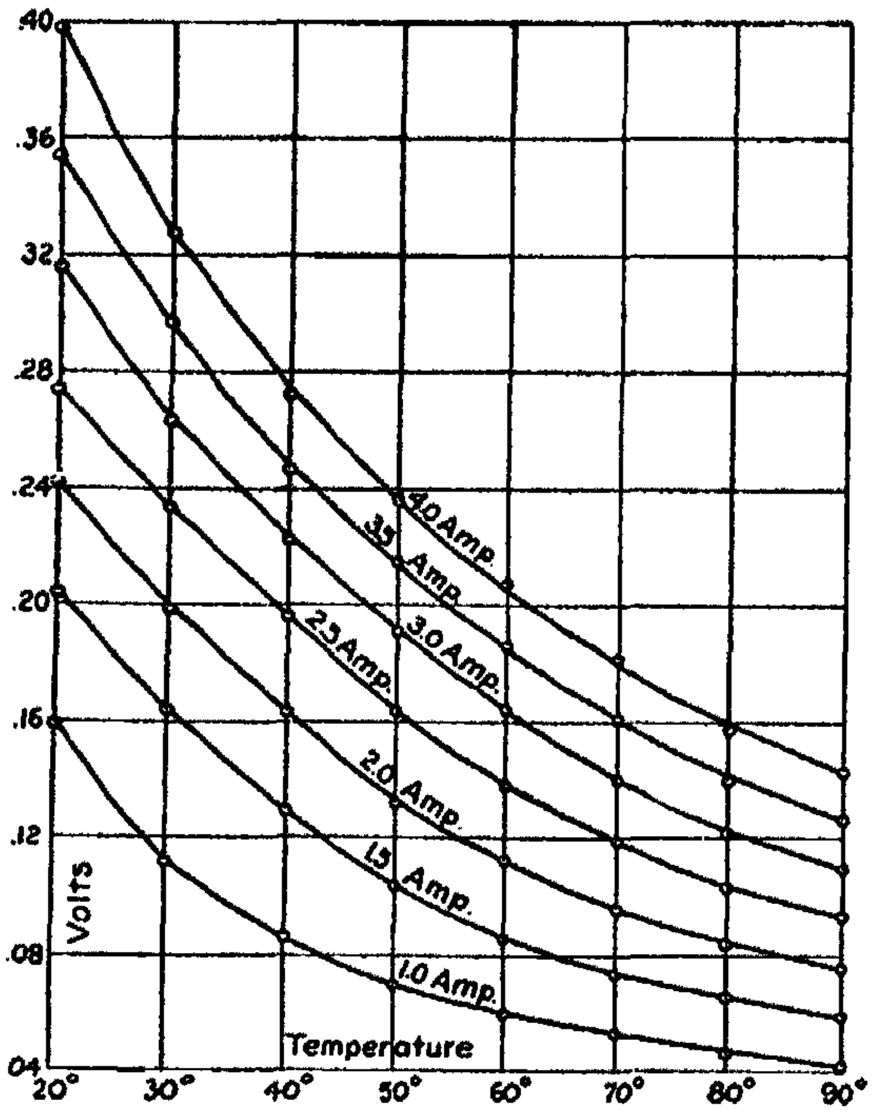

Fig. 3

Discussion of voltage run

The results obtained from this run are tabulated on the preceding pages. Two sets of curves are drawn for solution A, the other solutions being very similar. The first set of these curves, Fig. 2, shows the relation between voltage and current density, a curve being drawn for each temperature. The other set, Fig. 3, shows the relation between voltage and temperature, a curve being drawn for each current density at which readings were made.

Interpreting the voltage current density curves, we see a slightly curious effect; instead of the voltage rising in some direct proportion to the current density, thus giving a straight line as the result, the curves for the lower temperatures at first begin to bend towards the current density axis and then, on reaching the higher densities, a point of inflection is reached and the curve bends in the opposite direction. This point of inflection gradually proceeds away from the voltage axis with a rise of temperature; for the 20° curve inflection takes place at a current density of 2.5 amperes, while for the 30° and 40° curve it is not reached until we come to a current density of 3 and 3.5 amperes respectively. The radius of curvature rapidly increases as the temperature rises, until at 80° and 90° the curves become a straight line.

The reason for this point of inflection is more or less a matter of conjecture. What appears to us to be a satisfactory explanation of the matter is, that the small counter electromotive force of the cell is not a constant quantity, that is, at the lower current densities, it seems to be a decreasing variable, while after the point of deflection is reached, it begins to increase as the current density increases. When working at higher temperatures this counter electromotive force evidently becomes a constant quantity, as a right line indicates. This right line, when produced, cuts the axis of ordinates at a point somewhat above the axis of abscissæ, thus indicating that the electromotive force is not zero, but has a constant value.

In comparing the relative advantages of the different solutions as electrolytes, it can readily be seen that the voltage between the electrodes is materially less when using the 9 percent acid solution than the voltage required to overcome the resistance of the 6 percent solution. The addition of the sodium chloride to the solution increases the voltage at the lower temperatures, while at the higher temperatures the rise in voltage is hardly appreciable.

Tables for voltage runs

20° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	19.7	19.7	20.0	20.0
Voltage	0.160	0.173	0.167	0.171
Temp.	19.6	19.6	19.9	19.9
Voltage	0.156	0.167	0.167	0.171
Current density 1.5 amp/qdm				
Temp.	19.7	19.6	19.9	19.9
Voltage	0.205	0.221	0.211	0.221
Temp.	19.6	19.7	20.0	19.9
Voltage	0.209	0.234	0.218	0.238
Current density 2.0 amp/qdm				
Temp.	19.6	19.7	20.0	19.9
Voltage	0.244	0.262	0.252	0.267
Temp.	19.9	19.9	20.1	20.1
Voltage.	0.251	0.277	0.259	0.275
Current density 2.5 amp/qdm				
Temp.	19.7	19.7	20.0	20.0
Voltage	0.275	0.299	0.284	0.306
Temp.	20.0	20.0	20.3	20.2
Voltage	0.289	0.318	0.298	0.315
Current density 3.0 amp/qdm				
Temp.	19.8	19.8	20.1	20.1
Voltage	0.317	0.342	0.322	0.350
Temp.	20.1	20.2	20.4	20.4
Voltage	0.322	0.354	0.334	0.359
Current density 3.5 amp/qdm				
Temp.	19.8	19.8	20.1	20.1
Voltage	0.354	0.384	0.366	0.396
Temp.	20.3	20.1	20.5	20.4
Voltage	0.359	0.391	0.369	0.398
Current density 4.0 amp/qdm				
Temp.	19.8	19.8	20.1	20.1
Voltage	0.399	0.424	0.414	0.439
Temp.	20.3	20.3	20.6	20.5
Voltage	0.395	0.429	0.402	0.434

30° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	29.7	29.5	29.8	29.8
Voltage	0.114	0.129	0.127	0.129
Temp.	29.7	29.7	30.1	30.0
Voltage	0.120	0.134	0.123	0.132
Current density 1.5 amp/qdm				
Temp.	29.8	29.6	29.9	29.8
Voltage	0.165	0.180	0.173	0.181
Temp.	30.0	29.9	30.4	30.1
Voltage	0.165	0.187	0.170	0.184
Current density 2.0 amp/qdm				
Temp.	29.9	29.7	29.9	29.8
Voltage	0.200	0.223	0.211	0.224
Temp.	30.1	30.0	30.4	30.2
Voltage	0.203	0.232	0.212	0.228
Current density 2.5 amp/qdm				
Temp.	29.9	29.6	29.9	29.8
Voltage	0.237	0.262	0.247	0.264
Temp.	30.2	30.1	30.2	30.1
Voltage	0.240	0.271	0.248	0.268
Current density 3.0 amp/qdm				
Temp.	29.9	29.6	29.9	29.8
Voltage	0.264	0.292	0.274	0.299
Temp.	30.1	30.1	30.4	30.3
Voltage	0.269	0.303	0.278	0.302
Current density 3.5 amp/qdm				
Temp.	29.8	29.6	29.9	29.8
Voltage	0.298	0.330	0.308	0.337
Temp.	30.5	30.2	30.6	30.4
Voltage	0.299	0.334	0.306	0.335
Current density 4.0 amp/qdm				
Temp.	29.8	29.6	29.9	29.8
Voltage	0.330	0.365	0.339	0.374
Temp.	30.3	30.1	30.4	30.2
Voltage	0.327	0.364	0.338	0.369

40° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	39.7	39.8	40.1	39.9
Voltage	0.088	0.099	0.098	0.103
Temp.	39.9	40.0	40.4	40.0
Voltage	0.097	0.113	0.102	0.110
Current density 1.5 amp/qdm				
Temp.	39.9	40.0	40.2	39.9
Voltage	0.130	0.146	0.142	0.149
Temp.	39.9	39.8	40.4	40.1
Voltage	0.140	0.161	0.143	0.148
Current density 2.0 amp/qdm				
Temp.	39.9	40.0	40.4	40.0
Voltage	0.165	0.188	0.178	0.190
Temp.	39.9	40.0	40.3	40.1
Voltage	0.172	0.198	0.175	0.194
Current density 2.5 amp/qdm				
Temp.	39.9	40.0	40.4	39.9
Voltage	0.197	0.223	0.211	0.226
Temp.	39.8	39.9	40.3	40.0
Voltage	0.202	0.229	0.204	0.227
Current density 3.0 amp/qdm				
Temp.	39.9	40.0	40.4	40.0
Voltage	0.225	0.255	0.238	0.259
Temp.	39.7	39.9	40.2	40.0
Voltage	0.229	0.257	0.231	0.255
Current density 3.5 amp/qdm				
Temp.	39.9	40.0	40.2	39.9
Voltage	0.248	0.287	0.260	0.288
Temp.	39.7	39.8	40.1	40.0
Voltage	0.249	0.281	0.254	0.284
Current density 4.0 amp/qdm				
Temp.	39.8	39.9	40.3	39.9
Voltage	0.274	0.314	0.289	0.318
Temp.	39.6	39.8	40.3	40.0
Voltage	0.274	0.314	0.284	0.314

50° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	49.7	50.0	50.3	49.9
Voltage	0.071	0.084	0.081	0.085
Temp.	49.5	49.5	49.9	49.9
Voltage	0.085	0.099	0.089	0.098
Current density 1.5 amp/qdm				
Temp.	50.0	50.0	50.4	49.9
Voltage	0.105	0.122	0.118	0.123
Temp.	49.5	49.5	50.1	49.9
Voltage	0.119	0.140	0.125	0.139
Current density 2.0 amp/qdm				
Temp.	49.9	49.9	50.3	49.9
Voltage	0.134	0.157	0.149	0.158
Temp.	49.5	49.7	50.2	49.9
Voltage	0.150	0.175	0.155	0.173
Current density 2.5 amp/qdm				
Temp.	49.8	49.9	50.3	49.9
Voltage	0.166	0.193	0.181	0.195
Temp.	49.7	49.8	50.2	49.9
Voltage	0.178	0.208	0.183	0.202
Current density 3.0 amp/qdm				
Temp.	49.9	49.9	50.3	49.9
Voltage	0.192	0.224	0.208	0.226
Temp.	49.9	49.9	50.3	49.9
Voltage	0.202	0.236	0.209	0.232
Current density 3.5 amp/qdm				
Temp.	50.0	50.0	50.4	49.9
Voltage	0.217	0.254	0.233	0.257
Temp.	49.7	49.9	50.3	49.9
Voltage	0.224	0.256	0.277	0.255
Current density 4.0 amp/qdm				
Temp.	50.0	50.0	50.4	49.9
Voltage	0.239	0.278	0.253	0.284
Temp.	49.5	49.7	50.1	49.9
Voltage	0.240	0.278	0.245	0.279

60° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	59.8	60.0	60.0	59.9
Voltage	0.062	0.074	0.067	0.074
Temp.	59.3	59.5	59.8	59.9
Voltage	0.069	0.081	0.074	0.082
Current density 1.5 amp/qdm				
Temp.	59.8	60.1	60.1	59.9
Voltage	0.088	0.104	0.096	0.104
Temp.	59.4	59.5	59.8	59.9
Voltage	0.098	0.116	0.104	0.115
Current density 2.0 amp/qdm				
Temp.	59.7	60.0	60.1	59.9
Voltage	0.114	0.136	0.125	0.137
Temp.	59.5	59.5	59.8	59.9
Voltage	0.126	0.148	0.132	0.147
Current density 2.5 amp/qdm				
Temp.	59.7	60.0	60.1	59.9
Voltage	0.140	0.166	0.153	0.168
Temp.	59.5	59.5	59.8	59.9
Voltage	0.151	0.179	0.159	0.177
Current density 3.0 amp/qdm				
Temp.	59.8	60.0	60.1	59.9
Voltage	0.166	0.196	0.180	0.199
Temp.	59.5	59.5	59.8	59.9
Voltage	0.174	0.208	0.182	0.205
Current density 3.5 amp/qdm				
Temp.	59.7	60.0	60.1	59.9
Voltage	0.188	0.223	0.206	0.227
Temp.	59.5	59.5	59.8	59.9
Voltage	0.196	0.234	0.205	0.232
Current density 4.0 amp/qdm				
Temp.	59.8	60.0	60.1	59.9
Voltage	0.213	0.250	0.229	0.254
Temp.	59.5	59.5	59.8	59.9
Voltage	0.216	0.256	0.226	0.258

70° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	69.8	70.4	69.8	69.9
Voltage	0.055	0.064	0.059	0.066
Temp.	69.5	70.0	69.5	70.0
Voltage	0.056	0.065	0.059	0.067
Current density 1.5 amp/qdm				
Temp.	70.0	70.4	70.0	69.9
Voltage	0.076	0.092	0.083	0.094
Temp.	69.5	70.0	69.5	69.9
Voltage	0.078	0.092	0.083	0.096
Current density 2.0 amp/qdm				
Temp.	70.0	70.4	70.0	69.9
Voltage	0.098	0.117	0.106	0.119
Temp.	69.5	70.0	69.5	69.9
Voltage	0.101	0.119	0.107	0.123
Current density 2.5 amp/qdm				
Temp.	69.9	70.3	70.0	69.9
Voltage	0.120	0.142	0.130	0.147
Temp.	69.5	70.0	69.5	69.9
Voltage	0.123	0.148	0.131	0.150
Current density 3.0 amp/qdm				
Temp.	69.7	70.3	69.9	69.9
Voltage	0.141	0.171	0.154	0.175
Temp.	69.5	70.0	69.5	69.9
Voltage	0.144	0.175	0.154	0.177
Current density 3.5 amp/qdm				
Temp.	69.6	70.3	70.0	69.9
Voltage	0.165	0.198	0.177	0.202
Temp.	69.5	70.0	69.5	69.9
Voltage	0.166	0.202	0.176	0.204
Current density 4.0 amp/qdm				
Temp.	69.7	70.3	70.0	70.0
Voltage	0.185	0.224	0.201	0.228
Temp.	69.5	70.0	69.5	69.9
Voltage	0.188	0.226	0.199	0.229

80° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	79.6	80.0	79.3	79.8
Voltage	0.048	0.058	0.050	0.059
Temp.	79.1	79.7	79.1	79.8
Voltage	0.048	0.058	0.049	0.059
Current density 1.5 amp/qdm				
Temp.	79.7	80.0	79.4	79.8
Voltage	0.068	0.082	0.071	0.083
Temp.	79.1	79.4	79.1	79.8
Voltage	0.067	0.082	0.071	0.083
Current density 2.0 amp/qdm				
Temp.	79.6	79.7	79.4	79.8
Voltage	0.086	0.105	0.091	0.107
Temp.	79.1	79.3	79.1	79.8
Voltage	0.085	0.104	0.090	0.107
Current density 2.5 amp/qdm				
Temp.	79.6	79.8	79.3	79.8
Voltage	0.105	0.129	0.110	0.131
Temp.	79.1	79.2	79.1	79.6
Voltage	0.104	0.129	0.110	0.131
Current density 3.0 amp/qdm				
Temp.	79.6	79.8	79.3	79.8
Voltage	0.124	0.153	0.133	0.156
Temp.	79.1	79.4	79.1	79.8
Voltage	0.122	0.152	0.131	0.154
Current density 3.5 amp/qdm				
Temp.	79.6	79.9	79.3	79.9
Voltage	0.142	0.175	0.152	0.180
Temp.	79.4	79.4	79.1	79.8
Voltage	0.140	0.174	0.150	0.179
Current density 4.0 amp/qdm				
Temp.	79.9	80.0	79.4	80.1
Voltage	0.160	0.199	0.171	0.204
Temp.	79.4	79.3	79.1	79.8
Voltage	0.160	0.199	0.172	0.204

90° voltage run

Solutions	A	B	C	D
Current density 1.0 amp/qdm				
Temp.	89.7	90.1	89.8	89.8
Voltage	0.044	0.053	0.045	0.054
Current density 1.5 amp/qdm				
Temp.	89.7	90.1	89.9	89.8
Voltage	0.061	0.076	0.064	0.078
Current density 2.0 amp/qdm				
Temp.	89.7	90.1	89.9	89.8
Voltage	0.078	0.097	0.081	0.099
Current density 2.5 amp/qdm				
Temp.	89.8	90.1	89.9	89.9
Voltage	0.096	0.120	0.099	0.122
Current density 3.0 amp/qdm				
Temp.	89.8	90.1	89.9	90.0
Voltage	0.112	0.142	0.118	0.144
Current density 3.5 amp/qdm				
Temp.	89.8	90.1	90.0	90.3
Voltage	0.129	0.164	0.135	0.166
Current density 4.0 amp/qdm				
Temp.	89.9	90.1	90.0	90.3
Voltage	0.146	0.187	0.153	0.189

The temperature-voltage curves require but little analysis. All are of single curvature, the voltage gradually decreasing as the temperature rises. At the lower temperatures this decrease is quite rapid, but becomes less and less as the temperature rises.

All the curves were plotted using only points on the up-run. The down-run points agree quite uniformly, hence there is no need to show them on the curve sheets.

TEST NO. 2

Current efficiency run

The object of this test was to determine the variations of the current efficiency when operating with the different electrolytic solutions at varying temperatures and different current densities. Heretofore, it has been claimed that the current efficiency drops off rapidly when working at temperatures above 50° C. It was to verify the correctness or prove the incorrectness of this claim that this test was made.

The apparatus used in this test was practically the same as was used in the voltage test (Test No. 1), with the addition of a a copper voltameter run in series with the four other cells.

The electrolyte for the voltameter was made up as follows:

$CuSO_4$	150 grams
H_2SO_4	100 grams
Alcohol	150 grams

Water to make up 1 liter

The electrolytes used for this run were the same as those of the voltage run, viz:—solutions A, B, C, and D. Before starting the run, the electrodes were carefully cleansed by immersing in a solution of nitric acid. They were then washed and further cleaned and brightened by sand-papering. They were once more washed and rinsed with strong alcohol, and dried gently over a Bunsen flame. After this preparation, they were accurately weighed. Two anodes and one cathode were used in each of the four cells; three anodes and two cathodes in the voltameter. The object of this was to increase the cathode surface in the voltameter in order to keep the current density below two amperes per square decimeter. The voltameter only gives accurate results when it is operated at the lower current densities, and as we had to run with a current as high as four amperes, the only remedy was to increase the cathode suiface, and thus cut down the current density.

After the different beakers were filled with their solutions to the proper height, the weighed anodes and cathodes were placed in their gutta-percha tops and immersed in the solutions to the depth of ten centimeters; stirring rods were coupled together, the driving belts rigged up and all electrical connections made with the four cells and the voltameter all in series. The water-bath in which the beakers were immersed was heated up to 20° C, and a current of one ampere was turned on. It might be here stated, that the voltameter was kept at room temperature throughout the entire series of runs. Three ampere hours were run in at this current density of one ampere per square decimeter. At the end of this time, the electrodes were removed from the baths and carefully washed, rinsed with alcohol and dried. Again they were weighed, and the loss of anodes and gain of cathodes noted.

Tables for current efficiency runs

Current efficiency run

Solution A

Temp.	Anode loss in g.	Cathode gain in g.	$\frac{\text{Anode loss}}{\text{Cathode gain}}$	Current efficiency
		Current density 1.0 amp/qdm		
20°	3.5930	3.5360	1.0161	0.9990
50	3.6528	3.4650	1.0542	0.9958
70	3.6910	3.3530	1.0710	0.9691
90	3.9382	1.1580	1.2461	0.9033
		Current density 2.0 amp/qdm		
20	3.5180	3.4840	1.0097	0.9997
50	3.6361	3.5537	1.0232	1.0038*
70	3.6594	3.4672	1.0553	0.9962
90	3.7935	3.3974	1.1163	0.9579
		Current density 3.0 amp/qdm		
20	3.5000	3.4560	1.0122	0.9988
50	3.5120	3.4730	1.0112	0.9990
70	3.6645	3.5670	1.0273	1.0088*
90	3.7377	3.3790	1.1061	0.9664
		Current density 4.0 amp/qdm		
20	3.4590	3.4213	1.0110	0.9986
50	3.5490	3.4840	1.0186	1.0000
70	3.5540	3.4720	1.0181	0.9973
90	3.1752	3.4316	1.0932	0.9821

Current efficiency run
Solution B

Temp.	Anode loss in g.	Cathode gain in g.	$\frac{\text{Anode loss}}{\text{Cathode gain}}$	Current efficiency
Current density 1.0 amp/qdm				
20°	3.5950	3.5387	1.0159	0.9997
50	3.6128	3.4715	1.0407	0.9985
70	3.6400	3.3500	1.0862	0.9682
90	3.8390	3.1890	1.2026	0.9121
Current density 2.0 amp/qdm				
20	3.5120	3.4850	1.0078	1.0000
50	3.6301	3.5531	1.0218	1.0037*
70	3.6358	3.4804	1.0446	1.0000
90	3.7902	3.4208	1.1080	0.9642
Current density 3.0 amp/qdm				
20	3.5030	3.4564	1.0134	0.9994
50	3.5580	3.4730	1.0241	0.9990
70	3.6435	3.5690	1.0288	1.0094*
90	3.7493	3.3590	1.1162	0.9609
Current density 4.0 amp/qdm				
20	3.4600	3.4098	1.0146	0.9951
50	3.5491	3.4817	1.0195	0.9997
70	3.5560	3.4923	1.0236	1.0031*
90	3.7280	3.4640	1.0762	0.9917

Current efficiency run
Solution C

Temp.	Anode loss in g.	Cathode gain in g.	$\frac{\text{Anode loss}}{\text{Cathode gain}}$	Current efficiency
Current density 1.0 amp/qdm				
20°	3.5800	3.5388	1.0110	0.9998
50	3.6660	3.4636	1.0584	0.9953
70	3.6730	3.3575	1.0938	0.9704
90	3.9332	3.1630	1.2431	0.9045

Current density 2.0 amp/qdm

20	3.5110	3.4828	1.0081	0.9995
50	3.6400	3.5505	1.0252	1.0030*
70	3.6548	3.4635	1.0552	0.9951
90	3.8045	3.4128	1.1148	0.9623

Current density 3.0 amp/qdm

20	3.5030	3.4562	1.0135	0.9994
50	3.5640	3.4730	1.0261	0.9940
70	3.6665	3.5670	1.0280	1.0088*
90	3.7555	3.3600	1.1147	0.9610

Current density 4.0 amp/qdm

20	3.4750	3.4080	1.0196	0.9947
50	3.5500	3.4840	1.0184	1.0000
70	3.5500	3.4870	1.0181	1.0016*
90	3.7280	3.4312	1.0866	0.9820

Current efficiency run

Solution D

Temp.	Anode loss in g.	Cathode gain in g.	$\frac{\text{Anode loss}}{\text{Cathode gain}}$	Current efficiency
Current density 1.0 amp/qdm				
20°	3.5850	3.5361	1.0138	0.9990
50	3.6144	3.4768	1.0400	0.9990
70	3.6440	3.3560	1.0861	0.9700
90	3.8430	3.1840	1.2070	0.9110
Current density 2.0 amp/qdm				
20	3.5278	3.4835	1.0130	0.9996
50	3.6285	3.5525	1.0214	1.0035*
70	3.6295	3.4710	1.0458	0.9773
90	3.8040	3.4156	1.1137	0.9629
Current density 3.0 amp/qdm				
20	3.5020	3.4560	1.0133	0.9991
50	3.5630	3.4725	1.0261	0.9989
70	3.6460	3.5510	1.0267	1.0043*
90	3.7305	3.3710	1.1068	0.9641
Current density 4.0 amp/qdm				
20	3.4640	3.4130	1.0149	0.9963
50	3.5470	3.4820	1.0187	0.9998
70	3.5400	3.4780	1.0179	0.9990
90	3.7305	3.4694	1.0752	0.9930

Tables for voltage and work relations

Voltage and work relations
Solution A

Temp.	Amp/qdm	$\frac{\text{Voltage } x^\circ}{\text{Voltage } 20^\circ}$	Watt hours per g. Cu	$\frac{\text{Watt hours } x^\circ}{\text{Watt hours } 20^\circ}$
20°	1.0	1.000	0.135	1.000
50	1.0	0.446	0.060	0.445
70	1.0	0.340	0.046	0.341
90	1.0	0.264	0.039	0.289
20	2.0	1.000	0.206	1.000
50	2.0	0.548	0.112	0.544
70	2.0	0.395	0.082	0.398
90	2.0	0.312	0.067	0.325
20	3.0	1.000	0.268	1.000
50	3.0	0.600	0.161	0.600
70	3.0	0.441	0.118	0.440
90	3.0	0.347	0.095	0.354
20	4.0	1.000	0.337	1.000
50	4.0	0.605	0.204	0.605
70	4.0	0.454	0.153	0.454
90	4.0	0.362	0.124	0.368

Voltage and work relations
Solution B

Temp.	Amp/qdm	$\frac{\text{Voltage } x^\circ}{\text{Voltage } 20^\circ}$	Watt hours per g. Cu	$\frac{\text{Watt hours } x^\circ}{\text{Watt hours } 20^\circ}$
20°	1.0	1.000	0.144	1.000
50	1.0	0.500	0.072	0.500
70	1.0	0.376	0.056	0.389
90	1.0	0.306	0.048	0.333
20	2.0	1.000	0.220	1.000
50	2.0	0.607	0.134	0.608
70	2.0	0.450	0.099	0.450
90	2.0	0.370	0.084	0.383
20	3.0	1.000	0.287	1.000
50	3.0	0.655	0.188	0.655
70	3.0	0.505	0.144	0.502
90	3.0	0.415	0.124	0.432
20	4.0	1.000	0.358	1.000
50	4.0	0.659	0.235	0.656
70	4.0	0.520	0.186	0.520
90	4.0	0.440	0.159	0.444

Voltage and work relations
Solution C

Temp.	Amp/qdm	$\frac{\text{Voltage } x^\circ}{\text{Voltage } 20^\circ}$	Watt hours per g. Cu	$\frac{\text{Watt hours } x^\circ}{\text{Watt hours } 20^\circ}$
20°	1.0	1.000	0.141	1.000
50	1.0	0.490	0.069	0.490
70	1.0	0.353	0.052	0.369
90	1.0	0.270	0.042	0.298
20	2.0	1.000	0.213	1.000
50	2.0	0.600	0.127	0.595
70	2.0	0.416	0.088	0.413
90	2.0	0.325	0.072	0.338
20	3.0	1.000	0.273	1.000
50	3.0	0.649	0.177	0.647
70	3.0	0.477	0.130	0.475
90	3.0	0.366	0.104	0.380
20	4.0	1.000	0.357	1.000
50	4.0	0.650	0.216	0.648
70	4.0	0.481	0.169	0.474
90	4.0	0.371	0.133	0.372

Voltage and work relations
Solution D

Temp.	Amp/qdm	$\frac{\text{Voltage } x^\circ}{\text{Voltage } 20^\circ}$	Watt hours per g. Cu	$\frac{\text{Watt hours } x^\circ}{\text{Watt hours } 20^\circ}$
20°	1.0	1.000	0.145	1.000
50	1.0	0.496	0.073	0.503
70	1.0	0.380	0.057	0.392
90	1.0	0.316	0.050	0.344
20	2.0	1.000	0.226	1.000
50	2.0	0.600	0.135	0.600
70	2.0	0.453	0.102	0.450
90	2.0	0.370	0.087	0.385
20	3.0	1.000	0.296	1.000
50	3.0	0.649	0.193	0.652
70	3.0	0.500	0.149	0.504
90	3.0	0.409	0.127	0.429
20	4.0	1.000	0.372	1.000
50	4.0	0.649	0.241	0.647
70	4.0	0.523	0.193	0.519
90	4.0	0.430	0.161	0.432

To find the current efficiency for any particular cell, divide the gain in weight of cathode of that cell by the gain in weight of cathodes of the voltameter.

After the completion of the first run, the electrodes were again cleansed, dried and weighed, and replaced in the cells. The current density was increased to two amperes per square decimeter and allowed to flow through the cells for 1 ½ hours, thus giving three ampere hours. This process was repeated for current densities of three and four amperes per square decimeter. Current efficiency runs were also made with the temperature of the electrolytes at 50° C, 70° C, 90° C, and with current densities of 1, 2, 3, and 4 amperes per square decimeter for each temperature. The results are given in two sets of tables, the first showing current efficiencies, the second the energy efficiencies.

Discussion of current efficiency run

By reference to the preceding data sheets it will be seen that the current efficiencies for temperatures below 70° C fall off but very little and are practically 100 percent. Even at a temperature of 90° C and a high current density of 4 amp/qdm, the efficiency runs as high as 98 percent, and 99 percent, for the 9 percent and 6 percent solutions respectively, while a current density of 1 ampere per sq/dcm gives an efficiency of 90 percent and 91 percent.[1] Between 50 and 70 degrees, the efficiency in some cases runs a trifle above 100 percent. This is no doubt due to the formation of cuprous sulphate, in small quantities in the electrolyte. In this salt, copper having a valency of unity, twice as much will be precipitated as from the solutions of cupric salts. This reduction seems to take place most readily at the higher current densities, which probably accounts for the high

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[1] While this result is apparently in flat contradiction with that of Foerster and Seidel, this is not really the case. These authors find 47 percent efficiency with 0.3 amp/qdm and 83 percent efficiency with 1.0 amp/qdm at 100°, while we find, at 90°, 91 percent efficiency with 1.0 amp/qdm and 99 percent efficiency with 4.0 amp/qdm. The highest current density of Foerster and Seidel is our lowest. Since no refinery in this country runs at as low a current density as 1.0 amp/qdm (except perhaps the Calumet and Hecla), the conclusions of Foerster and Seidel are not applicable to American practice.

current efficiencies obtained at the upper limits of temperature.

The deterioration of solution is proportional to the ratio of anode loss to cathode gain, since we used pure copper plates and there was no sediment or copper scrap on the bottom of the beakers. The solution deteriorates more rapidly at the higher temperatures and at the lower current densities. This deterioration of solution probably more than offsets the advantage of decrease in voltage which the higher temperatures give, but only when operating at the lower current densities. The ratio of anode loss to cathode gain, when operating at 70° C and 4 amp/qdm, is hardly any higher than this ratio for operating temperatures between 20° C and 50° C.

The results tabulated as

$$\frac{\text{Anode loss}}{\text{Cathode gain}};\ \frac{\text{Voltage at } x^\circ}{\text{Voltage at } 20^\circ};\ \frac{\text{Watt hours per gram of copper at } x^\circ}{\text{Watt hours per gram of copper at } 20^\circ}$$

are self-explanatory. Current efficiency is the ratio of the gain in weight of the cell cathode to the gain in weight of the voltameter cathode.

Watt hours per gram of copper were calculated from a formula deduced as follows: —

One ampere hour deposits $0.000328 \times 3600 = 1.1808$ grams copper from a solution when the current efficiency is 100 percent.

$$\frac{\text{Weight of copper deposited by voltameter}}{1.1808} = \text{number of ampere hours run.}$$

$$\frac{\text{Ampere hours run}}{\text{Current}} = \text{duration of run (hours).}$$

$$\frac{\text{Actual copper deposited for particular cell}}{\text{Duration of run (hrs)} \times \text{current} \times \text{voltage}} = \text{grams of copper deposited per watt hour for particular cell.}$$

$$\frac{1}{\text{Grams copper per watt hour}} = \text{watt hours per gram of copper.}$$

This all deduces to the following simple formula: —

$$\frac{\text{Voltage}}{1.1808 \times \text{current efficiency}} = \text{watt hours per gram copper.}$$

A set of curves was plotted (Fig. 4) showing the relation between the ratio of voltages and temperature. The voltage at 20° C was taken as unity. These curves are useful, in that they may be applied in general, and are not confined to any one particular case. The curves of the first run apply to the case when the electrodes are placed one centimeter apart. Knowing the voltage at any temperature, the voltage for any other temperature can be computed by use of these ratio curves.

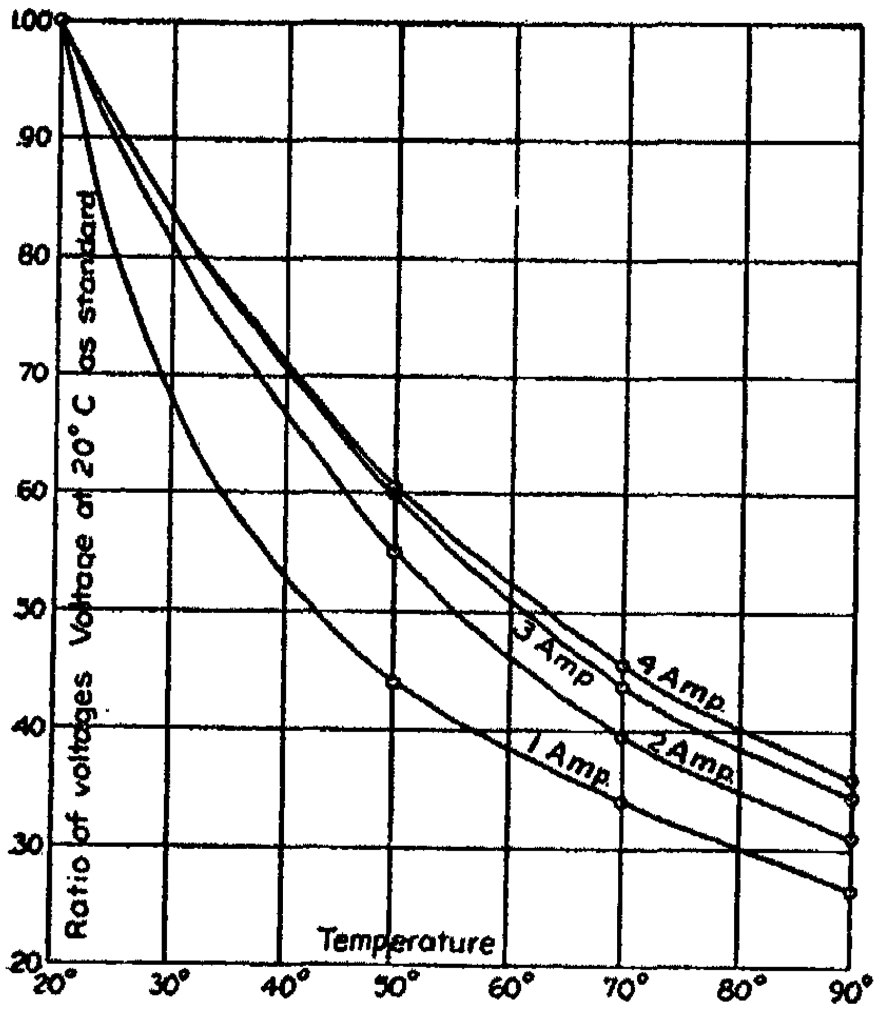

Fig. 4

A set of curves were also plotted (Fig. 5) showing the relation between watt hours required per gram of copper and the operating temperatures. These curves are self-evident and require no discussion.

Effect of iron in electrolyte

Frequent statements have been made that the presence of iron in the electrolytic solutions cuts down the current efficiency. To investigate this, we prepared the following solutions:—

Solution (*a*)	$CuSO_4.5H_2O$	16	percent
	H_2SO_4	5	percent
Solution (*b*)	$FeSO_4.7H_2O$	18.4	percent
	H_2SO_4	6	percent

3 cc HNO_3 per liter of solution (*b*)

We then mix 9 volumes (*a*), 1 volume (*b*) — (Solution 1)
8 " " 2 " " (Solution 2)
7 " " 3 " " (Solution 3)
6 " " 4 " " (Solution 4)

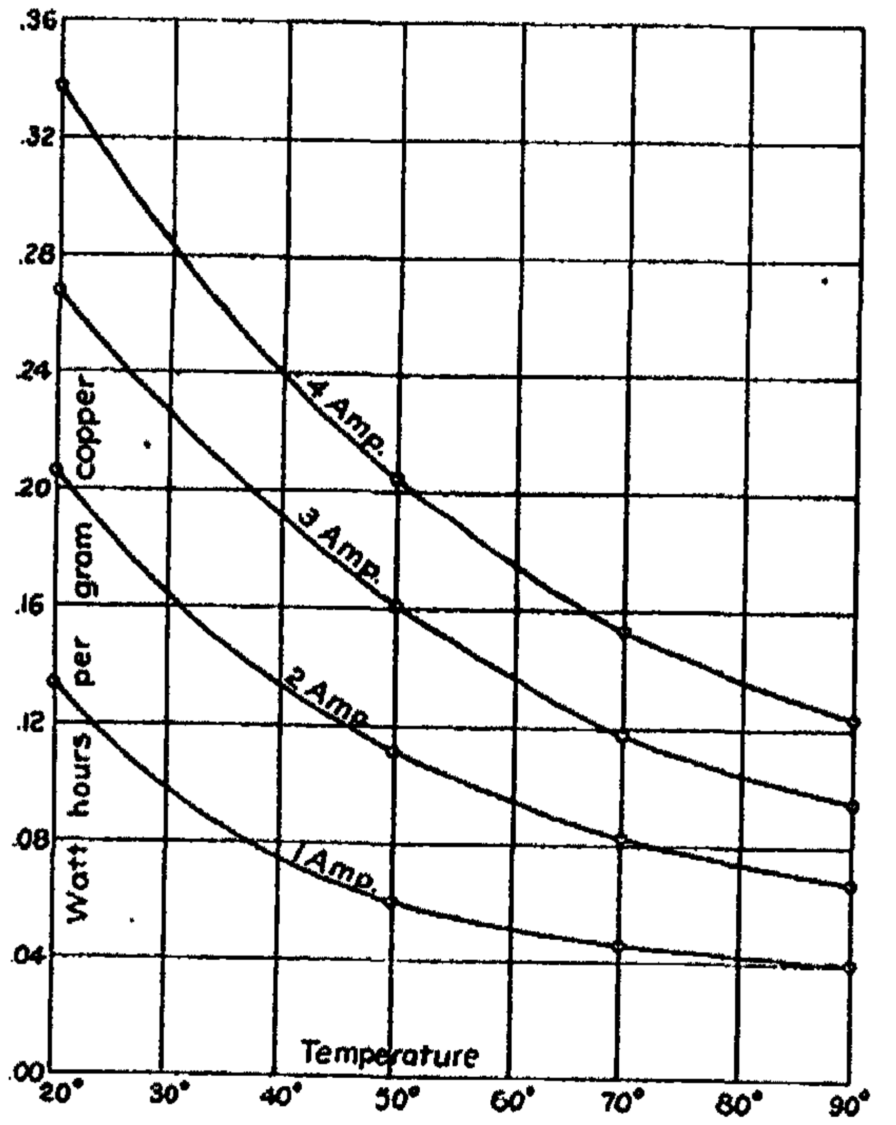

Fig. 5

These solutions were electrolyzed between weighed copper electrodes at a temperature of 45° C and a current density of 2 amp/qdm, with a voltameter in series. The same apparatus was used as in the current efficiency run. The results obtained show that there is no falling off in the current efficiency. Thinking that perhaps enough nitric acid had not been added to change a sufficient quantity of ferrous iron to the ferric condition, we made up another solution of iron to contain 20 cc nitric acid per liter, instead of 3 cc. The run was continued, using this new solution. The results obtained tallied with the first, showing no decrease in current efficiency. After the test the precipitate on the cathode was dissolved in nitric acid, and the solution was tested for iron. None was found, thus demonstrating that iron was not precipitated from the solution.

Table for iron in electrolyte

Effect of iron in electrolyte

Current density 2 amp/qdm

Temperature 20°

Solution	Anode loss in g.	Cathode gain in g.	$\frac{\text{Anode loss}}{\text{Cathode gain}}$	Current efficiency
3 cc HNO$_3$ per liter solution (*b*)				
1	3.6255	3.5260	1.032	0.9986
2	3.6190	3.5295	1.025	0.9996
3	3.6265	3.5310	1.028	1.0000
4	3.6195	3.5270	1.025	0.9988
5	3.6760	3.5310	1.011	1.0000
20 cc HNO$_3$ per liter solution (*b*)				
1	2.3650	2.2886	1.035	0.9980
2	2.3690	2.2925	1.035	0.9997
3	2.3775	2.2920	1.035	0.9996
4	2.3700	2.2880	1.040	0.9978
5	2.3441	2.2931	1.019	1.0000

TEST NO. 3

Radiation run

One of the important items in electrolytic copper refining is the cost of maintaining the electrolytes in the vats at operating temperature. To form some idea of the relative costs of operating at various temperatures was the object of this test.

To this end we proceeded in the following manner. Of course, it was impossible for us to make a radiation run with a vat of such a size as is used in an electrolytic copper refining plant, but we endeavored to duplicate commercial conditions on a small scale.

The vats in a plant using the Hayden system, are 9 feet long, 2 feet wide, and 2.5 feet deep, and are filled with copper plates 0.5 inch apart. Accordingly, we constructed a small tank out of 0.5 inch stock, with inside dimensions of 9″ × 2″ × 2.5″, and filled it with copper plates 0.5 inch apart. The joints of the tank, as well as the inside, were lined with tar, thus effectually preventing leaks.

As a means of heating up the tank, a platinum coil was placed on the bottom and connections brought out to binding posts on the sides of the tank. Next, the tank was filled up with electrolytic solution (Solution A) and its temperature brought up to near the boiling-point by passing an alternating current through the platinum coil. The object of using an alternating current was to prevent precipitation of copper on the platinum coil, which would thereby increase its conductivity and cut down the heating powers when working with a current for which the coil was designed. When the solution had reached the temperature of about 95° C, the current was turned off and the run started.

A standard thermometer was placed in the electrolyte, and readings of its temperature taken at varying intervals of time, until the temperature had dropped to about 40° C. Two radiation runs of this sort were made, the first with the tank uncovered, and the second with a cover over the top.

The tank was again heated up to 90° C, and the current so adjusted that the temperature of the solution was maintained constant. A wattmeter and ammeter were placed in series with the tank. In order to make accurate readings of the power required to overcome radiation at 90° C, the potential side of the wattmeter was stepped up to ten times the pressure at the terminals of the vat by means of a ten-to-one transformer. This reduces the error of reading to practically a negligible amount, since the actual watts required will be only one-tenth of the wattmeter reading. The power required to overcome radiation at 90° was determined both for covered and uncovered tanks.

Radiation run

Room temperature 24.8°

Tank covered				Tank uncovered			
Temp.	Time	Temp.	Time	Temp.	Time	Temp.	Time
96.1°	0.0	78.7°	23.0°	94.5°	0.0.	69.8°	14.5
95.0	0.5	76.0	27.5	92.2	0.5	67.7	16.5
94.2	1.0	73.1	32.5	90.7	1.0	65.9	18.5
93.6	1.5	70.5	37.5	88.1	2.0	63.7	21.0
93.1	2.0	68.2	42.5	85.6	3.0	61.5	24.0
92.2	3.0	66.0.	47.5	83.5	4.0	59.0	27.5
91.5	4.0	63.9	52.5	81.4	5.0	56.8	31.0
90.8	5.0	61.9	57.5	79.6	6.0	55.0	34.0
89.7	6.5	59.9	62.5	77.2	7.5	52.4	40.0
88.6	8.0	56.5	72.5	75.2	9.0	48.2	50.0
87.2	10.0	53.3	82.5	73.2	10.5	44.7	60.0
85.7	12.0	50.6	92.5	71.4	13.0		
84.2	14.0	48.2	102.5				
82.4	17.0	46.0	112.5				
80.5	20.0	44.1	122.5				

Constant temperature — Power data

Tank covered				Tank uncovered			
Temp.	Watts	Temp.	Watts	Temp.	Watts	Temp.	Watts
90°	44.0	65°	25.2	90°	145.0	65°	42.0
85	40.1	60	21.7	85	118.0	60	34.4
80	36.6	55	18.8	80	90.4	55	26.4
75	33.5	50	14.5	75	67.3	50	20.6
70	28.8			70	50.6		

The results obtained were very surprising. Two radiation curves were plotted, using temperature as ordinates and time as abscissæ. The radiation curve for the uncovered tank differs greatly from the curve for the covered tank, as can readily be seen by reference to Fig. 6. As would naturally be expected, radiation takes place much more rapidly from the uncovered tank. The power required to overcome radiation at any particular temperature is directly proportional to the slope of the radiation curve at that temperature. Hence, to find the number of watts at any particular temperature necessary to overcome the radiation, we simply multiply the watts required at 90° by the ratio of the tangent to the curve at the particular temperature and the tangent at 90°. The power required at several different temperatures was computed for both curves, and the relation between this power and the temperature is graphically shown by another set of curves, Fig. 7.

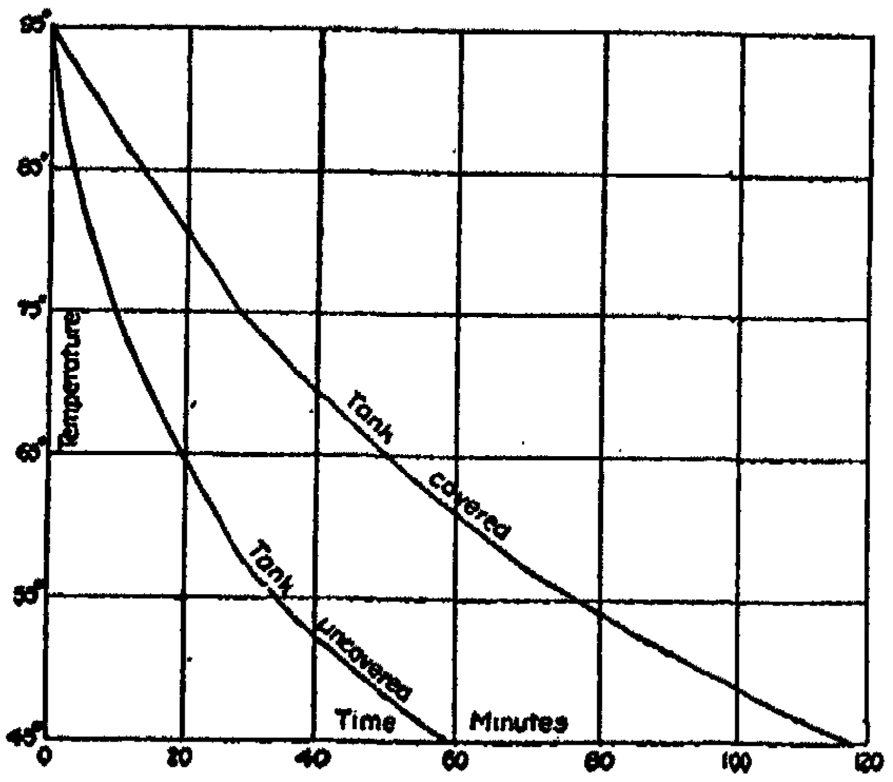

Fig. 6

Since the radiation of any two similar bodies is directly proportional to the area of their radiating surfaces, these values of power as determined for our small tank can be easily translated to figures for a tank of commercial size. This has been done, and two curves showing the power required to overcome radiation at different temperatures in a commercial tank were plotted. Of course, we do not expect these results to be entirely accurate, as the temperature gradient for the small tank enters in to a far greater extent than for the larger commercial tanks. But the results obtained can be safely said to be accurate to within 10 or 20 percent, since, in a subsequent run on a larger tank, we checked the results very closely.

In our further discussion, we shall confine ourselves entirely to covered tanks, as it is obvious that the most efficient results can be obtained from their use. At 50° the uncovered tank needs 42 percent more power; and 75 percent more power at 70°.

COMMERCIAL TEST

In this test we endeavored to duplicate commercial conditions in the precipitation of electrolytic copper. Through the courtesy of the Baltimore Copper Company, we were able to obtain several hundred pounds of their commercial anode plates. These plates were 24¼ inches long, 11 inches wide, and ¼ inch

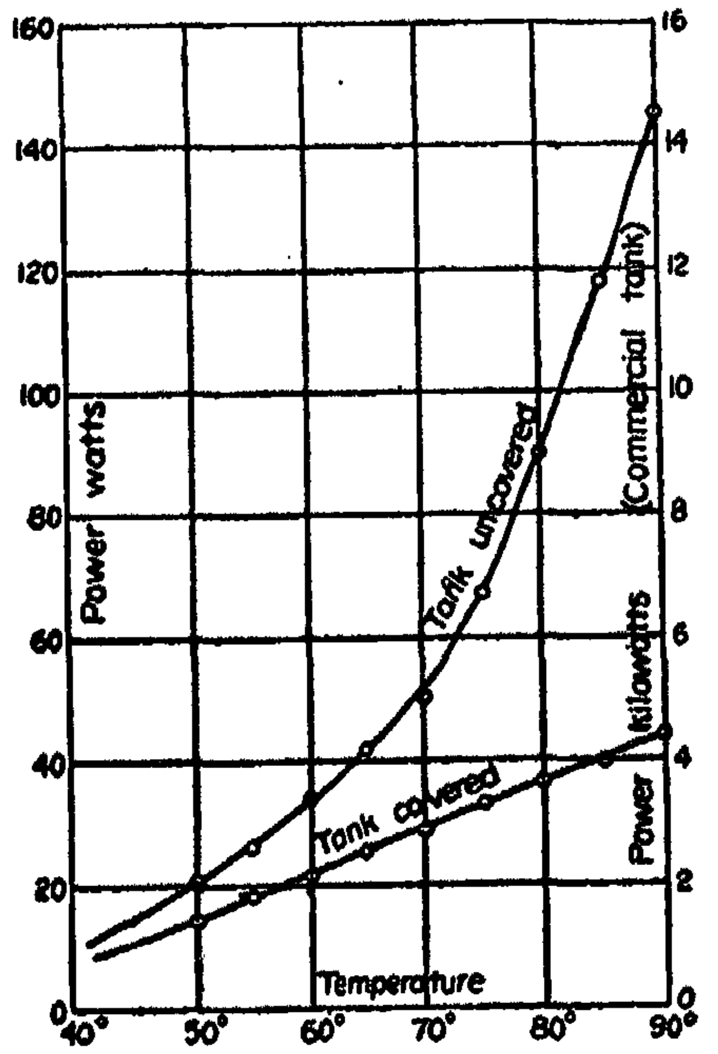

Fig. 7

thick. They were cut in half, thus giving anode plates 11 × 12⅛ inches.

The tank used was built of ¾ inch stock of inside dimensions 13″ × 13″ × 13″, and lined with tar to make it water-tight. A piece of sheet glass was fitted in the bottom, covering it completely, for the purpose of preventing the slimes from sticking to the tar lining. Small, rectangular pieces of wood, having ¼ inch grooves cut their entire length, were used as distance pieces, allowing the plates to be stacked ½ inch apart.

Ten commercial anode plates were used, and a thin sheet of copper composed of end cathode. The method of arranging the plates was according to the Hayden system. The plates did not rest upon the bottom of the tank, but were suspended about an inch therefrom. The tops of the plates were likewise an inch from the top of the tank. The tank was then filled with solution, covering the plates completely.

The composition of this electrolyte was

$CuSO_4.5H_2O$	16 percent
H_2SO_4	9 percent

Water to make one liter

As a means of maintaining the tank at a temperature of 45° C, we employed a half inch glass tube, one end of which extended to within an inch of the tank's bottom, while the other end extended down only an inch below the top of the tank. The tube was heated by means of a Bunsen burner, which not only kept the electrolyte up to the required temperature, but provided a good circulation from the bottom of one end of the tank to the top of the other. Thinking that this circulation might not be adequate, a stirring rod, operated by a small motor, was also provided.

Current to the cell was supplied during the day by a small direct current generator, and at night by a battery of storage cells. In the circuit was inserted an ammeter, ampere hour meter, and a recording ammeter, while a voltameter was placed across the terminals of the cell. The current was adjusted to 20 amperes, which gave a current density a little over 2 amp/qdm.

The voltage across the terminals of the tank rose from 1.75 volts, at the beginning of the run, to 2.10 volts, three and a half days later. This was due to the deterioration of the solution, that is, to the neutralization of the acid.

After a run of about two hundred hours, it was discovered that some of the plates had become short-circuited by a growth of copper along the bottom of the plates. In stacking up the plates, to raise them from the bottom of the tank, we used a strip of wood upon which the distance pieces rested, thus giving a liquid joint extending clear across the tank. In the actual Hayden system, the grooves in the distance pieces are not cut all the way to the bottom, thus holding up the plates and doing away with this liquid joint. The short-circuiting in our case was caused by a growth of copper along this joint. This occurrence rendered all readings of power consumed incorrect, and therefore useless as data. The run was here concluded, the slimes washed from the plates and collected from the tank, washed carefully and dried. In all, about 90 grams were taken out. The slimes were analyzed, and found to contain 41 percent silver and quite an appreciable amount of silica, which probably came from the linings of the blast-furnace. The silver in the slimes was recovered by dissolving them in nitric acid, evaporating to dryness and taking up the residue in a dilute solution of sulphuric acid, then precipitating from this solution by means of copper strips.

As we could not compute the current efficiency from the results of this run, we made an extra determination with a commercial anode, using our current efficiency apparatus previously described. The results obtained are tabulated below.

$$\frac{\text{Anode loss}}{\text{Cathode gain}} = 1.0330$$

$$\text{Current efficiency} = 0.9915$$

This run was made at 45° C and a current density of 2 amp/qdm. From the current efficiency obtained we see that the impurities in the anode do not cut down the current efficiency to any great extent. The current efficiency of commercial tanks does not reach this high figure, probably due to leakage of the current through the slimes on the bottom.

The color of the solution at the end of the commercial run was a decided green. This aroused our curiosity and we decided

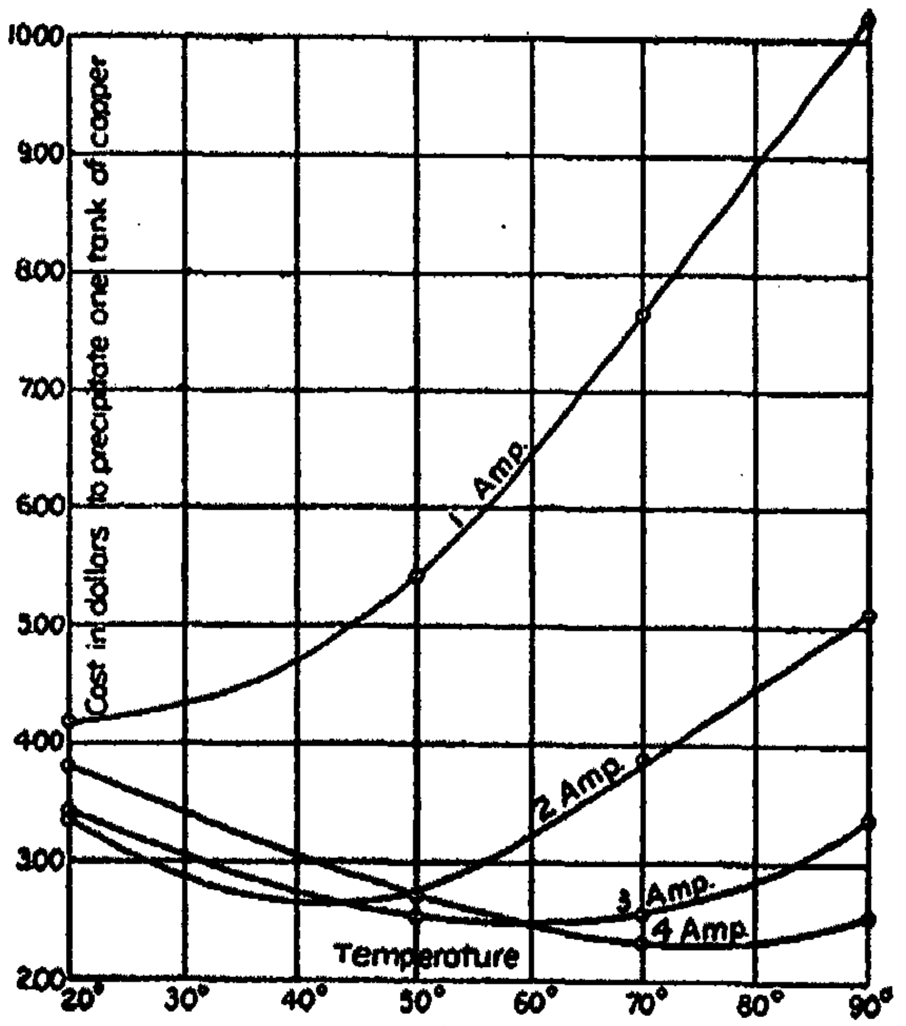

Fig. 8

to discover what caused it. After numerous trials and experiments we arrived at the conclusion that the green color is due to the presence of ferro-arsenate in solution.

CALCULATIONS FOR COST OF REFINING

Basis.—One tank, inside dimensions 2 feet × 2½ feet × 9 feet. Outside dimensions taken as 29″ × 34″ × 112″, giving a radiating surface of 16000 square inches. Ratio of radiating surface of small experimental tank to commercial tank is about 1 to 100.

The basis for the following figures on the cost of production are as follows:—

One tank, containing 130 electrodes of two plates each.

Weight of copper per tank = 5700 lbs.

Value of copper per tank = \$800.00.

Cost of power = \$20.00 per H.P. per year.

Plant temperature = 20° C.

We have figured on the basis that the heating of the electrolyte is done by means of the electric current. In such cases, where the cost of heating the solution is greater than the cost of precipitating the copper, we have taken as the figures of cost, the former, and vice-versa, since, in precipitating the copper, the energy is consumed simply in overcoming the resistence of the electrolyte, and thereby heating it.

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1 lb. = 453.6 grams.

5700 lbs. = 2,684,000 grams copper = N.

Area of electrodes $= 22'' \times 23'' = 506$ sq. in. $= 32.65$ qdm. Current density of 1 amp.sq/dcm = 32.65 amp., which will deposit $32.65 \times 1.181 \times 24 \times 130 = 120{,}500$ grams copper per day per tank. Therefore it requires $2{,}684{,}000/120{,}500 = 22.3$ days or 535 hours to precipitate one tank full of copper, operating at a current density of 1 amp/qdm. Interest on one tank of copper (value \$800) for 22.3 days at 6 pct = \$2.975.

At 2 amp/qdm, interest $= 2.975 \div 2 = \$1.487$.

At 3 amp/qdm, interest $= 2.975 \div 3 = \$0.992$.

At 4 amp.sq/dcm, interest $= 2.975 \div 4 = \$0.744$.

At 20° C, 1 amp/qdm it requires $0.145 \times N = 390{,}000$ watt hours to precipitate one tank of copper.

At \$20 per H.P. year, 1 K.W. hour costs \$0.00306.

Therefore 390 K.W. hours cost \$1.195.

Therefore total cost to deposit one tank of copper at 20° C and 1 amp/qdm $= \$1.195 + \$2.975 = \$4.170$.

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1 amp/qdm 50° C.

Cost to deposit $= \$1.195 \times 0.503 = \$0.601$.

Required to heat $= 1.48 \times 22.3 \times 24 = 793$ K.W. hours.

Cost to heat = 793 × $0.00306 = $2.425.
Interest = $2.975.
Total cost = $2.425 + $2.975 = $5.400.

1 amp/qdm 70° C.

Cost to deposit = $1.195 × 0.392 = $0.468.
Cost to heat = 2.9 × 22.3 × 24 × 0.00306 = $4.750.
Interest = $2.975.
Total cost = $4.755 + $2.975 = $7.730.

1 amp/qdm 90° C.

Cost to deposit = $1.195 × 0.344 = $0.411.
Cost to heat = 4.4 × 22.3 × 24 × 0.00306 = $7.205.
Interest = $2.975.
Total cost = $7.205 + $2.975 = $10.180.

In a similar manner the costs for other current densities were computed and the results are shown on the data sheet.

Data for cost of refining tank of copper

Amp/qdm	Temp.	K. W. hours to deposit	Cost to deposit	K. W. hours to heat	Cost to heat	Interest on copper	Total cost
1.0	20°	390	$1.195	000	$0.00	$2.975	$ 4.17
1.0	50	196	0.601	793	2.425	2.975	5.40
1.0	70	153	0.468	1550	4.755	2.975	7.73
1.0	90	134	0.411	2360	7.205	2.975	10.18
2.0	20	608	1.86	000	0.00	1.487	3.35
2.0	50	362	1.11	396	1.21	1.487	2.70
2.0	70	274	0.84	775	2.38	1.487	3.87
2.0	90	233	0.71	1180	3.60	1.487	5.09
3.0	20	795	2.43	000	0.00	0.99	3.42
3.0	50	519	1.59	264	0.81	0.99	2.58
3.0	70	400	1.22	517	1.58	0.99	2.57
3.0	90	341	1.04	787	2.40	0.99	3.39
4.0	20	1000	3.06	000	0.00	0.74	3.80
4.0	50	647	1.98	198	0.61	0.74	2.72
4.0	70	519	1.59	388	1.19	0.74	2.33
4.0	90	433	1.33	590	1.80	0.74	2.54

While these figures are based on experiments with the series system, it is probable that the chief results obtained would be the same for the multiple system. The kilowatt hours needed to deposit a kilogram of copper will be larger for a multiple tank owing to the greater distance between plates. The radiation losses are probably also greater owing to the wider tanks. Otherwise there is but little difference, since the extra interest charge on account of thick anodes is offset by the possibility of removing the cathodes before the end of the run.

Exception may be taken to our estimates on the ground that, in practice, the solutions are heated by steam coils, and that this costs less than electrical heating. To meet this objection we have calculated our results on the basis of electrical power at $20 per horse-power year and of steam heating at one-thirtieth the price of electrical heating. The data for the two calculations are given in the following table, and show cost per ton of copper. The two columns represent practically the two extremes, since the cost of steam heating cannot exceed that of electrical heating.

Table for cost per ton

Cost per ton of copper

Amp/qdm	Temp.	Cost 20–20	Cost 20–2/3
1	20°	$1.46	$1.46
1	50	1.89	1.28
1	70	2.78	1.25
1	90	3.57	1.27
2	20	1.17	1.17
2	50	0.95	0.91
2	70	1.36	0.83
2	90	1.79	0.80
3	20	1.20	1.20
3	50	0.91	0.91
3	70	0.90	0.78
3	90	1.19	0.72
4	20	1.33	1.33
4	50	0.95	0.95
4	70	0.82	0.82
4	90	0.89	0.89

Conclusion

Summing up the results obtained for the different runs, we are now prepared to draw our conclusions, as to what are the most financially economical conditions under which to refine copper electrolytically.

All the results were figured down to the cost of precipitating one tank of copper. Two sets of curves were plotted, the

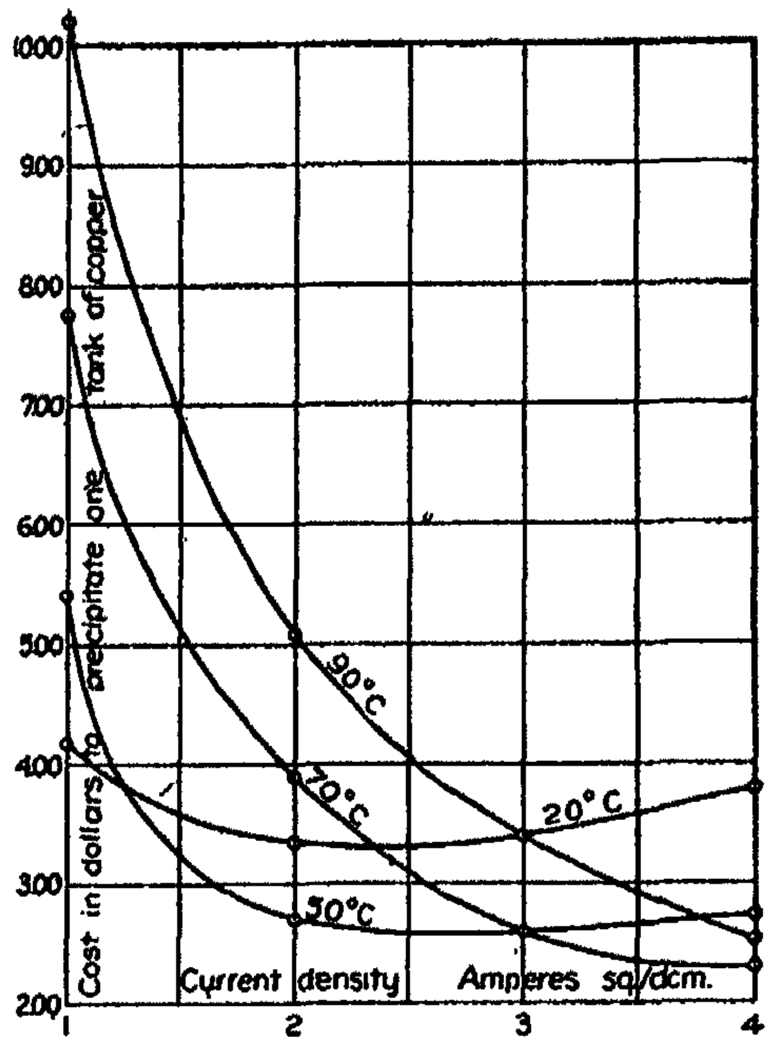

Fig. 9

first showing the relation between the cost to precipitate a tank of copper and the operating temperature; the second set showing the relation between the cost to precipitate a tank of copper and the operating current density. From these curves it is evident that to operate at a temperature of 90° C and a low current density is entirely out of the question, not only on account of the cost of power to heat up the solution and to precipitate the copper, but also on account of the deterioration of solution which takes place most rapidly under these conditions. At this high temperature and the higher current densities, the cost rapidly approaches a minimum, but here also the deterioration probably more than offsets the advantage of reduced cost of power. To operate at 20° C is not so costly as would seem at first thought. The cost is maximum at the lowest and the highest current densities, reaching a minimum between 2¼ and 2½ amp/qdm.

At 50° C it would not be economical to operate at 1 amp/qdm, but the cost drops off very rapidly between 1 and 2 amperes. At the higher current densities the cost fluctuates but very little, reaching a minimum at about 2.5 amp/qdm.

The 70° C curve seems the most prolific of good results, and it is here that we must look for our most advantageous point. Although at this temperature the cost runs very high at a current density of 1 amp/qdm, it begins to drop off very rapidly as the current density increases, until at the higher current densities it assumes a practically constant value. Between 3.5 and 3.75 amp/qdm we would say would be the best current density for obtaining economic results, for at this density no extra power would be required to heat the solution. Operating at this current density and with the *tanks covered* the current alone would be sufficient to heat up the electrolyte to over 80° C. In order to secure a good circulation, the present method of procedure could be adopted, and if the gutters, leading to and from the pump, were properly insulated the temperature of the solution would not drop below 70° C before returning to the tanks. Moreover, running at this high current density, there would be a considerable saving in the first cost of the plant, inasmuch as the same amount of copper can be precipitated in a given time in half the number of tanks, when working at, say, 4 amperes as when working at 2 amperes. The lower the cost of heating, the greater is the advantage of a high temperature. Lowering the rate of interest decreases the advantage of a high current density. With covered tanks it will be possible for men to work in the tank room even with the electrolyte at 70°.

Therefore we would say, that in order to operate a plant most economically and to secure the best financial returns, copper should be refined electrolytically under these conditions: —

(1) *Covered tanks.*
(2) *Current density 3½ to 3¾ amp/qdm.*
(3) *Temperature 70° C.*

The writers of this paper express their thanks to Professor Bancroft, under whose direction the work was done, for his hearty co-operation and the interest which he has shown; also to Dr. H. R. Carveth, for his valuable suggestions and advice; and to Mr. E. S. Shepherd and Mr. G. H. Burrows for the kind assistance which they have rendered.

Cornell University,
June, 1903.

THE COMPOSITION OF THE SURFACE LAYERS OF AQUEOUS AMYL ALCOHOL

BY CLARA C. BENSON

In October, 1900, J. von Zawidski[1] published the results of some experiments on the composition of the foam of aqueous solutions of hydrochloric acid and of acetic acid which indicated that the concentration of the acid in the surface layers of these solutions was slightly greater than in the rest of the liquid. In order to obtain a durable foam a small quantity of saponin was mixed with the solutions.

It was suggested to me by Dr. F. B. Kenrick that I should examine a dilute solution of amyl alcohol which itself produces a sufficiently durable foam, the concentration of which can be estimated by measurements of surface tension.

Since these experiments were begun, von Zawidski has published the results of measurements[2] with dilute saponin solutions, the amount of the latter substance being determined by the refractive index. His measurements show that in this case also the surface layers are more concentrated than the rest of the liquid. These experiments with amyl alcohol were nevertheless continued in order to ascertain whether the amyl alcohol behaves in the same way.

The solution of amyl alcohol in water was prepared by making up 4 cc of the alcohol (a preparation from Kahlbaum, which had been re-distilled) to a volume of 1 liter. About 40 cc of this solution were shaken vigorously in a separating funnel holding about 200 cc of the liquid, and as much as possible of the drainings from the walls of the vessel were run out through the tap. The froth left in the bulb settled to a clear liquid after a few minutes and was run into a small stoppered bottle.

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[1] Zeit. phys. Chem. 35, 1 (1900).

[2] Zeit. phys. Chem. 42, 1 (1903).

The compositions of the various solutions were determined from the number of drops which fell from a pipette provided with a capillary tube, ground to a flat surface at the tip. While this method requires certain corrections in order to determine actual surface tensions, it is quite satisfactory for comparative measurements when the differences in value are slight.[1] The method, moreover, gives very accurate determinations of concentration since a slight alteration in the amount of amyl alcohol, in the neighborhood of the concentration used, corresponds to a considerable change in surface tension.

The pipette used in most of the measurements held about 30 cc. It was kept at constant temperature by immersion in the vessel A (Fig. 1), which was connected by a large siphon and pump to a water-bath whose temperature was maintained at 31 degrees. By the arrangement shown, the drops were formed in a space whose temperature was the same as that of the rest of the liquid. After closing the lower end of the pipette by a rubber cap attached to a glass rod, the solution to be analyzed was run in quickly from the stock, which had been kept in the water-bath, and the whole allowed to stand for a few minutes in order to bring the solution to the temperature of A, which was

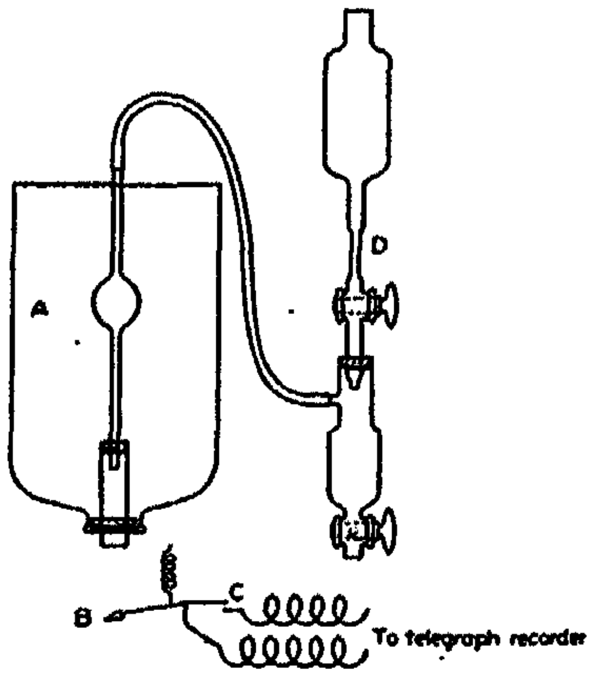

Fig. 1.

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[1] Duclaux. Ann. Chim. Phys. (5) 13, 82 (1878).

0.3 degree below that of the bath. This temperature did not vary more than 0.2 degree during the entire measurements.

In order to obtain accurate results the rate of dropping must be slow and constant. The flow of liquid was regulated at first by using a pipette with a constriction in the capillary tube, but it was found that this was easily stopped with particles of dust. The pipette used in these measurements, therefore, had no constriction, but the rate was regulated by connecting the top of the pipette by fine rubber tubing to a small air reservoir into which glycerine was dropping (see Fig. 1). Owing to the viscosity of the glycerine, a slow enough rate was obtained even with fairly large tubing at D, and the difficulty of stoppage by dust was avoided. With this arrangement the rate of flow could be kept constant to within a few percent.

A record of the number of drops was kept by a mechanical counter, which is a modification of that used by Duclaux. The impact of the drop on the inclined plate, B, broke an electrical current at C, which actuated a telegraph recorder, thus leaving a mark on a moving tape.

That both temperature and rate of flow affect the number of drops will be seen from the following tables:

TABLE I.

INFLUENCE OF TEMPERATURE

Amyl alcohol solution: 4 cc in 1 liter; rate: 36 drops per minute.
Volume of liquid: 30 cc.

Temperature	Number of drops
30.7°	693
36.7°	700
36.7°	699.5

A rise of 1 degree causes an increase of 0.16 percent in the number of drops.

An increase of 50 percent in rate decreases the number of drops by about 1 percent.

In the experiments (Table IV) for the comparison of the foam with the liquid the alterations of temperature and rate of dropping were therefore negligible in their effect on the number of drops.

Another possible source of error lay in the fact that the foam might become more concentrated by evaporation. In order to investigate this point, a solution was set aside to evaporate at the room temperature for about three days, after which time its composition was compared with that of the original solution. (See Table III.)

TABLE II.

INFLUENCE OF RATE OF DROPPING

Amyl alcohol solution: 4 cc in 1 liter; temperature: 30.7°.
Volume of liquid: 8.8 cc.

Drops per minute	Number of drops
44	212
35	212
52	210
8 to 17	217
Volume of liquid: 30 cc.	
32	693
36	693
75	678

TABLE III.

EFFECT OF EVAPORATION ON CONCENTRATION

Amyl alcohol solution: 4 cc in 1 liter; temperature: 30.7°; rate: 30 drops per minute

Pct. loss in weight by evaporation	Volume of liquid	Number of drops original solution	Number of drops evaporated solution
11	11 cc	270	213
12	30 cc	694	548

It is clear, therefore, that any change in composition due to evaporation would be in the opposite direction to that actually observed. (See Table IV.)

In the above table, Expt. No. 10 was made with the original (unfrothed) liquid; Nos. 6, 11, 13, and 15 were made with the liquefied foam; the rest with the liquid from which the foam had been separated. In Expt. No. 15 greater care was taken to thoroughly remove the drainings from the foam and for this reason, no doubt, its composition shows a greater deviation from that of the liquid than is seen in the other cases.

TABLE IV.

COMPARISON OF LIQUID AND FOAM

Amyl alcohol solution: 4 cc in 1 liter; temperature: 30.7°

Number of experiment	Volume of liquid	Drops per minute	No. of drops Liquid	No. of drops Foam	Comp. of foam cc per liter
1	8.8 cc	34	212	—	—
2	"	34	213	—	—
3	"	35	212	—	—
4	"	44	213	—	—
5	"	44	213	—	—
6	"	44	—	214.5	4.12
7	"	44	212	—	—
8	30 cc	32	693	—	—
9	"	32	693.5	—	—
10	"	33	694	—	—
11	"	33	—	697	4.086
12	"	34	694	—	—
13	"	33	—	699.5	4.135
14	"	36	693	—	—
15	"	36	—	703	4.235

It is therefore evident that the foam from amyl alcohol contains a larger proportion of the alcohol than the rest of the liquid. The composition of the foam, calculated by the use of Duclaux's measurements on the surface tensions of different solutions of amyl alcohol, is given in the last column, Table IV. No difference could be observed in the composition of the original solution and the liquid from which the froth had been separated.

In conclusion I wish to express my indebtedness to Dr. F. B. Kenrick for his assistance and interest in these experiments.

University of Toronto,
Chemical Laboratory,
May, 1903.

A CORRECTION

BY GEO. H. BURROWS

In a paper entitled "Experiments on the Electrolytic Reduction of Potassium Chlorate,"[1] it was shown that potassium chlorate when electrolyzed in aqueous solution with copper electrodes gives rise to an amount of chloride far in excess of that calculated from the hydrogen equivalent of the current.

In the analyses involved, the fact was overlooked that nitric acid containing oxides of nitrogen rapidly reduces potassium chlorate to chloride. Elimination of the error due to this oversight does not affect the nature of the results, but does decrease the numbers expressing the efficiencies, the true maximal efficiency found being 160–170 pct instead of 200 pct as stated.

This correction made, it is found that the ratio between weight lost by the anode of the electrolytic cell and that gained by the copper voltameter cathode equals or exceeds in each case the ratio between the efficiency found and what we may call the theoretical efficiency. This is seen to be a necessary consequence of the partial explanation given.

Two verbal errors also stand in the paper. Page 418, line 22, for 3 × 26.8, read 6 × 26.8; page 422, line 7 from bottom, for 'cathode' read 'anode.'

Brochet[2] objects to the phrase 'electrolytic reduction of potassium chlorate' being applied to the action described, and attributes the formation of chloride to the instability of copper chlorate in the presence of metallic copper. This he expresses as a side reaction and points out that if not interfered with, it would give an efficiency of 600 pct; the main reaction, that between the caustic potash formed at the cathode and the copper chlorate, prevents the realization of this and gives rise to reformation of potassium chlorate and precipitation of copper oxide.

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[1] Jour. Phys. Chem. 6, 417 (1902).

[2] Zeit. Elektrochemie, 9, 160 (1903).

This view of the action at the anode appears reasonable and may be correct. It cannot be considered as proved, however, by the fact that metallic copper reduces copper chlorate in concentrated solution. Further, it would be expected that by preventing the mixing of the caustic potash of the cathode with the anode products, as, through use of a porous cup, the yield of 600 pct might be approximated. Such does not appear to be the case. In experiments tried, the efficiencies were well below 100 pct.

Brochet states that potassium chlorate cannot be made to yield chloride by means of cathodic reduction and accounts for the non-appearance of hydrogen in the present case by assuming that it reduces the copper oxide formed to metallic copper. Part of the hydrogen, or its equivalent, taken up may be accounted for in this way, but not all.

Gladstone and Tribe[1] have shown that hydrogen occluded by copper reduces potassium chlorate. If finely divided copper be deposited on a copper cathode and this, after washing with water, be introduced as cathode in a solution of potassium chlorate, under the conditions of temperature and concentration employed in my experiments and using a platinum anode, reduction to chloride takes place with some readiness. An indirect reduction through copper chlorate is excluded. In the experiments on potassium chlorate, using copper anodes, a deposit of spongy copper is found on the surface of the cathode. It appears certain that this copper, either after the manner indicated by the theory of Binz or through its power of occluding hydrogen, is instrumental in bringing about a direct reduction of potassium chlorate to potassium chloride.

Cornell University.

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[1] Jour. Chem. Soc. 33, 306 (1878).

NEW BOOKS

Modern Electrolytic Copper Refining. *By Titus Ulke. First Edition. 14 × 22 cm; pp. viii + 170. New York: John Wiley and Sons, 1903. Price: bound, $3.00.* — The industry of electrolytic copper refining has become so important that a monograph on the subject has been long needed. The present volume fills this need as well perhaps as could be expected. The first chapter deals with the development, methods, and apparatus of electrolytic copper refining; the second with a description of electrolytic copper-refining works; and the third with cost estimates of an American electrolytic copper and nickel refinery. In an appendix there is a chronological list of patents, books, and special articles on electrolytic copper-refining methods and apparatus.

The book is essentially a compilation from printed sources. While this is very welcome, it necessarily follows that much of the information is behind the times and that some of it is wrong. The account of the Hayden system in use at Baltimore is singularly incomplete. The whole of the third chapter is to be thrown out of consideration because the process described is not to be used at the Sault St. Marie and because there is no evidence as yet that the process will be a commercial success. While this book will be valuable, it would be more valuable if the accuracy of the author's statements had been questioned less often.

Wilder D. Bancroft

Die Aluminium-Industrie. *By F. Winteler. 16 × 24 cm; pp. xi + 108. Braunschweig: Friedrich Vieweg und Sohn, 1903. Price: 6 marks.* — In the historical part, the process of Héroult gets two pages and those of Hall eight lines. The technical part is no better, and it would puzzle any one who did not already know to find out under whose patents aluminum actually is made. No mention is made of Acheson graphite, though ten pages are given to carbon electrodes. Over thirty pages are given to bauxite and cryolite, less than four pages to the physical properties of aluminum, one and a half pages to the chemical properties of aluminum, six pages to methods of working aluminum, eight pages to the applications of aluminum, and less than four pages to the alloys. In other words, forty-five pages out of the hundred and eight are devoted to bauxite, cryolite, and methods of electrical measurements. Most of the twenty-four pages on operating the aluminum bath might well have been omitted so as to make room for facts in regard to the matter.

Wilder D. Bancroft

Quantitative Chemical Analysis by Electrolysis. *By Alexander Classen. Authorized translation, fourth English from the fourth German edition, revised and enlarged by Bertram B. Boltwood. 14 × 22 cm; pp. vi + 315. New York: John Wiley and Sons, 1903. Price: $3.00.* — This book is more than a mere translation of the fourth German edition. The translator has introduced much of the more recent work including the determinations of

Gooch with a revolving cathode. This work of Gooch has so revolutionized electrolytic analysis that all the old methods are already out of date, and we continue to use them only until the new directions are forthcoming.

Wilder D. Bancroft

Die Herstellung der Akkumulatoren. *Ein Leitfaden. By F. Grünwald. Dritte Auflage. 10 × 16 cm; pp. vi + 158. Halle: Wilhelm Knapp, 1903. Price: bound, 3 marks.* — There is a preliminary chapter on the electric current and then one on the development of the lead accumulator. This is followed by chapters on raw materials, on the treatment of accumulators, and on their application. Some useful tables are given in the appendix. There is a great deal of information contained in a small space. The author considers the work of Dolezalek. Errors are few in number, though putting the melting-point of antimony at 440° is one. *Wilder D. Bancroft*

Physics of Thermo-Chemistry. *By G. M. Westman. 15 × 23 cm; 122 pp. New York: G. M. Westman, 1903.* — "By isotherm expansion of the gas, the volume of the molecule also expands, and consequently its heat capacity is changed. The molecule takes a part of the heat introduced into the system in order to satisfy its greater heat capacity, when the system is isothermally expanded, and consequently the growth of the inner energy cannot be considered null as the Second Law [of Thermodynamics] presumes." This paragraph from the introduction is really the starting point for all of the author's deductions. The argument involves the explicit assumption that the volume of the molecule expands during the isothermal expansion of an ideal gas. This is a matter about which we have no proof. We find, however, that the specific heat of different gases is more nearly independent of the volume, the more nearly the gas approaches the condition of an 'ideal' gas. It therefore becomes a very plausible assumption that the specific heat of an ideal gas is independent of the volume. While the author has a right to substitute some other assumption for this, it would be more satisfactory if he had stated the facts as they are.

The author starts with the following postulate: — "All forces in nature can be referred to the force of attraction, and to the force of repulsion. While the force of attraction, which is called living force, emanates from the centrum, and acts towards it, the force of repulsion emanates from the surface and acts in the direction of the tangent. When the latter, which could better be named the radiant force, is freely developed, it is of equal value to the living force." This is supplemented by the hypothesis that "gases are considered to consist of molecules, and a gaseous matter around each molecule, as the phenomena of expansion cannot be explained if the gases were only a continuous medium; and on the other hand a continuous medium is necessary, because vibration travels to the space which cannot be propagated by matter."

Starting from these premises, the author discusses: the energy of gases and laws controlling them; determination of volume and energy of gaseous molecules; latent heat; determination of the volume and energy of the elements by heat evolved or absorbed in chemical reactions; the coefficient for transferring the volume of the compound into the volume of the components; volume and energy of twenty-seven elements; determination of the radiant energy of some oxides by the heat evolved in combination with H_2O, CO_2, and SO_3; determination of the radiant energy of some sulphates and chlorides through the heat evolved in combination with different members of molecules of water; energy evolved by dissolving bodies in different proportions of water; heat of neutralization; melting-point of the elements; boiling-point of the elements; the modern kinetic gas theory and the author's formula for kinetic energy; valence and the supposed composition of the elements; energy of bodies as deduced from the refraction of light; the liquid state of a compressed gas; the conditions for a chemical reaction.

This is an interesting programme. While the reviewer has been unable to follow all the steps in the reasoning based on this theory of elastic molecules, it must be admitted that the formulas obtained do, in some cases, represent the facts very well. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

Permanent changes and thermodynamics, IX. *P. Duhem. Zeit. phys. Chem.* 43, *695* (*1903*).—The author shows that if we admit the existence of hysteresis, we may believe in the Clausius inequality $\int \frac{dQ}{T} > 0$, but we must give up the inequality

$$\int \frac{dQ}{T} + S(x_1T_1) - S(x_0T_0) > 0. \qquad \textit{W. D. B.}$$

Note on the probable atomic weight of tellurium and on atomic weights in general. *K. Seubert. Zeit. anorg. Chem.* 35, *205* (*1903*).—A reply to Köthner (7, 475). *W. D. B.*

Law of atomic weights. *G. J. Stoney. Phil. Mag.* [*6*] 4, *411* (*1902*).—It is shown that the succession of atomic weights, when arranged as in Mendeléeff's table, follows two nearly coincident laws, one for the elements of even atomicity; and the other for the elements of odd atomicity. Two slightly sinuous curves intersect respectively equidistant, vertical lines representing the successive steps of the Mendeléeff series. These two curves lie near to a simpler curve without sinuosities which can be represented by a simple equation and which the author calls the central curve. Taking the central curve as logarithmic and plotting according to polar co-ordinates, a diagram is produced which represents the views put forward by the author very clearly. A number of interesting facts are brought out by the arrangement. *H. T. B.*

On the law of atomic weights. *G. J. Stoney. Phil. Mag.* [*6*] 4, *504* (*1902*).—This is a letter forecasting certain facts in regard to the recently discovered elements. Their position on his diagram of atomic weights (preceding review) makes it appear probable that they possess the greatest atomic volume. Experimental work is looked for in the case of xenon, krypton, argon and neon in order to verify the theoretical conclusions. *H. T. B.*

On a numerical connection between the atomic weights. *J. H. Vincent. Phil. Mag.* [*6*] 4, *103* (*1902*).—All the atomic weights are arranged in ascending order of magnitude. Calling the order in this list n, from $n = 3$ to $n = 60$, the atomic weight of the nth is given by the equation:

$$W = (n + 2)^{1.21}.$$

With a few exceptions close coincidence is obtained between the observed and calculated values. According to the method of treatment, it is possible to form conclusions about the position of gaps in the periodic table, and that, although the list starts abruptly at hydrogen, it has no end. *H. T. B.*

On the weights of atoms. *Lord Kelvin. Phil. Mag.* [*6*] 4, *177* (*1903*). — From the first suggestions of Young in regard to a method of estimating the dimensions of molecular structure in ordinary matter, the author reviews all the work that has since been done to gain a measure of the actual sizes involved in molecular space. As a further estimate, the kinetic theory of gases forms a basis upon which, with the help of the theory of Boscovich, the author arrived at a value for N equal to 10^{20}. The paper is to be continued. *H. T. B.*

On the weights of atoms. *Lord Kelvin. Phil. Mag.* [*6*] 4, *281* (*1902*). — Starting out with the dynamical theory of Rayleigh in regard to the absorption of light from direct rays through the air, the author points out that it leads to an inferior limit for the number of atoms in a cubic centimeter. Rayleigh's numbers were founded on some very old experiments by Bouguer. The more recent work by Majorana at Catania and Etna, and by Sella at Monte Rosa, carried out to determine the ratio of the brightness of the sun's surface to the brightness of the sky seen in any direction, is taken by the author for the basis of the new calculations for the size of the atom.

Taking the number of atoms in the cubic centimeter to be 10, some data are given of the weights of atoms, and molecular dimensions of liquefied gases, water, ice, and solid metals. *H. T. B.*

On the conception of independent components. *J. J. van Laar. Zeit. phys. Chem.* 43, *741* (*1903*). — A reply to Wegscheider (7, 395) which will do more harm than good. So long as a thing is held constant, it is not a variable.
W. D. B.

On the electric origin of molecular attraction. *W. Sutherland. Phil. Mag.* [*6*] 4, *625* (*1902*). — The author endeavors to bring forward a theory based on the electron theory. After a brief statement in which the idea of the electric doublet in molecules is considered, the principle of electric doublets is applied to the ether as well as to matter. A consideration of the range of molecular force and a comparison of the results with known laws of molecular attraction then follow. Helmholtz's electric theory of chemical valency is discussed. Various properties of electric doublets are considered at some length. These with molecular gyrostatic properties, the author points out, must play the most important part in the formulation of a dynamic theory. *H. T. B.*

One-Component Systems

On the comparison of vapor-temperatures at equal pressures. *J. D. Everett. Phil. Mag.* [*6*] 4, *335* (*1902*). — The mathematical expression of Ramsay for the comparison of vapors is changed so as to be rendered more symmetrical. The law is shown to be deducible from Rankine's formula. *H. T. B.*

A new method of determining the vapor density of metallic vapors, and an experimental application to the cases of sodium and mercury. *F. B. Jewett. Phil. Mag.* [*6*] 4, *546* (*1902*). — The amount of vapor filling a bulb of known volume at any particular temperature is determined by finding the amount of condensed metal present on cooling the bulb. The bulb was two liters capacity with small side tubes; one for the metal to be vaporized, and the other for exhausting. Fresh bulbs were used for each observation in the case of sodium as the side tubes had to be removed in order to wash out the metal. With mercury the change in level of the metal in the side tube was observed, and the amount vaporized was calculated from the known coefficient of expansion of the metal and glass. A comparison of the results with those of Regnault and Hertz shows a very good agreement. *H. T. B.*

On the composition of brittle platinum. *W. N. Hartley. Phil. Mag.* [*6*] 4, *84* (*1902*). — A number of small pieces of platinum wire, which had become brittle, and crystalline in structure, were sent to the author for examination. A spectroscopic investigation by the arc and spark discharge showed that no other metal was present as an impurity in sufficient quantity at least to impair its toughness. The presence of phosphorus or carbon is suggested, although it is shown that silicon must be entirely absent. *H. T. B.*

Two-Component Systems

On the melting-points of mixtures of calcium and sodium silicates. *N. v. Kultascheff. Zeit. anorg. Chem.* 35, *187* (*1903*). —Sodium silicate, Na_2SiO_3, melts at about 1000°. Addition of calcium silicate lowers the freezing-point and there is a eutectic at 938°, the other phase being presumably $3Na_2SiO_3.2CaSiO_3$. The temperature then rises to 1090° where there is a quadruple point. The new phase is thought to be a solid solution and its freezing-point curve shows a maximum at 1160° and at a concentration approximating to $2Na_2SiO_3.3CaSiO_3$. The final eutectic is at 1128°, from which point a branch rises to the melting-point of calcium silicate which was not determined but which lies above 1400°. Addition of silica to sodium silicate lowers its freezing-point. Addition of silica to a mixture of sodium and calcium silicates first raises the freezing-point and then lowers it. *W. D. B.*

On the second anhydrous modification of calcium sulphate. *P. Rohland. Zeit. anorg. Chem.* 35, *194* (*1903*). —The author recognizes $CaSO_4 2H_2O$; $CaSO_4 \frac{1}{2} H_2O$, anhydrite, and three artificially-prepared forms of anhydrous calcium sulphate. The first is formed from the half-hydrate at 130°; the second from the first at 525°; and the third from the second at some still higher temperature. The half-hydrate and the second anhydrous modification have the power of setting with water. The first and third anhydrous modifications and the natural anhydrite have not. It is shown that salts which accelerate the hardening of the half-hydrate may retard the hardening of the second anhydrous form. *W. D. B.*

On the process of hydration and hardening with some sulphates. *P. Rohland. Zeit. anorg. Chem.* 35, *201* (*1903*). — It is pointed out that anhydrous sulphates only take up water if the ordinary temperature is lower than that of the quadruple point for hydrated salt, anhydrous salt, solution and vapor. The second requisite is that the partial pressure of water vapor in the air shall never fall below the dissociation pressure of the hydrated salt. The first condition is essential to the formation of hydrated salt at all; the second to the permanent existence of the hydrated salt. *W. D. B.*

On copper-cadmium alloys. *P. Denso. Zeit. Elektrochemie*, 9, *135* (*1903*). — Copper-cadmium alloys containing 1–10% Cu were made anodes in cadmium sulphate solutions. The residual crystals analyzed very well for $CuCd_3$.
W. D. B.

Multi-Component Systems

The solubility of homogeneous mixtures and of mixed depolarizers. *A. Thiel. Zeit. phys. Chem.* 43, *641* (*1903*). — A general classification of solubility curves in ternary systems when the two solid components crystallize together to a greater or lesser extent. The classification itself presents nothing new, but the author cites a number of interesting experimental investigations illustrating his types. *W. D. B.*

Some remarks on the vapor-pressures of ternary mixtures. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 43, *671* (*1903*). — Schreinemakers had previously discussed vapor compositions admitting the possibility that the addition of a third component to a constant-boiling binary mixture may change the ratio of the two components in the vapor. Ostwald has since maintained that the addition of the third component cannot change the ratio of the other two and Schreinemakers now replies to this. It is obvious that Schreinemakers is right and that Ostwald is wrong. Typical cases would be the addition of calcium chloride to benzene and alcohol; of sodium chloride or mercuric chloride to aqueous hydrochloric acid. It is very probable that the case imagined by Ostwald is one that is never realized experimentally. *W. D. B.*

The distribution of sulphur dioxide between water and chloroform. *J. McCrae and W. E. Wilson. Zeit. anorg. Chem.* 35, *11* (*1903*). — The distribution of sulphur dioxide between water and chloroform varies with the concentration, the chloroform solution being the weaker when the solutions are fairly dilute and the stronger when the solutions are more concentrated. Addition of hydrochloric acid decreases the solubility of sulphur dioxide in water. When the concentration of the hydrochloric acid is *n*/10 or greater, the distribution ratio is practically independent of the absolute concentration of the sulphur dioxide.
W. D. B.

The action of calcium on alcoholic ammonia. *G. Doby. Zeit. anorg. Chem.* 35, *93* (*1903*). — When metallic calcium is brought in contact with alcoholic ammonia there is first formed calcium amide and then calcium ethylate, according to the equations

$$Ca + 2NH_3 = Ca(NH_2)_2 + H_2$$
$$Ca(NH_2)_2 + 4C_2H_5OH = Ca(C_2H_5O)_2.2C_2H_5OH + 2NH_3.$$

This was confirmed by making calcium amide and letting it act on absolute alcohol. *W. D. B.*

On some physical-chemical constants of the mercury halides and the formation of complex salts. *M. S. Sherrill. Zeit. phys. Chem.* 43, *705* (*1903*). —

The author has determined the solubility in water, ether, and benzene of mercuric chloride, bromide, iodide and cyanide; also the distribution coefficients for these salts in water and ether, and in water and benzene. From the solubility products of the mercurous halides in water, he has calculated the solubilities of these salts. Electromotive force measurements gave the constants for the complex salts, from which a number of calculations were made. In chloride solutions there is some reason for assuming the existence, to a limited extent, of an anion $(HgCl_2)_3(Cl')_2$. *W. D. B.*

The combustion of carbon in the calcium carbide reaction. *F. v. Kügelgen. Zeit. Elektrochemie,* 9, *411* (*1903*). — Experiments on the reduction of oxides by calcium carbide were made in an atmosphere of nitrogen. When the oxide is easily reduced, no carbon monoxide is formed. With an oxide which is more difficultly reduced and with an excess of calcium carbide, there is formation to a certain extent of carbon monoxide. *W. D. B.*

On spontaneous nucleation and on nuclei produced by shaking solutions. *C. Barus. Phil. Mag.* [*6*] 4, *262* (*1902*). — Condensation was produced by the method of expansion in the case of gasoline, benzine, petroleum, benzol, carbon bisulphide and water. The first three hydrocarbons showed no spontaneous nucleation. Benzol, although apparently productive of nuclei, was subsequently shown to be free from them. For carbon bisulphide nuclei are emitted, while for water with new apparatus and special precautions to insure cleanliness and perfect filtration, air above the water remained free from nuclei. Nuclei produced by shaking the hydrocarbons showed no tendency to vanish until removed by gravity. The persistency of the nuclei obtained by shaking, including those obtained from water and solutions, is discussed at length. The author does not consider they can be due to ionization since the effect is equally marked for hydrocarbons and other insulators. The author endeavors to explain the phenomenon in terms of surface tension. *H. T. B.*

Osmotic Pressure and Diffusion

The displacement of osmotic equilibria by capillarity. *F. Kaufler. Zeit. phys. Chem.* 43, *686* (*1903*). — A discussion of the change in osmotic pressure and distribution coefficient when a solvent has a cellular structure. *W. D. B.*

Velocities

The rate of solution of solids, III. *L. Bruner and S. Tolloczko. Zeit. anorg. Chem.* 35, *23* (*1903*). — Experiments were made with alabaster, the solution being stirred at known rates. The rate of solution is directly proportional to the rate of stirring and inversely proportional to the volume. The latter of these two conclusions had previously been disputed by the authors on the strength of earlier experiments which appeared to prove that the volume had no effect. *W. D. B.*

The catalysis of hydrogen peroxide by iodine as ion. *G. Bredig and J. H. Walton, Jr. Zeit. Elektrochemie,* 9, *114* (*1903*). — The decomposition of hydrogen peroxide in presence of iodides is a reaction of the first order and proportional to the concentration of iodine as ion. Addition of iodine, mercuric iodide or caustic potash decreases the reaction velocity. It seems probable that the reaction takes place in two stages.

$$H_2O_2 + I' = H_2O + IO'$$
$$H_2O_2 + IO' = H_2O + I' + O_2.$$

The first reaction is the one measured and the second is assumed to take place practically instantaneously. *W. D. B.*

The change of the rate of inversion with the temperature. *C. Kullgren. Zeit. phys. Chem.* 43, *701* (*1903*). — The author shows that the change in the rate of inversion of cane sugar with the temperature can be accounted for quantitatively by known facts in regard to the dissociation of water and of cane sugar. The weak point in the reasoning is that reactions between highly dissociated substances do not have a small temperature coefficient, though this would seem to be a necessary corollary. *W. D. B.*

Electromotive Forces

The thermodynamics of the cadmium cell. *R. A. Lehfeldt. Zeit. phys. Chem.* 43, *745* (*1903*). — If we take the values

$$1\ \text{cal}_{18} = 4.184$$
$$\text{and } F = 96600\ \text{coulomb}$$

the heat effect in the Weston cell becomes 197540 joules by calorimetric measurement and 197450 joules as calculated from the electromotive force measurements. *W. D. B.*

The electromotive force of the Daniell cell. *E. Cohen and J. W. Commelin. Zeit. Elektrochemie*, 9, *431* (*1903*). — The authors find that the electromotive force of the Daniell cell increases continuously from 1.081 volts with saturated zinc sulphate solution to 1.146 volts with a solution containing 1/12 g $ZnSO_4 7H_2O$ per 100 g water, the copper sulphate solution being always saturated. There is therefore no such maximum as had been found by Chaudier. *W. D. B.*

On oxidation and reduction potentials. *K. Schaum and R. von der Linde. Zeit. Elektrochemie*, 9, *406* (*1903*). — Measurements with ferrocyanide-ferricyanide cells from which the authors calculate the equilibrium constant and the heat of reaction. The results hang together better when the actual concentrations are taken than when assumptions are made in regard to the dissociation. No results could be obtained with sulphate-sulphite cells. *W. D. B.*

On the electrochemistry of permanganic acid. *J. K. H. Inglis. Zeit. Elektrochemie*, 9, *226* (*1903*). — The author finds that the potential of a platinum electrode in an acid solution of permanganate of potash and a manganese salt cannot be determined accurately owing to the polarization resulting from the disappearance of the manganous salt, presumably according to the equation

$$2MnO'_4 + 3Mn^{\cdot\cdot} + 2H_2O = 5MnO_2 + 4H^{\cdot}.$$

Attention is called again to the fact that permanganate has little or no oxidizing power in the absence of a manganese salt. *W. D. B.*

On the decomposition curves for copper salt solutions. *M. E. Heiberg. Zeit. Elektrochemie*, 9, *137* (*1903*). — The author noticed that the current begins to increase about 0.1 volt below the decomposition point of a copper salt solution. Special experiments showed that this was not due to any impurity in the salt used and was not due to the acid. It seemed probable, therefore, that the phenomenon was due to cuprous salt. A previous heating with metallic copper emphasized the phenomenon while repeated electrolysis caused it to disappear. No similar effect could be obtained with silver. *W. D. B.*

On the decomposition curves for copper salt solutions. *E. Abel. Zeit. Elektrochemie, 9, 268 (1903).* — Heiberg (preceding review) accounted for the two breaks in the copper salt solutions by assuming that the first was due to cuprous salt. The author points out that the break due to cuprous salt would come below that for cupric salt if the solution is supersaturated with respect to univalent copper; but that it should come above the other when the reverse is true. The author's explanation is that the first break is due to the reaction

$$Cu'' \longrightarrow Cu'.$$

This explanation does not account for the first break being more marked after the solution had been heated with metallic copper and then cooled.

W. D. B.

Observations on thermoelectric currents and on a new thermopile. *A. Heil. Zeit. Elektrochemie, 9, 91 (1903).* — From a table given by the author, it appears that constantan gives the greatest thermoelectric effect when combined with an alloy of antimony and zinc. This latter alloy is unfortunately very brittle and a little iron is therefore added to give it more toughness. Details are also given of a thermopile which is to be far better than any yet known. It is the invention of the author and is not yet on the market.

W. D. B.

On an anodically-polarized light-sensitive gold electrode. *H. Kochan. Zeit. Electrochemie, 9, 33, 61, 79 (1903).* — A gold electrode becomes sensitive to light after having been made anode in sulphuric acid. Yellow light has very little effect; green light lowers the potential 1-2 millivolts, blue light as much as 0.05 volt. Ultra-violet rays seem not to have any marked effect, while Röntgen rays are as efficacious as blue rays. The temperature coefficient is − 0.00025 in the dark and + 0.00169 in the light. *W. D. B.*

On the electrical resistance of bismuth to alternating currents in a magnetic field. *G. C. Simpson. Phil. Mag. [6] 4, 554 (1902).* — This is a continuation of the author's previous work (6, 157). The present paper contains the determination of the variation of the angle of lag with different field strengths, the frequency being constant and the variation of the magnitude of the bismuth E. M. F. with different field strengths keeping the frequency constant.

Temperature variations of the bismuth E. M. F. were also made showing a decided maximum value at − 70° C. *H. T. B.*

The electrical conductivity of metals and their vapors. *R. J. Strutt. Phil. Mag. [6] 4, 596 (1902).* — Mercury and its vapor forms the subject of the present paper. Attempts are made to observe the critical condition, but with little success, owing to the great difficulties involved. It is found that the vapor is a very poor conductor of electricity. It seems probable, however, that as the critical temperature is approached the vapor begins to conduct freely, while the liquid changes its electrical character to a much less extent.

The author proposes to make some extended tests on the resistence of mercury as the temperature rises as soon as necessary appliances can be obtained.

H. T. B.

On the electrical properties of thin metal films. *J. Patterson. Phil. Mag.* [*6*] 4, *650* (*1902*). — A very complete description of the experiments is given and a thorough study made of various properties of the thin metal films deposited by spattering from a cathode in vacuo on glass strips. The work is of importance in its relation to the corpuscular theory of metallic conduction advanced by J. J. Thomson. The results enable the mean free path of the corpuscle in the metal to be calculated. *H. T. B.*

Electrolysis and Electrolytic Dissociation

The laws of electrolysis of alkali salt vapors. *H. A. Wilson. Phil. Mag.* [*6*] 4, *207* (*1903*). — The character of the dissociation of salt vapors is the subject of the present investigation which shows that above 1300° C a close analogy exists between salt vapors and liquid electrolytes. Faraday's laws of electrolysis are shown to hold very closely. The author considers it is probable that the gaseous ions attract neutral molecules, the positive ions having the greater power. This power of condensing neutral molecules accounts for the small velocity of the ions. The results are discussed in the light of the corpuscular theory, but as there remain still more unexplained points further experiments are promised. *H. T. B.*

On the cathodic precipitation of lead. *K. Elbs and F. W. Rixon. Zeit. Elektrochemie*, 9, *267* (*1903*). — The electrolytic precipitation of lead in large crystals occurs only so long as there is no plumbic sulphate in the solution. When plumbic sulphate is present, the lead precipitates in microscopic crystals. The authors show the presence of plumbic sulphate in accumulator acid and refer the self-discharge to it. *W. D. B.*

The preparation of potassium from fused caustic. *R. Lorenz and W. Clark. Zeit. Elektrochemie*, 9, *269* (*1903*). — By putting a magnesite capsule round the cathode, the diffusion to the anode is checked and there is no difficulty in obtaining metallic potassium by electrolysis of fused caustic potash.

W. D. B.

The electrochemical reduction of some stilbene derivatives. *K. Elbs and R. Kremann. Zeit. Elektrochemie*, 9, *416* (*1903*). — The electrochemical reduction of the dye-stuff "*Sonnengelb*" shows that it is *p*-azoxystilbene sulphonic acid. In alkaline solution the end-product of the reduction is *p*-azotoluene disulphonic acid. When reduced in an acid tin chloride solution, *p*-diamino benzene disulphonic acid, and *p*-toluidine sulphonic acid. Experiments were also made with *p*-dinitrostilbene, *p*-dinitrostilbene disulphonic acid, and *p*-azostilbene disulphonic acid. *W. D. B.*

The electrochemical reduction of *m*-nitroacetophenone and *m*-nitrobenzophenone. *K. Elbs and A. Wogrinz. Zeit. Elektrochemie*, 9, *428* (*1903*). —

It is easy to reduce *m*-nitroacetophenone to *m*-azoacetophenone and to *m*-aminoacetophenone. Attempts to form the azoxy compound gave mixtures of azo and azoxy compounds. The hydrazo and benzidine compounds cannot be obtained in satisfactory amounts. From *m*-nitrobenzophenone it is easy to make the azoxy, azo, and amino compounds, but the hydrazo and benzidine compounds present difficulties. In no case was there any reduction of the carbonyl group.
W. D. B.

On the electrolytic oxidation of *p*-toluene sulphonic acid. *J. Sebor. Zeit. Elektrochemie*, 9, *370* (*1903*). — When *p*-toluene sulphonic acid is electrolyzed in sulphonic acid solution with a platinum anode, a twenty percent oxidation was the best that could be obtained. With lead peroxide anodes an efficiency of eighty percent was obtained. The first oxidation product is the *p*-sulphobenzoic acid; but the actual yield is low because this acid oxidized to carbonic and sulphuric acids.
W. D. B.

On the electrolysis of potassium iodide solutions. *F. Foerster and K. Gyr. Zeit. Elektrochemie*, 9, *215* (*1903*). — Under ordinary circumstances, iodate is due to the decomposition of hypo-iodite. Since this decomposition takes place readily and rapidly, the anodic evolution of oxygen is only observed under special conditions instead of being an almost inevitable accompaniment as in the chlorate formation. By making the iodide solution dilute, very alkaline, or very hot, it is possible to get evolution of oxygen. A high current density is also favorable.
W. D. B.

On a so-called electrolytic reduction of potassium chlorate. *A. Brochet. Zeit. Elektrochemie*, 9, *160* (*1903*). — The author does not believe that potassium chlorate is reduced electrolytically by a copper anode (6, 417). He claims that there is formation of copper chlorate which is then decomposed by copper

$$Cu(ClO_3) + 6Cu = CuCl_2 + 6CuO.$$

Apart from the fact that this reaction permits a possible yield of 700 percent, it seems to be a matter of definition whether a reduction which takes place only under the influence of the current is to be called an electrolytic reduction or not. [Subsequent unpublished experiments by Mr. Burrows have shown that the loss in weight of the copper anode is greater than the theoretical loss by approximately the excess of reduction above 100 percent.]
W. D. B.

On the theory of the electrolysis of alkali chloride solutions. *F. Foerster and E. Müller. Zeit. Elektrochemie*, 9, *171*, *195* (*1903*). — In a moderately concentrated chloride solution, the chloride set free at the anode reacts with water forming hypochlorite

$$Cl_2 + H_2O = HClO + HCl.$$

Hypochlorite as ion can give chlorate as ion

$$3ClO' = ClO' + 2Cl'.$$

This reaction is accelerated by free hypochlorous acid. If hypochlorite be set free at the anode, it will decompose

$$6ClO + 3H_2O = 2ClO'_3 + 4Cl' + 6H^{\bullet} + 3O.$$

This reaction calls for 33.3 percent waste of current evolving oxygen, and the chlorate efficiency does approximate 66.6 percent when a constant state has been reached and when there is no cathodic reduction. This latter decomposition takes place only when the hypochlorite concentration is high. It would disappear if the rate of the other chlorate formation could be increased. *W. D. B.*

Contribution to the electrolytic preparation of persulphates. *M. G. Levi. Zeit. Elektrochemie, 9, 427 (1903).* — Special experiments showed that the yield of ammonium persulphate, when prepared electrolytically without a diaphragm, does not fall off perceptibly until the temperature gets above 30°. The yield is the same whether the cathode is nickel, platinum, carbon or lead. On the other hand, the yield varies very much with the state of the platinum anode. *W. D. B.*

On the formation of lead-white by electrolysis with soluble anodes. *A. Isenburg. Zeit. Elektrochemie, 9, 275 (1903).* — A lead anode in a 1.5 percent solution of sodium chlorate and sodium carbonate shows no sign of lead peroxide until the sodium carbonate is thirty-five percent of the total salt. Experiments were made to obtain a white lead having the composition $Pb(OH)_2.2PbCO_3$. Starting with a 1.5 solution containing eighty parts of sodium chlorate to twenty of sodium carbonate, it was possible to get anything between a carbonate containing 83.5 percent PbO and one containing 88.4 percent PbO, depending on the rate at which carbonic acid was supplied. To get a particular product with 86.3 percent PbO, it is necessary to stick closely to the required conditions.

In some experiments with a solution to which sodium nitrate had been added, a difference of potential of 30 volts was observed after some hours. Special experiments showed that this was due to the formation at the anode of a film having a high resistance and not to the existence of a high counter-electromotive force. *W. D. B.*

Electrolytic dissolving of platinum by an alternating current. *R. Ruer. Zeit. Elektrochemie, 9, 235; Zeit. phys. Chem. 44, 81 (1903).* — A continuation of the experiments made by Margules (3, 126) on the behavior of a platinum anode when subjected to the simultaneous action of a direct and alternating current. The author finds that, for each current density of alternating current, there is a corresponding current density of direct current which causes the maximum amount of platinum to go into solution. The author believes that the direct current forms an infinitely thin coating of a conducting oxide which is then reduced by the alternating current. Under the same circumstances in sulphuric acid solution, lead forms lead sulphate which separates from the electrode. *W. D. B.*

A new electrochemical synthesis of prussic acid. *J. Gruszkiewicz. Zeit. Elektrochemie, 9, 83 (1903).* — When the spark discharge is passed through a gas mixture having the composition 38.44 CO, 19.32 N_2, and 42.34 H_2, traces of prussic acid are formed. The amount of prussic acid increases on increasing the percentage of carbon dioxide and decreasing the percentage of hydrogen. There seems to be a reduction of carbon monoxide, the carbon uniting with hydrogen and nitrogen. The best results are obtained when the spark is short and broad. *W. D. B.*

The direct combination of carbon and chlorine, II. *W. v. Bolton. Zeit. Elektrochemie*, 9, *209* (*1903*). -- When chlorine is passed between a carbon arc, hexachlorethane is the primary product. If this substance pass again and again through the arc, traces of hexachlorbenzene are formed. The author has now succeeded in obtaining an analysis of this latter substance. *W. D. B.*

A new interrupter for conductivity determinations. *C. W. Kanolt. Zeit. Elektrochemie*, 9, *415* (*1903*). — The circuit is opened and closed by means of an air-blast which makes a stretched wire vibrate. *W. D. B.*

Electrolytic galvanometer. *R. Heilbrun. Zeit. Elektrochemie*, 9, *111* (*1903*). — In order to show the passage of a current through an electrolyte, spiral coils of glass or rubber are laid round the magnet of a galvanometer. On passing a current, the galvonometer needle is deflected. *W. D. B.*

On the formation of hydrogen ions from the methylene group in succinic, malonic and glutaric acids. *R. Ehrenfeld. Zeit. Elektrochemie*, 9, *335* (*1903*). — When a sodium hydroxide solution is added drop by drop to a solution of succinic, malonic or glutaric ester, the conductivity first decreases, passes through a minimum, and then increases. From the position of the minimum the author calculates the dissociation of the esters. *W. D. B.*

On the dissociation of electrolytes. *C. Liebenow. Zeit. Elektrochemie*, 8, *933* (*1902*). — A discussion of the dilution law based on the dissociating action of the solvent on the undissociated electrolyte. The conclusion is reached that the dilution should hold more exactly the more complex one of the ions is. This receives a confirmation in the fact that many organic acids do follow the dilution law. This can hardly be said to be a statement of the whole truth. *W. D. B.*

Dielectricity and Optics

The discharge of positive electrification by hot metals. *R. J. Strutt. Phil. Mag.* [*6*] 4, *98* (*1902*). — By means of a gold leaf electroscope, the author has succeeded in detecting the effect observed by Guthrie, that red-hot metals are capable of discharging positive electrification, at as low a temperature as 270° C. The effect was found to increase rapidly with the temperature. *H. T. B.*

On spectra arising from the dissociation of water vapor, and the presence of dark lines in gaseous spectra. *J. Trowbridge. Phil. Mag.* [*6*] 4, *156* (*1902*). — A careful comparison is made of photographs of the solar spectrum with gaseous spectra in which water vapor is invariably found to be present (6, 446). The conclusions are that oxygen must be present in the sun's atmosphere resulting from the dissociation of water vapor. In the spectra of gases, dark lines occur which are photo-chemical in origin, and which are obscured by the brilliancy of the dissociation spectrum of water vapor. *H. T. B.*

The effect of hydrogen on the intensity of the lines of the carbon spectrum.

A. M. Herbert. Phil. Mag. [6] 4, *202* (*1902*). — The author investigates the observation made by Sir William Huggins that the carbon spectrum is altered by the presence of hydrogen. The red line of carbon, which is slightly less refrangible than the red hydrogen line, becomes very faint and behaves quite differently to the other carbon lines, when hydrogen is introduced. The spark spectrum was used in CO_2 and H, CO and H, and coal gas. The experiments seem to show, according to the author, that the red and violet carbon lines belong to different spectra of carbon. *H. T. B.*

On the spectra of the more volatile gases of the air. *S. D. Liveing and J. Dewar. Ann. Chim. Phys.* (*7*) 22, *482* (*1901*). — Air from above the roof of the Royal Institute was cooled by liquid hydrogen, and the uncondensed portion found to contain approximately 43 parts hydrogen, 6 parts oxygen, and 51 parts nitrogen, argon, helium, etc. Many lines were observed which probably coincide with some of the coronal lines; but none of the unknown auroral lines were detected. The yellow neon line is more brilliant than the yellow helium line in the volatile portion of the atmospheric air, while the reverse is the case in the gas from the spring at Bath. *W. D. B.*

On the nature and constitution of the spectrum of the Aurora borealis. *H. Stassano. Ann. Chim. Phys.* (*7*) 26, *40* (*1902*). — The author shows that the lines in the spectrum of the *Aurora borealis* coincide, as closely as could be expected from the accuracy of the measurements, with lines found by Liveing and Dewar in the spectrum of the more volatile components of the air. The lines in the spectrum of the sun's protuberances have been more carefully determined and here the agreement with the results of Liveing and Dewar are quite startling. Neon, helium, argon, and hydrogen are therefore the important gases in the auroral displays and in the sun's protuberances. *W. D. B.*

Determinations of wave-length in absolute values. *C. Fabry and A. Perot. Ann. Chim. Phys.* (*7*) 24, *98* (*1902*). — Reviewed (6, 363) from Comptes rendus, 133, 153 (1901).

On radiation of heat and light from heated solid bodies. *J. T. Bottomley Phil. Mag.* [*6*] 4, *560* (*1902*). — The main point which the author has under investigation, and which he clearly describes in the present paper is the difference in the emissivity of dull and polished metal surfaces. Two similar platinum strips, one polished and the other covered with a thin coating of lamp-black, are enclosed in a vacuum chamber. Measurements are made of the electrical energy expended in heating the strips, to the first gray light, dull red, bright red and white heat.

Difficulties are met with in the breaking of the strips. Under the repeated heating and exhaustion to get rid of occluded gases the metal appears to become "rotten".

Although the present paper is considered as a preliminary note to further work, the general conclusions are that the polished surface is much more economical for the production of light than the sooted surface, and that the two surfaces are practically at the same temperature when they present a similar appearance to the eye. *H. T. B.*

Calorific and luminous radiation of some oxides. *C. Féry. Ann. Chim. Phys.* (*7*) 27, *433* (*1903*). — A careful study of the radiation from heated oxides, with special reference to the Welsbach lamp. Thorium oxide gives a higher radiation in the oxidizing flame than in the reducing flame, while the reverse is the case for cerium oxide. With the latter the radiation is greater than with a black substance at the same temperature. This seems to be a case where one can speak of a real luminescence. The author propounds the following theory of the Welsbach lamp.

A mantel of cerium oxide does not give a good light because its emissive power is so great that the temperature does not rise to a high enough point. Thorium oxide, by its porousness, permits the gaseous mixture to burn in direct contact with the cerium oxide; by its transparency, it permits of free radiation; by its strength, it forms a supporting frame for the ceria; by its feeble heat radiation, it makes a high temperature attainable. *W. D. B.*

On a new optical method for the measurement of temperatures in absolute value. *D. Berthelot. Ann. Chim. Phys.* (*4*) 26, *58* (*1902*). — A detailed description of the author's optical method for measuring high temperatures. The following points are believed by the author to be known with an accuracy of ± 2°:

B. Pt. Selenium $690° + \frac{H - 760 \text{ mm}}{10}$
B. Pt. Cadmium $778° + \frac{H - 760 \text{ mm}}{9}$
B. Pt. Zinc $918° + \frac{H - 760 \text{ mm}}{8}$
M. Pt. Silver 962°
M. Pt. Gold 1064° *W. D. B.*

Practical methods for spectroscopic analysis of gases. *M. Berthelot. Ann. Chim. Phys.* (*7*) 23, *447* (*1901*). — The author examines the spectra of gases under atmospheric pressure in a very simple tube. Tables are given for the more important lines for many gases and also a table for a mixture of gases. *W. D. B.*

Color sensitiveness of the eye. *A. Pflüger. Drude's Ann.* 9, *185* (*1902*). — From the result of a long series of tests with different observers the author finds that the eye is much more sensitive to green than to either the red or violet. He experimented on light varying from $\lambda = 413 \mu\mu$ to $717 \mu\mu$. A number of curves are given which show a remarkable correspondence. *H. T. B.*

Photography of the ultra-red spectrum of the alkali metals. *H. Lehmann. Drude's Ann.* 9, *246* (*1902*). — The author discusses a paper by Kayser and Runge, which he had overlooked at the time of the publication of his main paper (6, 78). *H. T. B.*

On the chemical action of the canal rays. *G. C. Schmidt. Drude's Ann.* 9, *703* (*1902*). — The author's previous study on the reducing action of cathode rays, which he attributes to the replacing of a positive valency in the chemical substance by a negative electron, led him to investigate the chemical action of canal rays. These rays carry a positive charge, and it was thought they would produce an oxidation. This was not, however, shown to occur, but the only action was that of decomposition. The fluorescence excited in the substance by the rays at first resembled spectroscopically that from cathode rays, but after a short interval the spectrum became continuous. The canal rays were found to decompose gases. In an atmosphere of oxygen, substances were oxidized, while in an atmosphere of hydrogen they were reduced. *H. T. B.*

Studies on radium. *M. Berthelot. Ann. Chim. Phys.* (*7*) 25, *458* (*1902*). — The decomposition of iodine pentoxide by radium does not take place when the tube containing the radium is covered with black paper. An approximate calculation showed that the amount of iodine pentoxide decomposed is about what it should be from the amount of energy given off by the radium.

W. D. B.

Some chemical reactions caused by radium. *M. Berthelot. Ann. Chim. Phys.* (*7*) 25, *452* (*1902*). — Reviewed (6, 364) from Comptes rendus, 133, 659 (1901).

Comparison of the radiations from radioactive substances. *E. Rutherford and H. T. Brooks. Phil. Mag.* [*6*] 4, *1* (*1902*). — The authors compare the rays from uranium, thorium and radium by the electrical method. They show that the rays not deflected by a magnetic field, given out by all these substances, differ in penetrating power, and are not therefore from a common radioactive impurity. The difference in the rates of decay of the emanation from thorium and radium is found to be considerable. The connection between the emanation and excited radioactivity is studied. Much more light has been thrown on the whole subject of radioactivity by Rutherford in later papers. (See succeeding reviews.) *H. T. B.*

Deviable rays of radioactive substances. *E. Rutherford and A. G. Grier. Phil. Mag.* [*6*] 4, *315* (*1902*). — It was found that thorium compounds and the excited radioactivity due to thorium give out deviable rays. For both thorium and radium excited radioactivity, it is shown that the deviable and non-deviable rays decay at the same rate. No durable rays could be detected from polonium or from the emanation of thorium. A comparison of the amount of ionization produced by the α and β rays is given, and of the energy radiated by them. It is found that for uranium only about 1/1000 of the total energy radiated is carried off by the β rays in the form of electrons. The authors discuss the relation between the two types of rays in the light of the recent work of one of the authors as the chemical separation of the secondary products. (See reviews of later papers.) *H. T. B.*

The cause and nature of radioactivity. *E. Rutherford and F. Soddy. Phil. Mag.* [*6*] 4, *370*, *569* (*1902*). — Reviewed (7, 60) from Jour. Chem. Soc. 81, 321 (1902), the present papers containing, however, more recent views.

H. T. B.

Excited radioactivity and ionization of the atmosphere. *E. Rutherford and S. J. Allen. Phil. Mag.* [*6*] 4, *704* (*1902*). — The authors undertake a thorough study of the phenomena of excited radioactivity from the atmosphere, and the cause of the spontaneous ionization.

It is found that for a fixed voltage the excited activity in a given wire decays to half its value in 45 minutes, the decay being regular and independent of conditions.

Weather conditions have little effect, the presence or absence of wind being the most important factor.

In considering the penetrating power, the authors conclude that the excited radiation from air cannot be ascribed to the presence of any known radioactive substance in the atmosphere.

It is found that the number of ions produced spontaneously in air is 15 per cc per second, which agrees fairly well with the number found by Wilson, i. e., 19.

The ionization theory is applied to the experimental results with a very fair agreement.

The velocity of the ions is worked out, and it is shown that those produced spontaneously in the atmosphere travel at about the same rate in the electric field as the ions produced by Röntgen and Becquerel rays. *H. T. B.*

Crystallography, Capillarity and Viscosity

The microscopic determination of the rare earths. *R. F. Meyer. Zeit. anorg. Chem.* 33, *31, 113* (*1902*). — After a critical study of the facts, the author expresses the opinion that it is utterly impossible to detect the different rare earths by a microscopical examination of the crystalline form of the succinates, as had been proposed by Behrens. *W. D. B.*

The surface tension at the boundary between alcohol and salt solutions. *G. Quincke. Drude's Ann.* 9, *1* (*1902*). — The present paper is one of a long series of papers on surface tension, and adds much of interest. A whole host of experimental facts are given in regard to the formation of crystals from alcohol and water mixtures. The surface tension between water and ether is found to be 1.25 mg/mm, and to decrease with time. The surface tension between alcohol and water is very small. Water salt solutions have a surface tension with alcohol of 0.3 mg/mm. A thorough study is made of the drops and bubbles formed when various salt solutions are run into pure alcohol. These become poorer in water as the bubble moves through the alcohol, and the salt crystallizes out. The forms taken by these crystals are studied at length. The paper is illustrated with excellent diagrams. *H. T. B.*

ERRATA

The following corrections are to be made in Mr. Scudder's paper which appeared in the April number: —

P. 274. First table is for acetonedicarboxylic acid and belongs on p. 273 between lines 2 and 3 from the bottom.

P. 285. Line 2 from bottom, 10 K should be 10 *k*.

P. 287. Line 2 from botton, read T = 17° instead of T = 170.

P. 291. Last line. Instead of diazo phenols read diazo compounds.

P. 292, First line. There should be a space between OH and K.

HISTORY OF THE WATER PROBLEM

(MRS. FULHAME'S THEORY OF CATALYSIS)

BY J. W. MELLOR

Up to the middle of the seventeenth century combustion was explained by assuming that all combustible substances contained an "inflammable principle"—sulphur—in virtue of which they were able to burn. Becher (1669) recognized that sulphur itself could not be *the* principle because many inflammable substances were known which did not contain sulphur. He, therefore, postulated the existence of another principle which he called *terra pingua*—inflammable earth. Stahl (1697) still further refined this hypothesis. According to Stahl, a combustible substance is a compound containing "fixed fire" or phlogiston. The "inflammable earth" of Becher became Stahl's "phlogiston." In the act of combustion phlogiston is transferred from a fixed to a free state. When the transfer is complete the substance becomes incombustible. If the calcined substance—say an oxide—be heated with another substance (reducing agent) capable of giving up its phlogiston, it again becomes combustible.

Lavoisier (1775) then showed that the increase in weight which bodies acquire during combustion, depends on the quantity of air absorbed, and he was led to the belief that a combustible body is one which has the property of uniting with the oxygen of the air and becoming again combustible when the oxygen has been taken from it by another body which has a stronger affinity for that substance. Lavoisier's idea was sometimes called the "anti-phlogistic theory" in contrast with the "phlogistic theory" of Stahl.

Lavoisier's theory is the one now prevalent in our textbooks. The combustion of carbon monoxide, for instance, is said to be "satisfactorily explained by the equation

$$2CO + O_2 = 2CO_2,$$

in which two molecules of carbon monoxide unite directly with one molecule of oxygen." In 1880, H. B. Dixon announced to the British Association[1] that the union only takes place in the presence of water vapor. The reaction thus necessitates an entirely different explanation. Dixon has put forward the hypothesis that the reaction really takes place in two stages:

First stage. The carbon monoxide decomposes the water, forming carbon dioxide and liberating hydrogen,

$$CO + H_2O = CO_2 + H_2.$$

Second stage. The hydrogen then unites with the free oxygen to re-form water,

$$2H_2 + O_2 = 2H_2O.$$

The only other hypothesis which has attracted much attention was suggested by M. Traube.[2] It is based upon the facts that carbon monoxide and steam do not interact in the absence of oxygen and that hydrogen peroxide can always be detected when moist carbon monoxide burns in air. Traube thinks that the first action ought to be represented by the equation,

$$CO + 2H_2O + O_2 = CO(OH)_2 + H_2O_2;$$

the hydrogen peroxide so formed then reacts with more carbon monoxide,

$$CO + H_2O_2 = CO(OH)_2;$$

and finally,

$$CO(OH)_2 = CO_2 + H_2O.$$

The relative merits of these two hypotheses are still *sub judice*.

The influence of water on chemical changes was suspected a century before Dixon's discovery. T. O. Bergman,[3] for example, in 1780, noticed that "regulus of manganese" retained its bright appearance in dry air, but not in moist air, and that "in ordinary air, . . . phosphorus is consumed very slowly, and scarcely at all unless water be present". Six years later the illustrious

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[1] H. B. Dixon, B. A. Reports, 1880, 593.

[2] M. Traube. Ber. chem. Ges., Berlin, 15, 666 (1882).

[3] T. O. Bergman, "Opuscula physica et chimica", 2, 206 (1780), Upsala; "Physical and Chemical Essays", 2, 206 (1784), London.

Scheele[1] (1786) stated that "the water present in common atmospheric air is the chief cause of the burning of pyrophorus". This he proved by the following experiment: "I made a very dry air by putting some very small pieces of quicklime into a small flask. I then put the neck of another flask into that of the first so that the air of both might be in communication. I then luted the junction with wax. Two days afterwards I separated the empty flask and poured half an ounce of pyrophorus from my phial into it, and immediately shut the aperture up. But I did not observe that it grew in the least warm. An hour after this I put a sponge moistened with water into the same flask and shut it up again. A few minutes afterwards the pyrophorus became strongly heated and some pieces kindled spontaneously".

Mrs. Fulhame[2] (1794) appears to have been the first to give a clear statement of the influence of water on chemical transformations,[3] and it is the object of this note to call attention to some of her observations which appear to have been quite overlooked. This is the more interesting as her theory of the influence of water in chemical changes is identical, in many respects, with that H. B. Dixon, just outlined.

In 1790, Mrs. Fulhame commenced an investigation on the deposition of gold, silver, and other metals upon silk fabrics so as to imitate "cloths of gold and silver". The results of her observations were published in a remarkable work entitled "An Essay on Combustion with a view to a new art of dying and painting wherein the phlogistic and antiphlogistic hypotheses are proved erroneous". (p. 182, London, 1794.)

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[1] K. W. Scheele, Crell's Annalen, 1, 483 (1786); "Experiments on Fire and Air", English edition, pp. 112, 130, London: Sämmtliche physische und chemische Werke," 1, 183 (1793) Berlin; Priestley, "On Air," 6, 443 (1786), publishes a letter from James Keir on this subject."

[2] Mrs. Fulhame, "An Essay on Combustion" 1794, London. See Annales de Chimie, 26, 58 (1798).

[3] It is generally believed that "Wanklyn was the first, in 1869, to draw attention to the fact that the presence of water is necessary for the interaction of certain substances". Mellor and Russell, however, have drawn attention to a number of observations made prior to that date. (Journ. Chem. Soc. 81, 1272 (1902).) This bibliography was reproduced in this Journal by H. E. Patten, present volume, page 154.

In the first chapter she describes her observations on "the reduction of metals by hydrogen gas". The experiments were conducted in a glass apparatus made of two vertical bulbs. The materials required for the generation of the gas were placed in the lower bulb. The silk fibre under investigation was placed in the upper bulb. The hydrogen, obviously impure, was prepared from iron nails and dilute sulphuric acid. The hydrogen was not dried in any way.

In "Expt. 5" some fibres of white silk were steeped in an aqueous solution of gold chloride, dried in air, and then exposed to hydrogen gas. No reduction was observed. More fibres were then dipped in the same solution of gold chloride and exposed, while still wet, to the action of the gas. Reduction commenced instantly and in the course of half an hour the fibre was covered with a film of the reduced metal.

Similar results were obtained with aqueous solutions of silver nitrate, lead acetate, platinum chloride, mercuric chloride, copper sulphate, stannous chloride, arsenic chloride, bismuth nitrate, antimony tartrate, ferrous sulphate, and zinc chloride. It is therefore evident that the reduction of metals by hydrogen gas "depends on the presence of moisture".

Mrs. Fulhame then tried "if alcohol and ether would produce the same effect by passing a stream of hydrogen through solutions of dry gold chloride in alcohol". The metal was reduced in some cases but not in others. She traced the reduction to "the presence of water contained in the alcohol or the gas and deposited on the silk... It is difficult to obtain ether or alcohol free from the least possible quantity of water and equally difficult to expel all moisture from the surface of the glass". With a solution of gold chloride in ether the metal is not reduced "until the silk has collected a sufficient quantity of water from the gas". Similar results were obtained with ethereal and alcoholic solutions of salts of silver, mercury and lead.

From these observations it is inferred:

"1. Hydrogen is capable of reducing the metals at the ordinary temperature of the atmosphere.

" 2. Water promotes and accelerates the reduction in a very remarkable manner.

" 3. Ether and alcohol do not promote the reduction without the aid of water ".

It was first thought that " water promoted these reductions by minutely dividing the particles of the metallic salt, and by condensing the gas, and by bringing the hydrogen and the metallic oxide within the sphere of attraction; the hydrogen either uniting to the metallic earth or reducing it, as the Phlogistians suppose; or uniting (directly) with, and separating the oxygen of the metal, and thus restoring it to the metallic form, as the Antiphlogistians maintain.

" But it is evident from the experiments related, that water does not promote these reductions solely by minutely dividing the particles of the metallic salt; for, were this the case, ether and alcohol should promote the reduction of the metallic salts which they dissolve, since they divide their particles as minutely as water can.

" Since metallic solutions in ether and alcohol cannot be reduced by hydrogen gas, it follows that the above supposition concerning the mode of agency of water does not account for the reduction of the metals in this way ".

Mrs. Fulhame then assumes that the reduction is always effected by " a double affinity in preference to a single affinity ". This, in modern parlance, means that a reaction will take place indirectly rather than directly, that it will go *via* " intermediate stages " rather than by a direct path.

" Now as water does not promote the reduction merely by dissolving, and minutely dividing the particles of the metallic salts and condensing the hydrogen gas, and since a double affinity takes place in preference to a single affinity, it is obvious that the water must be decomposed in these reductions in the following manner. The hydrogen of the gas unites with the oxygen of the water, while the hydrogen of the latter unites, while in nascent state, with the oxygen of the metal, reduces it and forms water ".

In Chapter II experiments are described on "the reduction of the metals by phosphorus". Fibres were first dipped in a solution of the metallic salt and then into a solution of phosphorus in ether or alcohol. If the fibre was dried after steeping in the metallic salt, little or no reduction took place. The experiments were modified so as to expose the dry and moist fibres to the vapors of phosphorus. The metallic salts tried were gold chloride, silver nitrate, platinum chloride, mercuric chloride, mercuric nitrate, copper sulphate, and stannous chloride. In all cases,

"1. Water is essential to the reduction of metals by phosphorus; for these experiments show that the reduction is effected only in proportion to the quantity of water present.

"2. Phosphorus does not reduce metals by giving them phlogiston.

"3. Phosphorus does not reduce the metals by uniting with and separating their oxygen.

"How then is the reduction effected? Are we not to conclude that it is effected by the decomposition of the water in the following manner?

"The phosphorus attracts the oxygen of the water, while the hydrogen of the latter unites, in the nascent state, with the oxygen of the metal, and effects the reduction.

"Hence it follows that the phosphorus is oxidizèd by the oxygen of the water, while the metal is restored to its combustible state".

Chapter III treats of "the reduction of the metals by sulphur". Fibres dipped in salts of the above-mentioned metals were exposed to sulphur dioxide[1] and to the vapors.

The subject of Chapter IV is "the reduction of metals by alkaline sulphides". Fibres were dipped in aqueous, or alcoholic solutions of potassium sulphide and then in an aqueous, alcoholic, or ethereal solution of salts of manganese and cobalt,

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[1] "Fumes obtained from a burning match," — 1794, of sulphur. The reductions in all cases resemble those with phosphorus.

as well as of the metals previously employed. The results confirm the preceding deductions.

Chapter V. "The reduction of metals by sulphuretted hydrogen". The conclusions recorded in this chapter were rediscovered fifty years later by E. A. Parnell,[1] and yet again a hundred years later by R. E. Hughes.[2]

"Exp. 5. Silver.—A piece of silk which was immersed in a solution of fused silver nitrate in alcohol and dried in the air, was exposed to a current of the gas; but no change could be perceived for some time. It was then wetted with alcohol, still no alteration could be observed until the silk attracted moisture from the gas, when small particles of reduced silver began to appear, attended with a brown stain.... Another piece of silk was then dipped in the same solution of nitrate of silver and exposed, while wet, to the gas. The silver was instantly reduced all over the sides of the silk exposed to the current" of gas. Salts of the metals gold, silver, platinum, mercury, copper, lead, tin, arsenic, bismuth, antimony, iron, and zinc were either converted into sulphides or reduced to the metallic state. The results, in all cases, resemble those which precede.

The same thing might be said of the results recorded in Chapter VI on "reduction of metals by phosphuretted hydrogen".

Chapter VII. "The reduction of metals by charcoal". A small bit of well-burned charcoal was suspended by a thread in a phial containing a diluted solution of gold chloride in distilled water; and in about two hours metallic gold was deposited on the charcoal. A similar piece of charcoal was then "suspended in a solution of gold in ether... not a vestige of reduced gold could be perceived".

Experiments were then made with most of the metals discussed in the preceding chapters, using different forms of charcoal. The conclusions were quite analogous.

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[1] E. A. Parnell. B. A. Reports, 1841, 51.

[2] R. E. Hughes. Phil. Mag. (5) 33, 471 (1892); 34, 117 (1892); 35, 551 (1893).

"1. Charcoal is capable of reducing the metals in the ordinary temperature of the atmosphere.

"2. Water is essential to the reduction of the metals by charcoal; for these experiments prove that the reduction cannot be effected without water.

"3. Charcoal does not reduce the metals by giving them phlogiston; or by uniting with and separating their oxygen; for, were either of these opinions true, metallic solutions in ether and alcohol should be as effectually reduced by charcoal as metallic solutions in water are.

"4. Ether and alcohol do not promote the reduction of metals without the aid of water; but when this is present in sufficient quantity, they effect the reduction in the same manner that charcoal and other combustible bodies do.

"It is evident then that charcoal reduces the metals by decomposing water which seems to be effected in the following manner:

"The carbon of the charcoal attracts the oxygen of the water, while the hydrogen of the latter unites, in its nascent state, with the oxygen of the metal and reduces it.

"Hence it follows that the carbon is oxidized by the oxygen of the water, and forms carbon dioxide, while the metal is restored to its combustible state".

Mrs. Fulhame's objection to Lavoisier's theory of combustion will be understood from her remarks on the following quotation:

"It cannot be doubted", says Lavoisier, "that charcoal at a red heat takes oxygen from all metallic substances: this is a fact against which no exception can be made, and it is the foundation of the whole theory of metallic reduction".

"The experiments in this essay", says Mrs. Fulhame, "demonstrate that this assertion is erroneous in every instance of metallic reduction; for, so far is it from being true, that charcoal takes oxygen from all metallic substances, that it never does so in one single instance; since its carbon always unites with the oxygen of the water, while the hydrogen of the water unites immediately with the oxygen of the metal and reduces it ".

Chapter VIII embodies some astute observations on " the reduction of metals by light ".

" Exp. 2. Silver.—A bit of silk, which was dipped in an aqueous solution of silver nitrate, was suspended in a phial over water . . . no alteration could be observed after standing in a dark closet from the 20th of July to the 20th of October. The silk was now taken out of the phial, and the silver was immediately reduced by means of a solution of phosphorus in ether. Hence it appears that water alone has not the power of reducing metals in the ordinary temperature of the atmosphere ".

Further experiments "detailed in this chapter, prove beyond the power of contradiction,

" 1. That water is essential to the reduction of metals by light: for these experiments demonstrate that the reduction cannot take place without water, and that it is always in proportion to the quantity of that fluid present.

" 2. That light does not reduce metals by giving them phlogiston (energy), as Macquer and Scheele supposed ; for were this opinion true, light would reduce them without the aid of water, and as well with alcohol as with water.

" 3. Light does not reduce metals by fusing and expelling their oxygen, as the Antiphlogistians imagine, for were this the mode of agency, the reduction would happen without the assistance of water, and as well with alcohol as with water".

The aim of Chapter IX on "the reduction of metals by acids " is to show that solutions of salts of gold, silver, platinum, tin, mercury, arsenic, manganese, iron, and zinc in water and in acids, frequently form films of reduced metal on the sides of the vessel and on the surface of the liquid.

Chapter X, " the oxidation of combustible bodies " contains some interesting observations.

" The combustion of hydrogen gas in air is explicable only on the assumption that the water contained in these airs is decomposed. Thus when a flame or a glowing body is applied to a mixture of hydrogen and air, the attraction of the principles of water for each other is diminished, therefore the hydrogen ... unites (directly) with the oxygen of the water, while the hydrogen of the latter seizes the oxygen of the air. Thus all the gases which are changed into water disappear... Hence it appears that water is not formed during the combustion of hydrogen gas in air in the manner the Antiphlogistians suppose... Indeed it is obvious that, if these gases contained no water, they could never be burned... The same reasoning applies to the combustion of all other gases".

Air always contains a large quantity of moisture, and "when phosphorus is burned in this air it attracts the oxygen of the water and forms phosphoric acid while the hydrogen of the water unites with the oxygen of the gas and forms water" once more. This is confirmed by the observation of Bergman previously quoted.

"In like manner during the combustion of charcoal in air, the carbon attracts the oxygen of the water, and forms carbon dioxide, while the hydrogen of the water unites with the oxygen of the air to form a new quantity of water equal to that decomposed.. Hence the carbon of the charcoal does not unite with the oxygen of the air, as Lavoisier supposes, but with the oxygen of the water contained in that gas".

The same reasoning is applied to the combustion of sulphur in air, and to the union of oxygen and nitrogen under the influence of electric sparks.

Mrs. Fulhame then extends her theory to the precipitation of one metal by another, say of copper from a solution of copper sulphate by metallic iron.

"There is no reason to suppose that nature deviates, in this particular case, from that uniform simplicity which she constantly observes in all her operations.

"Therefore it is obvious that, when one metal precipitates another in a form more or less metallic, the precipitant unites with the oxygen of the water while the hydrogen of the latter combines with and separates the oxygen of the precipitated metal and thus reduces it.

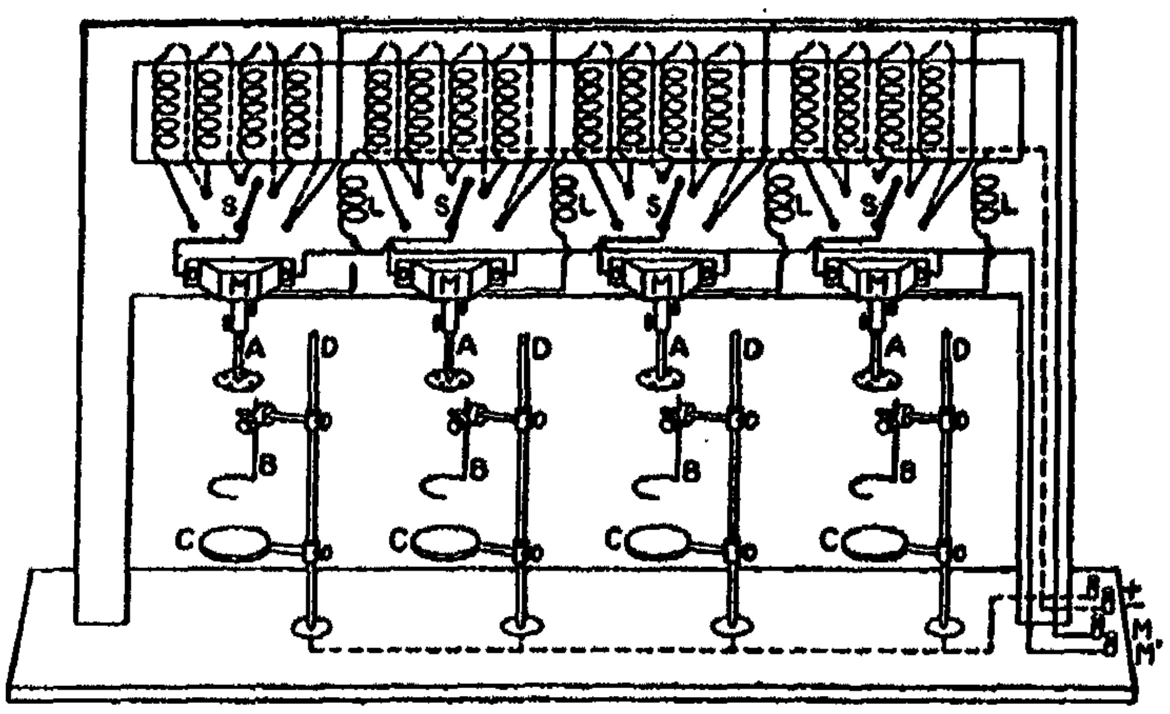
"The experiments made with phosphorus and metallic salt solutions in ether, alcohol, and water prove the truth of this explanation, and show that when one metal precipitates another in the metallic form it first decomposes the water".

Newcastle, Staffordshire.

AN APPARATUS FOR THE ELECTROLYTIC DETERMINATION OF METALS, USING A ROTATING CATHODE

BY E. S. SHEPHERD

Gooch and Medway[1] have shown that by the use of a rotating cathode the time necessary for the quantitative precipitation of metals can be very much shortened. It has occurred to the writer that a much more convenient form of apparatus would be the one herein described. A sketch of the one now in use in this laboratory is here given.



Instead of a platinum crucible, I have used the ordinary disk anode, shortening the stem to about 6 cm, and fastened it by a screw connector directly to the shaft of the armature. The connection to the battery is made through the iron frame of the motor. The motor used is a toy motor, a very poor affair in its way, but sufficient for the purpose, and cheap enough to permit each cathode having its own motor. The use of belts as suggested by Gooch is very unsatisfactory, owing to the slipping, etc. It was found best to arrange a rheostat for each motor,

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[1] Am. Jour. Sci. (4) 15, 320 (1903).

since no two motors run on the same current, and it is also desirable to slacken the speed when removing the beaker and washing the cathode.

This rheostat consisted of one zero, two one-ohm and two two-ohm coils connecting through the switch (S), the other motor connection being through the wire leading to M′. And a 110-volt circuit lamp may of course replace this form of rheostat.

The cathode connection was made through four 8-volt 6-C. P. lamps in multiple (L) for storage-battery work, or these are replaced by the ordinary 110-volt lamp for dynamo circuit. The current was then regulated by loosening or tightening the lamps in their sockets. No difficulty was experienced in getting a good connection through the motor frame to the cathode.

The beaker containing the electrolyte was supported by the wood support (C) on the brass posts (D). The screw for tightening the collar of (C) should be of such size as to allow manipulating this support with one hand, leaving the other free to manage the wash bottle, etc.

The anode was a stiff platinum wire held in the usual electrode holder, connection being made through the brass posts (D).

The distance from the motors to the base board is about 30 cm, and between motors 10 cm.

The disk electrode was used because we happened to have that form in stock. A more desirable form would consist of a disk of platinum gauze, thus allowing a stronger current to be used and shortening the time required.

The brass connector which connects the cathode to the shaft is protected from corrosion by a rubber tube. A finger stall does very well.

A number of determinations were made to see if the apparatus could not advantageously replace volumetric methods in commercial laboratories. A rather good chalcopyrite was treated with 10 cc nitric acid, and after the reaction had subsided, with 7 cc strong sulphuric acid. It was then evaporated until white fumes of SO_3 appeared; taken up with water; filtered, 1 gram NaCl added, and electrolyzed. The salt aided materially in preventing the deposit burning toward the close of the electrolysis. The time required was from 25 to 40 minutes, using 1.5 to 2 amperes. If a better motor were available the time could be shortened to at most 20 minutes. Doubtless, as the advantages of the rotating cathode are better appreciated, our manufacturers will turn out a better quality of motor, allowing the desired high speed. The copper plate was bright, smooth and free from iron. We are thus able to omit the precipitation with zinc, and the time from the filtration to the calculation of the result need not exceed forty minutes, and with more rapid rotation can easily be reduced to twenty minutes. No iron came down with the copper. The following analyses of chalcopyrite and zinc blende show what an ordinary student is able to do and warrant the belief that the apparatus is of practical importance.

Chalcopyrite			Blende		
	Percent Cu	Time Minutes		Percent Zn	Time Minutes
a	22.57	25	A	67.25	30
b	22.75	30	B	67.84	40
c	22.88	30	C	67.80	40
d	22.89	35			
e	22.87	35			

The zinc was prepared as directed by Smith.[1] It is essential that no free acid other than acetic be present, and if one starts with a hot solution, the solution need not be warmed during the electrolysis. It will be seen that the results give more zinc than the theory requires for pure zinc sulphide, an analysis of the plate yielded no iron, but an appreciable amount of cadmium. The zinc plate was firm and bright. The apparatus has been used successfully in the separation of lead and copper. In this case a platinum gauze is substituted for the wire anode.

This apparatus should commend itself both to commercial laboratories and to schools. Not only because of its rapidity, but because it means a saving of at least seventy-five percent in the weight of platinum.

Cornell University,
August, 1903.

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[1] Jour. Am. Chem. Soc. 24, 1073 (1902).

SOLUBILITY OF CALCIUM SULPHATE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID[1]

BY F. K. CAMERON AND J. F. BREAZEALE

In the course of an investigation now in progress, we have had occasion to study certain solutions containing various amounts of sulphuric acid and saturated with respect to calcium sulphate. Some apparent abnormalities which appeared in this work led us to believe that the solubility of calcium sulphate in solutions of the corresponding acid was not in accordance with prevailing views as to the effect of one electrolyte upon another when both are supposed to yield a common ion; and for the proper interpretation of the data we were obtaining, a more precise knowledge of the solution curve for this pair of electrolytes would be necessary. Ostwald[2] has published some results of work by Bantisch on the solubility of calcium sulphate in solutions of hydrochloric, nitric, monochloracetic and formic acids, respectively, from which it appears that, qualitatively at least, the indications of the electrolytic dissociation hypothesis are followed. No systematic study, however, seems to have been made of the solubility in sulphuric acid, solutions, and it was therefore determined to make the investigation, the results of which are here recorded.

The calcium sulphate used was prepared by triturating very pure precipitated calcium carbonate with successive portions of pure sulphuric acid until no trace of carbonic acid remained, and then washing the product free of sulphuric acid with distilled water. The product thus obtained was carefully examined, found to be a very pure salt, and was most satisfactory for solubility work, as it was in a finely precipitated form, offering a large surface for the action of the solvent, and shortening much

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[1] Published by permission of the Secretary of Agriculture.

[2] Jour. prakt. Chem. 29, 52 (1884).

the time required to produce conditions of definite equilibrium between solvent and solute. The sulphuric acid used was obtained from Baker & Adamson and labeled "chemically pure." It was taken from a bottle, freshly opened for the purpose, and appeared to be entirely satisfactory as regards its freedom from other substances.

A series of solutions of sulphuric acid of the concentrations indicated in the table was prepared, and an excess of the dried calcium sulphate introduced into each in the proportion of one gram of the salt to every 100 cc of the solution. The solutions were then immersed in a bath kept at a temperature of 25° C, the containing bottles being shaken occasionally. Portions of these solutions were withdrawn from time to time and analyzed for calcium, until successive analyses showed that final equilibrium had been established in all cases. This was effected in about 70–80 hours, but the solutions were retained in the constant temperature bath for six days to establish final equilibrium beyond any possible question. Portions of 50 cc were then withdrawn and analyzed.

The calcium was precipitated from a hot solution by adding ammonia to excess and then ammonium oxalate. The precipitate was carefully washed, dried, ignited, and the calcium weighed as oxide. The filtrate and washings, containing considerable quantities of ammonium sulphate and oxalate, were in all cases brought to dryness in porcelain dishes, which were then carefully ignited to remove ammonium salts, the residue taken up with small quantities of hydrochloric acid, washed into cylindrical bottles and the small quantities of calcium present estimated by a modification of the well-known "soap" method originally suggested by Clarke. The small amounts of calcium found were added as corrections to the amounts determined gravimetrically. By this procedure the error due to the solubility of the precipitated calcium oxalate in rather concentrated solution of ammonium sulphate was avoided, since the modification of the soap method in use in this laboratory has been found to be accurate to about one part of calcium per million of solution.

The amounts of free sulphuric acid present were checked by titration against a standard solution of potassium hydrate, using both phenolphthaleine and methyl orange as indicators, before and after the introduction of the solid calcium sulphate into the solutions of the acid.

After making the determinations for 25° C, the flasks were brought to 43° C, being held at this temperature for six days before being analyzed. They were then brought to 25° C again and held at this temperature for several days and again analyzed, yielding results in such good accord with those formerly obtained at this temperature, that it is not thought worth while to state them here. A few determinations were made at 35° C, in which, however, the calcium sulphate used was finely powdered gypsum from a sample employed in some earlier solubility work already described in this Journal.

The weights of solutions at 25° C were carefully determined, the volume of the pycnometer used being standardized by determining the weight of boiled, air-free, distilled water it would contain and finding the corresponding volume from Gray's tables. These data will enable any one who may desire it, to compute the solubilities on the basis of the mass of solvent; rather than the volume of solution. But conceding the latter form to be the less rational, we have retained it here in order to show the comparison of the results obtained at the different temperatures. There does not appear to be any particular advantage in stating the results in terms of reacting weights, and they are therefore only given as grams per liter of solution.

The significance of the results is more readily seen when they are plotted to some convenient scale, as in the accompanying chart. It will be observed that increasing the temperature increases the solubility of the calcium sulphate in the presence of the sulphuric acid over the range covered by our experiments, and the maximum point on the solubility curve for calcium sulphate in pure water at various temperatures[1] disappears at least

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[1] 37.5° C according to Marignac. Ann. Chim. Phys. (5) 1, 274 (1874), and 40° C according to the recent work of Hulett and Allen. Jour. Am. Chem. Soc. 24, 667 (1902).

within the range here considered. In this respect, the system seems to be quite different from those composed of calcium sulphate and solutions of other electrolytes, such as sodium or magnesium chloride, etc.,[1] formerly studied in this laboratory.

Solubility of Calcium Sulphate in Solutions of Sulphuric Acid

Weight of 1000 cc of solution at 25° C Grams	Grams H_2SO_4 per liter Grams	Grams $CaSO_4$ per liter at		
		25° Grams	35° Grams	43° Grams
999.1067	0.00	2.126	—	2.145
1002.493	0.48	2.128	2.209	2.236
1002.553	4.87	2.144	2.431	2.456
1005.091	8.11	2.203	—	2.760
1009.787	16.22	2.382	—	3.116
1030.151	48.67	2.727	3.397	3.843
1043.470	75.00	2.841	—	4.146
1075.613	97.35	2.779	3.606	—
—	146.01	2.571	3.150	4.139
1113.392	194.70	2.313	—	3.551
1141.755	243.35	1.901	—	2.959
1168.143	292.02	1.541	—	2.481

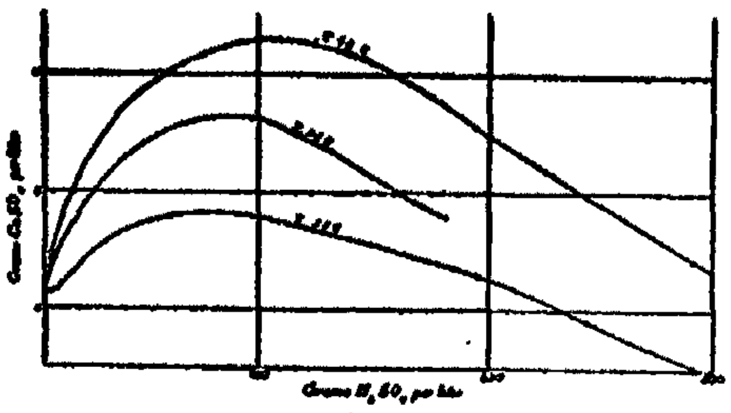

Fig. 1

At the three temperatures studied, the curves show maxima points, which by interpolation appear to correspond to the following concentrations:

At 25° C, 75 gms. H_2SO_4 and 2.84 gms. $CaSO_4$ per liter.
" 35° " 85 " " " 3.70 " " " "
" 43° " 105 " " " 4.26 " " " "

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[1] Jour. Phys. Chem. 5, 556, 643 (1901). Bulletin No. 18, Division of Soils, U. S. Department of Agriculture, 1901.

A remarkable feature presented by this system is that the solubility of the calcium sulphate increases with increasing amounts of sulphuric acid, up to comparatively high concentrations with respect to the latter. We seem to have here another of the increasing number of known cases where the indications of the hypothesis of electrolytic dissociation in aqueous solutions do not hold. It is difficult to see how calcium sulphate could dissociate any way other than that indicated thus:

$$CaSO_4 \rightleftarrows Ca + SO_4;$$

but on the basis of conductivity, freezing-point and similar measurements, we are accustomed to regard sulphuric acid as dissociating thus:

$$H_2SO_4 \rightleftarrows H + HSO_4,$$

and, then a further dissociation of one of the ions, thus:

$$HSO_4 \rightleftarrows H + SO_4,$$

and that at lower concentrations this latter dissociation is approximately complete. This would suggest in the system we are considering, the presence of two electrolytes which yield a common ion, and that we should obtain a decrease in the solubility of the calcium sulphate with increasing amounts of sulphuric acid. That the reverse was actually found at all concentrations suggests several hypotheses:

1. Sulphuric acid, possibly influenced by the presence of dissolved calcium sulphate, may dissociate with the formation mainly of HSO_4 ions. Opposed to this view is the work to which reference has just been made.

2. Possibly the calcium sulphate, in dissolving, more or less completely unites with the sulphuric acid to form complexes. yielding such ions, for instance, as $Ca(SO_4)_2$ or $HCa(SO_4)_2$. No evidence in support of this view could be obtained from a critical examination of the solid phases and the determination of the acidity of the solutions before and after adding the calcium sulphate, yielding practically identical results, failed to give any information on this point.

3. Possibly the two dissolved substances, or the substances

and the water may have other effects, one upon another of such magnitude as to mask those normally to be expected from the ions which they might yield. There does not seem to be any known reason why even strong electrolytes might not exert such effects which are well known though not well understood in the case of other and especially not dissociating solutes.

No satisfactory methods of testing these several hypotheses at present suggest themselves, and it only seems worth while to bring these views forward to show that while the facts established by this investigation are not in harmony with the indications of the dissociation hypothesis as we know it, it would be going too far to say that they are in actual opposition to the hypothesis, and to emphasize the desirability of further study along this line.

Another point brought out by this work as in our former studies[1] is that there seems to be a condensation, not alone of the solution, but of the solvent itself, brought about by the introduction of these solutes. For instance, a liter of solution at 25° C and containing 0.49 gram of sulphuric acid with 2.128 grams of calcium sulphate weighs 1002.493 grams, so that the weight of the water present is actually 999.875 grams, while the weight of an equal volume of pure water at the same temperature is given as 997.12 grams.[2]

Finally, it seems worth while to call attention to the figures given for the solubility in pure water. The figure corresponding to 25° C especially, was determined with unusual care and is the average of eight determinations, six of which were practically identical. This matter is of some moment in view of the careful work on the solubility of gypsum recently done by Hulett and Allen.[3] The figures given by these authors represent what they term a *normally saturated* solution, that is, a solution in equilibrium with a solid presenting only a plane surface to solvent action, whereas Hulett[4] has shown that by secur-

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[1] Loc. cit.

[2] Gray. Smithsonian Physical Tables, 1896.

[3] Jour. Am. Chem. Soc. 24, 667 (1902).

[4] Zeit. phys. Chem. 37, 388 (1901). See also Ostwald. Ibid. 34, 495 (1900).

ing sufficiently convex surfaces, through powdering or otherwise reducing the size of the particles, he could obtain an apparent increase in the solubility, of about 20 percent. But the solubility of calcium sulphate or gypsum with which one most commonly has to deal, and probably is most interesting on that account, is not that which would be obtained either by bringing the solution into equilibrium with plates of selenite or gypsum free from powder or with particles less than 0.3 micron in diameter. And the fact that this figure 2.126 has been obtained so often in this laboratory,[1] working with calcium sulphate of widely different origin, leads us to think that it represents with considerable accuracy the solubility, under ordinary conditions, to be expected at 25° C. Hulett and Allen's suggestion that former investigators have had present varying amounts of material consisting of particles less than 0.3 micron in diameter, does not seem very probable, since no matter what the physical character of the calcium sulphate, whether precipitated from solution or powdered mineral, we have obtained such concordant figures.

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[1] Loc. cit.

THE SOLUBILITY OF MAGNESIUM CARBONATE IN AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES[1]

BY F. K. CAMERON AND A. SEIDELL

The work herein described was done in connection with and for the most part antedated that upon the solubility of calcium carbonate in solutions of other salts, which has already been described.[2]

The solubility of magnesium carbonate is obviously dependent upon the partial pressure of the carbon dioxide in the atmosphere or gas phase in contact with the solution. This has led to the development of this investigation in three parts:

1. When the solutions were in contact with ordinary atmospheric air containing a small and practically constant percentage of carbon dioxide.
2. When the atmosphere in contact with the solutions contained practically nothing but carbon dioxide and water.
3. When the solutions were in contact with an atmosphere practically free from carbon dioxide.

Under these several conditions the ratio of normal carbonate to hydrogen carbonate or bicarbonate for any given concentration of solution might be expected to vary greatly.

Moreover, it was found, in the case of solutions of magnesium carbonate, that temperature changes frequently produced relatively large changes in the solubility, and it was therefore necessary to take precautions to prevent variations in this respect during the progress of the work.

Unless otherwise stated the work described here was done at 23° C.

As is well known, solution studies of magnesium carbonate, when other salts are present, have always given great difficulty

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[1] Published by the permission of the Secretary of Agriculture.

[2] Jour. Phys. Chem. 6, 50 (1902).

it is generally believed on account of an unusually strong tendency toward the formation of complex or double carbonates.[1] The work here described has involved these difficulties to a large degree, and they have delayed the announcement of the results obtained. On account of these difficulties, the results obtained when measurable quantities of carbon dioxide were present in the vapor phase, are not satisfactory, at least from a quantitative point of view, although an unusual amount of labor was expended in obtaining them. It has seemed wisest, therefore, to present them for what they are worth as at least approximately correct, since it has become inexpedient for us to give further time to this particular investigation.

In Equilibrium with Air

A series of solutions of sodium chloride was prepared, pure powdered magnesium carbonate added, and, by means of an aspirator and appropriate connections, a stream of air was conducted through the solutions for periods ranging from 20 to 100 days. Portions of the solutions were then withdrawn with a pipette, the relative amounts of carbonates and bicarbonates determined by titrating with a standard acid, using phenolphthaleine and methyl orange,[2] respectively, as indicators. The total amount of magnesium in solution was determined gravimetrically as the pyrophosphate; and the sodium chloride by titrating with a standard solution of silver nitrate, using potassium chromate as indicator.

A number of such series of determinations was made, yielding results which approximated each other, but which could not, however, be regarded as in satisfactory agreement. It is not, therefore, thought worth while to tabulate the figures actually obtained, but the nature of the solubility curve and its approximate position are given in the accompanying chart.

In the attempt to obtain conditions which would bring

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[1] Bodländer. Zeit. phys. Chem. 35, 31 (1900), suggests that magnesium carbonate, in going into solution, forms more or less indefinite complexes of the type $m\text{Mg(OH)}_2, n\text{MgCO}_3$, to which the difficulties encountered are due.

[2] Vide. Am. Chem. Jour. 23, 471 (1900).

about final, definite equilibria in these solutions, several devices were used. The solutions were brought to boiling, then allowed to cool and stand for long periods while a current of air was drawn through them. In another series, magnesium carbonate was precipitated in the solutions by adding equivalent amounts of magnesium chloride and sodium carbonate. Still another plan was tried, the series of solutions being prepared as usual, but instead of bubbling air through them, a carbon dioxide generator was attached and a stream of the gas drawn through the series of solutions. It was evident that the gas rapidly caused the solution of the solid magnesium carbonate in contact with the solutions, since in several of the flasks the amount originally added soon disappeared, and it was necessary to add more. After introducing carbon dioxide for about 3 or 4 hours, in order to insure the solution of much more of the magnesium carbonate than would dissolve without its aid, the gas generator was removed and air drawn through for the purpose of displacing the excess of carbon dioxide which had been added, and at the same time precipitate from solution the excess of magnesium carbonate which had been dissolved. The current of air which was drawn through the solutions for about 10 hours did not cause the precipitation of magnesium carbonate in any of the solutions except one, where a cloudiness, which might have been due to this cause, was observed. It is needless to say satisfactory results could not be expected from these solutions. Even

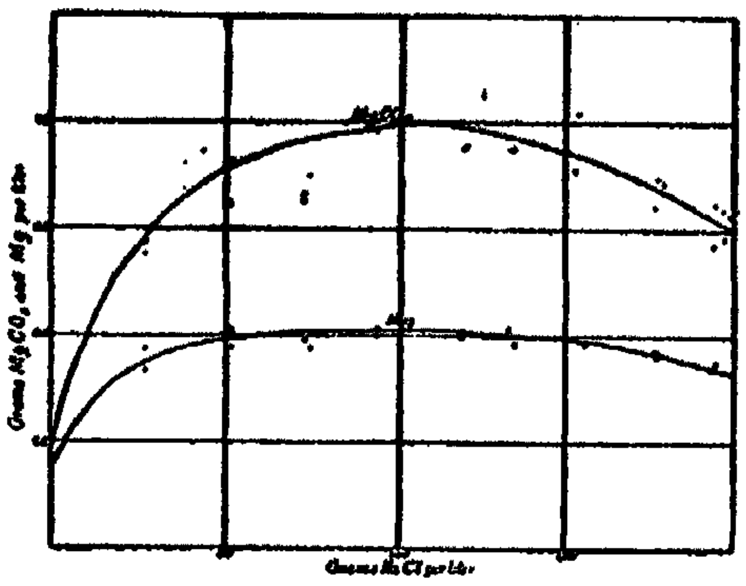

Fig. 1

long-continued boiling failed to completely remove the excess of carbon dioxide, as titration with phenolphthaleine and methyl orange as indicators showed.

The results of these different methods of work, in general, confirmed those diagrammatically presented here. In no case were they of such a character as to lead us to believe that they could be regarded as more than rough approximations to the truth.

In Equilibrium with an Atmosphere of Carbon Dioxide

Sodium chloride solutions of various concentrations were prepared as described for the previous experiments. The volumes of the solutions for convenience, however, were kept somewhat less, about 100 cubic centimeters. The solutions were introduced into small bottles of about 250 cc capacity, which were of such dimensions that they fitted into the places provided for them in a very efficient shaking apparatus. An excess of magnesium carbonate was added to each bottle and at the same time a few drops of phenolphthaleine. Carbon dioxide gas from a tube of liquid carbon dioxide after being passed through dilute sulphuric acid, was bubbled into each bottle separately until the red color disappeared. The bottles were then placed in the shaking apparatus and shaken for several hours. The red color reappeared in each flask, and upon the removal of the stopper for the purpose of introducing the tube for bubbling in more carbon dioxide, a "popping" sound was produced, caused by a diminished pressure in the inside, due to the absorption of the carbon dioxide gas which was above the solution in the bottle before it had been shaken in the apparatus.

The introduction of more carbon dioxide gas served to dispel the red color of the phenolphthaleine the second time, and after a second period of shaking, the color again reappeared in some of the bottles. It is to be noted, however, that the popping sound, caused by the removal of the stoppers, continued with every bottle, even after a great many introductions of carbonic acid gas and subsequent shaking of the bottles. Indeed, the apparently large volume of carbon dioxide which seemed to be absorbed by the solutions in each flask, led to the idea that part of the solid carbonate in each bottle might be uniting with the gas, and therefore becoming transformed into the unknown solid magnesium bicarbonate. An attempted demonstration of this by analysis of some of the solid phase proved futile, however, since the results apparently showed that the solid material was undoubtedly still in the form of the normal carbonate. The solubility of magnesium bicarbonate in solutions of sodium chloride is shown in the following table, and illustrated in the accompanying chart.

Solubility of Magnesium Bicarbonate in Aqueous Solutions of Sodium Chloride

Grams NaCl per liter	Grams $Mg(HCO_3)_2$ per liter
7.0	30.64
56.5	30.18
119.7	27.88
163.9	24.96
224.8	20.78
306.6	10.75

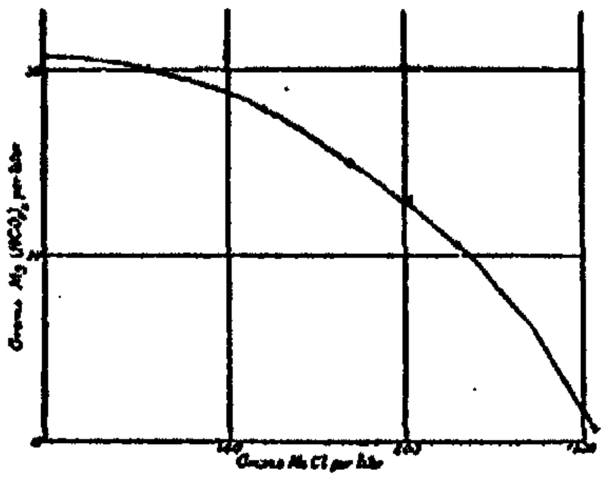

Fig. 2

The first experiment made upon a series of solutions prepared and saturated with carbon dioxide as described above gave results which, when plotted on cross-section paper, yielded a very smooth curve throughout its whole length. From this curve it appears that the solubility of magnesium bicarbonate is greatest in pure water, being about 3.06 grams $Mg(HCO_3)_2$ per 100 cc, and decreases gradually as the concentration of sodium chloride increases, to about one-third the above amount in a nearly saturated solution of sodium chloride. When this experiment was subsequently repeated, however, under as nearly similar conditions as possible, the curve obtained was somewhat irregular and, in addition, lay for most of its length below the one plotted for the results obtained from the analysis made upon the first series of solutions. The solubility of magnesium bicarbonate in pure water, as determined the second time, was only about 2.0 grams per 100 cc, instead of 3.0 grams as found above. In the second experiment, although the course of the curve was more or less irregular, it descended, as had the first, as the concentration of the sodium chloride ascended. The solubility, as found for the nearly saturated sodium chloride solution, was very nearly the same in the two instances. It was not deemed worth while to record the results obtained with the second series of solutions which undoubtedly did not represent final equilibria conditions. They are cited to illustrate the difficulties to be expected when working with magnesium carbonate, and the tendency toward what are probably "false equilibria" when the substance is dissolved in solutions of more soluble salts.

It will be further observed that, assuming this to be the case of the solubility of magnesium bicarbonate, [$Mg(HCO_3)_2$], and sodium chloride, ($NaCl$), it is one where there is a decreasing solubility of the one salt with the increasing concentration of the other, although no common ion is yielded by the dissociation of the two solutes. No reasonable explanation of this discrepancy with the indications of the hypothesis of electrolytic dissociation suggests itself, and it is probable that this case may be regarded as a real exception to the hypothesis.

One more experiment with solutions of magnesium carbonate and a soluble salt in contact with an atmosphere of carbon dioxide will be cited. In this case the soluble salt used was sodium sulphate instead of the chloride. The saturation with carbon dioxide was accomplished exactly as has been noted for the two experiments already described. The carbon dioxide was introduced into the solutions at room temperature, and the temperature of the shaking apparatus kept the same at each period of shaking until the last, when the temperature was raised to 37.5° and the bottles revolved for forty hours at this temperature. It was noted that as each bottle was unstoppered the difference in the ease with which each of the stoppers could be withdrawn indicated a different gas pressure inside each bottle. Another and more striking evidence of the gas pressure existing in each bottle was found in the fact that, on removing the stoppers, bubbles of gas could be seen ascending from the solid magnesium carbonate in the bottom of each bottle, and in most cases it was evolved at such a rate that the solid material itself was dispersed throughout the liquid. This increased gas pressure resulted, no doubt, from the fact that each solution had been saturated with carbon dioxide at a temperature of about 20° C, and afterwards subjected for a long time to a temperature of 37.5°, whereupon a varying amount of carbon dioxide was liberated from each solution and created a slightly different gas pressure in each bottle. The results of the titrations of these solutions with standard half-normal acid solutions, using methyl orange as indicator, showed that the amount of magnesium bicarbonate dissolved in 100 cc of pure water, and in each of the sodium sulphate solutions was very nearly the same in all. The variations being from 1.463 grams in the pure water to 1.916 grams, being the highest amount and found in a solution of a concentration of about 12 percent sodium sulphate, the amount of the bicarbonate then decreasing very gradually to about 1.612 grams in a saturated solution of sodium sulphate.

In Equilibrium with an Atmosphere Free from Carbon Dioxide

In Solutions of Sodium Chloride. — A series of solutions of sodium chloride was prepared, and solid magnesium carbonate added in about the proportion of 2 grams of solid to each 100 cc of solution. The solutions were all brought to vigorous boiling, transferred to bottles, which were then closed with rubber stoppers, and allowed to cool. It was thought wiser to momentarily remove the stoppers, from time to time, during the cooling in order to equalize the pressures within the bottles, and possibly traces of carbon dioxide may have thus found entrance and been absorbed by the solutions. On cooling, the solutions were vigorously agitated for about 3 days at a temperature of 23° C, allowed to stand until the major part of the suspended solid material had subsided and quickly filtered. Aliquot portions of the solution were then weighed and analyzed by the methods indicated above. It was assumed that the magnesium went into solution in the form of the carbonate alone, and that the resultant solution would therefore contain only normal carbonates and no bicarbonates. Titrations with a standard acid, using phenolphthaleine and methyl orange respectively as indicators, showed this assumption to be not quite true and that small amounts of bicarbonates probably existed in all the solutions, but in amounts so small as to be negligible. Repeated experiments showed that vigorous boiling of the solution containing suspended solid was necessary to eliminate the excess of carbon dioxide and decompose the last traces of hydrogen carbonate. The results obtained are given in the following table and represented graphically in the accompanying chart.

Solubility of Magnesium Carbonate in Aqueous Solutions of Sodium Chloride

Weight of liter of solution	Grams NaCl per liter	Grams $MgCO_3$ per liter	Reacting weights. NaCl per liter	Reacting weights. $MgCO_3$ per liter
996.92	0.0	0.176	0.000	0.00210
1016.82	28.0	0.418	0.482	0.00500
1041.09	59.5	0.527	1.025	0.00630
1070.50	106.3	0.585	1.831	0.00699
1094.53	147.4	0.544	2.539	0.00650
1142.48	231.1	0.460	3.981	0.00550
1170.14	272.9	0.393	4.701	0.00470
1199.28	331.4	0.293	5.709	0.00350

It will be observed that with increasing concentration of sodium chloride up to about a 12 percent solution, there is an increase in the solubility of magnesium carbonate, but as the concentration of sodium chloride further increases there is a gradual diminution of the solubility of the magnesium carbonate, yielding a solubility curve with a maximum point, being, in this respect, analogous to the curve representing the solubility of calcium carbonate in solutions of sodium chloride.

In Solutions of Sodium Sulphate. — A series of solutions of sodium sulphate was prepared, magnesium carbonate added, and then treated exactly as the sodium chloride series just described, except that instead of chlorine determinations, the sulphates present in the various solutions were estimated as barium sulphate precipitated from appropriate portions of the solutions. After having satisfactorily determined the solubility curve at 23° C, another series of solutions was prepared, brought to equilibrium at 35.5° C and analyzed. The results brought out the unlooked-for fact that the solubility of magnesium carbonate in solutions of sodium sulphate is decreased by increasing the temperature, and that the solubility curve at 35.5° is lower at every point than the one corresponding to 23° C. The curves are similar in general respects to that representing the solubility of calcium carbonate in solutions of sodium sulphate. The results obtained are tabulated below and are graphically represented in Figure 3.

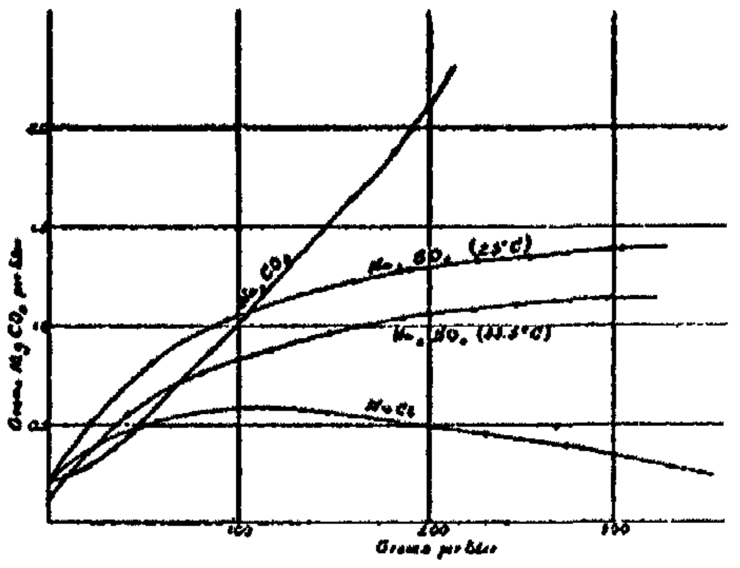

Fig. 3

In Solutions of Sodium Carbonate. — A series of solutions was prepared by dissolving anhydrous normal sodium carbonate in water which had been previously boiled to expel dissolved carbon dioxide, magnesium carbonate added as in the series above described. The solutions were not boiled subsequent to

Solubility of Magnesium Carbonate in Aqueous Solutions of Sodium Sulphate

At 24° C.

Weight of liter of solution	Grams Na_2SO_4 per liter	Grams $MgCO_3$ per liter	Reacting weights. Na_2SO_4 per liter	Reacting weights. $MgCO_3$ per liter
997.52	0.00	0.216	0.000	0.00258
1021.24	25.12	0.586	0.178	0.00700
1047.60	54.76	0.828	0.388	0.00990
1080.95	95.68	1.020	0.678	0.01219
1133.85	160.80	1.230	1.140	0.01470
1157.34	191.90	1.280	1.360	0.01530
1206.03	254.60	1.338	1.804	0.01600
1223.91	278.50	1.338	1.973	0.01600
1241.99	305.10	1.388	2.162	0.01660
		At 35.5° C.		
995.15	0.32	0.131	——	0.00156
1032.89	41.84	0.577	0.296	0.00689
1067.23	81.84	0.753	0.579	0.00900
1094.77	116.56	0.904	0.826	0.01080
1120.38	148.56	0.962	1.052	0.01149
1151.70	186.70	1.047	1.323	0.01251
1179.82	224.00	1.088	1.587	0.01300
1196.32	247.20	1.100	1.751	0.01314
1236.52	299.20	1.130	2.120	0.01350

the addition of the magnesium carbonate, but were at once tightly stoppered in appropriate bottles and shaken vigorously and continuously for 3 days. After coming to equilibrium, they were analyzed, the magnesium being precipitated as the double ammonium phosphate in the presence of a large excess of ammonia and ammonium chloride, and the amount of carbonates being determined by titrating with a standard solution of hydrochloric acid, using methyl orange as indicator. From these data the total amounts per 100 cc of solution of sodium and magnesium carbonates present were computed and compared with actual determinations made by evaporating 100 cc portions of the solutions to dryness in weighed platinum dishes, heating cautiously below dull redness to expel water of crystallization, but not combined carbon dioxide, and weighing the residues. The figures obtained in this comparison follow:

Found	Computed
0.0520	—
2.36	2.34
5.11	5.13
8.66	8.73
12.74	12.86
16.05	16.24
18.42	18.39
21.62	21.55

From the analysis as above described the results presented in the accompanying table were obtained, and from them the curves given in the diagram (Fig. 3) were plotted.

Solubility of Magnesium Carbonate in Aqueous Solutions of Sodium Carbonate at 25° C.

Weight of liter of solution	Grams Na_2CO_3 per liter	Grams $MgCO_3$ per liter	Reacting weights. Na_2CO_3 per liter	Reacting weights. $MgCO_3$ per liter
996.84	0.00	0.223	0.000	0.00266
1019.89	23.12	0.288	0.220	0.00344
1047.72	50.75	0.510	0 482	0.00620
1082.47	86.42	0.879	0.820	0.01027
1118.91	127.30	1.314	1.209	0.01570
1147.66	160.80	1.636	1.526	0.01955
1166.05	181.90	1.972	1.727	0.02357
1189.38	213.20	2.317	2.024	0.02770

It will be observed that, except for the lower concentrations, the increase in solubility of the magnesium carbonate with increase in the amount of sodium carbonate is represented by an approximately straight line.

It appears striking that the solubility of magnesium carbonate should increase so rapidly with the increase in the concentration of the sodium carbonate, since we are dealing with a pair of electrolytes supposedly having a common ion. Such cases as this have been found, however, in the previous work which has been done in this laboratory and elsewhere, and in former instances an explanation based upon the formation of double salts has been the one usually offered. An unsatisfactory feature of most of these cases, as with the present one, is that an inspection of the residue as solid phase in contact with the solution does not give any evidence of the formation of a new component, nor is there any sudden change in the direction of the solubility curve, indicating the formation of a new component at any particular concentration. Such component, though formed, would not necessarily separate, however, should it possess a relatively high solubility. At present there does not appear any satisfactory method of testing this or any other explanation of the phenomena which has been suggested. It seems wisest, therefore, to refrain from speculation until sufficient data of this kind have been accumulated to furnish possibly a clearer insight of the phenomena.

Conclusions

In this paper it has been shown:

1. That when appreciable quantities of carbon dioxide are present in the vapor phase in contact with solid magnesium carbonate and solutions of other salts, there is a marked tendency toward conditions of false equilibria. The usual explanation advanced to account for these observations, that double carbonates are formed, is unsatisfactory.

2. The solubility of magnesium carbonate in solutions of sodium chloride when in contact with ordinary air, increases with increasing concentration of sodium chloride up to a maximum and then decreases.

3. The solubility of magnesium carbonate, as the bicarbonate, in solutions of sodium chloride when in contact with an atmosphere containing only carbon dioxide and water vapor at atmospheric pressure, decreases regularly with increasing concentration with respect to sodium chloride. This appears to be a real exception to the hypothesis of electrolytic dissociation for which no explanation based upon that hypothesis can be offered.

4. The solubility of magnesium carbonate in solutions of

sodium sulphate, in contact with an atmosphere containing only carbon dioxide and water, increases slightly and then decreases with increasing concentrations of sodium sulphate.

5. In contact with an atmosphere free from carbon dioxide, the solubility of magnesium carbonate increases to a maximum and then decreases, with increasing concentration of sodium chloride; it increases regularly with increasing concentration with respect to either sodium sulphate or sodium carbonate.

6. The solubility of magnesium carbonate in solutions of sodium sulphate, in contact with an atmosphere free from carbon dioxide, appears to decrease with increasing temperature.

7. The solubility curve for magnesium carbonate in solutions of sodium carbonate is not in apparent accord with the theory of electrolytic dissociation.

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NEW BOOKS

Thermodynamik und Kinetik der Körper. *By B. Weinstein. Zweiter Band. 14 × 22 cm; pp. xviii + 586. Braunschweig: Friedrich Vieweg und Sohn, 1901. Price: paper, 16 marks.* — Weinstein's Thermodynamics and Kinetics of Bodies is essentially a critical review of the literature of thermodynamics. An account of the character and contents of its first volume, which appeared in 1901, was given in this Journal at that time (5, 604). The work is continued in the present second volume, whose five chapters deal successively with absolute temperature, liquids, solids, thermodynamic mechanics and irreversible processes, and mixtures and solutions.

An introductory chapter on absolute temperature, which is the ninth chapter of the whole work, deals with the definition of the thermodynamic scale of temperatures and with the calibration of the scales of constant volume gas thermometers. The next chapter, on liquids, is more extensive. It presents a critical analysis of the literature on the characteristic equation of a liquid, on capillarity, viscosity, thermal conductivity, osmosis, and the specific heats of liquids, and on evaporation and fusion. The section on capillarity discusses the theories of Laplace and Gauss, the investigations of Ramsay and Shields, and the thermodynamic theories of Gibbs and van der Waals; and that on osmosis outlines the early history of the study of osmotic phenomena, and examines the theory of van 't Hoff and the various theories of diffusion. Next comes a chapter, of one hundred pages, on solids. This is arranged in five sections, which treat, respectively, the characteristic equation, specific heats, and fusion, sublimation, and transformation of solids, coexistence and stability of states of aggregation, and equilibrium and deformation of solid bodies. The last of these sections is especially interesting because of the exposition given of the theories of Gibbs and of Voigt.

A chapter on "thermodynamic mechanics and irreversible processes" is here inserted as a general introduction to succeeding chapters. It deals first with the equality of the chemical potential in coexistent phases, the phase rule, and the conditions of stability of thermodynamic equilibria. Then the forms of the entropy, energy, and thermodynamic potential for ideal gases and gas mixtures are found, and some of the phase equilibria studied by Roozeboom and Schreinemakers are described. The last section is made unclear by the absence of diagrams. The following section, on irreversible processes, gives an account of the interesting theories of Wiedeburg, Duhem, and Natanson; and the chapter is brought to a close by a section on thermodynamic kinetics, which chiefly consists of a few examples of the application of the law of mass action. The concluding chapter, entitled Mixtures and Solutions, is concerned with the capillarity and viscosity of solutions, and with their specific heats, heats of solution and of dilution, vapor pressures, and fusion phenomena.

The author's idea in writing the book has apparently been to give a condensed account of the literature of his field, rather than to work up the subject

as a whole from any definite point of view. For this reason its value is primarily that of a work of reference. The present volume is a bulky one, of nearly six hundred closely printed pages. A forthcoming third volume is to treat electrolysis, and the special topic of dilute solutions. An extensive index is to be provided.
J. E. Trevor

La Compressibilité des Gaz réels. *By L. Décombe.* (*Scientia, No. 21.*) *12 × 19 cm; pp. 99. Paris: C. Naud, 1903. Price: bound, 2 francs.* — This number of the *Scientia* series gives in outline an account of the work that has been done in the study of the compressibility and thermal expansion of gases. The introductory chapter is on the "Law of Mariotte". It tells of the early statement of the law of Boyle in 1661, and by Mariotte in 1676; of its acceptance without question for a century, although Boyle had stated that it did not accurately correspond to the expermental data; that its accuracy was later called in question by a number of experimenters, especially by Regnault, in 1847, who showed that at ordinary temperatures no gas strictly follow's Boyle's law, and that all but hydrogen are more compressible than the law indicates, and indeed the more so the more readily they are liquefiable. Then follows an account of the work of Natterer, Cailletet, and Amagat under pressures greater than one hundred atmospheres, which exhibited a minimum of the product *pv* for all the gases examined except hydrogen. A short chapter here deals with the contradictory results of the various researches that have been executed at very low pressures. The next two chapters describe Amagat's famous determinations of the isotherms of several fluids throughout wide ranges of pressure and temperature, and the discovery of the critical phenomena by Cagniard de Latour and Andrews. The sixth chapter introduces some dozen and a half forms that have been proposed for the characteristic equation of a fluid, with incidental comment on the kinetic theory of gases, and on James Thomson's suggestion of the analytical continuity of the liquid and vapor states. Another chapter presents a brief exposition of van der Waals's theory of corresponding states, and of its essential verification by Amagat, who effected the superposition of the isotherms of carbon dioxide, ethylene, ether, and air. The volume is concluded by a short chapter on the families of isotherms of two-component fluids. The whole treatment is sketchy; merely an outline of the subject is provided, and the citations of the original papers are not as full as they should be.
J. E. Trevor

Recherches sur l'Hydrodynamique. *By P. Duhem. Première Série. Principes fondamentaux de l'Hydrodynamique; Propagation des Discontinuités; Des Ondes and des Quasi-Ondes. 22 × 28 cm; pp. 210. Paris: Gauthier-Villars, 1903.* — In the classical form of the theory of dynamics, the thermal changes that mechanical processes always involve are omitted from consideration. When these thermal aspects of the phenomena are not disregarded, the theory assumes a far more general form. The theory of hydrostatics has been recast in this form by Duhem, chiefly in a paper published in 1893 in the *Annales de l'École Normale superieure.* This indefatigable investigator has now undertaken a corresponding revision of the dynamics of fluids. The present introductory volume of this research is reprinted from the *Annales* *de la Faculté des Sciences de Toulouse*, in which it has been appearing serially during the past three years. Its text is arranged in three parts, in which are successively considered the fundamental principles of hydrodynamics, the propagation of waves, and "quasi-waves". The typography of the volume is of the highest order. *J. E. Trevor*

Ostwald's Klassiker der exakten Wissenschaften.

No. 21. Ueber die Wanderungen der Ionen während der Elektrolyse. Abhandlungen von W. Hittorf. Erster Teil. Zweite, erweiterte Auflage. Herausgegeben von W. Ostwald. 115 pp. Price: 1.60 marks.

No. 134. Experimental-Untersuchungen über Elektricität. Von Michael Faraday. Herausgegeben von A. J. von Oettingen. 102 pp. Price: 1.60 marks.

No. 135. Allgemeine Grundlagen einer Theorie der Gestalt von Flüssigkeiten im Zustand des Gleichgewichte. Von Carl Friedrich Gauss. Uebersetzt von Rudolf H. Weber. Herausgegeben von H. Weber. 73 pp. Price: 1.20 marks.

No. 136. Experimental-Untersuchungen über Elektricität. Von Michael Faraday. XVIII. und XIX. Reihe. Herausgegeben von A. J. von Oettingen. 58 pp. Price: 1.20 marks.

No. 137. Abhandlungen zur Thermodynamik chemischer Vorgänge. Von August Horstmann. Herausgegeben von J. H. van 't Hoff. 73 pp. Price: 1.20 marks.

No. 139. Thermodynamische Abhandlungen über Molekulartheorie und chemische Gleichgewichte. Von C. M. Guldberg. Aus dem Norwegischen übersetzt und herausgeben von R. Abegg. 85 pp. Price: 1.50 marks.

Leipzig: Wilhelm Engelmann, 1903.

We are in receipt of a half dozen new volumes of Ostwald's *Klassiker* series. The first of them is a new edition of the first part of Hittorf's papers on the migration of ions. It differs from the first edition in the inclusion of controversial material from Hittorf's third paper, which was omitted from the former edition on Hittorf's request. The papers in the present part appeared between the years 1853 and 1858.

Two numbers continue the translation of Faraday's Experimental Researches in Electricity, including the sixteenth, seventeenth, eighteenth, and nineteenth series. These are devoted mainly to a defense of the chemical theory of the voltaic current, and to the discovery of the magnetic rotation of the plane of polarization of light. An Appendix on the latter topic, from the Philosophical Transactions of 1847, is included.

Another number contains a carefully annotated reprint of the German translation of Gauss's famous paper on capillarity. The remaining two numbers are collections of the thermodynamic papers of Horstmann and of Guldberg, the former edited by van 't Hoff, and the latter translated from the Norwegian and edited by Abegg. To the former, van 't Hoff has contributed an appreciative sketch of Horstmann's life. *J. E. Trevor*

An Elementary Text-Book on the Differential and Integral Calculus. *By William H. Echols. 15 × 22 cm; pp. x + 36. New York: Henry Holt and*

Company, 1902. Price: bound, $2.00.—This new introductory treatise on the calculus is an exceptionally brilliant performance. The author has presented the subject very clearly and in a thoroughly modern way. This is indicated by the following statement from his preface. "The calculus is essentially the science of numbers and is but an extension of Arithmetic. The inherent difficulties which lie about its beginning are not those of the Calculus, but those of Arithmetic and the fundamental notions of number. Our elementary algebras are beginning now to define more clearly the number system and the meaning of the number continuum. This permits a clearer presentation of the calculus than heretofore, to elementary students. ... An equation must express a relation between finite numbers. The differentials are defined in finite numbers according to the best modern treatment."

As an introduction, and by way of supplying a connecting link between algebra and calculus, the text begins with a review of the topics of arithmetic and algebra that are necessary for the calculus, and which are often omitted from elementary algebras. This is followed by a treatment of the calculus of one variable, the subtopics being: the principles of the differential calculus, applications to geometry, the principles of the integral calculus, and applications of integration. The latter half of the book treats functions of more than one variable, and discusses successively the principles and theory of differentiation, application to surfaces, and multiple integrals. A number of interesting special topics are considered in appendices. The scope of the book is thus seen to be very satisfactory. It is cordially to be recommended to students who wish to begin a serious study of the calculus, even though they intend to take up the subject without a teacher. *J. E. Trevor*

Vorlesungen über Experimentalphysik. *By August Kundt. Herausgegeben von Karl Scheel. 15 × 23 cm; pp. xxiv + 852. Braunschweig: F. Vieweg und Sohn, 1903. Price: paper, 15 marks; bound, 17.50 marks.*—This volume presents Kundt's brilliant lectures on experimental physics at the University of Berlin, as delivered in the academic year 1888-89. The text is a revision, by Karl Scheel, of a manuscript report of the course. In order to preserve Kundt's characteristic style, the manuscript has been altered as little as possible, and no effort has been made to incorporate in the book any account of the progress of the last fifteen years. The presentation is very simple and clear, and the chief stress is laid on the experimental illustration of the subject. No mathematical developments are given. The book is profusely illustrated, chiefly by drawings of apparatus. The frontispiece is an excellent portrait of Kundt, and the volume is introduced by an interesting account of Kundt's life, written by his brother-in-law, G. Schwalbe. *J. E. Trevor*

Leçons de Mécanique élémentaire, *a l'usage des Élèves des Classes de Première (Latin Sciences ou Sciences-Langues vivantes), conformément aux programmes du Mai, 1902. By P. Appell and J. Chappuis. 11 × 17 cm; pp. viii + 177. Paris: Gauthier-Villars, 1903. Price: 2.75 francs.*—A feeling that the sciences of experiment and observation have been neglected in French secondary teaching has led to a new government programme, extending the instruction in mechanics in these schools, and bringing it more into harmony with that in the physical sciences. To meet the new requirements, Appell and Chappuis, a mathematician and a physicist, have collaborated in the preparation of the present introductory schoolbook on mechanics. It is designed for use in the courses in which physical science is combined with either ancient or modern languages. The authors have carefully avoided an exaggerated systematization, and they have freely chosen their illustrative applications from familiar phenomena. Another volume is to appear for use in the "*Classe de Mathematiques*." The work has been surpassingly well-done, and the typography of the volume is excellent; it is in all respects a beautiful little book. The treatment is confined to kinematics, with an introductory chapter on the geometrical ideas that are made use of. *J. E. Trevor*

Papers on Etherification and on the Constitution of Salts. *By Alexander W. Williamson (1850-1856). Alembic Club Reprints, No. 16. 12 × 18 cm; pp. iv + 62. Chicago: The University of Chicago Press, 1902. Price: bound, $0.40.* — Williamson's papers on etherification are now issued, as No. 16 of the Alembic Club Reprints, by both the Alembic Club of Edinburgh and the University of Chicago Press. The papers are so well known that this convenient and neatly printed issue required no comment other than the information contained in the heading of this note. *J. E. Trevor*

Mathematical papers of the late George Green. *Edited by N. M. Ferrers. Facsimile Reprint. 14 × 22 cm; pp. x + 336. Paris: A. Hermann, 1903. Price: paper, $4.00.* — This volume is a facsimile reprint of the collected papers of George Green, as edited by Ferrers in 1870. The collection comprises nearly a dozen papers, which appeared in the interval between 1828 and 1839, mostly in the Transactions of the Cambridge Philosophical Society. The first of them is the famous paper, An Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism, originally published by subscription at Nottingham in 1828. The volume is printed on a good, tough paper, and is to be welcomed as rendering more accessible the work of this self-taught scientific genius. It is a curious fact that this reproduction of an English classic should appear in France. *J. E. Trevor*

Problems in Astrophysics. *By Agnes M. Clerke. 15 × 23 cm; pp. xvi + 567. London: Adam and Charles Black, 1903. Price: bound, $6.00, net.* — This rather large book is a popular treatise on the active new science of astrophysics. Its two parts deal successively with solar physics and with sidereal physics, the latter including the study of nebulæ. These parts are preceded by an introductory chapter on the rise and scope of the whole subject. Entertainingly written and well illustrated, the book appears to give a thoroughly adequate account of the marvels that the spectroscope has disclosed in the sky. *J. E. Trevor*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Conditions of progress in electrochemistry. *J. W. Richards. Trans. Am. Electrochemical Soc.* 3, *59* (*1903*). — A presidential address in which the progress of electrochemistry is discussed under the headings: discovery of new facts; clearer understanding of the laws correlating facts; more rational theories of the why and the wherefore; increasing application of the facts to the welfare of mankind; increasing dissemination of scientific literature; an increasing vision, on the part of the scientist, of the possibilities of scientific achievement. *W. D. B.*

On the teaching and practice of electrochemistry in the United States. *F. Haber. Zeit. Elektrochemie,* 9, *291, 347, 379* (*1903*). — The author came to this country to investigate and report on American methods. He was given great facilities, and this article is his official report. It contains a very interesting sketch of the electrochemical industries of the country and an epitomized statement of the methods of teaching at different universities. *W. D. B.*

On the deduction of the intensity law of energetics from the second law of thermodynamics. *Scheye. Zeit. phys. Chem.* 44, *495* (*1903*). — The author considers the cases of an adiabatic change and of two spheres colliding. He draws the conclusions that Helm's deduction of the generalization, that each form of energy tends to pass from a higher to a lower potential, is unsound. *W. D. B.*

Reply to Scheye's article. *G. Helm. Zeit. phys. Chem.* 44, *498* (*1903*). — An answer to the criticisms of Scheye (preceding review). *W. D. B.*

An automatic Sprengel mercury pump. *W. Donle. Drude's Ann.* 10, *313* (*1903*). — The author describes the construction and working of his form of pump, which he has slightly modified as a result of the important papers of Kahlbaum (6, 276). This brings the speed of the pump well up to that attained by the Kahlbaum pump. *H. T. B.*

An automatic mercury fall pump, together with details of the glass technique. *L. Zehnder. Drude's Ann.* 10, *623* (*1903*). — The author's aim is to describe an automatic pump that may be easily constructed with ordinary skill. Having no patents, he endeavors to make his paper as clear as possible, and at the same time describes the best methods of performing the more difficult glass work. *H. T. B.*

Description of a bomb-calorimeter and method of its use. *W. O. Atwater and J. F. Snell. Jour. Am. Chem. Soc.* 25, *659* (*1903*). — The authors now use a gold-lined, copper bomb for calorimetric purposes and find it very satisfactory. Full descriptions are given of the bomb itself and of the way to use it.

W. D. B.

One-Component Systems

An attempt to determine the relative amounts of krypton and xenon in the air. *W. Ramsay. Zeit. phys. Chem.* 44, *74* (*1903*). — The ratio of the absolute boiling-points of krypton under various pressures to the absolute boiling-points of mercury under the same pressures is found to be nearly constant, the value being 0.19. For xenon and mercury, the corresponding ratio is 0.258. The melting-point of krypton is —169°, and the boiling-point under atmospheric pressure is —151.7°. The corresponding values for xenon are —1.40° and 109.1°. There is believed to be one part of krypton by volume in twenty million parts of air, and one part of xenon by volume in 170 million parts of air. From density determinations, the atomic weight of krypton should be 81.62, while the mean of the former determinations was 81.55.

W. D. B.

The vapor-densities of some carbon compounds. *W. Ramsay and B. D. Steele. Zeit. phys. Chem.* 44, *348* (*1903*). — The volume, pressure, and masses of a number of carefully purified vapors have been determined with great care. The consensus of opinion is that Avogadro's law does not hold for these substances and that accurate atomic weights cannot be obtained from density determinations.

W. D. B.

Determination of vapor densities in an electric furnace. *W. Nernst. Trans. Am. Electrochemical Soc.* 3, *75* (*1903*). — Vapor density determinations by the V. Meyer method were made up to 2200° in an electrically-heated, iridium tube. Mercury, sodium chloride, and potassium chloride gave values slightly higher than the normal; but a suitable correction would bring them out where they should be. Water gave an apparent molecular weight of 18, which would be decreased if we apply the correction just referred to.

W. D. B.

The velocity of sound and the ratio of the specific heats of air at high temperatures. *A. Kalähne. Drude's Ann.* 21, *225* (*1903*). — The method of measuring the velocity of sound is a resonance method after the principle proposed by Quincke and adapted by Seebeck and Low. It is specially adapted for high temperatures up to 1000°. At 900° the value of the ratio $\frac{C_p}{C_v} = 1.39$.

H. T. B.

On the relation between the formula of J. Stefan and the equation of condition of van der Waals. *A. Brandt. Drude's Ann.* 10, *783* (*1903*). — Stefan's formula which reads:

$$\int_{P_1}^{P_2} v dP = C \log \frac{P_2}{P_1} + P_2 v_2 - P_1 v_1,$$

involving terms representing the cohesion pressure and specific volume of fluid and vapor, was put by that author equal to 2 B, where B represents the equivalent of the inner heat of vaporization. No sufficient reason was given for this equation.

In the present paper the author shows how the formula can be derived from the well-known equation of van der Waals. This not only gives direct proof, but indicates the truth of the two formulas. *H. T. B.*

The kinetic theory of monatomic bodies. *G. Mie. Drude's Ann.* 11, *657* (*1903*). — The author gives a theoretical treatment of the molecular relation of liquid and vapor for monatomic bodies, touching at the same time, in a general way, polyatomic bodies. The great inequality in the specific heats of liquid and vapor, which is experimentally demonstrated for such bodies as mercury and water, is not in accord with van der Waals's hypothesis, and the author attempts to go over the whole matter, and to harmonize theory and fact more satisfactorily. It is admitted, however, that the results of the investigation so far are but an approximation. *H. T. B.*

The isotherm of dissociating sulphur at 448°. *G. Preuner. Zeit. phys. Chem.* 44, *733* (*1903*). — From an analysis of the vapor density-pressure curve for sulphur at 448°, the author concludes that the vapor must contain S_8, S_6, S_4, and S_2. *W. D. B.*

Investigations on the gaseous and liquid states. *A. Schükarew. Zeit. phys. Chem.* 44, *548* (*1903*). — The author has determined for isopropyl alcohol, acetone, methyl alcohol, and ether, the heat necessary to carry one gram of liquid from 22° to the critical temperature. As was to be expected, the value found varies with the pressure. *W. D. B.*

A determination of the thermal conductivity of argon and helium. *W. Schwarze. Drude's Ann.* 11, *303* (*1903*). — The method of Schleiermacher is used in the measurements. Through the axis of a tube containing the gas, a platinum wire is placed, heated by an electric current. The glass walls are kept at a constant temperature and the temperature of the wire becomes finally stationary. The heat conducted and radiated by the wire is found by measuring the current strength and resistance. By knowing the temperature coefficient of the wire and its resistance, the temperature is known. From the dimensions of the apparatus and special experiments to determine the radiation, the conductivity of the gas can be calculated. The values obtained are as follows: air 0.00005690, argon 0.00003894, helium 0.0003386. The author is satisfied that convection currents in no way affected his results. The measurements for air are in very good agreement with previous results. *H. T. B.*

On the expansion of fused quartz. *L. Holborn and F. Henning. Drude's Ann.* 10, *446* (*1903*). — The value obtained for the expansion of fused quartz between 0° and 1000° is 0.00000054. The method was the authors' well-known one used in the Reichsanstalt. *H. T. B.*

An apparatus for the measurement of the expansion of gases by heat under constant pressure. *T. W. Richards and K. L. Mark. Proc. Am. Acad.* 38, *417* (*1902*); *Zeil. phys. Chem.* 43, *475* (*1903*). — "The desirability of new determinations of the coefficient of expansion by heat under constant pressure for various gases is pointed out. An apparatus is described which possesses the advantages of having all the gas at known temperature, of affording the means of measuring pressure to within one-hundredth of a millimeter of mercury, of using a small temperature-interval, and of eliminating many possible constant errors by making the observations of pressure always under similar conditions.

"A table of results on the expansion of hydrogen under constant pressure, as compared to its previously determined tension in constant volume, shows the possibility of attaining an accuracy equal to that desired, namely, one part in thirty-six hundred. Two other sets of measurements are appended which show that nitrogen expands at, essentially, the same rate as hydrogen, while carbon dioxide exhibits a very great deviation. It is proposed to make a large number of experiments on different gases at different pressures with the aid of this apparatus." *W. D. B.*

Apparatus for measuring small volumes. *L. Zehnder. Drude's Ann.* 10, *40* (*1903*). — The general principle of the apparatus depends on the depression of a barometer column, by introducing a small bottle containing air. The density of the body to be determined, which is placed in the bottle, is found from the amount of air it displaces from the bottle. The theory of the apparatus and the various sources of error are described at length. *H. T. B.*

Two-Component Systems

On saturated aqueous solutions of sparingly soluble salts, I. *F. Kohlrausch Zeit. phys. Chem.* 44, *197* (*1903*). — The author gives solubility determinations for forty-one so-called insoluble salts by the conductivity method. The temperature coefficient was also determined over a small range of temperatures. Work like this gives a definiteness to our knowledge of these salts. *W. D. B.*

The freezing-points of dilute solutions. *T. W. Richards. Zeit. phys. Chem.* 44, *563* (*1903*). — Reviewed (7, 479) from Jour. Am. Chem. Soc. 25, 291 (1903).

Contributions to the determinations of molecular weights, VII. *E. Beckmann. Zeit. phys. Chem.* 44, *161* (*1903*). — Various improvements have been made in the Beckmann form of the Landsberger apparatus, and these changes are described in full. The freezing-point apparatus has been improved by cheapening the stirrer and by changing the construction of the electromagnet and the metronome. There is a chapter on exact measurements and another in answer to criticisms that have been made. *W. D. B.*

On amorphous sulphur. *A. Smith and W. B. Holmes. Decennial Publications, 1902; Ber. chem. Ges. Berlin,* 35, *2992* (*1902*); *Zeit. phys. Chem.* 42, *469* (*1903*). — The freezing-point of pure sulphur is 119.25°. From the lowering of the freezing-point caused by amorphous sulphur, the authors conclude that the latter has a molecular weight of 8 × 32, and that it is an isomer of liquid, monoclinic sulphur. Special experiments showed that the amount of amorphous sulphur in the melt was increased by the presence of air, sulphur dioxide, or hydrochloric acid, and decreased by the presence of nitrogen, carbon dioxide, hydrogen sulphide or ammonia. The authors refer to the work of Malus, but seem scarcely to appreciate its importance. *W. D. B.*

On the formation of nitric acid by electric energy. *C. W. Volney. Trans. Am. Electrochemical Soc.* 3, *285* (*1903*). — Some experiments were made on the decomposition of nitric oxide by the spark. Nitrogen peroxide and nitrogen are formed according to the equation

$$2NO = NO_2 + N.$$

The author believes that the decomposition of nitrogen peroxide under the same conditions may be represented by the three equations,

$$N_2O_4 = NO + NO + O_2$$
$$NO + O = NO_2$$
$$N + O = NO.$$

These three equations could be condensed into two as follows :

$$NO_2 \rightleftarrows NO + O$$
$$N + O = NO.$$

From Richardson's measurements, which are not cited by the author, we know that the reversible reaction actually takes place above 500°.

Starting with atmospheric air instead of nitric oxide, about one-eighth as much nitrogen peroxide was obtained under what were otherwise the same conditions. *W. D. B.*

Multi-Component Systems

Contributions to the thermodynamics of water gas. *O. Hahn. Zeit. phys. Chem.* 44, *513* (*1903*). — The author has studied the equilibrium represented by the equation

$$CO_2 + H_2 \rightleftarrows CO + H_2O.$$

The mass law relations hold up to 1400°, and the change of the equilibrium constant with the temperature can be calculated up to 1100° by means of the van't Hoff formula. At higher temperatures the equilibrium constant increases less rapidly than the formula requires. The equilibrium was reached from both sides, but the results thus obtained showed a curious tendency to overlap, for which no explanation is forthcoming. *W. D. B.*

On the effect of salts on the solubility of hydrogen sulphide, iodine and bromine. *W. H. McLauchlan. Zeit. phys. Chem.* 44, *600* (*1903*). — Henry's law appears to hold for the solubility of hydrogen sulphide in aqueous salt solutions. Urea increases the solubility, but the other substances decrease it. The author believes that the percentage decrease of the solubility is a linear function of the concentration of the salt added, but his experiments do not furnish a brilliant confirmation of this in the case of bromine, though the results with hydrogen sulphide are better. Experiments were also made on the solubility of hydrogen sulphide, and of iodine in aqueous alcohol and in aqueous acetic acid. *W. D. B.*

The basic oxalates of bismuth. *F. B. Allan. Jour. Am. Chem. Soc.* 25, *722* (*1903*). — At 75° there are two basic oxalates of bismuth, $Bi_2O_32C_2O_3.H_2O$ and $3Bi_2O_3.2C_2O_3$. *W. D. B.*

A new double oxalate of bismuth and ammonium. *F. B. Allan and J. S. DeLury. Jour. Am. Chem. Soc.* 25, *728* (*1903*). — The authors have separated and analyzed the double oxalate of bismuth and ammonium, $Bi_2(C_2O_4)_3K_2C_2O_4$-$9.5H_2O$. *W. D. B.*

A new double oxalate of bismuth and ammonium. *F. B. Allan and F. A. Phillips. Jour. Am. Chem. Soc.* 25, *729* (*1903*). — The authors have separated and analyzed the double oxalate of bismuth and ammonium,

$Bi_2(C_2O_4)_3(NH_4)_2C_2O_48H_2O$. *W. D. B.*

Mercuric chloride and water. *D. Strömholm. Zeit. phys. Chem.* 44, *63* (*1903*). — In order to explain the solubility relations for mercuric chloride in ether and water, the author is forced to assume the existence of a number of hydrates of mercuric chloride. Even then, the result is admitted to be unsatisfactory. *W. D. B.*

On molecular compounds of iodine. *D. Strömholm. Zeit. phys. Chem.* 44, *721* (*1903*). — The assumption is made that the solubility of a solute in mixed solvents can be calculated from the solubilities in the pure solvents provided no molecular compounds are formed. Applying this criterion to iodine, he concludes that addition compounds are formed in the brown solutions with water, alcohol or ether as solvent; but not in the red or violet solutions. While the conclusion may be correct, the reasoning is not. *W. D. B.*

On the solidification and swelling of gelatine. *P. v. Schroeder. Zeit. phys. Chem.* 46, *75* (*1903*). — When gelatine is heated and cooled in presence of water, there are three phenomena which have to be distinguished. The sol changes to a gel with increased viscosity. This change is reversible. Thermal changes occur in the gel increasing the viscosity. This also is reversible. The water has a gradual saponifying effect on the gel, decreasing its viscosity and tending to liquefy it. This change is not reversible. The rate of saponification can be described by a logarithmic formula. Sulphates increase the rate of solidification, while chlorides, nitrates, bases and acids decrease it, the effect of the anion being greater than that of the cation. Acids and bases increase the rate of saponification. The formation of gel under the influence of salts is to be distinguished from coagulation by salts.

Special experiments, which are not finished, seem to show that there is an increase in the vapor pressure of water when gelatine swells in it. A gelatine will therefore swell in water while it will contract in saturated water vapor. This is to be studied further. *W. D. B.*

On the precipitation of colloidal solutions by electrolytes. *H. Freundlich. Zeit. phys. Chem.* 44, *129* (*1903*). —

1. The precipitating action of electrolytes on sols is to be explained by an action requiring time, such as diffusion; and not by a displacement of static equilibrium. The precipitation is dependent on the concentration of the solution and also on the rate at which the solution of the electrolyte is added to the sol.

2. When sols show anodic convection, the nature of the anion is immaterial; when there is cathodic convection the cation plays no part.

3. The valency of the ions is the most important factor in determining the coagulation, the rate being higher the greater the valence.

4. A minor factor, especially noticeable with univalent ions, is the migration velocity, the rate of coagulation increasing with the migration velocity.

5. Equivalent quantities of two electrolytes have the same precipitating action when the two salts are equally dissociated and when the ions have the same migration velocities.

6. There are also chemical factors to be considered. *W. D. B.*

Silver as a reducing agent. *W. S. Hendrixson. Jour. Am. Chem. Soc.* 25, *637* (*1903*). — Chloric, iodic, and chromic acids oxidize finely divided silver, six equivalents of silver being oxidized for one molecular weight of the acid reduced. Dilute sulphuric acid dissolves finely divided silver, but only when the solution contains air. *W. D. B.*

Reducibility of some metallic oxides by hydrogen and carbon monoxide. *T. W. Fay and A. F. Seeker. Jour. Am. Chem. Soc.* 25, *641* (*1903*). —

"1. The minimum temperature of reduction of both silver and gold oxide by hydrogen is much below zero, and that for carbon monoxide lower than that for hydrogen.

"2. Carbon monoxide is a more rapid and efficient reducing agent than hydrogen.

"3. The differences in the temperatures of reduction of the yellow and red oxides of mercury make them exhibit properties of two different substances." *W. D. B.*

The protective action of zinc chloride on metallic iron. *C. J. Reed. Trans. Am. Electrochemical Soc.* 3, *149* (*1903*). — When a nail is allowed to remain in a zinc chloride solution, the surface keeps bright and there is no sign of ferric oxide. Under a sodium chloride solution, the nail rusted. No explanation is offered. *W. D. B.*

Velocities

On the decomposition of potassium chlorate. *J. Scobai. Zeit. phys. Chem.* 44, *319* (*1903*). —

1. Pure potassium chlorate does not decompose perceptibly at 390°, 395°, or 411°.

2. At 395° potassium chlorate decomposes in the two ways indicated by the equations,

$$4KClO_3 = KCl + 3KClO_4$$

and

$$KClO_3 = KCl + 3O.$$

3. At 395°, the first, or main, reaction is of the fourth order, while the minor reaction is of the first order.

4. Pure potassium nitrate does not decompose at 400°.

5. The order of the reaction is the same when potassium chloride is present in the fused mass, as when it is not.

6. Sodium chlorate decomposes practically the way the potassium salts do. *W. D. B.*

On the velocity of flow of a metal. *N. Werigen, J. Lewkejeff and G. Tammann. Drude's Ann.* 10, *647* (*1903*). — At a temperature of about 200° C, the metal is subjected to a high pressure in double steel cones, and allowed to flow out of a small orifice in tubular form. The apparatus has been carefully described and illustrated in a previous paper by Tammann, Drude's Ann. 7, 198 (1902), and is therefore only briefly mentioned in the present paper. On account of the wide divergence in the results for the different metals at different temperatures, the authors are unable to give the temperature variation of the plasticity. The following series however begins with the most plastic and this property decreases in order:

K, Na, Pb, Tl, Sn, Bi, Cd, Zn, Sb.

In the case of tin at 200° a sudden decrease in velocity of flow occurs, while in the case of thallium at 180° the reverse takes place. In general, it is found that a temperature increase of 10° under equal conditions of pressure and orifice nearly doubles the velocity of flow. *H. T. B.*

The action of metallic magnesium upon aqueous solutions. *C. F. Roberts and L. Brown. Jour. Am. Chem. Soc.* 25, *801* (*1903*). —

"1. Magnesium is without action on distilled water, boiled to free it from gases, and carefully cooled out of contact with air.

"2. Magnesium acts on undistilled water and on unboiled distilled water, setting free varying amounts of gas; also on water boiled and afterwards charged with oxygen or carbon dioxide.

"3. The hydrogen equivalent of magnesium can be obtained from aqueous solutions of varying strengths of the chlorides of sodium, potassium, magnesium, barium, calcium, and strontium; also very slowly from the sulphate of magnesium (probably also of sodium and potassium); also from such dilute solutions of hydrochloric and sulphuric acids as contain in themselves but a small proportion of the hydrogen liberated.

"4. With the same surface of magnesium the action of the chlorides is much more rapid than that of the corresponding sulphates. With chlorides of the same metal, the rate is dependent upon the concentration, though no strict proportionality can be traced. The maximum rate is more quickly attained in the stronger solution than in the weaker and is greater in amount, but the length of time for completing the reaction does not differ very much in the two cases.

"5. With equimolecular solutions of chlorides of sodium, potassium, magnesium, calcium, strontium, and barium, the order of rapidity of action upon magnesium ribbon was as follows: magnesium, barium, strontium, calcium, sodium, and potassium."

With the salts, the rate of evolution of hydrogen is at first low, then increases and passes through a maximum, afterward falling off gradually to zero. It would be well if these experiments could be repeated with efficient stirring and with removal of magnesia crusts as fast as formed. *W. D. B.*

On the physics of flames. *H. Mache. Drude's Ann.* 10, *408* (*1903*). — The author studies a homogeneous mixture of detonating gas, and develops an expression for the flame, connecting the explosion velocity with the other physical properties of the gas, which resembles in form the fundamental equation of heat conduction. He then considers the temperature relations of the flame, and the protective nature of wire netting against gas explosion. *H. T. B.*

Electromotive Forces

Single potentials of zinc in aqueous solutions. *H. E. Patten and W. R. Mott. Trans. Am. Electrochemical Soc.* 3, *317* (*1903*). — Measurements of the potentials between zinc and various solutions showed that the so-called solution pressure of zinc is a very variable value. As was to be expected, the residual current is very large when a mixture of ferrous and ferric salt is taken between platinum electrodes. The authors account for the precipitation of zinc before hydrogen by assuming that a thin film of zinc separates below the decomposition point and that the excess voltage of Caspari is developed on this.

W. D. B.

Thermoelectromotive force without difference of temperature. *H. S. Carhart. Trans. Am. Electrochemical Soc.* 3, *137* (*1903*). — A discussion of concentration cells with special reference to the Peltier effect. *W. D. B.*

An experimental study of some electrode effects. *H. M. Tory and H. T. Barnes. Trans. Am. Electrochemical Soc.* 3, *95* (*1903*). — Experiments showed that the differences of potential between pieces of the same metal in the same solution depend very largely on the amount of air dissolved in the water. Experiments were also made with a large number of metals, in pure water charged with either air, oxygen, or hydrogen against air-free water. Oxygen-charged water behaves usually like air-charged water. The authors believe that they are studying a process of occlusion rather than a process of oxidation or reduction. *W. D. B.*

Electromotive force of alloys. *W. D. Bancroft. Trans. Am. Electrochemical Soc.* 3, *297* (*1903*). — It is pointed out that conclusions as to the composition of alloys are erroneous if not based on equilibrium conditions. In the measurement of the electromotive force of alloys, no attention has been paid to this point. *W. D. B.*

Experiments with metallic diaphragms. *W. D. Bancroft. Trans. Am. Electrochemical Soc.* 3, *133* (*1903*). — It is shown that two interposed electrodes connected by a wire are not the same as a single interposed electrode equal in length to the distance between the two electrodes. It is also shown that the voltage at which a metal is deposited on an interposed plate, which does not divide the solution into two parts, is less than the decomposition voltage owing to partial depolarization. *W. D. B.*

On polarization capacity. *F. Krüger. Zeit. phys. Chem.* 46, *1* (*1903*). — The measurements on large capacities were made by the Wien method and those on small capacities by the Gordon method. Starting from the theory of electrical double layers, the author develops a theory of polarization capacity which is to cover all the ground covered by the Warburg theory and more. The value of 6-7 M. F. per cm^2 for mercury in solutions of iodides, sulphocyanates, etc., is not in accord with the Lippmann-Helmholtz theory of electrocapillarity. In order to account for the effects due to diffusion and dissociation, the author makes the hypothesis that the rate of dissociation is not infinitely high but is comparable with the period of an alternating current. *W. D. B.*

The electrolysis of water. *J. W. Richards and W. S. Landis. Trans. Am. Electrochemical Soc.* 3, *105* (*1903*). — When working with a sealed tube filled with solution, no current could be observed with an applied voltage of 3 volts while a current passed as soon as one end of the tube was opened. No explanation is offered for this. The other experiments are valuable chiefly as showing that the residual current is dependent on the gases dissolved or dissolving in the solution. The conclusions reached would be more convincing were the authors not hazy about the relation between the applied voltage and the decomposition voltage. The authors are firm believers in Thomson's law.

W. D. B.

On the cathode fall of potential of the alkali metals. *K. Mey. Drude's Ann.* 11, *127* (*1903*). — Clean surfaces of the metals are used in nitrogen, hydrogen and helium. It is found that under the influence of electric discharge in nitrogen the compounds NK_3 and NNa_3 are formed, and in hydrogen probably KH and NaH.

Measurements of the fall of potential showed that where this was small at the cathode there was a correspondingly high fall at the anode. Values of the cathode fall are given. *H. T. B.*

On the acceleration and retardation of reactions in electrical reduction and oxidation. *R. Russ. Zeit. phys. Chem.* 44, *641* (*1903*). —

1. The depolarization by nitrobenzene, *p*-nitrophenol, hypochlorite, and quinhydrone has been measured at different metal electrodes, chiefly gold, platinum, silver, iron and nickel. The depolarization is, in general, strongest with gold and weakest with nickel, the least noble of the metals studied. The effect of the different metals varies with the different depolarizers.

2. There was noticed a peculiar effect of the past history of the electrode on its readiness to polarize. By continuous cathodic polarization the electrode can be made more active, its readiness to polarize can be decreased. This activity is not permanent and decreases gradually when the current decreased rapidly; it often decreases suddenly when the circuit is broken.

3. The current-potential curves and the concentration-potential curves are very regular and are logarithmic especially with those electrodes which show a readiness to depolarize. With other electrodes the curves are more irregular and less satisfactory. These latter electrodes are readily made more active by a previous polarization and these curves are then more like those of the depolarizable electrodes.

4. The retarding and accelerating effects of the electrodes must be referred to different causes, one a change in the reaction velocity constant and the other a change in a special expenditure of work of some other sort.

5. These two effects of the electrode metal sometimes work together, as with gold in acid nitrobenzene solution; sometimes in opposite directions, as with iron in alkaline nitrobenzene solution. Either may predominate.

Gold, especially electrolytic gold, as electrode decreases the tendency to depolarize very markedly in comparison with platinum in the electrolytic reduction of nitrobenzene in acid solution or in the reversible reduction and oxidation of quinhydrone. This effect appears to be chiefly of the nature of a catalytic acceleration. This is very clear with quinhydrone where there is a similar change in both the cathode and anode potential without any displacement of equilibrium. *W. D. B.*

Electrolysis and Electrolytic Dissociation

The universally exact application of Faraday's law. *T. W. Richards and W. N. Stull. Proc. Am. Acad.* 38, *409* (*1902*); *Zeit. phys. Chem.* 42, *621* (*1903*). — A silver voltameter with an aqueous silver nitrate solution was placed in series with a silver voltameter containing silver nitrate dissolved in a mixture of fused sodium and potassium nitrates. The first voltameter was kept at 20° and the second at 250°. When corrections were made for the mother liquor occluded in the crystals, the amounts of silver precipitated in the two voltameters differed by less than 0.005 per cent. This proves conclusively that Faraday's law is not affected by change of solvent or of temperature.

W. D. B.

Uniformity in electrochemical equivalents. *C. Hering. Trans. Am. Electrochemical Soc.* 3, *291* (*1903*).— This is a plea for the adoption of 0.0011180 g Ag as the electrochemical equivalent of one coulomb. While this value is the legal one and the one ordinarily in use, it is now known to be wrong by at least four units in the last place. *W. D. B.*

Electro-deposition on rotating cathodes. *J. G. Zimmerman. Trans. Am. Electrochemical Soc.* 3, *245* (*1903*). — A burnished deposit of copper can be obtained with a current density of 200 amp/sq. ft. if the peripheral velocity of the cathode be about 1000 ft/min. Nickel can also be precipitated in a polished form from a hot, slightly acid solution. The author believes that the polished look is due to the burnishing effect of the surface friction. *W. D. B.*

Constant voltage and constant current separations. *W. D. Bancroft. Trans. Am. Electrochemical Soc.* 3, *85* (*1903*). — This is an abstract of a paper by Root (Jour. Phys. Chem. 7, 428). In Table I the position of tin is incorrect.

W. D. B.

The use of a mercury cathode in electrochemical analysis. *E. F. Smith. Jour. Am. Chem. Soc.* 25, *884* (*1903*). — A glass beaker with a platinum wire in the side near the bottom is filled with mercury above the wire and made the cathode. Copper, nickel, iron and zinc can easily be precipitated in the mercury from solutions of sulphates or nitrates and the free acids titrated. No reduction of the nitric acid takes place. The halides can be determined by using a platinum gauze anode coated with silver. When the mercury cathode is not used, the resulting alkali can be titrated direct. It seems surprising that a beaker with mercury can be weighed twice in succession to the tenth of a milligram. Iron can readily be separated from uranium by means of a mercury cathode. *W. D. B.*

Metal separations in the electrolytic way. *E. F. Smith. Jour. Am.*

Chem. Soc. 25, *892* (*1903*).—Silver, mercury or copper may be separated from selenium either in an alkaline cyanide solution or in a nitric acid solution. A separation from tellurium can be effected only in a nitric acid solution.

W. D. B.

Notes on the electro-deposition of nickel. *W. McA. Johnson. Trans. Am. Electrochemical Soc.* 3, *255* (*1903*).—The author says that, with proper care, good deposits of nickel can be obtained from cold solutions. The only advantage of the hot solution is that less gas is dissolved in it. The curling of electrolytic nickel sheets is attributed to the formation of nickel hydride and it is said that a much more tenacious nickel is obtained when the depositing is done from a gas-free electrolyte. *W. D. B.*

The electrolytic production of calcium. *J. H. Goodwin. Jour. Am. Chem. Soc.* 25, *873* (*1903*).—The author uses an iron cathode projecting through a copper water-cooled base. The floor of the furnace is made of lime and the electrolyte is calcium chloride. The anode is a disc of Acheson graphite. It is said that this furnace gives a high current efficiency but the actual value is not stated. There is no obvious reason why the chlorine should not recombine with the calcium to a very considerable extent. The working temperature is 950° and a current of 100 amperes passes. *W. D. B.*

The disintegration of the anode. *E. Wohlwill. Zeit. Elektrochemie*, 9, *311* (*1903*).—When a pure copper plate is made anode in a dilute sulphuric acid solution, the surface becomes coated with a fine copper dust, part of which can be rubbed off easily. The amount of this dust varies with the nature of the surface of the electrode and with the current density. While the experiments vary considerably, more dust is formed when the copper surface is cleaned with emery than when it is polished with tripoli or etched with nitric acid. The author refers the phenomenon to the formation and decomposition of cuprous sulphate. In a copper sulphate solution there is much less dust formed because of the solvent action of the copper sulphate. In a cyanide solution there is no change of valence and no anode dust.

To account for the so-called mechanical disintegration of the anode, the author assumes that the current acts on the unchanged anode plate behind the deposited dust. In time, pieces of the corroded plate break off. *W. D. B.*

The influence of some impurities in salt upon the yield of caustic soda by the amalgam process. *J. W. Walker and C. S. Paterson. Trans. Am. Electrochemical Soc.* 3, *185* (*1903*).—The presence of small amounts of potassium, calcium or magnesium chlorides in a sodium chloride solution has little or no effect on the yield of caustic soda in the mercury diaphragm cell. If traces of iron or nickel salts are present in addition, there is a very marked falling off in the yield. No satisfactory explanation for this is offered and the authors make no reference to the action of iron in the sulphuric acid voltameter nor to the effect of nickel and iron on the hypochlorite formation.

W. D. B.

Concentration changes in the electrolysis of brine. *W. H. Walker. Trans. Am. Electrochemical Soc.* 3, *177* (*1903*).—When a sodium chloride solution is electrolyzed in a diaphragm cell, the concentration of sodium as chloride and hydroxide increases in the cathode chamber. The author shows that this increase can be predicted qualitatively from the transference numbers.

W. D. B.

Notes on modern electrolytic copper-refining. *T. Ulke. Trans. Am. Electrochemical Soc.* 3, *219* (*1903*). — A brief account of the methods of electrolytic copper refining, of the improvements made during the last ten years, and of the plants now in operation. *W. D. B.*

Electrolytic production of metallic compounds. *C. F. Burgess and C. Hambuechen. Trans. Am. Electrochemical Soc.* 3, *299* (*1903*). — A discussion of the commercial conditions affecting the electrolytic production of salts of the metals, and a description of a small laboratory plant for the electrolytic production of white lead. *W. D. B.*

Notes on the composition of electroplating solutions. *N. S. Keith. Trans. Am. Electrochemical Soc.* 3, *227* (*1903*). — The ideal conditions for electroplating are that the loss in weight of the anode should exactly equal the gain in weight of the cathode and that there should be no chemical change in the electrolyte. The first of these conditions cannot hold for electrolytic refining under any circumstances, and the second can hold only when the impurities are completely slimed either as metals or oxides. *W. D. B.*

Corrosion of metals by electrolysis. *A. A. Knudson. Trans. Am. Electrochemical Soc.* 3, *195* (*1903*). — The author gives a sketch of experiments made in New York City during the past few years on the stray currents from street railway systems. A map is also furnished which shows the general direction of these currents. *W. D. B.*

Note on corrosion of aluminum. *J. A. Steinmetz. Trans. Am. Electrochemical Soc.* 3, *217* (*1903*). — The free-board plates on the "Defender" were made of a nickel aluminum alloy and were fastened with steel rivets to the manganese bronze hull. As a result of this, the aluminum plates were badly corroded by the salt water. *W. D. B.*

Contributions to the direct measurements of transference numbers. *R. B. Denison. Zeit. phys. Chem.* 44, *575* (*1903*). — The author concludes that Steele's method gives satisfactory results for the simple salts of all the alkali metals except lithium, when account is taken of the electrical endosmose. In a solid gelatine solution the values differ somewhat from those in water; but this difference is said to disappear when the gelatine liquefies. When complexes are formed or when hydrolysis takes place, the results obtained by Steele's method differ from those obtained by Hittorf's. The author thinks that Steele's method gives the more accurate results under these circumstances but his argument is not very convincing. In some cases there is some evidence that the gelatine moves with the cation and it is generally true that solid gelatine decreases the migration velocity of the cation. It seems to the reviewer that the general theory of the transference at the surface of two different solutions is still a bit shaky. *W. D. B.*

The theory of the residual current. *U. Grassi. Zeit. phys. Chem.* 44, *460*

(*1903*). — It seems possible that Salomon's results had been vitiated by convection currents due to the facts that his electrodes were placed vertically and that they hung free in the solution. Experiments were therefore made with a vertical tube, the electrodes filling the cross-section completely. This gave better results but it was not absolutely satisfactory. The solution was then solidified with agar-agar and no further difficulties were encountered.

W. D. B.

Note on electrical endosmose. *W. D. Bancroft. Trans. Am. Electrochemical Soc.* 3, *261* (*1903*). — Since the degree of endosmose varies with the nature of the diaphragm, this factor must be taken into account. In the Hargreaves and Bird process it is essential that the endosmose shall not exceed a certain value. *W. D. B.*

Electrolytic conduction without electrodes. *A. B. Marvin. Trans. Am. Electrochemical Soc.* 3, *347* (*1903*). — The author describes an apparatus for showing the existence of an induced current in an electrolytic circuit.

W. D. B.

An historical review of the storage battery. *H. B. Coho. Trans. Am. Electrochemical Soc.* 3, *159* (*1903*). — A brief sketch of the development of the storage battery. *W. D. B.*

The use of pyroxyline in electric storage batteries. *E. A. Sperry. Trans. Am. Electrochemical Soc.* 3, *169* (*1903*). — The author believes that the peroxide plate must be covered by a protecting envelope if it is to last and to resist the surface wash. To be successful the material of which this envelope is made should have toughness and flexibility, should be very thin, should have the maximum degree of porosity, and should have a certain amount of elasticity to accommodate itself to the creeping or expansion and contraction of the positive. Pyroxyline is a nitrated cheesecloth and satisfies these conditions fairly well. Although explosively inflammable when dry, it will not burn when damp. It will not withstand hydrogen and can therefore only be used on the peroxide plate. *W. D. B.*

Ions and electrons. *L. A. Parsons. Trans. Am. Electrochemical Soc.* 3, *265* (*1903*). — An outline of the electron theory. *W. D. B.*

On the basis of the solution theory. *M. Cantor. Drude's Ann.* 10, *205* (*1903*). — The author starts out by a criticism of Planck and endeavors to show that the hypothesis upon which the deductions of Planck depend does not lead to accurate results. The same is applied to the extended theory of Jahn, both having to do with very dilute solutions. The object of the present work is to develop mathematically a theory applicable to more concentrated solutions. The theory is based on the Helmholtz expression for the E. M. F. of a concentration cell. *H. T. B.*

On the basis of the solution theory. *M. Planck. Drude's Ann.* 10, *436* (*1903*). — This is a reply to M. Cantor (preceding review). The author points out that the criticism made by Cantor of his theory is incorrect. *H. T. B.*

Free ions in aqueous solutions. *W. R. Whitney. Trans. Am. Electro-*

chemical Soc. 3, *101* (*1903*). — A criticism of Olsen's attempt to prove the existence of free ions. "While it is perfectly true that electrochemical phenomena are most readily explained by the assumption of charged ions, and while many investigators are firm in their belief of the actual existence of such charged particles, an experiment actually proving their existence would be of great interest." *W. D. B.*

Molecular force and the electrical charge of the molecule. *M. Reinganum. Drude's Ann.* 10, *334* (*1903*). — The author assumes that neutral molecules possess a positive and a negative charge, localized in definite positions. The size of the charges is that obtained in electrolytic phenomena. After citing various properties and making certain assumptions, he discusses the potential of the molecular force which involves a little gas theory. The application to the solid condition follows and it is shown that the distance between the charges on the molecule is of the order 10^{-9} cm. The paper closes with a short reference to chemical properties. *H. T. B.*

The mechanism of electrochemical reactions. *M. Reinganum. Drude's Ann.* 10, *354* (*1903*). — The author introduces the idea of a double pair of charges on a molecule. The dissociation of a hydrochloric acid molecule then leaves the hydrogen with a positive charge alone and the chlorine atom with a positive and two negative. The reason for this assumption is that the metal atoms appear to hold the negative charges less securely as illustrated in cathode rays and the Zeeman effect.

The electrolysis of silver nitrate between silver electrodes is illustrated, and many points connected with the reaction between metals and metalloids and between acids and bases are considered. *H. T. B.*

An electric test retort. *C. F. McKenna. Jour. Am. Chem. Soc.* 25, *415* (*1903*). — The apparatus consists of a glass globe made in two parts, with a platinum wire inside for heating purposes, and a delivery tube for carrying off the gases. It is intended, primarily, for rapid distillation of small samples of wood, but can be used for other purposes. It is not yet known how long the platinum spiral will withstand the reducing gases formed. *W. D. B.*

Note on a laboratory furnace. *B. McNutt. Trans. Am. Electrochemical Soc.* 3, *367* (*1903*) — The essential feature of this furnace is a crucible made from arc carbons held together by an iron band, the interstices being filled with crushed arc carbons. *W. D. B.*

Insulating materials, a field for the chemists. *M. v. Recklinghausen. Trans. Am. Electrochemical Soc.* 3, *153* (*1903*). — The author classifies and discusses insulating materials under the headings: organic materials, liquid and solid; mixtures of organic and inorganic materials; inorganic materials.

W. D. B.

ACTION OF SODIUM AND POTASSIUM AMALGAMS ON VARIOUS AQUEOUS SOLUTIONS

BY GUSTAVE FERNEKES

INTRODUCTION

In working with magnesium upon different aqueous solutions, Tommasi[1] found that there is a difference in the rate at which hydrogen is liberated. His investigations were of a qualitative character. Solutions of salts of the following formulæ were tried by this investigator: NaCl, KCl, LiCl, NH_4Cl, $CaCl_2$, $BaCl_2$, $SrCl_2$, $FeCl_3$, $FeSO_4$, $CrCl_3$, $NaSO_4$, $CuCl_2$, $CdCl_2$, $PbCl_2$, $HgCl_2$, $PtCl_4$, $AuCl_3$, and $CuSO_4$. G. Lemoine[2] noticed that magnesium liberated hydrogen more rapidly from aqueous solutions of its salts, than from pure water, or solutions of other salts. The same fact was noticed by H. Mouraour.[3] At the suggestion of Prof. Kahlenberg, Mr. O. W. Brown and Dr. H. V. Black made some preliminary experiments in this laboratory for the purpose of comparing the rates at which magnesium liberates hydrogen from various aqueous solutions. They, however, discontinued their work on this subject, and it was then taken up by Prof. Kahlenberg himself, whose results have recently been published.[4]

The question then presented itself to Prof. Kahlenberg whether other metals would act in a similar way towards solutions of their salts, and at his suggestion I undertook to solve this question. Sodium and potassium naturally suggested themselves for such investigations, as both metals decompose water at ordinary temperatures. But on account of the violence of the reaction, and because the metals are so easily oxidized, their amalgams were used. With but few exceptions, which will

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[1] Bull. Soc. Chim. Paris (3) 21, 885–887 (1899).

[2] Comptes rendus, 129, 291 (1899).

[3] Ibid. 130, 140 (1900).

[4] Jour. Am. Chem. Soc. 25, 380 (1903).

be mentioned below, these amalgams have not hitherto been used for this purpose, although a great amount of work has been done to determine the constitution of amalgams.[1] The tendency of most investigators seems to have been to consider amalgams as definite chemical compounds rather than as solutions of the metals in mercury.

Baeyer[2] seems to have been the only one who made investigations as to the rate at which hydrogen is evolved from various aqueous solutions by the action of sodium amalgam. He investigated the behavior of solutions of sodium hydroxide, sodium sulphate, sodium chloride, sodium carbonate, and the sodium salts of the following organic acids: isophthalic acid, succinic acid, benzoic acid, acetic acid, tartaric acid, citric acid, and malic acid. He claims no great quantitative accuracy for his results, however, and simply gives the relative rates without any further explanation how the experiments were made. Baeyer found that the order of action was as follows, the substance causing fastest action being mentioned first:

Sodium isophthalate
" succinate
" benzoate
" hydroxide (ten drops)
" hydroxide (one drop)
" acetate
Sodium sulphate
" chloride
" carbonate
" tartrate
" citrate
" malate

He found that water acts slowly at first, then faster, and at great concentrations of sodium hydroxide slower again. Sodium chloride, sodium sulphate, and sodium acetate act like water, whereas sodium carbonate retards the action. Of the organic salts Baeyer says: —

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[1] On the constitution of amalgams see: Guntz. Comptes rendus, 122, 465-467 (1896); 131, 182-184 (1900); V. Merz and Weith. Ber. chem. Ges. Berlin, 14, 1438 (1881); F. Haber. Zeit. phys. Chem. 41, 399 (1902); G. Meyer. Zeit. phys. Chem. 7, 477 (1891); J. Schumann. Wied. Ann. 43, 101-125 (1891); Zeit. phys. Chem. 3, 443 (1889); Aug. Schoeller. Zeit. Electrochemie, 5, 259 (1898); W. Kerp. Zeit. anorg. Chem. 17, 284-309 (1898); M. Le Blanc. Zeit. phys. Chem. 5, 467 (1888); Rud Boettger. Jour. prakt. Chem. 1, 303 (1834); 3, 283 (1836); Georg Langbein. Zeit. phys. Chem. 36, 746 (1900); Gouy. Jour. de Phys. 4, 320-321 (1895).

[2] Liebig's Ann. 251, 265 (1888).

"Der negative Phenylrest scheint beschleunigend zu wirken, da Benzoësäure dreimal soviel Wasserstoff entwickelt als essigsaures Natron. Am Auffallendsten ist aber der Gegensatz zwischen Bernsteinsäure einerseits und der Aepfel-, Wein-, und Citronensäure andrerseits welche zehnmal weniger Gas entwickelt als erstere. Dieses Verhalten scheint mir den Schlüssel für den räthselhaften Vorgang zu liefern.

"Diejenigen Säuren welche wie die Aepfelsäure ein alkoholisches Hydroxyl enthalten, befinden sich bei Gegenwart von Natronlauge vermuthlich als basische Salze in Lösung wodurch die Fähigkeit des Salzes Natrium aufzulösen verringert wird Worauf diese Fähigkeit beruht ist mir unklar, da das passive Verhalten der Salze unorganischen Säuren die Erklärung des Vorganges durch Dissociation unwahrscheinlich macht."

In 1893, Svante Arrhenius[1] in electrolyzing aqueous solutions of salts of alkali metals, found that some time elapsed before hydrogen was given off from the amalgam formed at the cathode. From the standpoint of his theory, he attributed this to the ions of sodium or potassium in the solution which would hinder the entrance of more of these metals into solution in form of ions.

EXPERIMENTAL WORK

In studying the rate of reactions, the volumes of hydrogen liberated at given intervals of time were measured. This is a method which is common in measuring the rate of chemical reactions in which a gas is evolved.[2] The experiments were performed in the following way. Two hundred cubic centimeters of solution were poured into beakers 14 cm high and 9 cm in diameter. These beakers contained evaporating dishes 7 cm in diameter, on which were set eudiometer tubes whose upper ends were provided with stop-cocks above which the tubes were widened out so as to form funnels. These tubes also had small funnels inserted into their lower end by means of

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[1] Zeit. phys. Chem. 11, 805 (1893).

[2] Millon. Ann. Chim. Phys. (3) 6, 73 (1842); W. Spring. Zeit. phys. Chem. 2, 13 (1888); Bredig. Ibid. 39, 125 (1902).

rubber stoppers. By suction, the eudiometer tubes were filled almost to the top with the solution, and 5 cc of sodium amalgam was placed in the upper portion of the tube which had been thoroughly dried. The stop-cock was now opened and the amalgam allowed to drop through the solution in the eudiometer into the evaporating dish, and the eudiometer was then quickly filled with solution by suction at the upper end of the tube as before. Bubbles of gas would be prevented from getting to the top before a reading could be taken. With a little practice this method gave fairly quantitative results. Some factors which might seem to be a source of error in these experiments must be mentioned. Small quantities of air might be carried down mechanically by the amalgam. Experiments performed with mercury alone showed that this quantity was very small. The amount was 0.02 of a cubic centimeter, which was as small a reading as could be estimated on the eudiometers employed. Then the fact must be considered that the height of the column of solution in the eudiometer tube exerts a downward pressure. The column is 4.4 cm high, which corresponds to about 3 mm of mercury. All readings are therefore 0.08 of a cubic centimeter too large. The solubility of the hydrogen also influenced the readings. Finally, slight variations of temperature could not be avoided. A change in temperature of 1° C might change the total volume of 20 cc of gas by about 0.08 cc. It can be seen from these data that the maximum error on 20 cc of gas evolved could amount to 0.1–0.15 cc. As the solution of different salts in most cases showed a greater variation than this, they must be looked upon as real differences in the rates of liberation of hydrogen.

To prevent bubbles from adhering and accumulating on the sides of the apparatus, the funnels, evaporating dishes and eudiometers were treated with a chromic and sulphuric acid mixture.

Impurities on the surface of the amalgam were carefully guarded against, although impurities purposely introduced had no marked effect on the rate of liberation. The mercury used was obtained from Bausch and Lomb (Rochester, N. Y.) and was marked C. P. redistilled. It was cleaned before using according to the method of Brühl.[1] The sodium was obtained from Schuchardt and was scraped free from oxide before using. The sodium amalgam was prepared by throwing pieces of sodium upon mercury in a covered porcelain casserole and then shaking until combination took place. A rather strong amalgam was first made and this then diluted until 5 cc liberated 23 cc of hydrogen from water, i. e., 5 cc contained 0.0472 g of sodium. After being thus prepared, the skin of oxides was scraped off the top with a piece of filter-paper, and the amalgam was then poured into bottles which were well stoppered and kept under a bell-jar in a dry atmosphere. In this way the amalgam can be kept indefinitely without change of concentration. The potassium amalgam was prepared in a similar manner. When the amalgam was at the bottom of the evaporating dish, it had a diameter as measured by a pair of dividers of about four centimeters. This would give a thickness of 3.2 mm to this layer as calculated by the formula $h = \frac{v}{r^2\pi}$, where h = height, v = volume, and r = radius. The evolution of hydrogen was watched and readings were taken every five minutes. Two or three samples of the same solution were run side by side in different apparatuses and only slight variations were noticed, which must be attributed to the causes mentioned above. In all cases where salt solutions were used, a little frosted white area was noticed on the amalgam from which the hydrogen seemed to emanate, and this was larger the more rapid the reaction. In concentrated potassium hydroxide or pure sodium hydroxide no such area was observed. It is very probable that these areas are simply small bubbles of hydrogen adhering to the mercury.

The salts of the inorganic acids used were obtained from various sources. From Kahlbaum were obtained: K_2SO_4, $NaCl$, KCl, KNO_3, KBr, $SrCl_2$, Na_2HPO_4, $Na_2P_2O_7$. From Schuchardt: Na_2SO_4, $Na_2B_4O_7$, $NaBr$, KI, NaI, ordinary $NaOH$

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[1] Ber. chem. Ges. Berlin, 12, 204 (1879).

by alcohol, $CaCl_2$, $BaCl_2$, Na_3AlO_3, CH_3COONa, KOH. The sodium hydroxide from metallic sodium was from Eimer and Amend.

The results obtained are presented in the tables which follow. To facilitate comparison and to show the general trend of the results at a glance, they have also been plotted in the form of curves, ordinates indicating minutes and abscissæ the number of cubic centimeters of gas evolved. In most cases the readings were taken every five minutes. Normal, one-tenth normal and saturated solutions were employed. In all tables the numbers indicate the volume of hydrogen gas evolved in cubic centimeters. The term normal solution as used here always means a solution containing one gram equivalent per liter.

Table I with accompanying Fig. 1 represents results obtained by the action of sodium amalgam on solutions of sodium salts. The curve for water is also shown for the purpose of comparison. Among the salts which acted faster than water are: Na_3AlO_3, $NaHCO_3$, Na_2HPO_4, Na_2SO_3, and NaOH. Those acting slower

TABLE I.

Min.	NaCl sat. cc.	NaCl *n*/1 cc.	NaCl *n*/10 cc.	NaI sat. cc.	NaBr *n*/1 cc.	NaBr *n*/10 cc.	NaOH *n*/1 cc.	NaOH *n*/10 cc.	Na_2HPO_4 sat. cc.
5	—	0	—	—	0.1	—	2.0	2.5	—
10	—	—	—	—	0.5	—	16.0	19.0	—
15	—	0.1	0.4	—	0.7	0.5	22.0	—	1.2
20	—	0.3	—	—	1.0	—	—	—	—
25	—	0.5	—	—	1.4	—	—	—	—
30	0.7	0.6	1.4	0.6	1.8	1.0	—	—	2.2
35	—	0.8	—	—	2.3	—	—	—	—
40	—	1.0	—	—	2.9	—	—	—	—
45	—	1.1	3.0	—	3.4	1.7	—	—	3.6
50	—	1.2	—	—	4.4	—	—	—	—
55	—	1.3	—	—	5.1	—	—	—	—
60	1.5	—	4.8	0.9	5.8	2.5	—	—	5.6
65	—	—	—	—	6.4	—	—	—	—
70	—	—	—	—	7.0	—	—	—	—

TABLE I.—(*Continued.*)

Min.	Na_2HPO_4 n/1. cc.	Na_2HPO_4 n/10. cc.	Na_2SO_4 sat. cc.	Na_2SO_4 n/1 cc.	Na_2SO_4 n/10 cc.	Na_2SO_3 cc.
5	0.5	0.1	—	0	—	0.9
10	1.0	0.8	—	—	—	2.0
15	1.5	1.2	—	0.3	0.3	4.5
20	2.0	1.5	—	0.4	—	—
25	3.0	2.0	—	0.5	—	14.0
30	4.0	2.4	—	0.6	0.8	18.0
35	4.5	—	—	0.8	—	20.2
40	5.0	—	—	1.1	—	—
45	5.5	—	—	1.3	1.5	—
50	6.0	—	—	1.5	—	—
55	—	—	—	1.7	—	—
60	—	—	0.4	2.0	2.0	—
65	—	—	—	2.3	—	—
70	—	—	—	2.6	2.9	—

Min.	$Na_2B_4O_7$ n/10. cc.	$Na_4P_2O_7$ cc.	Na_3AlO_3 cc.	NaOH pure cc.	$NaHCO_3$ n/1. cc.	H_2O. cc.
5	0.2	—	0.5	—	1.0	0.2
10	0.5	—	1.0	—	1.8	0.6
15	0.8	—	1.5	—	2.2	0.9
20	1.0	—	2.0	—	2.8	1.2
25	1.2	—	2.5	—	—	1.6
30	1.5	0.4	3.0	—	3.8	2.2
35	1.8	—	3.5	—	4.3	2.7
40	2.0	—	3.9	—	4.7	3.2
45	2.2	—	4.4	—	4.9	4.0
50	2.5	—	4.8	—	5.2	4.5
55	2.7	—	5.2	—	5.6	5.2
	—	0.8	5.7		Stop'd	
	—	—	6.0		at	
60	—	—	6.5	0.3	9.5	6.0
65	—	—	—	—	—	—
70	—	—	—	—	—	—

than water are: NaBr, $Na_2B_4O_7$, Na_2SO_4, NaCl, $Na_4P_2O_7$, NaI, CH_3COONa, and pure NaOH from metallic sodium.

The solutions of salts acting slower than water will be taken up first. The slowest of these are the saturated solutions of sodium sulphate and the solution of sodium hydroxide containing 50 g to a liter. Only about 0.2 of a cubic centimeter of hydrogen was evolved at the end of an hour in these cases. Next to these stand the saturated solutions of sodium iodide and sodium pyrophosphate, which gave about 1 cc each in one hour. Saturated sodium chloride and normal sodium chloride liberated 1.5 cc and 1.3 cc of hydrogen respectively at the end of the same period. Sodium acetate stands next in the list. Normal sodium sulphate and one-tenth normal sodium sulphate again fall very close together, both liberating 2 cc of hydrogen at the end of an hour. The next in order is a tenth-normal sodium borate solution. One-tenth normal sodium bromide and sodium chloride solution stand nearest to water.

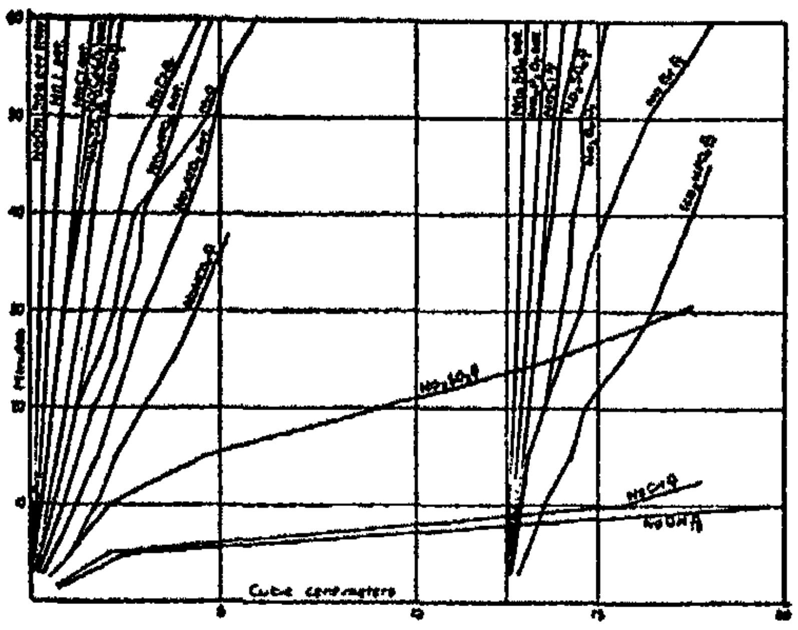

Fig. 1

Action of sodium amalgam on the aqueous solutions of sodium salts

Among those salts acting faster than water are the acid salts, normal and one-tenth normal sodium acid phosphate solutions, sodium acid carbonate and also sodium sulphite, normal and one-tenth normal sodium hydroxide. One would expect the acid salts to act faster on account of the replaceable hydrogen atom, but this explanation can not hold in the case of sodium sulphite. Sodium hydroxide is an anomaly in the list of these solutions. It is seen that sodium hydroxide from metallic sodium acts very slowly, in fact as slowly as saturated sodium sulphate solution; whereas sodium hydroxide from alcohol acts extremely fast, even exceeding that of a one-hundredth normal solution of hydrochloric acid (see Fig. 3). An explanation of

TABLE II.

Min.	KCl *n*/1 cc.	KBr *n*/1 cc.	KBr *n*/10 cc.	KI *n*/1 cc.	KI *n*/10 cc.	K_2SO_4 *n*/10 cc.
5	0	—	0	0	—	—
10	—	—	0.2	0.1	—	—
15	—	—	0.4	0.2	0.6	—
20	—	—	0.6	0.3	—	—
25	0.1	—	0.8	0.5	—	—
30	0.2	0.3	0.9	0.7	1.5	0.2
35	0.3	—	1.0	0.8	—	—
40	0.4	—	1.1	0.9	—	—
45	0.5	0.6	1.3	1.0	2.4	—
50	0.6	—	1.5	1.1	—	—
55	0.7	—	—	1.3	—	—
60	0.8	0.8	—	1.5	3.4	0.5
65	—	—	—	—	—	—
70	—	—	—	—	—	—

Min.	K_2SO_4 *n*/1 cc.	K_2SO_4 sat. cc.	$KHCO_3$ cc.	H_2O. cc.	KOH *n*/1 cc.
5	0	—	0.9	0.2	—
10	—	—	1.6	0.6	—
15	—	—	2.5	0.9	—
20	—	—	3.1	1.2	—
25	0.1	—	—	—	—
30	0.12	—	4.0	1.6	—
35	0.2	—	4.6	2.2	—
40	0.25	—	5.2	2.7	—
45	0.3	0.2	5.8	3.2	—
50	0.4	—	6.0	4.0	—
55	—	—	6.2	4.5	—
60	—	0.3	6.8	5.2	—
—	—	—	—	—	—
—	—	—	—	—	—

this phenomenon will be given later. It is seen from these curves that in general the greater the dilution the faster the action, although a tenth-normal solution does not act ten times as fast as a normal one. In some cases in fact there is very little difference observable between the action of the saturated, normal and tenth-normal solutions; such a case is sodium sulphate for instance. In other cases the difference asserts itself more distinctly, as is the case with sodium chloride and sodium bromide.

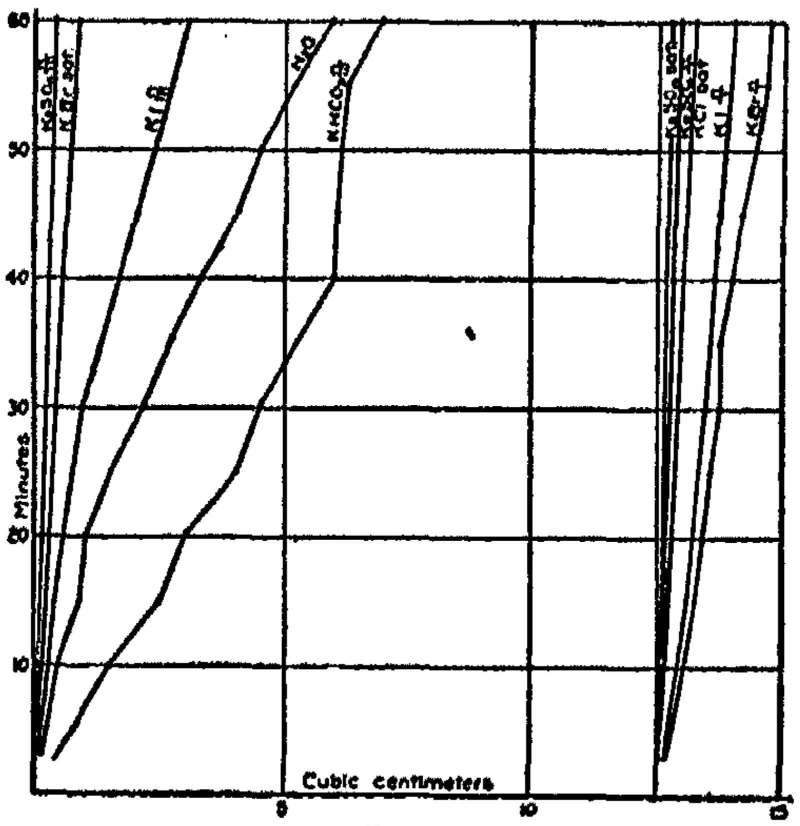

Fig. 2

Action of sodium amalgam on aqueous solutions of potassium salts

Table II and Fig 2 represent the results of the action of sodium amalgam on solutions of potassium salts. Here again the acid salt, potassium acid carbonate, acts faster than water. Potassium iodide, bromide and sulphate act slower than water. Normal, tenth-normal and saturated solutions of potassium sulphate again act with about the same degree of readiness. Potassium chloride, iodide and bromide follow each other successively, the first being a saturated and the other two normal solutions of these salts. There is again a distinct difference between normal and tenth-normal potassium iodide, and also between saturated and normal solutions of potassium bromide. Thus it appears that the bromides seem to act fastest, the chlorides somewhat slower, and finally the iodides and sulphates act very slowly. Solutions of equivalent strength of sodium sulphate, bromide and chloride seem to correspond very closely to those of potassium sulphate, iodide, bromide and chloride of the same strength. The similarity of the salts will fully account for this phenomenon. In solutions, potassium sulphate would combine with water with the same degree of tenacity as sodium sulphate, although a slight difference might be expected.

TABLE III.

Min.	HCl *n*/100 cc.	HCl *n*/500 cc.	HCl *n*/1000 cc.	NH_4OH *n*/1 cc.	HNO_3 *n*/100 cc.	HNO_3 *n*/1000 cc.	$CaCl_2$ *n*/4 cc.	$SrCl_2$ *n*/4 cc.	$BaCl_2$ *n*/4 cc.
5	1.9	0.5	0.3	—	0.6	0.1	0.9	0.2	—
10	2.7	1.2	0.7	1.0	0.9	0.5	3.0	1.1	0.4
15	4.0	3.0	1.1	2.0	1.4	0.9	4.2	1.9	0.6
20	6.0	4.8	2.0	4.5	1.9	1.2	5.1	2.1	0.9
25	11.0	7.0	2.7	6.0	—	1.5	6.2	2.5	1.0
30	18.0	10.0	3.5	7.7	3.1	1.7	6.9	3.0	1.5
35	19.0	12.0	4.5	9.0	—	2.0	8.0	3.5	2.0
40	—	14.0	5.8	10.0	4.7	—	—	4.0	2.7
45	—	16.3	7.1	10.6	5.5	3.0	11.7	4.4	3.3
50	—	18.0	8.5	11.6	6.2	—	—	—	4.0
55	—	—	10.2	12.5	6.9	4.0	—	—	4.5
60	—	—	11.3	13.5	7.5	—	—	—	—
65	—	—	—	—	—	—	—	—	—
70	—	—	—	—	—	—	—	—	—
75	—	—	—	—	—	—	—	—	—

Table III and Fig. 3 represent the results obtained with still other solutions which were treated with sodium amalgam. Nitric and hydrochloric acids were tried. The former was reduced and did not give 23 cc of gas. One-hundredth normal hydrochloric acid acted even slower than normal sodium sulphite. This shows that even though a salt might contain a very slight excess of acid as an impurity, it would make very little difference in its rate of reaction. One-fourth normal solution of calcium, strontium and barium act slower following the increase of their atomic weights. The rapidity with which they act is not proportional to their atomic weights, however. These results are influenced by the formation of the difficultly soluble hydroxides.

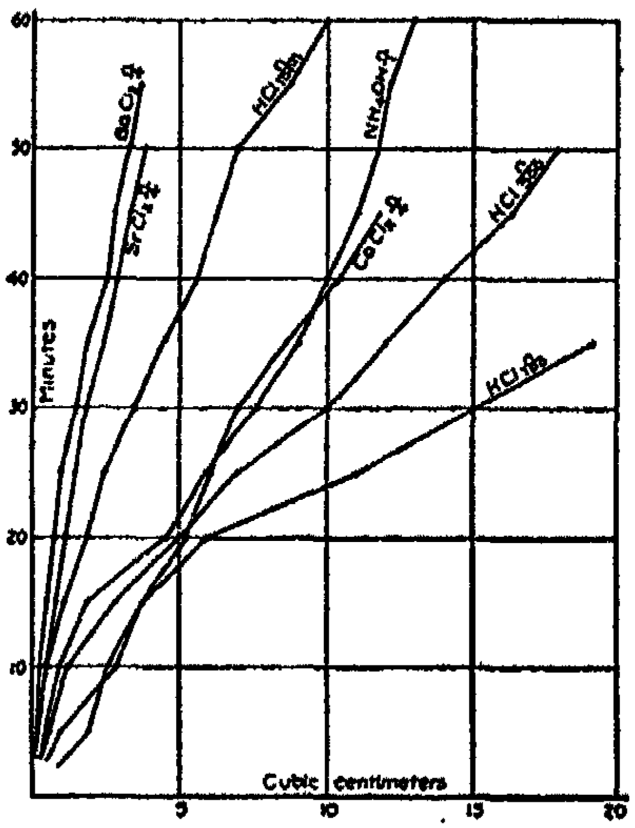

Fig. 3
Action of sodium amalgam on solutions of various other compounds

The only other curve represented in this chart is that of ammonia. A normal ammonia solution acts faster than water, but very much slower than a sodium hydroxide solution of equivalent strength.

Table IV and Fig. 4 present the results yielded by the action of potassium amalgam on various solutions. Normal and tenth-normal sodium hydroxide purified by alcohol again acted faster than all the others. Water was acted upon more violently by potassium amalgam than by sodium amalgam of the same strength. Here again solutions of the sulphates acted slower than those of the iodides or chlorides. It might be said that potassium amalgam acts more violently on most solutions than does sodium amalgam. The most interesting curves in these figures are the ones which represent the action of ordinary sodium

TABLE IV.

Min.	NaCl *n*/1 cc.	NaCl *n*/10 cc.	Na_2SO_4 *n*/1 cc.	Na_2SO_4 *n*/10 cc.	NaOH *n*/1 cc.	NaOH *n*/10 cc.	Na_2HPO_4 *n*/1. cc.	KCl *n*/10 cc.	KI *n*/1. cc.
5	0.2	0.3	0.2	0.2	—	0.5	—	0.5	—
10	0.5	0.7	0.5	0.5	—	3.5	—	1.1	—
15	1.0	1.2	0.7	1.0	9.3	10.1	0.4	1.5	0.3
20	1.5	2.5	1.0	1.7	—	20.1	—	2.9	—
25	2.0	3.0	1.1	2.5	—	—	—	4.3	—
30	2.6	4.0	1.4	3.2	20.0	—	1.0	4.8	1.0
35	3.9	4.8	1.7	—	—	—	—	5.2	—
40	4.7	5.7	—	—	—	—	—	5.7	—
45	5.5	6.2	—	—	—	—	1.6	6.7	1.5
50	—	—	—	—	—	—	—	—	—
55	—	—	—	—	—	—	—	—	—
60	—	—	—	—	—	—	2.0	—	1.7
65	—	—	—	—	—	—	—	—	—
70	—	—	—	—	—	—	—	—	—
75	—	—	—	—	—	—	2.3	—	2.0

Min.	KOH *n*/1 cc.	K_2SO_4 *n*/10 cc.	K_2SO_4 *n*/1 cc.	$KHCO_3$ *n*/10 cc.	H_2O. cc.
5	—	0.2	—	—	4.0
10	—	0.3	—	—	7.0
15	—	0.4	—	0.2	9.5
20	—	0.5	—	—	13.0
25	—	0.6	—	—	15.0
30	0.3	0.8	0.1	1.0	16.6
35	—	1.1	—	—	—
40	—	1.3	—	—	—
45	0.5	—	1.2	1.5	—
50	—	—	—	—	—
55	—	—	—	—	—
60	0.9	—	0.4	2.4	—
65	—	—	—	—	—
70	—	—	—	—	—

hydroxide solution on both sodium and potassium amalgams. As has been mentioned before, there is little or no action of these amalgams on a solution of pure sodium hydroxide prepared from metallic sodium. The fact that sodium hydroxide from metallic sodium retards the action, and sodium hydroxide purified by alcohol hastened the evolution of hydrogen was somewhat puzzling, and so analyses of both sodium hydroxides were made, which gave the following results:

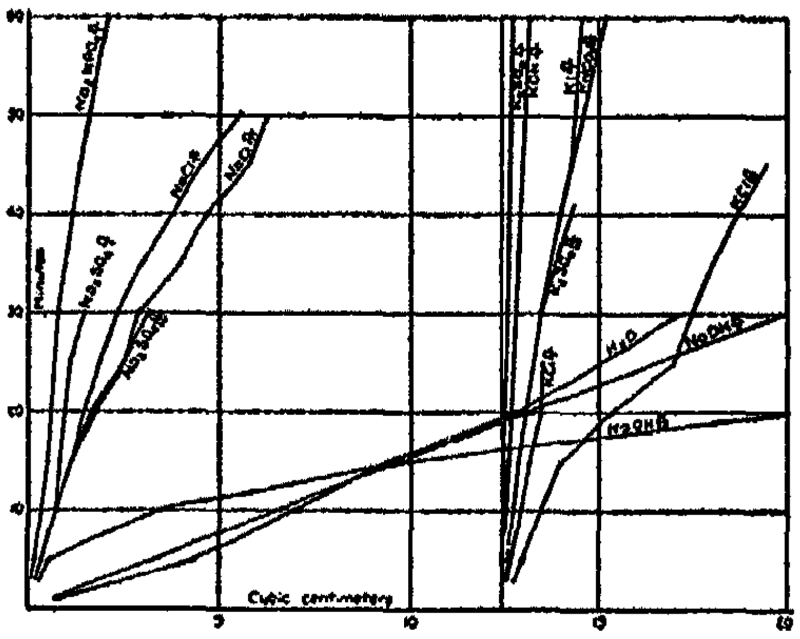

Fig. 4
Action of potassium amalgam on solutions of potassium and sodium salts

Sodium hydroxide purified by alcohol		Sodium hydroxide from metallic sodium
NaOH	85.31 %	90 %
Al$_2$O$_3$	1.75	none
CaO	0.26	none
FeO	trace	trace
SO$_3$	trace	none
Cl	trace	none
Heavy metals	none	none

Various impurities were now purposely introduced into the solution of sodium hydroxide from metallic sodium to see whether they would accelerate the reaction. The chlorides of aluminum, calcium and iron (both ferrous and ferric) were successively introduced into the solution, as was also sodium sulphite. The addition of iron salts increases the rapidity of the action somewhat, although this increase is so slight that it does not account for the enormous rate observed with sodium hydroxide purified by alcohol. Small quantities of sodium sulphite introduced had little effect. A normal solution of the latter salt acted rather vigorously, but still very much slower than a solution of sodium hydroxide (purified by alcohol).

At this point Prof. Kahlenberg suggested another line of work which diverted my attention from the above work for a time. On inspecting the list of substances tried by me, he noticed that it contained but few organic compounds. The solutions of organic compounds that had been tried, such as aqueous solutions of amyl alcohol, ethyl alcohol, glycerine and cane-sugar (see tables that follow) were acted upon much more rapidly by sodium amalgam than was pure water. The fact that amyl alcohol which is not copiously soluble in water, nevertheless showed an increased activity suggested that other organic compounds which are very slightly soluble in water might produce a similar acceleration of the chemical action in question; and so a goodly number of organic substances that are but very slightly miscible with water were tested.

The following compounds employed were obtained from Schuchardt: methyl alcohol, propyl alcohol, glycerine, grape-sugar, cane-sugar, milk-sugar, dextrine, pentane, amylene, paraffine, M. P. 30° to 37° C, benzene, toluene B. P. 110° at 744 mm, *p*-xylene B. P. 136.5° at 744 mm, naphthalene, thymol, cumenol, menthol, camphor, terpineol, acetonitrile, tri-propylamine, butylamine, di-amylamine, aniline B. P. 185°, toluidine B. P. 195.5° at 151 mm, diphenylamine, dibenzylamine, benzamide, benzylamine, pyridine, quinoline, blood albumen and egg albumen.

From Kahlbaum were obtained: ethyl alcohol, amyl alcohol, acetone, hexane, petroleum ether, phenol, borneol, mesitylene, and naphthylamine. The acetanilide was of Merck's manufacture, and the carbon bisulphide came from Bausch and Lomb. The water used in these experiments was distilled from a tin-lined copper still of about eight liters capacity and condensed in a block-tin spiral. Barium hydrate was added to the water before it was distilled. This would combine with the carbon dioxide and also liberate the ammonia which would be contained in the first 300 to 400 cc of distillate. The water would also be free from any grease. The importance of the latter fact will become apparent from the data that follow below.

The solutions were usually made up in the afternoon and allowed to stand over night. The experiments were made the next morning. The substances thus remained in contact with the water for 16 to 18 hours. While working up the solutions they were frequently shaken. The shaking was invariably repeated before using them. Paraffine and vaseline were melted just before pouring them into the water. Many of the results found were confirmed by Mr. F. L. Shinn. Duplicates and sometimes three samples of the same solution were run side by side. The results of the different samples agreed very closely, and the average of the values obtained is given in the tables. It might be well to add that the physical properties of these solutions were of course not appreciably different from those of pure water. The viscosity, surface tension (by Traube's method) and the electrical conductivity were tested, as were also the refractive power and the rotatory power, though the refractometer and polariscope are of course less sensitive instruments, relatively, and it was not to be expected that such very dilute solutions as here used could be distinguished from pure water by means of these.

Table V and Fig. 5 represent results obtained with solutions of hydrocarbons on sodium amalgam. The solutions were prepared by shaking up the water with a great excess of the hydrocarbon. A glance at Table V shows that all the solutions act faster on the amalgam than pure water. It may be observed further that in most cases the rapid action seems to start after the lapse of five minutes, and in some of the cases ten, fifteen, or even more minutes are necessary, before rapid action begins. Solutions of hexane, terpineol,[1] heptane, and xylene act more rapidly after five minutes. Solutions of naphthalene, petroleum

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[1] This substance is a terpene hydrate and ought, strictly speaking, not be classed as a hydrocarbon.

TABLE V.

Hexane	Terpineol	Heptane	Naphthalene	Petroleum ether	Benzene
0.9	0.7	0.5	0.3	0.4	0.9
5.4	3.9	1.6	1.5	1.0	2.5
11.0	10.5	5.5	3.5	2.5	4.0
15.5	—	10.3	7.5	5.0	6.0
18.0	18.6	14.8	10.5	8.8	8.5
20.7	20.5	17.8	14.0	11.0	11.0
21.3	—	19.9	16.0	13.0	13.0
—	—	—	17.8	15.0	15.0
—	—	—	19.3	—	17.0
—	—	—	—	—	—
—	—	—	—	—	—
—	—	—	—	—	—

Toluene	Xylene	Paraffine	Mesitylene	Vaseline
0.7	0.5	0.2	0.2	0.2
1.8	1.0	0.8	0.6	0.65
2.7	3.0	1.5	0.8	1.1
3.7	—	2.5	1.1	1.7
4.9	—	6.0	1.8	2.4
6.0	—	9.0	3.4	3.3
6.7	12.9	11.2	5.2	4.2
7.5	14.2	15.2	6.5	5.2
—	15.9	17.0	9.0	6.2
9.2	17.0	—	11.5	7.2
10.5	18.2	—	13.8	8.3
11.6	—	—	15.8	9.0
—	—	—	—	1.00

ether and benzene do not show an increase of action until ten minutes have elapsed.

A solution of paraffine began to act rapidly after twenty minutes; one of mesitylene after twenty-five, and vaseline after thirty minutes. Toluene gives a curve which is very nearly a straight line, althouhg it has a slight bend after the five minute mark. The increase of action can be readily seen (Fig. 5) by the sudden bend in the curves. After this bend the curve continues in the new direction until with the exhaustion of the amalgam it again makes a sudden bend upwards.

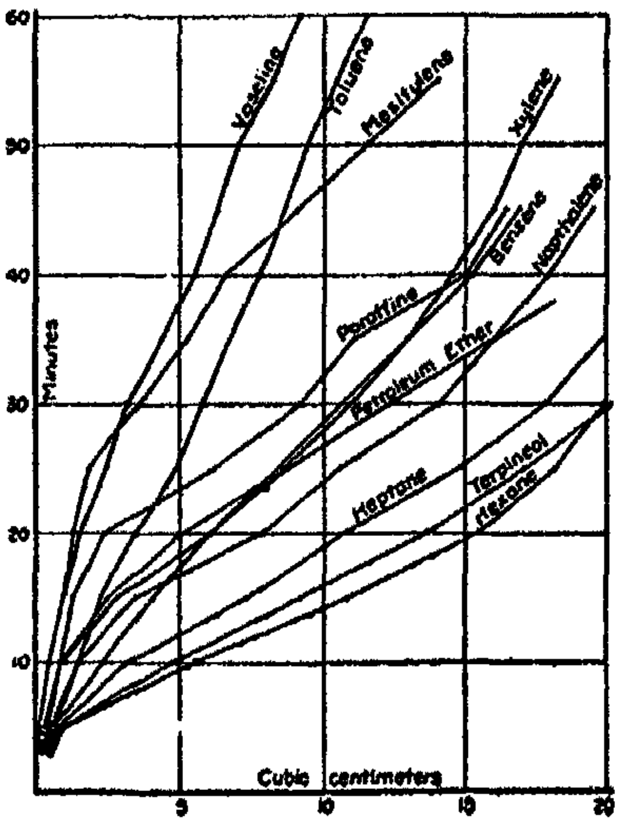

Fig. 5
Saturated aqueous solutions of hydrocarbons

Table VI and Fig. 6 show the results obtained by the action

TABLE VI.

Min.	Hexane cc.	Naphthalene cc.	Heptane cc.	Terpineol cc.	Toluene cc.	Mesitylene cc.
5	1.0	0.8	0.2	0.5	0.2	0.2
10	4.0	2.9	1.0	2.5	1.9	0.5
15	7.0	5.0	2.4	4.0	1.6	1.0
20	10.0	8.0	5.0	5.5	2.6	1.5
25	13.5	10.0	—	7.0	3.5	2.0
30	16.0	13.0	10.0	9.0	4.5	2.5
35	18.0	15.5	13.0	11.5	5.5	3.0
40	—	17.5	15.5	14.0	6.2	3.5
45	—	—	17.0	16.0	8.6	4.0
50	—	—	—	—	7.1	5.0
55	—	—	—	—	7.5	5.5
60	—	—	—	—	—	—

of half-saturated solutions of the same hydrocarbons on sodium amalgam. These solutions were made up in the following manner: a liter of water was saturated with the hydrocarbon by constant shaking for some time. The hydrocarbon was then allowed to collect on the surface of the liquid, and then separated from it by means of a separating funnel. Five hundred cubic centimeters of this solution thus saturated was then diluted up to a liter. The strength of these solutions was then one-half that of the saturated solutions. The action of these half-saturated solutions on sodium amalgam was in all cases slower than was the action of saturated solutions. In most cases the rate of liberation of hydrogen was more than half as fast as in saturated solutions. A half-saturated solution of terpineol, however, liberated even less than half the quantity of hydrogen that was liberated by a saturated solution of the same compound at the end of the same period of time. The curves do not follow each other in the same order as in Fig. 5. A saturated solution of terpineol acts faster than a saturated solution of heptane or naphthalene. On comparing half-saturated solutions of the

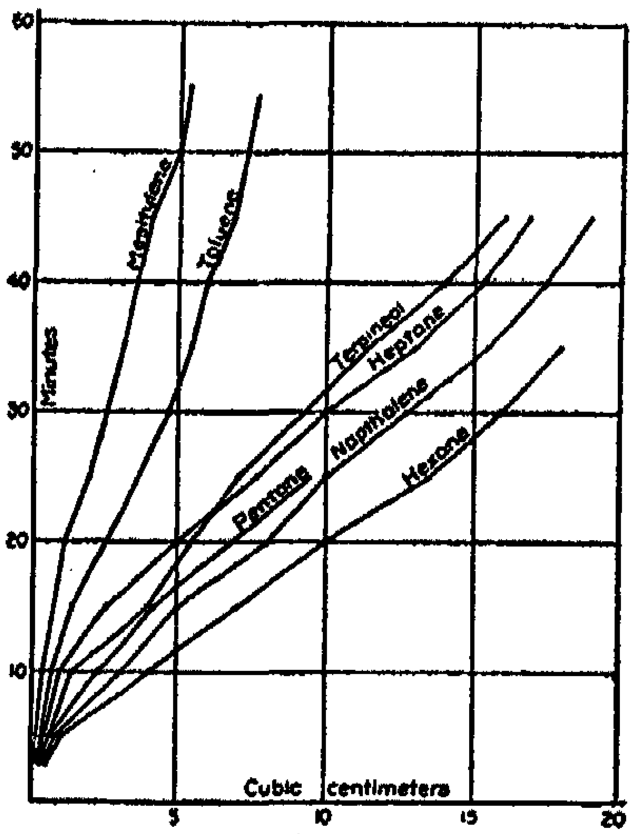

Fig. 6

Action of sodium amalgam on half-saturated solutions of hydrocarbons same compounds it will be observed that a solution of terpineol acts slower than solutions of naphthalene or heptane. The curves representing the results for solutions of toluene and mesitylene follow in the same order in Fig. 6 as in Fig. 5.

The results in these two tables very strongly favor the view that these hydrocarbons are actually in solution. The presence of a certain quantity of the hydrocarbon in the water increases the rate of reaction on the sodium amalgam. If only one-half the concentration of the hydrocarbon is used in the water we might expect this solution to act more nearly with the rate that pure water acts. Further it might be expected that the action would be one-half as rapid as with the saturated solution, if we compare the rates of both the saturated and half-saturated solutions with water. All solutions represented in Table VI satisfy the first requirement, i. e., they all act slower than saturated solutions of the same hydrocarbons. The second requirement is, however, only approximately satisfied. The rate of action is sometimes greater, and in a few instances half that of the concentrated solutions.

Table VII and Fig. 7 present results obtained by using amines and various organic compounds containing oxygen. The amines are placed at the right-hand side of the figure. The solutions used were all saturated unless otherwise stated. Glycerine solution containing four molecules to a liter acts extremely fast, the action starting rapidly from the very beginning. Amyl alcohol and methyl alcohol solutions (the latter containing two gram-molecules per liter) show a slight bend in the curve which means an initial slow action. The same is true of ethyl alcohol containing four gram-molecules per liter. Methyl alcohol with 200 g per liter acts very much slower than the same solution containing two molecules per liter. It is comparable with the sodium salts of inorganic acids which have already been discussed. One would expect propyl alcohol to act like methyl and ethyl alcohols on account of its similarity to these. Different concentrations of propyl alcohol in water were, however, not tried. Ether acts extremely fast. The total amount of gas evolved in this case was greater on account of the vapor pressure at the temperature of the experiment. Solutions of

TABLE VII.

Ether (Sat.)	Glycerine 4 mols/liter	Amyl alcohol (Sat.)	Methyl alcohol 2 mols/liter	Thymol	Cumenol	Camphor	Ethyl alcohol 4 mols/liter
1.4	4.0	3.3	1.0	0.9	0.2	0.3	0.6
4.0	8.0	7.5	—	3.2	—	0.7	1.5
9.5	12.0	12.0	9.0	7.2	—	1.2	3.0
16.0	15.5	15.5	13.5	10.7	2.5	2.7	4.0
21.0	18.5	18.5	17.7	13.8	4.0	5.0	5.2
—	20.7	21.0	20.5	16.2	7.0	7.6	6.8
—	—	—	—	17.2	10.2	9.2	8.5
—	—	—	—	—	13.0	12.0	10.8
—	—	—	—	—	16.5	13.8	12.5
—	—	—	—	—	—	16.5	—
—	—	—	—	—	—	17.6	—

Methyl alcohol 200 g/liter	Menthol	Phenol	H_2O	Propyl alcohol 200 g/liter	Xylidine	Toluidine	Aniline
1.2	0.4	0.7	0.2	0.2	0.2	0.1	0.3
2.0	1.0	1.4	0.6	0.3	0.5	0.6	0.7
2.8	1.4	2.1	0.9	0.4	0.9	0.9	1.1
3.5	1.7	2.7	1.2	0.5	1.2	1.3	1.7
4.7	3.0	3.4	1.6	0.7	1.6	1.9	2.3
6.0	5.5	4.1	2.2	0.8	1.8	2.1	2.7
13.0	6.9	4.5	2.7	0.9	2.2	2.5	3.2
—	—	5.2	3.2	1.0	2.7	3.2	4.0
—	—	5.9	4.0	1.1	3.1	3.6	5.0
—	—	6.6	4.5	1.2	3.6	4.0	5.8
—	—	—	5.1	1.3	4.1	4.6	7.0
—	—	10.0	—	—	—	—	—
—	—	—	6.7	1.35	4.6	5.0	8.0
—	—	12.7	—	1.4	5.3	5.8	9.0
—	—	—	—	1.5	—	—	10.0
—	—	—	—	1.6	—	—	11.0
—	—	—	—	—	—	—	12.0

thymol, cuminol, camphor, and menthol all act faster than water, and they all show a sudden bend in the curve where rapid action commenced. A saturated solution of phenol acts but little faster than water.

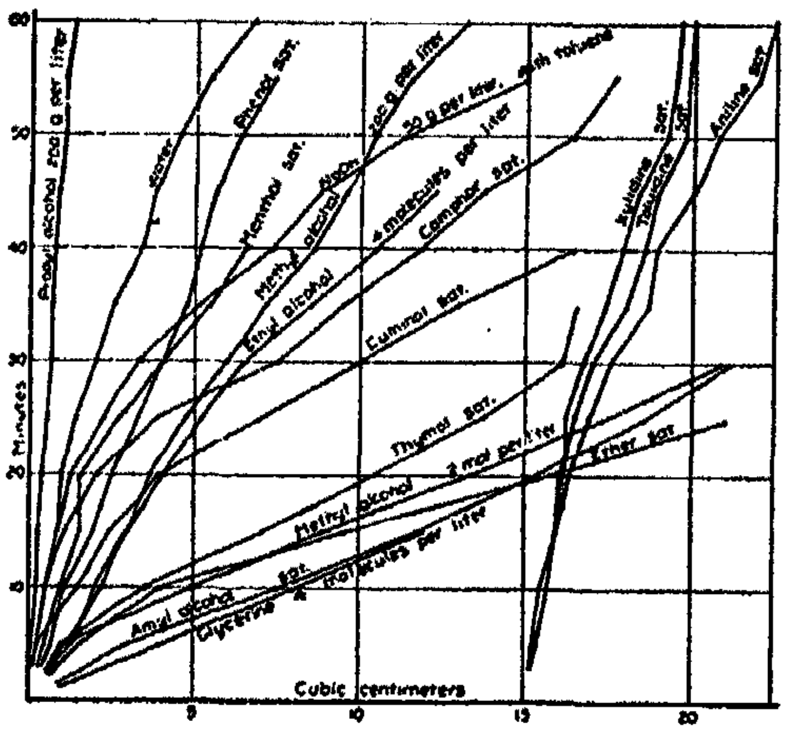

Fig. 7

Aqueous solutions of amines, alcohols, and miscellaneous oxygen compounds

Saturated solutions of the amines, aniline, toluidine, and xylidine act with about the same speed upon the sodium amalgam as does water. Toluidine and xylidine even retard the action somewhat. The same results were obtained with many other amines and amides tried, the action of the water on the amalgam being hardly influenced by these substances.

It might be of interest to add a number of substances, whose action on the amalgam was tried at dilutions of one gram per liter. Fig. 8 and Table VIII present the results obtained with these dilute solutions. Glycerine, cane-sugar and butyl alcohol still show a more rapid action at this dilution than pure water. The solution of glycerine, however, acts slower than a solution of the same substance where four molecules per liter were used (Fig. 7). A grape-sugar solution acts with about the same speed as water. Acetone, milk-sugar and amyl alcohol solutions retard the action of the amalgam. Again referring to Fig. 7, one may observe that a saturated amyl alcohol solution acts very fast. The curve in this figure (Fig. 8) shows that amyl alcohol retards the action when only one gram is used to a liter of water. The fact that solutions which are as dilute as this still affect the reaction is very remarkable. A solution of cane-sugar containing one gram of sugar per liter can hardly be detected by the sense of taste. Glycerine, phenol, and the alcohols can, however, be tasted quite distinctly at this dilution. The latter may also be detected by the sense of smell. The dilu-

TABLE VIII.

Min.	Acetone	Phenol	Amyl alcohol	Butyl alcohol
5	—	1.0	0.1	0.2
10	0.4	1.9	0.3	0.8
15	0.8	3.2	0.6	1.5
20	1.0	4.8	0.8	—
25	1.3	6.2	1.0	—
30	1.8	9.5	1.3	—
35	2.2	11.3	1.5	—
40	—	13.5	—	—
45	—	15.5	—	7.8
50	3.5	17.5	—	—
55	4.2	18.5	2.8	11.5
60	4.8	—	—	—
65	5.2	—	—	15.5
70	6.0	—	—	—

Min.	Glycerine	Grape-sugar	Cane-sugar	Milk-sugar
5	0.5	—	0.1	0.1
10	1.8	0.3	1.0	0.6
15	4.2	0.7	1.8	0.8
20	7.3	1.0	3.2	1.1
25	11.0	1.5	5.4	1.4
30	14.4	2.1	7.9	1.8
35	17.0	2.9	10.3	2.0
40	19.4	3.8	13.0	—
45	20.5	4.5	14.5	—
50	22.0	5.5	16.5	3.2
55	—	—	—	4.3
60	—	—	—	—

tion at which various substances can still be detected by the sense of taste has been very carefully studied by Prof. Kahlenberg.[1] It is clearly shown in this article that a substance must be soluble in order that it may be tasted, and furthermore it is shown how extremely delicate must be the reaction between the solution and the nerve endings which govern the sense of taste.

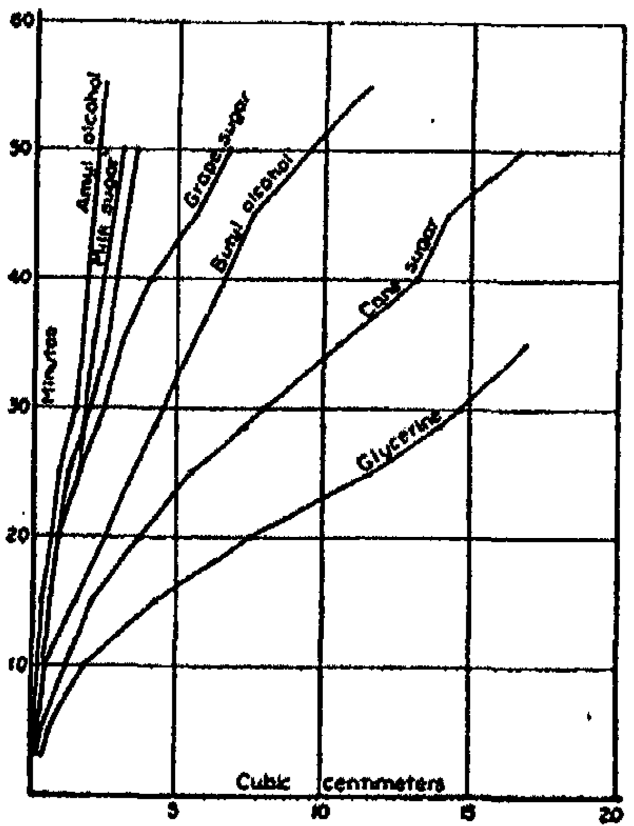

Fig. 8

Solutions in which one gram of the substance was used per liter of water

A five-thousandth normal solution of silver nitrate and a two-thousandth normal solution of mercuric chloride could still be tasted. There is no doubt that there are substances which can be tasted in still greater dilutions. The sense of taste also assists us in detecting the presence of hydrocarbons in solution. It is a well known fact that water shaken up with benzene or toluene will retain a distinct taste characteristic of the respective hydrocarbon used.

From these facts we can draw the conclusion that the hydrocarbons and other compounds frequently regarded as in-

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[1] "The action of solutions on the sense of taste." Read before the Wisconsin Academy of Sciences, Arts and Letters at its meeting at Milwaukee, December, 1897.

soluble, actually go into solution. The action of these solutions on sodium amalgam can serve as a method of detecting the presence of minute quantities of these compounds in water. To remove all doubt that the action might be due to finely suspended particles of these hydrocarbons, a number of experiments were performed. Precipitated barium sulphate and calcium carcium carbonate were employed. But the action of the amalgam on water containing these finely divided substances was not increased. An explanation of these facts is now incumbent.

Viewed from the standpoint of catalytic actions it is possible to classify all these reactions under two heads. First there are those substances which, dissolved in water, retard the action of the amalgam so that the speed with which the latter liberates hydrogen is less than with pure water. These substances are "negative catalytic agents" and include most of the salts of the inorganic acids and also some organic compounds. Then there are those substances which in solution increase the action of the amalgam. These substances are "positive catalytic agents" and include most of the organic substances employed, especially the hydrocarbons. The term catalytic action of course does not give an explanation of these phenomena, but it merely serves as a convenient term for the classification of these results. As we are here dealing with solutions entirely we are confronted with the problem to find an explanation as to the nature of these solutions.

It would seem that the action of the sodium and potassium amalgams on solutions of sodium and potassium salts should be fully accounted for by the ionic theory of Arrhenius. As stated above, this investigator attributed the slow action of sodium amalgam, for example, on solutions of sodium salts to ions of sodium in solution, which by mass action would prevent the entrance of more sodium ions into the solution. Although this theory is very plausible in the case of solutions of sodium salts with sodium amalgam, it fails to explain the slow action of the same amalgam on solutions of potassium salts. It is just as difficult to explain the slow action of potassium amalgam on solutions of sodium salts by this theory. The increased action of the sodium amalgam on water containing organic compounds in solution cannot be accounted for by this theory, and the problem of finding the cause for the anomalous behavior of the amalgam on these solutions would remain unsolved. Numerous examples of the untenability of the ionic theory have been found since its establishment in 1887, and it is especially the series of investigations which have been carried out in this laboratory for a number of years under the direction of Prof. Kahlenberg, which show conclusively that this theory has outlived its usefulness. Prof. Kahlenberg has also been the first to suggest a new theory, which not only explains satisfactorily the facts whose interpretation required the complicated ionic theory, but which also throws light upon the whole subject of solutions, explaining the facts whose interpretation by the old theory was difficult or absolutely impossible.

Chemical affinity, the affinity between solvent and dissolved substance, and the formation of a true chemical compound whose properties are different from either constituent form the basis of this new theory. It will be seen how simple the interpretation of the behavior of the amalgam on the different solutions is.

To begin with, the solutions of the sodium and potassium salts of inorganic acids, whose action on the amalgams could not be explained by the ionic theory, will show how well the new theory applies. A solution of sodium chloride should retard the action of the sodium amalgam according to the ionic theory, because sodium ions in the solution will tend to prevent the entrance of more sodium in the ionic state. On the other hand, a solution of potassium chloride should not retard the action of the sodium amalgam. The potassium ions can offer no resistance to the entrance of sodium ions. A glance at Figs. 1 and 2 will however, show that potassium chloride retards the action, and furthermore that a normal potassium chloride solution retards about as much as a normal solution of sodium chloride. Prof. Kahlenberg's theory satisfactorily explains this by assuming that potassium chloride has about the same affinity for water as has sodium chloride on account of the similarity of the two salts.

The water would in each case be held with the same degree of tenacity, and the action of the sodium amalgam on the new compound would in each case suffer an equal retardation. The same explanation of course holds in the case of potassium and sodium salts in general if we compare isotonic solutions of these salts. The theory also accounts for the same phenomenon observed with potassium amalgam (see Figs.). The similarity in the ebullioscopic and cryoscopic behavior and the electric conduction of solutions of sodium and potassium salts can also be readily interpreted by this theory. A new chemical compound then is formed between the water and the salt which, if similar, will also have similar action on the respective amalgams.

There still remains the list of organic solutions, the results of which on sodium amalgam are represented in Figs. 5 to 8. As the majority of organic compounds are considered undissociated in aqueous solution, the ions can not be held responsible for the peculiar behavior of these solutions on sodium amalgam. By the application of the new theory presented above the results can, however, be readily explained. The formation of a compound of the solvent and dissolved substance is again assumed. The compound must in this case be extremely unstable toward sodium amalgam, as is shown by the rapid inroads that the latter makes upon the solution. The action as has been mentioned, was in most cases more rapid than with pure water. The assumption of such an unstable compound is nothing extraordinary. Numerous instances of the great reactivity of such unstable compounds are known. It will suffice here to mention but one instance to illustrate what is meant. Nitrous oxide, for example, is a more reactive compound than are either of the elements of which it is composed. Everybody knows that a splinter of wood will burn even more violently in nitrous oxide than in pure oxygen. These facts give the clue for the explanation of the anomalous behavior of these organic solutions, and justify the view that the rapid action of these organic solutions is due to such unstable compounds. It is also clearly shown by comparing the results presented in all the tables that the rate of action of inorganic as well as organic solutions on the amalgams is not proportional to the number of dissolved molecules. A one-tenth normal sodium chloride solution does not act ten times as fast as a normal solution of the same salt. A half-saturated solution of any of the organic solutions does not act half as fast as a saturated solution. This simply means that the first particles of a substance going into solution are attracted more strongly and held more firmly by the water than are the particles which enter when the solution is already partially saturated. The firmness with which the particles are held by the water diminishes with increasing concentration. Therefore the particles which enter when the solution is already partially saturated will not influence the rate of action of this solution on the amalgam as much as the first particles which went into solution. This then accounts for the fact that in most cases of the inorganic salt solutions very little difference appears between the rate of action for different concentrations of the same salt. It is for the same reason that a half-saturated solution of a hydrocarbon, for example, acts slower than a saturated one, but not with half the rate.

There is still one more fact to be explained, and that is the sudden increase of action on the amalgam of most organic solutions. This sudden increase is shown in the figures by the sudden bend in the curves. This can also be easily interpreted by the new theory. The amalgam in acting on the solution forms sodium hydroxide. It is very probable that this sodium hydroxide brings about this increase in action. A compound formed by the action of the three substances water, hydrocarbon and sodium hydroxide need only be assumed in these cases to explain these phenomena. At this place, attention must again be called to the rapid action of sodium hydroxide purified by alcohol, on both sodium and potassium amalgams. The results of this action are presented in Figs. 1 and 4. A probable explanation of these results follows, from what has been stated above; small quantities of organic substance may be present in this sodium hydroxide. The combination of the water, sodium hydroxide and the organic substance again might cause this rapid action which was observed.

All the results obtained by the action of the different solutions on sodium and potassium amalgams are now satisfactorily explained by Prof. Kahlenberg's theory. A few of the possibilities of applying this theory to phenomena which are closely allied to these results should be mentioned. It has been convenient to term these actions catalytic actions. To solve the nature of catalytic reactions is one of the most important problems of modern chemistry. Catalysis plays an important rôle not only in pure science, but also in many branches of chemical industry. The manufacture of indigo from naphthalene, and the manufacture of sulphuric acid are only two of the numerous reactions which are termed catalytic. Many of these catalytic reactions find a ready explanation by the application of this new theory, and by using the term solution in the broad sense which includes solid, liquid and gaseous solutions, it is not improbable that all catalytic actions can be explained satisfactorily.

It is then simply the attraction between solvent and dissolved substances and the formation of a true chemical compound which is more or less stable and which may be made up of more than two substances, which has been set down as the cause of the different rates of reaction. To how great an extent this theory will be substantiated by further investigation cannot be foretold at the present time, but its simplicity must certainly appeal to all who have followed the development of the ionic theory and are cognizant of its weaknesses. Many very able investigators have been aware of the meager evidence upon which the theory of Arrhenius has been built up and have repeatedly set forth views similar to Prof. Kahlenberg's. None, however, took a firm stand to uphold these views nor did they attempt to confirm them experimentally.

I wish at this place to express my sincere gratitude to Prof. Kahlenberg, not only for the many compounds which he placed at my disposal, but also for the many suggestions and the advice which he offered me throughout the work.

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Madison, July, 1903.

THE RATE OF FORMATION OF IODATES IN ALKALINE SOLUTIONS OF IODINE

BY E. L. C. FORSTER

Up to the year 1861, in which Schönbein's "*Beiträge zur nähern Kenntniss des Sauerstoffs und der einfachen Salzbildner*"[1] appeared, it was generally believed that iodine and caustic potash in solution react instantaneously to form potassium iodate. Schönbein showed that the reaction takes place in two stages, and, relying on the close analogy between the chemical behaviour of iodine and chlorine, assumed that the intermediate product was potassium hypoiodite.

With regard to the first stage—formation of hypoiodite—his experiments show that the reaction is incomplete and reversible, leading to an equilibrium between potash, iodine, iodide, and hypoiodite; with regard to the second—formation of iodate—which differs from the first in requiring a measurable time for its completion, Schönbein says little, merely pointing out that rise in temperature increases the rate.

In 1894 there appeared a paper by Lonnes[2] containing measurements of the amount of iodate formed in solutions of iodine and sodium carbonate at measured intervals of time, which show that the rate of the reaction is influenced by the concentrations of the iodide and of the alkali; and in the following year Schwicker[3]—in the only formal study of the "rate of transformation of potassium hypoiodite" that has as yet appeared—found that the rate was proportional to the square of the concentration of the "iodine," and that increase in the quantity of potash caused a retardation almost proportional to the excess of KOH over that needed to form hypoiodite. In a few experiments in which the iodine was present in slight excess,

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[1] Jour. für prakt. Chem. 84, 385 (1861).

[2] Zeit. anal. Chem. 33, 409 (1894).

[3] Zeit. phys. Chem. 16, 303 (1895).

the rate was thought to be proportional to the cube of the concentration of the iodine; no account was taken of the influence of the potassium iodide.

In the opinion of Taylor,[1] Schwicker's results "do not appear to have been altogether satisfactory;" this he ascribes to that author's neglect of the effect due to the potassium iodide in his "iodine" solution. That the rate is in reality largely dependent on the concentration of the iodide, was again shown by Förster and Gyr[2] in a paper on "the action of iodine on alkalis," published in January of the present year.

In the experiments described in the present paper, I have examined the effect of changing the quantities of potash, iodine, and potassium iodide, on the rate of formation of potassium iodate in alkaline solutions of iodine. When the potash is present in large excess — colourless solutions — the results are simple, and can be expressed with a fair degree of accuracy by saying that the rate is proportional to the concentration of the iodion $\bar{I}$, the hypoiodion $\overline{OI}$, and the hypoiodous acid HOI. In brown solutions, on the other hand, where the iodine is in excess, the relations are more complex; and, until the numerical values of certain constants have been determined, it cannot be asserted that the laws suggested by the experiments with colourless solutions are valid for all.

My measurements show that Förster's equation

$$KOI + 2HOI = KIO_3 + 2HI,$$

which in that author's opinion "corresponds in all details" with the reaction itself, must be rejected equally with the older theory adopted by Schwicker and others

$$3KOI = KIO_3 + 2KI,$$

and that in all probability it must be replaced by some equation of which the left member is

$$(?\ H_2O +)\overline{OI} + HOI + \bar{I},$$

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[1] Chem. News, 76, 17 (1897).

[2] Zeit. Elektrochemie, 9, 1 (1903).

and of which the right can be filled in, for the present, only by a draft on the imagination.

I. Colourless Solutions

The solution of potash was mixed with the water in a 400 cc Erlenmeyer flask and brought to zero by immersion in a well-stirred bath of ice and water; the mixed solutions of iodine and potassium iodide, also at zero, were then quickly poured in, the whole well shaken and the time noted. After two minutes the first analysis was made; 10 cc was pipetted into a mixture of 50 cc water with 20 cc of a half-saturated solution of ammonium bicarbonate, by which further formation of iodate was prevented, and the residual "iodine" (hypoiodite) was then determined by *n/100* sodium arsenite with starch as indicator, 0.5 cc F^1-KI being added to make the end-point distinct; *n/100* iodine was used to "titrate back", and a correction of 0.1 cc was applied to the reading, being the amount of iodine needed to give the blue colour.

The stock solutions used in all the experiments described in this paper, with the exception of those of Tables XIII and XIV were: 1.092-normal potash, freed from carbonate by lime, 1.151-F potassium iodide, and 0.0936-normal iodine, the latter being prepared by dissolving about 12.7 grams of iodine in 100 cc of the 1.151-FKI and diluting to a liter. They were standardized in the usual manner, with sulphuric acid, silver, and sublimed iodine respectively. The volumetric solution of sodium arsenite was 0.01025-normal (against iodine) and the thiosulphate was 0.0104-normal (against the arsenite).

The potassium iodide employed contained small quantities of potassium iodate and potassium carbonate; these were removed by acidifying with sulphuric acid, boiling to expel CO_2, adding sodium thiosulphate until the solution just gave no blue with starch, and finally neutralizing with caustic potash freed from carbonate by lime. The water used in making up the reacting mixtures was freed from CO_2 by boiling for fifteen minutes, and was protected by soda lime.

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[1] One formula-weight in grams per liter.

The pipettes were calibrated by weighing the distilled water discharged; 30 seconds being allowed for draining.

At the head of each table is given the volume of each of these stock solutions employed. Under θ is entered the time in minutes reckoned from the first analysis (for which $\theta = 0$); under As, the number of cc of the volumetric arsenite solution required to remove the iodine in 10 cc of the reacting mixture, and under $K_2 \times 10^4$ the value of $10^4(1/As - 1/As_0) \times 1/\theta$.

Adopting Schönbein's assumption, that when iodine is dissolved in a solution of potash, potassium hypoiodite is formed, the quantities of the constituents $\overline{OH}$, $\bar{I}$, and $\overline{OI}$ may be determined by means of the equation

$$2\overline{OH} + \bar{I}_3 = \overline{IO} + 2\bar{I} + H_2O,$$

the quantity of $\bar{I}_3$ in colourless solutions obviously being zero.

Let A, B, and C represent the numbers of gram-molecules of KOH, KI, and KI_3 before mixing, multiplied in each case by 10^5. Thus for example, in Expt. 1:

50 cc potash: $A = 10^6 \times 0.050 \times 1.092 = 5460$
20 cc iodine: In making this up there was used
$10^6 \times 0.020 \times 0.1151$ units of potassium iodide, of which
$10^6 \times 0.020 \times 0.0936 \times 0.5 = 93.6 = C$ was converted into KI_3, leaving
$10^6 \times 0.020 \times 0.0683 = 136.6$ KI
20 cc iodide: containing $10^6 \times 0.020 \times 1.151 = 2302$ KI, to which must be added 136.6 in the iodine solution, giving $2439 = B$.

Then after mixing, when all the triiodion, $\bar{I}_3$, has been converted into hypoiodion, $\overline{OI}$, but before the formation of iodate has commenced,

the $\overline{OH}$ present $= A - 2C = 5560 - 187 = 5273$
" $\bar{I}$ " $= B + 2C = 2439 + 187 = 2626$
" $\overline{OI}$ " $= C = 94.6$

In the calculation it has been assumed that, owing to the large excess of potash, the concentration of the *HOI* might be neglected in comparison with that of the $\overline{OI}$ ions.

In addition to the experiments recorded in the tables, others were carried out which showed that the presence of a small quantity of potassium iodate (one gram in 100 cc) has no effect on the rate, and that the possible absorption of carbonic acid from the air during the progress of an experiment was likewise without influence on the result. In a few measurements the reacting mixture was exposed to direct sunlight; the same figures were obtained as in duplicates made in the diffuse light of the laboratory.

In Table VI, the initial compositions of the solutions in the experiments of Tables I to V are given in the terms of $\overline{OH}$, $\overline{I}$, and $\overline{IO}$, together with the average values of K_2. The initial rate, R_0, is obtained by multiplying K_2 into the square of the initial concentration of the hypoiodion,

$$R_0 = dx/d\theta(x = o) = K_2C^2.$$

From the constancy of K_2 in each of the Tables I–V, it is apparent that the rate is proportional to the square of the concentration of the $\overline{OI}$; this conclusion is confirmed (within 10 percent) by comparison of Tables I and II (see also Table VI).

TABLE I.

Potash, 50 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	9.06	—
3	8.52	23.3
10	7.54	22.2
15	7.24	25.1
19	6.40	24.1
22	5.99	25.6
		Av. 24.1

TABLE II.

Potash, 50 cc; Iodide, 20 cc; Iodine, 40 cc; Volume, 200 cc

θ	As	$K_3 \times 10^4$
0	17.25	—
4	14.70	25.1
9	11.77	29.9
13	10.06	31.8
17	8.68	33.6
22	7.53	34.0
27	7.27	29.4
		Av. 30.6

TABLE III.

Potash, 100 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	As	$K_3 \times 10^4$
0	8.75	—
4	8.37	13.2
8	8.18	10.0
12	7.62	14.1
16	7.60	10.9
20	7.09	13.4
24	6.93	13.9
		Av. 12.5

TABLE IV.

Potash, 25 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	As	$K_3 \times 10^4$
0	9.09	—
4	7.95	39.5
8	6.80	46.2
18	5.08	48.0
22	4.50	55.0
26	4.00	53.8
		Av. 48.5

TABLE V.

Potash, 50 cc; Iodide, 10 cc; Iodine, 20 cc; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	8.95	—
6	8.48	10.3
9	8.27	10.2
13	7.88	11.6
17	7.25	15.4
		Av. 11.8

TABLE VI.

Table	$\overline{OH}$	$\overline{I}$	$\overline{OI}$	$K_2 \times 10^4$	R_0	K[1] $\times 10^4$
1	5273	2626	93.6	24.1	21.1	47
2	5086	3050	187.2	30.6	107.3	51
3	10733	2626	93.6	12.5	11.0	50
4	2543	2626	93.6	48.5	42.5	46
5	5273	1475	93.6	11.9	10.4	43

Further comparison of the experiments, which is facilitated by the summary given in Table VI, shows that within the same limits (8 to 10 percent) the rate is directly proportional to the concentration of the $\overline{I}$, and inversely to that of the $\overline{OH}$. Since the product of $\overset{+}{H}$ and $\overline{OH}$ concentrations is constant, and since the concentration of the *HOI* is proportional to the product of those of $\overset{+}{H}$ and $\overline{OI}$, this is equivalent to saying that the rate is proportional to the concentrations of $\overline{OI}$, $\overline{I}$, and *HOI*.

II. Brown Solutions

In presence of a large excess of iodine, the plan of analysis described on page 642 would give very inaccurate results; it was therefore abandoned in favor of a direct determination of the iodate formed, according to the following method.

The iodine and hypoiodite were destroyed and the reaction stopped by pouring in a slight excess of fifth-normal sodium arsenite. The contents of the flask were then emptied into a beaker, 100 cc of water added, and then a measured quantity of

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[1] $Ro \times (OH) = K \times (I) \times (OI)^2$

hydrochloric acid diluted with 100 cc of water; the iodine which was thereupon liberated from the iodate was determined by sodium thiosulphate. Under x in the tables of this section is entered the number cc of 0.0104-*n* thiosulphate needed, and under θ the interval in minutes between mixing the reagents and adding the arsenite. By working quickly, using as little arsenite as possible, and adding in each case a definite excess (5 cc of 2-*n* HCl) of hydrochloric acid over that needed to neutralize the potash in the reacting mixture and the sodium bicarbonate in the arsenite solution, it was found possible to determine the iodate before any iodine was liberated by arsenic acid. It would have been better to remove the excess of arsenite before acidifying, but blank experiments show that the error arising from its presence is small.

A series of experiments analogous to those of Tables I–V were first carried out, but as no "constant" could be found, recourse was had to the "method of constant rates,"[1] the solutions being so made up that the changes in concentration during the progress of an experiment were almost negligible. In Tables VII–XII the rates (R) were obtained by dividing x (which is proportional to the amount of iodate formed) by the duration of the reaction in minutes. Duplicate experiments showed that the value of R so obtained was rather greater when θ was 3 or 4 minutes than when it was one; this suggests that the formation of hypoiodite may require an appreciable interval of time for its completion, but I have not examined the matter further.

TABLE VII.

Potash varies; Iodide, 20 oc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
1	Brown	2	2.1
2	Brown	1	11.3
5	Light brown	1	8.7
10	Green yellow	1	4.2
15	Light green	2	2.9
20	" "	4	2.1
25	" "	5	1.6

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[1] See Bray, Jour. Phys. Chem. 7, 92 (1903).

Table VIII.

Potash varies; Iodide, 40 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
2	Brown	1	4.2
5	Yellow brown	1	11.1
10	Yellow green	1	9.3
15	Green yellow	1	6.0
20	" "	1	3.8
25	" "	3	3.4

Table IX.

Potash varies; Iodide, 60 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
2	Brown	4	1.9
5	"	1	8.4
10	"	1	11.6
15	Yellow brown	1	10.7
20	Yellow green	1	6.4
25	Green yellow	1	5.0

Table X.

Potash varies; Iodide, 20 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	2	10.6	5.3
2	1	22.9	22.9
3	1	44.1	44.1

Table XI.

Potash varies; Iodide, 40 cc; Iodine, 40 cc; Volume, 200 cc

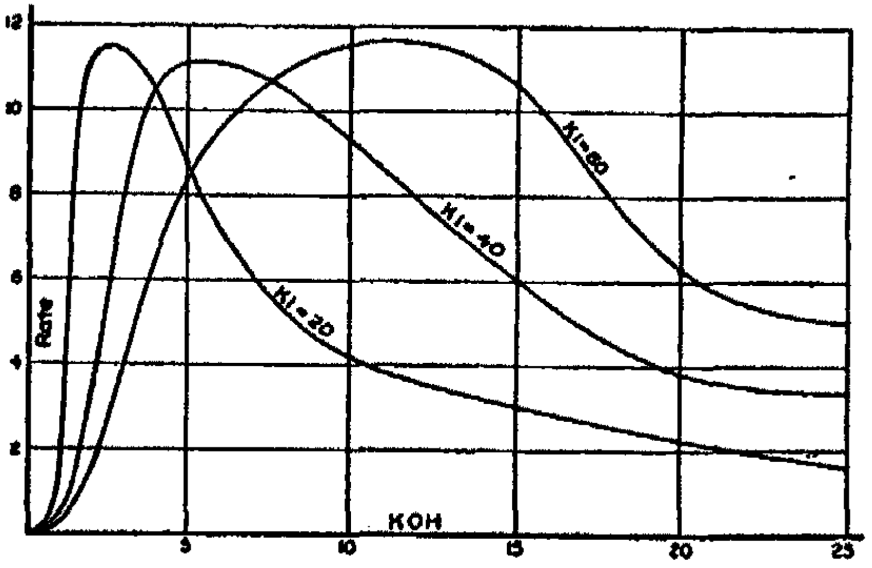
KOH	θ	x	R
1	2	3.3	1.6
2	1	9.6	9.6
3	1	23.1	23.1

TABLE XII.

Potash varies; Iodide, 60 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	3	2.2	0.7
2	1	4.5	4.5
3	1	12.3	12.3

From Tables VII–XII it appears that, in presence of a large excess of iodine, the rate of formation of iodate is increased by increasing the concentration of the iodine or of the potash, and decreased by increasing that of the iodide — the effect in the last two cases being the opposite of that produced when the potash is in excess. The existence of maximum rates, which is necessitated by this circumstance, is well shown by the curves.



Tables 7, 8, and 9

It would be interesting to know whether in the experiments of this section, as in those with colorless solutions, the rate is even roughly proportional to the concentrations of $\overline{OI}$, $\overline{I}$, and $\overline{HOI}$; in brown solutions, however, where only part of the iodine is converted into hypoiodites, it is not easy to determine the amounts of these three constituents.

Assuming the chemical equations: —

$$\overset{+}{H} + \overline{OH} \rightleftarrows H_2O$$

$$\overset{+}{H} + \overline{OI} \rightleftarrows HOI$$

$$\overline{OH} + \overline{I}_2 \rightleftarrows HOI + 2\overline{I},$$

and the corresponding conditions of equilibrium:—

$$(\overset{+}{H})(\overline{OH}) = W$$
$$(\overset{+}{H})(\overline{OI}) = D(HOI)$$
$$(\overline{OH})(\overline{I_3}) = E(HOI)(\overline{I})^2,$$

(where the symbols in brackets signify the amounts of the reagents in a fixed volume of solution, and W, D, and E are constants) and representing the initial quantities of potash, iodide, and iodine by A, B, and C as before, the following equations

$$Wy = Dz(A - 2y - z)$$
$$(A - 2y - z)(C - y - z) = Ez(B + 2y + 2z)^2,$$

determining y, the concentration of the $\overline{OI}$ ions, and z that of undissociated HOI (before the formation of $\overline{IO_3}$ has begun) may be obtained. These equations may be solved for y and z, and the results substituted in the expression for the rate of formation of iodate,

$$R = Kyz\,(B + 2y + 2z),$$

but without knowledge of the numerical values of D and E the relation so obtained cannot be compared directly with the experiments. I hope to determine these constants during the present winter; in the meantime the experiments of this section, though perhaps not so accurate as those in which the potash was in excess, and not leading to such simple results, serve to show how much the brown solutions differ from the colourless in respect to the influence exerted by the amounts of iodide and of potash on the rate of formation of potassium iodide.

Temperature Coefficient

A few experiments were undertaken at 30.3° in order to test the influence of the temperature on the rate; those with the colourless solutions are given in Table XIII, and those with brown solutions in Table XIV. In neither case is the temperature coefficient as great as usual, but as in all probability the dissociation of HOI and the equilibrium constant E (see above) change with the temperature, abnormal results are not to be wondered at. The experiments of Table XIII were carried out with solutions of potassium iodide that had not been freed from carbonate, and are therefore not directly comparable with the other experiments of this paper.

TABLE XIII. (Colourless)

Potash, 25 cc (0.929-*n*); Iodide, 20 cc (0.956-*F*); Iodine 20 cc (0.089-*n*); As (0.0101-*n*) Volume, 200 cc

θ	As(0°)	$K_2 \times 10^4$(0°)	As(30.4°)	$K_2 \times 10^4$(30.4°)
0	—	—	6.28	457.0
7	6.78	45.0	2.32	396.8
10	6.32	40.6	1.68	437.9
14	5.56	44.3	—	—
20	4.80	45.1	—	—
		Av. 43.7		Av. 431.

TABLE XIV. (Brown)

Potash, 1.0 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	x	R(0°)	θ	x	R(30.3°)
2	4.2	2.1	1	32.3	32.3

Summary

In the presence of a large excess of potash, the rate of formation of potassium iodate is, approximately, proportional to the concentrations of $\overline{OI}$, $\overline{I}$, and HOI.

In presence of a large excess of iodine, the rate is increased by increasing the amount of potash or iodine, and decreased by adding to that of the potassium iodide.

On continually increasing the amount of potash, so that the solution changes from brown to colourless, the rate passes through a maximum.

The temperature coefficient is smaller than is customary.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this investigation was undertaken, and under whose supervision it has been carried out.

University of Toronto,
October, 1903.

IRON SALTS IN VOLTAMETER SOLUTIONS

BY J. M. BELL

The presence of iron in the sulphuric acid solution of an oxy-hydrogen voltameter has been shown by Elbs[1] to decrease materially the amount of gas evolved. He points out that elements which have two different valencies should be eliminated from the solution of such a voltameter. The explanation offered is that successive reduction and oxidation take place, reduction of ferric to ferrous sulphate at the cathode, and oxidation at the anode. The actual amount of gas evolved depends on various conditions: on the rate of diffusion of ferrous salt to the anode and ferric salt to the cathode, on the current density, and on the concentration of iron in the solution. That the effect of a low current density is to cause a larger decrease in the gas product, is shown in the following table, taken from Elbs's paper:

Iron in the acid	Current density amp/qdm	Percent decrease in oxy-hydrogen gas
1%	2.230	48.3%
	0.920	64.3
	0.228	97.4
0.1	6.4	3.0
	4.9	3.6
	2.27	7.2
	1.123	11.9
	0.366	24.1
	0.355	25.1
0.01	2.217	1.7
	1.150	1.9
	0.360	6.3

Sulphuric acid of specific gravity 1.175 was used. The electrodes were of platinum.

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[1] Elbs. Zeit. Elektrochemie, 7, 261 (1901).

On the other hand the following table, taken from a paper by Schwab and Baum,[1] shows that the effect of iron in the solution of a copper voltameter is practically negligible:

Current density 2 amp/qdm

Temperature 20° C

Solution	Anode loss in g.	Cathode gain in g.	$\frac{\text{Anode loss}}{\text{Cathode gain}}$	Current efficiency
3 cc HNO_3 per liter solution (*b*)				
1	3.6255	3.5260	1.032	0.9986
2	3.6190	3.5295	1.025	0.9996
3	3.6265	3.5310	1.028	1.0000
4	3.6195	3.5270	1.025	0.9988
5	3.6760	3.5310	1.011	1.0000
20 cc HNO_3 per liter solution (*b*)				
1	2.3650	2.2886	1.035	0.9980
2	2.3690	2.2925	1.035	1.9997
3	2.3775	2.2920	1.035	0.9996
4	2.3700	2.2880	1.040	0.9978
5	2.3441	2.2931	1.019	1.0000

Sol. (*a*) $CuSO_4.5H_2O$ — 16% Sol. (*b*) $FeSO_4.7H_2O$ — 18.4%
H_2SO_4 — 5% H_2SO_4 — 6.0%
9 vols. (*a*) + 1 vol. (*b*) = Solution (1)
8 + 2 (2)
7 + 3 (3)
6 — 4 (4)

These two sets of experiments, although apparently contradictory, have one essential difference. In the oxy-hydrogen voltameter platinum electrodes are used, and these remain unchanged, while in the copper voltameter there is a soluble anode. The oxygen which appears at the anode in the first case oxidizes ferrous sulphate to ferric sulphate, while copper going into solution has no such effect. The amount of gas evolved in the first case is further diminished because of the reducing action of hydrogen on the ferric sulphate; in the second case no ferric sulphate is produced except by oxidation by the air, the rate of

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[1] Jour. Phys. Chem. 7, 497 (1903).

which oxidation has been shown by McBain[1] to be quite low. Two experiments will prove that the two cases are not contradictory.

In the first experiment two oxy-hydrogen voltameters with platinum electrodes were placed in series, one containing sulphuric acid solution, the other a solution of sulphuric acid and ferrous sulphate. The acid actually employed was 10 percent sulphuric acid.

TABLE A.

Percent iron as ferrous sulphate in solution	Current density amp/qdm	Percent decrease in oxy-hydrogen gas
1.0	1.0	29.5
1.0	0.5	39.7
1.0	0.2	53.0

The decreases are much less than in Elbs's experiments, and this is no doubt due to the presence of a large quantity of ferric salt in his solution. In the above experiments the iron was present at the beginning of the run as ferrous sulphate, practically no ferric salt being present, so that until ferric sulphate appeared at the cathode, the cathode efficiency was 100 percent.

In the second experiment three cells were placed in series: the first A, a copper voltameter; the second B, a cell with copper electrodes and with iron in the electrolyte; the third C, with platinum anode and with iron in the solution. The solutions had the following compositions:

$$\text{In A}\quad \left.\begin{array}{rr} CuSO_4.5H_2O & 150\text{ g} \\ H_2SO_4 & 50\text{ g} \\ \text{alcohol} & 50\text{ g} \end{array}\right\}\text{ pro L.}$$

$$\text{In B and C}\quad \left.\begin{array}{rr} CuSO_4.5H_2O & 150\text{ g} \\ H_2SO_4 & 50\text{ g} \\ \text{alcohol} & 50\text{ g} \\ FeSO_4.7H_2O & 50\text{ g} \end{array}\right\}\text{ pro L.}$$

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[1] Jour. Phys. Chem. 5, 623 (1901).

TABLE B.

Current density amp/qdm	Cathode gain A	Cathode gain B	Cathode gain C	Efficiency B	Efficiency C
1.0	1.794 g	1.781	1.642	0.993	0.915
0.5	1.185	1.182	0.997	0.997	0.841
0.2	1.543	1.533	1.045	0.994	0.679

The efficiency in the cell with soluble anode was found to be over 99 percent, confirming Schwab and Baum's contention. An insoluble anode, however, causes oxidation of ferrous to ferric sulphate, which is reduced at the cathode, forming ferrous sulphate.

Cornell University.

NEW BOOKS

Arbeitsmethoden für organisch-chemische Laboratorien, ein Handbuch für Chemiker, Mediziner und Pharmazeuten. *By Dr. Lassar-Cohn. Dritte, vollständig umgearbeitete und vermehrte Auflage. 16 × 24 cm; pp. xv + 1241. Hamburg: Leopold Voss, 1904. Price: paper, 40 marks.* — This bulky volume needs no recommendation to organic chemists. They know the preceding two editions and will need no urging to make them read the third. With the physical chemists this may not be true, and yet the book might have been written primarily for the physical chemist, so well does it meet his needs. The spirit of the author is the spirit of the physical chemist, though the language is that of the organic chemist.

In the general part the subjects treated are: shaking out; baths; distillation: dialysis; passage of vapors through heated tubes; sealed tubes; decolorizing and clearing of liquids; filtration of precipitates; crystallization, including salting out; solvents and diluents; molecular weight determinations; melting-point determinations; boiling-point determinations with small quantities of liquid; sublimation; prevention of superheating; drying of solids, liquids, and gases. In the special part there are chapters dealing with the various methods for introducing acetyl, benzoyl, oxime, and other groups; for making bromine, chlorine, iodine, and fluorine addition and substitution products; for preparing salts and alkaloids; for setting free acids and bases; for making diazo compounds, ethers and phenol ethers; for nitration and sulphonation; for oxidation, reduction and saponification. There is a short chapter on fusion with alkali, a long one on condensation, and a short one on the separation of isomers.

It is clear from this summary that the book covers a great deal of ground. What is more important is that the ground is well covered. The book deals with facts, and this in itself is a pleasure in these days when works on physical chemistry are apt to contain only so many facts as are absolutely necessary to float the theories and when books on organic chemistry are interested in facts only in so far as they bear on constitution formulas. This volume may really be said to be a book on chemistry, and as such we welcome it.

Any comprehensive statement of allied facts must necessarily suggest new problems to the physical chemist, and from this point of view this book of Lassar-Cohn's is a treasure-house. One can open anywhere and find a subject calling for investigation before one has read six pages. I myself marked one hundred and sixty places on the first hasty reading. The theory of distillation with steam is fairly simple, but the actual application of it is still in a rudimentary stage owing to our ignorance of the changes of solubility. Why a substance will crystallize readily from one solvent and not from another is a question which the physical chemist has not yet faced, though the experiments of Schreinemakers and others with dineric systems have been clearing the way for it. The effect of the nature of the solvent upon the yield is another interesting point about which all we can say is that the relative solubilities must be a factor. The relative stability of methyl alcohol in presence of bromine is very interesting when compared with the behavior of ethyl alcohol. While we know in some cases why caustic soda behaves differently from caustic potash, we are still far from a comprehensive generalization on the subject. On all these points and many others we find data ready to our hand in this book. If we are interested in bromine, chlorine or iodine 'carriers,' we turn to the proper chapters. If we wish to compare the chemical with the electrochemical methods of making the different reduction products of the aromatic nitro compounds, we find the chemical methods ready at our hand, though unfortunately not the electrochemical ones. Lassar-Cohn deals with facts, and it is still a fact that electrochemical methods are not common in organic laboratories.

One of the great difficulties in studying reaction velocities in organic systems is that of analysis. Many reactions can be made to run at a reasonable rate, but this is of little avail if the course of the reaction cannot be followed analytically with some approach to accuracy. While it is never safe to predict in this world, there are a number of reactions referred to in the book which look as though they might perhaps be followed successfully. Some of these are: the action of ammoniacal methyl alcohol on *o*-dinitro benzene, 82; the action of acetone on hydroxylamine, 249; the action of semicarbazides on ketones, 251; the action of diazo methane on phenol, 568; the action of alkaline formaldehyde on phenol, 652; the action of manganate on chloral hydrate, 855; the action of potassium oxalate on potassium chlorplatinate, 1003; the action of sulphur on sulphobenzide, 1011. These are but a few instances out of many; but they suffice to show the quality of the book.

The book is clearly written and is surprisingly comprehensive. The work of Sabatier and Senderens with pulverulent nickel is the only important omission noted by the reviewer. It is a book that no physical chemist should be without and which no physical chemist will be without if he once realizes the truth that the next great advance is to be the application of physical chemistry to organic chemistry. *Wilder D. Bancroft*

Kristallisieren und Schmelzen. *Ein Beitrag zur Lehre der Änderungen des Aggregatzustandes. By Gustav Tammann. 14 × 22 cm; pp. x + 348. Leipzig. Johann Ambrosius Barth, 1903. Price: paper, 8 marks.* — For seven years the author has been studying the equilibrium between a solid and its melt. The results of these investigations have been published from time to time; but we now have them all together and in a connected form. This is a great convenience, and the book is valuable for reference. Fluency and grace of language are not the author's strongest points; but the facts are there and are easily accessible. The one feature of the work, which strikes everyone, is the prevalency of polymorphous forms. A few years ago, relatively few substances were known to occur in different solid modifications. Now it seems quite possible that all solid substances can occur in two or more forms. Since the freezing-point curves were approached from both sides, we are justified in feeling great confidence in the accuracy of the author's results. Systematic and thorough work along definite lines is the crying need in the scientific world. The author is to be congratulated on the work that he has done and on the monograph that he has written about that work. *Wilder D. Bancroft*

Cyanid-Prozesse zur Goldgewinnung. *Nach einschlägigen Quellen bearbeitet von Manuel von Uslar, unter Mitwirkung von Georg Erlwein. 17 × 24 cm; pp. vi + 100. Halle: Wilhelm Knapp, 1903. Price: paper, 4 marks.* — The first chapter treats of the McArthur-Forrest and the Siemens and Halske processes. In the second chapter there is an account of some actual works. Chapter three deals with the chemistry of the process, while the fourth chapter has to do with modifications of the cyanide process, such as the use of bromcyanogen, etc. The last chapter is half the whole book. This is a very interesting and instructive volume. One would have liked a little more information in regard to the relative merits of the Siemens and Halske and the Andreoli processes, especially in view of the statement in Mineral Industry some years back that the Andreoli patents are owned by the Rand Central Reduction Co. (not by the firm of Siemens and Halske, as was erroneously stated in Volume IV of the American Electrochemical Society). There seems also some discrepancy about the reports from different sources as to the length of life of the iron anodes. In the theoretical part, a reference should have been made to Christy's measurements and their bearing on the question of a selective action by cyanide of potash.

These points however are not of vital importance, and on the other hand we find a very clear statement as to the difficulties to be overcome in treating the slimes. The statement in regard to the chemistry of the process is admirably put, while the chapter on the other processes is really a model of what such a report should be.

Wilder D. Bancroft

Grundriss der reinen und angewandten Elektrochemie. *By P. Ferchland. 14 × 22 cm; pp. 5 + 268. Halle: Wilhelm Knapp, 1903. Price: paper, 5 marks.* — The headings to the chapters are as follows: electrolytic conductivity and electrolysis; Faraday's law; the transference numbers of Hittorf; resistance and conductivity; the theories of Grotthuss, Clausius, and Arrhenius; relations between the theory of electrolytic dissociation, the gas laws and the modern theory of solution; degree of dissociation and dissociation constant; migration velocity of ions and Kohlrausch's law; calculation and measurement of electromotive force; electromotive force and thermodynamics; Nernst's osmotic theory of electrolysis; single potentials; the electromotive behavior of non-metals; polarization; electrothermal processes; technical electrolysis; generation of electrical energy by chemical means.

The outline of the topics will give a pretty good idea of the book without further comment. The applied electrochemistry is so unsatisfactory that it might well have been omitted. In eleven pages the author discusses electroplating with gold, silver, copper, nickel, steel, and platinum; the refining of copper and silver; the preparation of gold, aluminum, magnesium, and sodium; the electrolysis of the chlorides with preparation of chlorine, hypochlorite, chlorate, and perchlorate; and the preparation of persulphates and percarbonates. If one cannot give more than eleven pages to all these subjects, it would be much wiser to devote less space to them.

Wilder D. Bancroft

Physical Chemistry in the Services of the Sciences. *By Jacobus H. van 't Hoff. English version by Alexander Smith. The Decennial Publications,* *Second Series, Volume XVIII. 15 × 23 cm; pp. xviii + 123. Chicago: The University of Chicago Press, 1903. Price: bound, $1.50, net.*

La Chimie physique et ses Applications. *By J. H. van 't Hoff. Translated by A. Corvisy. 16 × 25 cm; pp. 78. Paris: A. Hermann, 1903. Price: 3 francs.*—

The German edition of this book has already been reviewed (7, 32), and it is only necessary to call attention to the prompt and simultaneous appearance of the English and French translations. The English edition is on heavy paper with small pages and is bound. Consequently it makes a volume by itself, though a small one. The French edition is on light paper, with large pages and is unbound. The result is that we have a pamphlet which can hardly be called a book. *Wilder D. Bancroft*

Radium, and Other Radio-active Substances; Polonium, Actinium, and Thorium, with a Consideration of Phosphorescent and Fluorescent Substances, the Properties and Applications of Selenium, and the Treatment of Disease by the Ultra-Violet Light. *By William J. Hammer. 15 × 23 cm; pp. viii + 72. New York: D. Van Nostrand Company, 1903. Price: bound, $1.00.*—The author delivered a lecture before the American Institute of Electrical Engineers and the American Electrochemical Society. This lecture was published in the third volume of the Transactions of the American Electrochemical Society and now appears in book form. The scope of the lecture may be gathered from the title. After a few words about fluorescence, the author discusses phosphorescence and then comes to the main feature, the properties of radium, polonium, actinium, and thorium. The selenium cell is next in order, and lastly comes an account of the Finsen treatment of disease by ultra-violet rays.

The lecture was illustrated by a surprising number of very interesting experiments. For this reason it suffers when reproduced in print. It is interesting to note that the author attributes the light-sensitiveness of the selenium cell to the selenium. *Wilder D. Bancroft*

Chemisches Praktikum. *By A. Wolfrum. II. Teil. Präparative und fabrikatorische Übungen. 12 × 18 cm; pp. xii + 580. Leipzig: Wilhelm Engelmann, 1903. Price: bound, 15 marks.*

Chemisches Praktikum. *By A. Wolfrum. Atlas zum zweiten Teil, darstellend die Apparate der chemischen Technik und des Laboratoriums sowie die Einrichtung vollständiger Betriebe. 23 × 30 cm; pp. viii + 156. Leipzig: Wilhelm Engelmann, 1903. Price: bound, 20 marks.*—

This work is designed to give students who are preparing for technical work a clear conception of the methods and apparatus employed in practice. To this end, the author treats first of all the conditions for obtaining the desired reaction and for separating and testing the products of reaction. This section is followed by a number of receipts for the preparation of various classes of inorganic and of organic compounds. After a few standard methods for the determination of reaction velocities have been detailed, factory operations are described and a few general statements in regard to the bookkeeping and conomics of the factory made. The last section introduces the student to the field of patent investigation and details a number of experiments to be carried out on a larger scale.

Instead of attempting to insert his illustrations in this volume, the author has very wisely issued, as the third of the series, an atlas whose diagrams are arranged to correspond with the various descriptive sections of the second volume.

The work is interesting as illustrative of a method which may be employed in training students for chemical engineering. It will prove a valuable adjunct to those whose text-books have been confined to Davis's Handbook and Parnicke's Hand- und Hilfsmitteln. *H. R. Carveth*

Les Industries chimiques et pharmaceutiques. *By Albin Haller. Tome I. pp. lxxxix + 405. Tome II. pp. 445. 19 × 29 cm. Paris: Gauthiers-Villars, 1903. Price: paper, 20 francs.* — These two volumes contain a report on the chemical exhibits at the Paris Exposition of 1900. In an introduction, there is given a sketch of the development of chemical industry in the different countries which sent exhibits. This includes a statement of the scientific organizations and of the methods of teaching at the universities and technical schools. The author speaks very frankly about the evil effects in France caused by excessive centralization and by too great respect for authority. In view of the great development of applied electrochemistry in France, it is surprising that electrochemistry should be recognized as an important subject only at Nancy.

The bulk of the two large volumes is taken up by data concerning the firms which exhibit, and by sketches of the various processes. While these are necessarily very brief, they are very well done and the volumes will be found very convenient for reference. To the physical chemist the most interesting things are, of course, the electrochemical processes and the contact sulphuric acid process. While the facts that are here given are all to be found in greater detail elsewhere, it is very convenient to have them all together and presented from a single point of view. *Wilder D. Bancroft*

Hypothese zur Thermodynamik. *By Viktor Grünberg. 16 × 23 cm; pp. vi + 73. Leipzig: Johann Ambrosius Barth, 1903. Price: paper, 3 marks.* — This pamphlet outlines an attempt to apply the planetary laws of motion to the kinetic theory of matter. It is assumed that each molecule revolves about a point, and that its energy is separable into the energy of rotation of the ether particles composing the system, the energy of rotation of the atoms, the energy of rotation of the whole molecule, and the energy of revolution of the molecule. On the basis of these assumptions expressions are found for pressure and molecular volume, and on multiplying these together the Boyle-Gay-Lussac law is obtained. The applications are extended to adiabatic change of state, the ratio of the specific heats at constant pressure and constant volume, and the law of Dulong and Petit. *J. E. Trevor*

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