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CONTENTS OF VOLUME IX

1. JANUARY

2. FEBRUARY

3. MARCH

4. APRIL

5. MAY

6. JUNE

7. OCTOBER

8. NOVEMBER

9. DECEMBER

ELECTROLYSIS OF COBALT AND NICKEL TARTRATES

BY JAY E. ROOT

In some experiments made on apparent decomposition voltages under the conditions used in electrochemical analysis, the value of 1.75 volts was found for cobalt in an alkaline tartrate solution and 2.8 volts for nickel.[1] If this difference continued to exist when both cobalt and nickel were present in the solution, a quantitative separation by the constant voltage method would be very simple. Vortmann[2] states that a separation can be effected in such a solution, but he gives no data and practically no details. He says that the addition of a few drops of potassium iodide solution prevents the formation of cobaltic oxide at the anode. In my work I found this not to be the case. Furthermore, the presence of iodide interferes with the precipitation of the metal at the cathode. The precipitation of any oxide at the anode can, however, be reduced to a minimum by making the anode current density high. If a few drops of concentrated nitric acid be added to the solution, there is still a deposit at the anode when the current density is low; but the deposit is then chiefly nickelic oxide.

It was soon found that the range of voltage is not as great as was hoped from the behavior of the metals when taken singly. If the voltage be kept below 2.1 volts the metallic cobalt contains no nickel. At higher voltages the cathode deposit always tests for nickel. As no detailed study of cobalt and nickel alloys has yet been made, the theory of this phenomenon cannot be discussed here. While pure cobalt is obtained at voltages below 2.1 volts, it has proved impracticable to get all of the cobalt out of the solution in any reasonable time. One reason for this is the oxidation of cobaltous salt to a green cobaltic salt

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

[2] Monatsheft, 14, 536 (1893).

at the anode. Addition of hydroxylamine sulphate, formaldehye, sodium bisulphite or even hydrogen peroxide helps somewhat, but does not make the precipitation satisfactory. With the bisulphite there is also precipitation of sulphur at the cathode.

In the experiments to be described, the salts used were crystallized $CoSO_47H_2O$ from the laboratory stock and crystallized nickel sulphate or nitrate. No one of the three salts was free from the metal of the other. The cobalt sulphate was recrystallized and contained no iron. It lost some water while being powdered and contained about 22.5–23.5 percent of cobalt instead of the more orthodox 21 percent. This introduces no error because it was only necessary to obtain metal, oxide, and solution which would pass the test. The following tests were used in all the work:—

Test for nickel in presence of cobalt. — The hydroxides of nickel and cobalt are filtered, washed and dissolved in the least possible amount of hot concentrated potassium cyanide solution. To this solution add three times its volume of strong NaOH solution, then bromine water in excess and warm. The appearance of a blackish coloration is due to nickelic hydroxide.

Test for cobalt in presence of nickel. — Solutions, if acid, are made alkaline with NaOH. Add slight excess of acetic acid, then large excess of saturated KNO_2 solution. The appearance of a yellow precipitate, after standing over night in a warm place, indicates traces of cobalt. This test will easily show 0.005 mg cobalt per cubic centimeter.

In the electrolytic runs, a Classen dish was always one electrode, while the other was either a platinum disk or a platinum wire. The distance between the electrodes was always 1 cm.

The first series of runs was made with the dish as cathode and the disk as anode. The solution was not stirred. The runs were made at 18°. The stock solution consisted of 10 g sodium potassium tartrate and 50 cc NaOH (sp. gr. 1.3), made up to 150 cc after the cobalt and nickel had been added.

RUN 1.

0.3070 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.9 volts; 0.45 amp; 6 hours.
Cathode deposit of 0.0645 g Co (= 21.1 %), free from nickel.
Slight anode deposit which is easily detached and is not weighable. Solution gives slight test for cobalt.

RUN 2.

0.7352 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.9 volts; 0.45 amp; 13 hours.
Cathode deposit of 0.1505 g Co (= 20.5 %), free from nickel.
Considerable anode deposit. Solution gives slight test for cobalt.

RUN 3.

0.2817 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.9 volts; 0.45 amp; 5 hours.
Cathode deposit of 0.0556 g Co (= 19.7 %), free from nickel.
Slight anode deposit. Solution tests for cobalt.

In all three runs a whitish insoluble salt was noticed after lengthy electrolysis at both electrodes and through the solution.

The second series of runs differed from the first in that the solution was stirred by rotating the anode.

RUN 4.

0.4575 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.9 volts; 0.45 amp; 20°; 2 hours.
Cathode deposit of 0.086 g Co, free from nickel.
Anode deposit of 0.0065 g cobaltic oxide,[1] free from nickel. Total cobalt 0.0895 g (= 17.8 %).

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[1] The anode deposit is approximately $Co_2O_3.3H_2O$; see Run 12. The anode was dried in air about one inch above the tip of the Bunsen burner flame. It was kept in motion while being dried. The anode was allowed to cool for fifteen minutes and was then weighed. The deposit was dissolved in boiling HNO_3 and tested in the usual way.

Solution tests for cobalt. This run was purposely made short to see whether the bulk of the cobalt precipitates in the first two hours.

RUN 5.

0.8440 g crystallized cobalt sulphate.
0.19 g nickel as nickel sulphate.
1.9 volts; 0.45 amp; 20°; 8 hours.
Cathode deposit of 0.1668 g Co, free from nickel.
Anode deposit of 0.0153 g cobaltic oxide, free from nickel. Total cobalt 0.175 g (= 20.7 %).
Solution tests for cobalt.

When using the rotating anode, the insoluble white salt is not formed. Rapid rotation tends, however, to detach the peroxide at the anode.

In the third set of runs a needle anode of platinum wire was used and the solution was not stirred. Owing to the increased resistance the current dropped almost to one-sixth its previous value.

RUN 6.

0.9288 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.95 volts; 0.08 amp; 18°; 20 hours.
Cathode deposit of 0.1948 g Co (= 19.9 %), free from nickel. No anode deposit.
Solution still contains cobalt.

RUN 7.

1.078 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.95 volts; 0.08 amp; 18°; 24 hours.
Cathode deposit of 0.1958 g Co (= 18.2 %), free from nickel. Anode wire coated with whitish insoluble salt. Solution contains cobalt.

RUN 8.

0.7443 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
1.95 volts; 0.08 amp; 18°; 24 hours.
Cathode deposit of 0.1558 g Co (= 20.9 %), free from nickel. Solution contains cobalt.

When using needle anode, care must be taken to prevent voltage rising during the run. The temperature should be kept between 15° and 18°. Some runs were made at 5° and at 10°, but there is then a green iridescent precipitate left on the cathode after the metallic cobalt has been dissolved. This precipitate disappears on ignition, sulphur dioxide being formed. In some cases as much as 0.0015 g of sulphur were found.

The results of these runs are that the cobalt precipitates pure, but that the last traces are very difficult to remove from the solution. Experiments were also made to see whether better results could be obtained by varying the concentrations of caustic soda and sodium potassium tartrate. Reducing the caustic soda from 50 cc to 5 cc reduces the amount of anode deposit, but increases the precipitation of nickel at the cathode. Decreasing the amount of tartrate increases the anode deposit and also the amount of nickel at the cathode. Increasing the amount of tartrate cuts down the anode deposit and prevents the precipitation of nickel at the cathode, but it makes the precipitation of the cobalt more difficult. Raising the temperature makes the nickel precipitate more readily. The best conditions seem to be 10 g sodium potassium tartrate, 50 cc NaOH (sp. gr. 1.3), temperature of 15°–20° and a voltage not to exceed 2.0 volts.

Since Vortmann recommends the use of potassium iodide a run was made to test the effect.

Run 9.

0.713 g crystallized cobalt sulphate.
0.1 g nickel as nickel sulphate.
2 g potassium iodide.
2.05 volts ; 0.75 amp ; 12° ; 22 hours.
There was a thick green deposit on the cathode and the solution was murky. There was a black residue at the anode. Cathode deposit of 0.079 g Co (= 11.1 %).

As one reason for the difficulty in precipitating the last traces is the formation of the green cobaltic salt at the anode, some experiments were made with reducing agents. Addition of pyrogallol prevents the precipitation of oxide for a while, but more must be added every hour. The solution, of course, becomes black and dirty. With a potential difference of 2.2 volts the cobalt was not all precipitated at the end of twenty-five hours. Sodium bisulphite prevents the anodic precipitation of oxide, but sulphur is precipitated with the cobalt and the last traces of cobalt come out hard. Addition of 2 g resorcine prevents the precipitation of cobalt. After the voltage had been kept four hours at 2.5 volts, there was no cobalt on the cathode. Formaldehyde, 10 cc, prevents the precipitation of oxide, but the cobalt was not all out at the end of six hours. Hydroxylamine sulphate does not change the decomposition voltage of cobalt perceptibly; but the last traces of metal do not precipitate under low voltages.

When there is no nickel present, there is no difficulty in getting all the cobalt out of the solution. The following experiments may be cited:

RUN 10.

0.7361 g crystallized cobalt sulphate.
5 g sodium potassium tartrate.
5 cc NaOH (sp. gr. 1.3).
Solution made up to 130 cc.
Rotating disk as anode.
A few crystals of hydroxylamine sulphate were added to prevent formation of oxide.
4.75 volts; 3.25 amp; 15°; 7 hours.
Cathode deposit of 0.1715 g Co (= 23.3 %).
Solution contains no cobalt.

RUN 11.

0.7430 g crystallized cobalt sulphate.
Other conditions as in Run 10.
Cathode deposit of 0.1730 g Co (= 23.28 %).
Solution contains no cobalt.

In the next run the hydroxylamine sulphate was omitted and the amount of caustic soda increased slightly to decrease the resistance.

RUN 12.

0.0870 g metallic cobalt dissolved in hot concentrated sulphuric acid. The excess acid was neutralized with caustic soda.
5 g sodium potassium tartrate.
7 cc NaOH (sp. gr. 1.3).
Solution made up to 150 cc.
Rotating disk as anode.
4 volts; 5 amp; 18°–45°; 2 hours.
Cathode deposit of 0.0802 g Co.
Anode deposit of 0.0122 g cobaltic oxide.
Solution gives no test for cobalt.

If we assume that the cobaltic oxide has the formula $Co_2O_3.3H_2O$ the total cobalt is 0.0868 g instead of 0.0870 g, a difference which is inside the experimental error. On any assumption the composition of the oxide must correspond very closely to the formula $Co_2O_3.3H_2O$, which confirms the results of Coehn[1]. Another run was made in which a needle anode was used, the solution being stirred by means of a rotating glass paddle. This was to prevent anodic precipitation of oxide.

RUN 13.

0.0802 g metallic cobalt dissolved in hot concentrated sulphuric acid. The excess acid was neutralized with caustic soda.
5 g sodium potassium tartrate.
7 cc NaOH (sp. gr. 1.3).
Solution made up to 150 cc.
19 volts; 3 amp; 18°–60°; 1.5 hours.
Cathode deposit of 0.0800 g Co.
Solution gives no test for cobalt.

This is a quick and accurate method of determining pure cobalt. As it requires a very high voltage two more runs are given in which the metal was dissolved in nitric acid instead of sulphuric acid. In making up the solution it is desirable to add the substances in the order given.

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[1] Zeit. anorg. Chem. 33, 18 (1902).

RUN 14.

0.0394 g metallic cobalt dissolved in least possible hot concentrated HNO_3.
7 cc water.
7 g crystallized sodium potassium tartrate dissolved in a very little water.
7 cc NaOH (sp. gr. 1.3) plus amount necessary to neutralize free acid.
Solution made up to 150 cc.
4 volts; 5 amp; 18°–50°; 2 hours.
Cathode deposit of 0.0393 g Co.
Solution gives no test for cobalt.

If there is any tendency for cobaltic oxide to precipitate at the anode, a drop or two of hot concentrated nitric acid should be added.

RUN 15.

0.0863 g metallic cobalt dissolved in nitric acid.
Time of electrolysis, 3 hours. All other conditions the same as in Run 14.
Cathode deposit of 0.0862 g Co.

The quantitative results of Runs 12–15 are given in Table I. The methods are entirely satisfactory for the case when one has to make determinations of cobalt only.

TABLE I.

Cobalt		Cobalt	
Taken	Found	Taken	Found
0.0870	0.0868	0.0394	0.0393
0.0802	0.0800	0.0863	0.0862

While the electrolytic determination of cobalt in itself is simple and easy, the separation from nickel in an alkaline tartrate solution takes so long that it is useless for analytical purposes. Experiments were then made on electrolytic purification, to see whether the bulk of the cobalt could be obtained free from nickel and the bulk of the nickel obtained free from cobalt.

Nickelic oxide, Ni_2O_3, precipitates more readily, the more carbonate and the less tartrate there is in the solution. As cobaltic oxide tends to come down with the nickel, it was found best first to precipitate nearly all the cobalt, then to add sodium carbonate and electrolyze with low current density. There are three cases to be considered: cobalt solutions with nickel as impurity; nickel solutions with cobalt as impurity; solutions containing nickel and cobalt, neither being present in large excess.

In the first run 150 cc of solution contained

5.01 g cobalt sulphate	10 g sodium potassium tartrate
0.50 g nickel nitrate	10 drops hot conc. HNO_3

50 cc caustic soda (sp. gr. 1.3).

A Classen dish was used as cathode and a needle anode. The solution was electrolyzed thirty hours at 20° and 2 volts. The cathode deposit weighed 1.069 g and gave no test for nickel. The solution still contained cobalt. A clean cathode was substituted and the run continued for twenty-four hours more. The cathode deposit weighed 0.058 g and was free from nickel. The solution gave only a faint test for cobalt. A platinum dish was now made anode and a rotating platinum disk the cathode. After adding 5 g Na_2CO_3 the solution was electrolyzed for another twenty-four hours. The cathode deposit weighed 0.0016 g and contained no nickel. The anode deposit did not adhere well and the solution was therefore filtered through a Gooch crucible. In this way there were obtained 0.1643 g nickelic oxide on the anode and 0.0356 g in the Gooch. This oxide gave a faint trace for cobalt, probably due to occluded mother-liquor.[1] The solution was colorless and gave no test for cobalt or nickel. The yield is 1.1285 g of pure cobalt and 0.1998 g of nickelic oxide containing the merest traces of cobalt. By dissolving and reprecipitating, this trace of cobalt could be removed. In a second run with 5.004 g cobalt sulphate and 0.1256 g nickel nitrate, 1.1233 g pure cobalt were obtained and 0.0638 g of nickelic oxide containing traces of cobalt.

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[1] Coehn. Zeit. anorg. Chem. 33, 22 (1902).

In the next run the conditions were the same as before, except that the solution contained 2.0 g cobalt sulphate and 2.041 g nickel nitrate, and that the voltage was 1.9 volts.

Electrolyzed 20 hours
  Deposit = 0.2672 g Co, pure
Electrolyzed with clean electrodes, 7 hours
  Deposit = 0.0452 g Co, pure
Electrolyzed with clean electrodes, 17 hours
  Deposit = 0.0752 g Co, pure
Electrolyzed with clean electrodes, 24 hours
  Deposit = 0.0478 g Co, pure
Electrolyzed with clean electrodes, 19 hours
  Deposit = 0.0067 g Co, pure
Electrolyzed with clean electrodes, 17 hours
  Deposit = 0.0017 g Co, pure
Electrolyzed with clean electrodes, 48 hours
  Deposit = 0.0044 g Co, pure
Added 10 g sodium potassium tartrate and 25 cc NaOH
Electrolyzed with clean electrodes, 48 hours
  Deposit = 0.0042 g Co, pure
Electrolyzed 5 hours, with a wire gauze anode, ½ in. by 4 in., wrapped in parchment paper. Solution stirred.
  Deposit = 0.0062 g Co, pure. Only slight deposit on gauze. Solution free from cobalt.
Added 5 g Na_2CO_3 and electrolyzed 24 hours with disk as anode and stationary disk as cathode.
  Anode deposit = 0.7718 g Ni_2O_3 free from cobalt. No cathode deposit. Solution free from nickel and cobalt.

The total yield is 0.0586 g cobalt free from nickel and 0.7718 g nickelic oxide free from cobalt. The exceptional purity of the nickelic oxide is due to the fact that all the cobalt was removed before the oxide was precipitated. It is, however, a very tedious job to remove the last traces of cobalt when there is much nickel present, over eight days in this particular case.

To test the separation of a large amount of nickel from a small amount of cobalt, a solution was taken containing 5.002 g nickel nitrate and 0.1007 g cobalt sulphate. At first a needle anode and a dish cathode were used. A voltage of 1.9 volts gave only 0.05 ampere. At the end of 49 hours there had been deposited 0.0102 g Co, pure. After 47 hours more there had been deposited 0.0042 g Co, pure. The needle anode was replaced by a rotating disk and the electrolysis continued for 2.5 hours at 1.8 volts (0.2 ampere). At the cathode there was 0.0010 g Co, pure; at the anode 0.0029 g cobaltic oxide free from nickel. Three grams of sodium potassium tartrate were added and the solution electrolyzed for 16 hours with continuous stirring. The cathode deposit consisted of 0.0042 g pure cobalt and the anode deposit of 0.0011 g cobaltic oxide free from nickel. As there was only very little cobalt left in the solution, the electrodes were reversed, 5 grams of sodium carbonate added, and the solution electrolyzed for twenty-four hours at 2.1 volts. At the cathode was 0.0011 g Co, showing faint traces of nickel. The nickelic oxide at the anode weighed 1.2561 g, and 0.6439 g was obtained by filtration. This oxide showed faint traces of cobalt. The total yield was 0.0196 g cobalt, pure; 0.0011 g cobalt, impure; 0.004 g cobaltic oxide, pure; 1.9 g nickelic oxide, containing traces of cobalt. In the second experiment there was no nitric acid in the solution and no sodium potassium tartrate was added during the run. Under these conditions the cobaltic and nickelic oxides come down together and there is no satisfactory separation. No experiments have yet been made with a diaphragm.

The general results are:

1. In presence of cobalt, the decomposition voltage for nickel in an alkaline tartrate solution is lowered.

2. Several methods were found for the electrolytic determination of cobalt alone.

3. It is possible to obtain nickel and cobalt pure from an alkaline tartrate solution if one is willing to take the time and pains.

4. The difficulty is due in part to the formation of cobaltic salt in the solution.

5. Coehn's results as to the composition of cobaltic oxide, $Co_2O_3.3H_2O$, have been confirmed.

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

Cornell University.

THE ACTION OF BARIUM AMALGAM ON SOLUTIONS OF SODIUM AND POTASSIUM SALTS

BY GEORGE MCPHAIL SMITH

In an article published recently in this journal, Gustave Fernekes[1] attempts to answer a criticism by me[2] of a thesis carried out by him[3] at the University of Wisconsin, on the action of sodium and potassium amalgams on various aqueous solutions. He begins by saying: "Smith, in an attempt to harmonize the facts observed by me with the theory of electrolytic dissociation, has drawn some rather hasty conclusions from very meager experimental evidence. In this paper I purpose to show that the great number of experiments which I have performed, and also the few additional ones of Smith can not only be readily explained without the aid of the electrolytic dissociation theory, but that it is impossible to explain the majority of them by means of that theory."

In the present paper I shall present one more "additional experiment", to which I would especially call the attention of Dr. Fernekes, viz: the easy replacement of barium in barium amalgam by sodium and potassium, by acting on the amalgam with a concentrated solution of the *hydroxide* of the metal in question.

It has long been known that sodium in sodium amalgam is replaceable by barium;[4] and in 1871 the following fact was discovered:[5] "Trägt man Natriumamalgam, wie es durch zusammenreiben von 3 Th. Natrium mit 97 Th. Quecksilber erhalten wird, in eine wässerige Lösung von kohlensaurem Kali oder Kalihydrat, so sieht man nach mehrtägigem Stehen in dem abgeschiedenen Quecksilber harte glänzende Krystalle eines

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[1] Jour. Phys. Chem. 8, 566 (1904).
[2] Ibid. 8, 208 (1904).
[3] Ibid. 7, 611 (1903).
[4] Jahresber. Chem. 1862, 126.
[5] Kraut und Popp. Liebig's Annalen, 159, 188.

Kaliumamalgams erscheinen. ... Aus essigsaurem Kali oder Chlorkalium werden sie nicht erhalten." Fernekes[1] gives at the beginning of his first article a reference to a paper[2] in which the following statements are made: "Ausserdem erhielt ich Kaliumamalgam, durch einbringen von Natriumamalgam in Kalilauge, wobei die Alkalimetalle nach längerer Zeit ihre Stellen auswechseln. ... Einprocentiges Natriumamalgam zersetzt die Chloride der meisten Metalle und bildet mit letzteren Amalgame."

And yet, in the same article Fernekes[3] says: "It would seem that the action of 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. ... 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."

In my former paper[4] I showed that the slow action of sodium amalgam on solutions of potassium salts, and of potassium amalgam on solutions of sodium salts could be readily explained by the ionic theory, as follows: "At the beginning, the main process[5] [i. e., in the action of sodium amalgam on potassium

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[1] l. c. 7, 612.

[2] J. Schumann. Wied. Ann. 43, 101–125 (1891).

[3] l. c. 7, 635.

[4] l. c. 8, 211.

[5] See explanation at the end of this paper.

salt solutions] consists in the replacement of sodium by potassium, and, as soon as an equilibrium has been approached in this direction, the resulting amalgam is free to act on the water of the solution with the formation of potassium (and sodium) hydroxide. It is now easy to see why this action is retarded. The sodium and potassium ions of the solution tend to prevent the entrance of more sodium and potassium in the ionic state.

"In the same way, the slow action of potassium amalgam on solutions of sodium salts is explained, a part of the potassium of the amalgam being replaced by sodium, according to the law of mass action."

My paper closed as follows:[1] "By treating potassium amalgam (or others) successively with fresh portions of a saturated solution of sodium chloride, for example, it should be possible to replace all the potassium (or other metal) by sodium in the course of a short time." This cannot be carried out as readily as I expected, for which fact an explanation will be offered at the end of this paper. That it is true in the case of barium amalgam, however, will be shown by the following experiments:

Preparation of Barium Amalgam

The barium amalgam used was prepared by treating sodium amalgam successively with fresh portions of a saturated solution of barium chloride.

The sodium amalgam for this purpose was made by the addition of sodium in small pieces to 250 grams of mercury. It was thoroughly washed with water and dried by means of filter-paper. It contained enough sodium to be of a pasty consistency when cold.

Thus obtained, the sodium amalgam was poured into about three times its volume of saturated barium chloride solution, which had previously been heated to 80° C, and the mixture let stand for five minutes. Upon coming into contact with the solution, the amalgam almost instantly solidified, notwithstanding the high temperature. This treatment was twice repeated

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[1] l. c. 8, 213.

with the same amalgam and fresh portions of barium chloride solution. During the second treatment the amalgam softened somewhat, and during the third it became almost liquid. The evolution of hydrogen was much more rapid during the first treatment than during the second and third.

The resulting amalgam was heated on a water-bath for fifteen minutes with a large excess of fresh barium chloride solution, the mixture being stirred from time to time. At the end of this period the amalgam was liquid at 80°, but after having been cooled with water to 20° it was still only semi-liquid.

In order to remove any sodium which might possibly have remained in it, the amalgam was permitted to stand over night with an excess of saturated barium chloride solution; the evolution of hydrogen was exceedingly slow. The next morning the amalgam was liquid at 20°. It was thoroughly washed with water, dried by means of filter-paper, and put into a glass-stoppered bottle. This amalgam did not remain homogeneous; after a few days a thin layer of crystals had separated out on the walls and bottom of the bottle.

Analysis of the Barium Amalgam

Immediately after the amalgam had been prepared, 48.68 grams of it was decomposed by heating with water on a water-bath. The extract was acidified with hydrochloric acid and the barium precipitated with sulphuric acid. The filtrate was evaporated to dryness and the residue weighed.

The amalgam gave:

0.8740 g $BaSO_4$ (i. e. 1.056 % Ba)
0.0023 g residue (Na_2SO_4).[1]

The Action of Barium Amalgam on Potassium Chloride Solution

I. To 40 grams of barium amalgam in a small beaker 50 cc of a saturated potassium chloride solution was added, and the mixture allowed to stand for three and one-half hours at 24° C.

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[1] This residue was of a reddish color and it was not dissolved on the addition of water. It probably consisted mainly of Fe_2O_3. A mixture of 2 or 3 cc each of the sulphuric and hydrochloric acids used in the analysis left a similar residue on evaporation. The residue therefore was not Na_2SO_4.

The evolution of hydrogen was extremely slow, but could be distinctly seen at two or three points on the surface of the amalgam, from each of which rose a continuous stream of microscopic bubbles.

At the end of the above period, the potassium chloride solution was decanted, and the amalgam carefully and thoroughly washed with distilled water. It was then decomposed by heating with water. The extract was acidified with hydrochloric acid and the barium precipitated from it with sulphuric acid. The filtrate was evaporated to dryness, and the residue taken up in water, filtered and evaporated to a syrup with platinum chloride. The excess of the latter was removed with absolute alcohol, and the precipitate dried and weighed. Result: 0.0086 g K_2PtCl_6.

II. The crystals of barium amalgam from the walls of the bottle (20.10 g) were allowed to stand five minutes with 40 cc of saturated potassium chloride solution. The amalgam was then thoroughly washed and analyzed as above. Result: 0.0060 g K_2PtCl_6.

The amounts of potassium platinum chloride obtained in the above experiments are so small that it is doubtful whether some of the potassium really entered into the amalgam. The washing of the amalgam after the action of the potassium chloride solution, however, was so thorough that it is much more likely that potassium was extracted from it by the wash-water, than that any potassium chloride was left behind.

From these experiments, then, it is probable that some, though very little, of the barium in the amalgam was replaced by potassium from the potassium chloride solution. It is seen that barium in its amalgam is not so readily replaced by potassium as is potassium in its amalgam by barium.

By acting on a concentrated solution of potassium hydroxide with barium amalgam, results were obtained, which, together with those obtained with potassium chloride, can readily be explained with the help of the ionic theory and the law of mass action. In the experiments with potassium chloride solution and barium amalgam there were no barium or hydroxyl ions in the solution. While the barium could readily come out of the amalgam, therefore, there was nothing to prevent its doing so by acting on the water of the solution. By using a solution of potassium hydroxide instead of the potassium chloride solution, however, the hydroxyl ions already in the solution tend to prevent the entrance there of more hydroxyl ions. From this it results that the easiest way in which the barium can enter the solution is by replacing potassium in the potassium hydroxide. The solubility product of the barium hydroxide formed is soon exceeded in the concentrated potassium hydroxide solution, so that, as fast as the barium replaces potassium in potassium hydroxide, the resulting barium hydroxide separates out in solid form. That this is really the case will be seen below.

In addition to his experiments with potassium and sodium chlorides, Fernekes performed some experiments with potassium and sodium sulphates, the object of which "was to throw insoluble barium sulphate out of solution, and thus give the potassium or sodium a better chance to combine with the mercury." He says:[1] "The difficulty which presented itself here is quite apparent. Barium sulphate would form at the surface of the amalgam and prevent further action. I therefore shook the amalgam violently with the solution; and continued the shaking with an occasional renewing of the solution until no more turbidity occurred. But when I now examined the amalgam I found neither barium nor alkali metal present. To complete this series of experiments, I tried various temperatures up to 40° C with the same result as above. This shows conclusively that barium in its amalgam is not replaceable by either sodium or potassium by the method which Smith thought possible by the ionic theory." That this conclusion is rather hasty will be seen below. In view of the results obtained with potassium hydroxide solution, I did not consider it worth while to repeat the above experiments.

Action of Barium Amalgam on Potassium Hydroxide Solution

I. 25 cc of saturated potassium hydroxide solution, made by

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[1] l. c. 8, 567f.

adding an excess of stick potassium hydroxide to water, stirring occasionally, and letting stand over night, was diluted with an equal volume of water, and to the resulting solution, 28.21 grams of barium amalgam added. The temperature of the mixture was 35° C.

The evolution of hydrogen could barely be detected, and in less than five minutes the amalgam was covered with white scales of barium hydroxide.

The mixture was allowed to stand for one hour, after which the amalgam was thoroughly washed, dried with filter-paper, and then washed again. It was then decomposed by heating with water, and the watery extract analyzed for barium and potassium.

The amalgam gave:

0.1030 g $BaSO_4$ (= 0.0606 g Ba)
0.2986 g K_2PtCl_6 (= 0.04812 g K).

The KOH mother-liquor gave:

0.1755 g $BaSO_4$ (= 0.1033 g Ba)
(0.04812 g K equivalent to 0.08446 g Ba).

II. To 25 cc saturated potassium hydroxide solution at 23° C was added 38.14 grams of barium amalgam. No evolution of hydrogen could be detected, but the amalgam was soon covered with grayish flakes of barium hydroxide.

After having stood for one hour, the potassium hydroxide was decanted, and the amalgam thoroughly washed. The wash-water was added to the potassium hydroxide mother-liquor.

The amalgam was then decomposed by heating it with water, the watery extract acidified with hydrochloric acid, and the barium precipitated from the boiling solution with sulphuric acid. The filtrate from the barium sulphate was evaporated to dryness, the residue taken up in a little water, the solution filtered, and then an excess of platinum chloride added. The resulting solution was evaporated to dryness on a water-bath and the excess of platinum chloride removed by means of absolute alcohol. The potassium platinum chloride was dried at 160° in a weighed platinum crucible.

The amalgam gave:

0.1589 g $BaSO_4$ (= 0.09354 g Ba)
0.4104 g K_2PtCl_6 (= 0.06615 g K).

The KOH mother-liquor gave:

0.2038 g $BaSO_4$ (= 0.11995 g Ba)
(0.06615 g K equivalent to 0.1161 g Ba).

Action of Barium Amalgam on Sodium Hydroxide Solution

To 100 cc of saturated sodium hydroxide solution, made by dissolving stick sodium hydroxide in water, was added 59.69 grams of barium amalgam. The temperature of the mixture was 45° C.

The evolution of hydrogen was imperceptible, but the amalgam was soon covered with grayish flakes of barium hydroxide.

After having stood for 65 minutes, the solution was decanted and the amalgam thoroughly washed. The amalgam was then decomposed with water, and the extract analyzed for barium and sodium.

The amalgam gave:

0.0415 g $BaSO_4$ (= 0.0244 g Ba)
0.1868 g Na_2SO_4 (= 0.06057 g Na).
(0.06057 g Na, equivalent to 0.1805 g Ba).

I shall now turn to the objections of Fernekes to my criticism of his thesis.

But first it may be stated that in this thesis Fernekes covered only the action of sodium and potassium amalgams on aqueous solutions, none of which contained more than one metal.

Besides acting on sodium amalgam with sodium salts, he also acted on it with potassium salts, then with hydrochloric and nitric acids, and finally with salts of ammonium, barium, calcium, and strontium. In this case K, NH_4, Ba, Ca, and Sr are all capable of replacing sodium in sodium amalgam.

Also, he acted with potassium amalgam on solutions of sodium and potassium salts. As shown in my first paper, sodium is capable of replacing potassium in potassium amalgam.

Finally, he acted with sodium amalgam on solutions of various organic compounds in water.

On page 566[1] he says: "Without attempting to make sodium amalgam from calcium, barium or magnesium amalgams, by treating these amalgams with a concentrated sodium chloride solution, Smith nevertheless proceeds to the following general statement: 'But nowhere have I seen that sodium amalgam has been prepared from potassium amalgam or from magnesium amalgam, etc., as should also be possible according to the ionic theory and the law of mass action.'" That this statement was made, rather to show that I intended to do further work along that line, than as a prophecy sure to be fulfilled, can be seen by referring to my article.[2]

On page 568[3] Fernekes says: "As Smith's objections were found not to hold for barium amalgam, it could be used for the purpose of testing the correctness of Prof. Kahlenberg's theory." This statement can no longer be maintained.

Fernekes[4] further says: "But to show that Smith has omitted consideration of the important factor, chemical attraction, in explaining the replacements in the mercury, I performed another experiment to show how essential this factor is.

"A solution containing equimolecular quantities of sodium and potassium chlorides was allowed to act on sodium amalgam. After fifteen minutes, the amalgam was examined, and found to contain only potassium, although more sodium than potassium was present in the solution at the end of the experiment. The experiment was now performed with potassium amalgam and the same solution. Again only potassium was found in the amalgam. This proves that potassium has a greater affinity for mercury than sodium."

While I did not exactly see Fernekes's object in perform-

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[1] l. c. 8, 566.
[2] l. c. 8, 213.
[3] l. c. 8, 568.
[4] l. c. 8, 568f.

ing the above experiments, since all that I said had reference only to the action of the amalgam of one metal on the solution of a salt of a single other metal, the results of his experiments nevertheless looked rather improbable, and I therefore repeated them with the following results.

A solution containing equimolecular quantities of sodium and potassium chlorides was made by dissolving a mixture of 29.2 g NaCl and 37.2 g KCl in as little water as possible, in a 250 cc flask, and then filling up to the mark with water.

An amalgam made from 101 g mercury and 1.15 g sodium was allowed to stand for one-half hour (instead of only fifteen minutes) at the ordinary temperature with 50 cc of the above solution, in a beaker 5 cm in diameter. The solution was then poured off and the amalgam thoroughly washed. It was then decomposed with water, the extract acidified with hydrochloric acid, and evaporated to dryness in a platinum dish. The chlorides obtained were first dried at 130° and then gently ignited, and after cooling weighed.

The chlorides were then dissolved in a little water, 45 cc of 10 percent H_2PtCl_6 solution was added and the mixture evaporated to dryness on a water-bath. The residue was then extracted with fresh portions of absolute alcohol as long as anything continued to be dissolved, and until the residue was of a pure golden yellow color. The residue of K_2PtCl_6 was finally dried in a platinum dish at 140°.

The amalgam gave:

1.2697 g NaCl + KCl.

This gave:

1.0115 g K_2PtCl_6.

Therefore the amalgam contained 0.16303 g K and 0.3779 g Na.

(0.16303 g K, equivalent to 0.09598 g Na).

An amalgam made from 102 g mercury and 1.0 g potassium was treated as above with 50 cc of the same solution for fifteen minutes. The amalgam was then thoroughly washed and decomposed, and the extract analyzed as above. 18 cc of

10 percent H_2PtCl_6 was used to convert the chlorides into the corresponding platinum chlorides.

The amalgam gave:

0.4935 g $KCl + NaCl$.

This gave:

0.6000 g K_2PtCl_6.

Therefore the amalgam contained 0.09670 g K and 0.1218 g Na.[1]

(0.1218 g Na, equivalent to 0.2070 g K.)

The Action of Potassium Amalgam on Barium Chloride Solution[2]

An amalgam made from 105.5 g mercury and 1.15 g potassium was treated at the ordinary temperature with 100 cc of a saturated barium chloride solution. The evolution of hydrogen was moderately rapid. After ten minutes the solution was decanted and the amalgam thoroughly washed. It was then analyzed for barium and potassium.

The amalgam gave:

2.9729 g $BaSO_4$ (= 1.7495 g Ba)
0.3428 g K_2PtCl_6 (= 0.0552 g K).
(1.7495 g Ba, equivalent to 0.99678 g K).

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[1] The alcoholic extracts from the K_2PtCl_6 were evaporated to dryness and strongly ignited in the air. The residues were extracted with water and the solutions filtered and evaporated to dryness. The residues were ignited and weighed. The first, from the sodium amalgam, weighed 0.6920 g; the second, from the potassium amalgam, weighed 0.2770 g. Both consisted of pure NaCl. No precautions were taken to make these results quantitative, and the operation was only performed to show conclusively that there was sodium in each of the amalgams, after the action of the above solution on them.

[2] The above experiment is given here to show that even barium, which Fernekes says forms such a stable compound with mercury, does not at once replace all the potassium in a one percent potassium amalgam, even when the latter is acted upon with a large excess of a saturated solution of pure barium chloride. The electrochemical series reads: + K, Na, Li, Ba, Sr, Ca, Mg, ..., Hg, ..., —. It is therefore easy to understand why potassium does not replace sodium as readily as Fernekes thinks. Besides, he has evidently failed to take into consideration the law of mass action. Also, the above experiments show that under like conditions potassium is more readily replaced in its amalgam by sodium, than is sodium in its amalgam by potassium, just as was to be expected according to the electrochemical series.

After having given some heats of formation for sodium and potassium amalgams, Fernekes[1] says: "... From these thermochemical data Berthelot has explained the replacement of sodium in sodium amalgam by potassium in a potassium hydroxide solution, and it did not require the assumption of ions to account for the facts satisfactorily. ...

"The reason why barium in barium amalgam is not replaced by sodium or potassium from solutions of their salts is perfectly obvious. In the case of barium amalgam there evidently exists a compound whose heat of formation so far exceeds that of either sodium or potassium amalgam, that a replacement by these metals is in no manner possible."

And yet the ionic theory has led to that very replacement, it having been found only necessary to act on the amalgam with a concentrated solution of the alkali hydroxide. Besides, even Berthelot did not foresee from his thermochemical data that potassium in potassium amalgam could be replaced by sodium in a sodium chloride solution.

Fernekes continues as follows: "From the fact that barium has such a strong affinity for mercury, we should expect the vapor tension of the solution of barium in mercury to be depressed correspondingly. In looking over the results obtained[2] for the molecular weight of barium and calcium where mercury was used as a solvent, I found that it was about one-half that obtained by other methods. Ostwald says that he could not harmonize these facts with the existing views. According to Prof. Kahlenberg's theory the explanation is again very simple."

Fernekes did not quote Ostwald in full. What Ostwald says is as follows:[3] "The numbers found for the molecular weights of calcium and barium are very noteworthy; they are about half as large as the atomic weights; the number found for potassium is also much smaller than the atomic weight. No

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[1] l. c. 8, 569.

[2] Ostwald. Solutions, p. 193.

[3] Ostwald. Solutions, p. 193.

satisfactory explanation of these numbers has yet been found."[1]

Fernekes[2] makes the following three claims at the end of his paper:

"I have thus shown in this paper that the reciprocal replacement of metals in mercury is not always possible as might be expected from 'the ionic theory and the law of mass action.' That a retardation of the evolution of hydrogen by the action of an amalgam, which is not thus replaceable, upon a solution is nevertheless observed. Furthermore the replacements which do take place in the amalgams can be explained on a purely thermochemical basis and [by] the laws of chemical attraction."

In regard to the first claim, Fernekes might be more successful in showing "that the reciprocal replacement of metals in mercury is not always possible", if he would try, for example, to replace silver in silver amalgam by sodium.

It has already been shown that the second claim is baseless.

As to the third, it is nevertheless very well to have the ionic theory to fall back on, in order to explain why barium in barium amalgam is so much more readily replaced by potassium and sodium in solutions of their hydroxides than in solutions of their chlorides.

It might also be well here to call Fernekes's attention to the fact that it is still an unsettled question, whether amalgams are compounds of other metals with mercury, or solutions of other metals in mercury; or whether both cases may not occur.

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[1] Through the courtesy of Prof. Bancroft, my attention has been called to the fact that in a paper on the electromotive force between amalgams, by Hamilton P. Cady, Jour. Phys. Chem. 2, 551 (1898), and 3, 107 (1899), these numbers have been satisfactorily explained by taking into account the heats of dilution of the amalgams in question. The amalgams which give normal results are those of which the heats of dilution are approximately equal to zero.

In the article cited (Jour. Phys. Chem. 2, pp. 556-7) it is shown that sodium amalgam also gives abnormal figures, as follows: molecular weight calculated from vapor pressure (Ramsay), 22.6-15.1; molecular weight calculated from E. M. F. (Cady), 16.3-17.3; atomic weight, 23.0. It is then shown experimentally that these results become normal when the heat of dilution of the amalgam is taken into account. This is probably true also in the case of calcium, barium, and potassium amalgams.

[2] l. c. 8, 570.

For example, on p. 61 of his "Text-book of Electrochemistry,"[1] Arrhenius says: "W. Ramsay investigated the vapor pressure of solutions of various metals in mercury. . . . A lowering of the vapor pressure was always observed on dissolving foreign metals in the mercury, and Ramsay was thus able to determine the molecular weight of the dissolved metal; for most metals, namely Li, Na, Mg, Zn, Cd, . . ., Au, he obtained results which agreed with the atomic weights within the experimental error. For K, Ca, and Ba he found numbers which are very appreciably lower (about half) than the atomic weights, a peculiar phenomenon which has not yet been explained.[2] The molecular weights found for Al, Sb, and Bi are considerably greater than the atomic weights of these elements, indicating that their molecules consist of several, probably two, atoms. On the whole the results agree remarkably well with what is known of the molecular weights of the metals in the gaseous state.

"Ramsay's observations have been confirmed by the experiments on the freezing-points of metal alloys made by Tammann. . . .

"The experiments of Roberts-Austen and of G. Meyer on the diffusion of metals in mercury confirmed the above results."

But F. Haber[3] concludes a recent article as follows: "Die Einatomigkeit der Metalle in Quecksilber ist durch die bisher bekannten elektrometrischen Messungen [by G. Meyer, etc.] nicht bewiesen. Diese lehren überall nur, dass *entweder* Einatomigkeit *oder* Metallquecksilberverbindungen der Form Hg_m M vorliegen."

Fernekes[4] begins his concluding paragraph as follows:

"But before concluding this paper it might be well to ask Smith how he would explain by the ionic theory the anomalous behavior of sodium hydroxide solutions towards both sodium

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[1] Translated by John McCrae (1902).

[2] But see note on preceding page.

[3] Zeit. phys. Chem. 41, 406 (1902).

[4] l. c. 8, 570.

and potassium amalgams. These phenomena he seems to have overlooked entirely. Besides this there is still the great number of solutions of organic compounds which he has failed to mention."

In regard to the action of the solutions of organic compounds on sodium amalgam, I shall not attempt to explain it by the ionic theory.[1] Neither has it been satisfactorily explained by the hypothesis of Prof. Kahlenberg.

In his attempt to explain it in his thesis, Fernekės[2] says that Prof. Kahlenberg has suggested 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 [those of] either constituent form the basis of this new theory."

To explain the action of the solutions of organic compounds on sodium amalgam, he[3] says: "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. 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 explana-

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[1] Though it might be ascribed to a higher concentration of hydrogen ions in most of these solutions, than in pure water.

[2] l. c. 7, 636.

[3] l. c. 7, 637.

tion 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."

Fernekes has, to say the least, been very unfortunate in his selection of an "instance to illustrate what is meant" by "such an unstable compound." For, in the first place, nitrous oxide is a definite chemical compound; and, secondly, it is not a more reactive substance than are either of the elements of which it is composed. On this subject Ostwald[1] says: "Dagegen verlischt Schwefel, wenn er ohne Erhitzen nur brennend in das Gas eingeführt wird." Erdmann[2] says: "Brennender Schwefel erlischt darin, wenn er nicht stark erhitzt ist." Holleman[3] says that a mixture of nitrous oxide and hydrogen explodes when ignited, like a mixture of oxygen and hydrogen, only a little weaker. Finally Richter[4] says: "A glimmering chip inflames in it, as in oxygen; phosphorus burns with a bright, luminous flame, while a sulphur flame is extinguished." A splinter of wood, therefore, will not "burn even more violently in nitrous oxide than in pure oxygen."

Fernekes[5] goes on to say: "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 can also be 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. ... A probable explanation [of the results of this action] follows from what has been stated above; small quanti-

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[1] Grundl. d. anorgan. Chem. (1900) p. 338.

[2] Lehrbuch d. anorgan. Chem. (1902) p. 192.

[3] Lehrbuch, (1900) p. 172.

[4] Inorganic Chem. 4th English Edition, p. 215.

[5] l. c. 7, 638.

ties 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."

A better explanation is that offered by W. Kerp.[1] It is as follows:

"Entsprechend der Theorie erfährt die Reaction [i. e. between water and sodium amalgam] mit der Menge der entstehenden Natronlauge eine fortwährende Verzögerung, Chlornatrium und Soda verzögern die Auflösungsgeschwindigkeit des Amalgams etwa dreimal so stark, als die bei der Zersetzung des Amalgams durch Wasser entstehende Natronlauge. Höchst auffallend jedoch war die Einwirkung von Natronlauge, welche aus dem sogenannten reinen Ätznatron des Handels hergestellt war. Das Amalgam wurde unter stürmischer Wasserstoffentwickelung zersetzt, und die Zersetzung verlief bei stärkeren als 1/4-norm.Lauge so ausserordentlich schnell, dass an ein quantitatives Verfolgen der Reaktion nicht zu denken war.

"Bei 1/4-norm.Lauge geht die Zersetzung des Amalgams noch etwa 40 mal, bei 1/10-norm.Lauge ungefähr 5 mal schneller vor sich, wie die Zersetzung durch Wasser bezw. die entstehende Natronlauge. Da die Natronlauge an sich somit nicht der Grund für die überraschende Erscheinung sein konnte, wurde das Ätznatron analysiert und neben Kieselsäure Eisen, Zink und Aluminium, wenn auch nur in geringen Mengen aufgefunden. Reine Natronlauge aus Natrium oder Natriumamalgam bereitet, zersetzt Natriumamalgam durchaus langsam. Versetzt man dieselbe aber mit der Auflösung eines Metalles, dessen Hydroxyd in Natronlauge löslich ist, in geringer Menge, z. B. mit Zinksulfat- oder Bleiacetatlösung, so erfolgt sofort mehr oder minder energische Wasserstoffentwickelung. Die stürmische Wasserstoffentwickelung bei der Einwirkung der gewöhnlichen Natronlauge auf das Amalgam beruht also unzweifelhaft auf der Anwesenheit jener Metalle und wird wahrscheinlich auf elektrische oder katalytische Ursachen zurückzuführen sein."

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[1] Zeit. anorg. Chem. 17, 308 (1898).

At this point it will not be out of place to offer an explanation why the reciprocal replacement of metals in mercury is probably not always possible, as might at first glance be expected from the ionic theory and the law of mass action.

Metals, like all other substances, possess when immersed in water a certain solution pressure, by which is understood an expansive force which seeks to drive the molecules of the metal into the solution. In the case of electrically neutral molecules, this expansive force is held in equilibrium by the osmotic pressure of the saturated solution; in the case of the metals, however, the particles which, by means of the solution-pressure, get into the solution are positively charged, and their solution-pressure is therefore called electrolytic.[1]

It is now easy to understand the processes that occur when a metal is immersed in pure water, or in a solution. If the ions of the given metal are absent from, or present only to a very limited extent in the solution, the solution-pressure of the metal drives a number of ions into the solution. As a result, the solution becomes positively charged and the metal negatively charged. These changes give rise to a force component, which on the one hand tends to prevent the entrance of more ions into the solution, and on the other hand, seeks to drive the positive ions in the solution back to the metal. On account of the enormous electrostatic capacity of the ions, this force attains an enormous magnitude, even before weighable amounts have entered the solution.

One of two things can now take place:

Either the solution-pressure of the metal is exactly compensated by the electrostatic charges, in which case there results an equilibrium, e. g., when silver is immersed in salt solutions.[2]

Or, as a result of the magnitude of the solution-pressure,

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[1] Nernst. Theoretische Chemie, 3 Aufl., p. 664f.

[2] The fact that silver does not dissolve under these conditions does not show that the solution-pressure of this metal is very small; it is more probable that it amounts to thousands of atmospheres, but its action is compensated by the electrostatic charge of the solution, caused by its contact with the metal (Nernst, l. c. p. 665).

the electrostatic charge attains such a high value, that other positive ions which are contained in the solution are driven out of it and deposited on the metal. We observe this in the case of the precipitation of one metal by a second, e. g., when a piece of zinc is dipped into the solution of a copper salt, ions of zinc go into the solution and the electrically equivalent amount of copper ions, driven by the electrostatic repulsion of the solution and the electrostatic attraction of the metal, are deposited on the zinc.[1] Another case is found in the evolution of hydrogen.

The decomposition of water by metals, with the evolution of hydrogen, is a most interesting reaction. The conditions for the evolution of hydrogen may be developed as follows:

In the electrolysis of a salt, where indifferent electrodes are employed, the cations separate out on the cathode, and the anions

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[1] It has long been customary to draw chemical conclusions from the electrochemical series of the metals. It should not be concluded, however, for example, that copper must always be precipitated by zinc. Ionic concentration is a second determining factor, which must be taken into consideration; and the experiment given below proves that under suitable conditions zinc is capable of being reduced by copper.

To a very concentrated solution of zinc sulphate was added one of potassium cyanide, until the precipitate at first formed was redissolved. Then enough of the zinc sulphate solution was added to produce a permanent precipitate, and then the solution was filtered. The filtrate was received in three test-tubes, each of which was about half filled by it. One sample was set aside; to the second was added about one-fifth its volume of the zinc sulphate solution, and to the third about the same amount of the potassium cyanide solution. In each sample was now immersed a piece (about 1 cm square) of bright copper foil, which had been polished with a new file. For a long time the copper remained unaltered, but after five or six hours a distinct trace of zinc could be seen on the copper foil in the solution to which an excess of potassium cyanide had been added; and a light, flocculent precipitate was present in this solution. After twenty-four hours the zinc precipitate on the foil was very distinct. During the whole time of the experiment hydrogen was slowly evolved by the copper in this solution. The copper in the solution to which an excess of zinc sulphate had been added remained perfectly bright, but that in the solution containing no excess of either zinc sulphate or potassium cyanide seemed to be coated after twenty-four hours with a very slight trace of metallic zinc.

The zinc sulphate, potassium cyanide, and copper foil used in the above experiment were obtained from Eimer and Amend. The zinc sulphate was marked "C.P.", and the potassium cyanide "Pure, 98%."

on the anode. The higher the concentration of the cations is, the more readily will they separate out, and the more dilute it is, the less readily will they separate out on the cathode. The same of course applies to the anions. If we designate the electromotive force necessary for the first process by ϵ, we have[1]

$$\epsilon_1 = \frac{RT}{n_1} \ln \frac{P_1}{p_1},$$

where P_1 is the electrolytic solution-pressure of the metal, p_1 the osmotic pressure of the monovalent ions of the metal; n_1 is the valency of the metal.

The electrical forces, considered above, work not only on the ions of the metal in question, but also on all the positive ions present, e. g., on the hydrogen ions, which are always present in aqueous solutions. The separation of hydrogen must take place as soon as the osmotic pressure of the hydrogen ions and the electrostatic pull are able to overcome the electrolytic solution-pressure of hydrogen of atmospheric pressure; i. e., the relation[2]

$$\epsilon_1 > \epsilon_2, \quad \text{or} \quad \sqrt[n_1]{\frac{P_1}{p_1}} > \frac{P_2}{p_2},$$

must hold, in which the index 1 refers to the metal, 2 to hydrogen, and n_1 is the chemical valence of the given metal.

From the above we see that the following conditions are favorable to the decomposition of water:

1. High osmotic pressure of the hydrogen ions.

2. Great electrostatic pull — i. e., high solution-pressure of the metal and low osmotic counter-pressure of the ions of this metal.

Zinc possesses sufficient solution-pressure for the evolution of hydrogen in acid solutions; but this is no longer the case when we make the concentration of the zinc ions great and that of the hydrogen ions small, e. g., when we dip zinc into a neutral solution of zinc sulphate. In strongly alkaline solutions zinc is again capable of evolving hydrogen, in spite of the ex-

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[1] Nernst. Theoret. Chem. pp. 668 and 674.

[2] Nernst. Theoret. Chem. 3 Aufl., p. 678.

traordinarily low concentration of the hydrogen ions,—since, as a result of the formation of zincates the concentration of the zinc ions is diminished to an infinitely small figure.

The above conditions apply also of course to the precipitation of one metal from solutions of its salts by another metal. In the case of the action of barium amalgam, for example, upon potassium salt solutions, there are three[1] kinds of positive ions that must be taken into consideration, viz., hydrogen, potassium and barium ions. We may distinguish the following four cases:

(1) If $$\sqrt[2]{\frac{P_{Ba}}{p_{Ba}}} > \frac{P_K}{p_K}, \text{ and } < \frac{P_H}{p_H},$$

only potassium will separate out. This is the case when 1 percent barium amalgam acts upon a saturated solution of potassium hydroxide.

(2) If $$\sqrt[2]{\frac{P_{Ba}}{p_{Ba}}} < \frac{P_K}{p_K}, \text{ and } > \frac{P_H}{p_H},$$

only hydrogen will separate out. This is the case when barium amalgam acts upon a dilute potassium chloride solution.

(3) If $$\sqrt[2]{\frac{P_{Ba}}{p_{Ba}}} > \frac{P_K}{p_K}, \text{ and also } > \frac{P_H}{p_H},$$

potassium and hydrogen can both separate out at the same time. In that case, the following will hold:

$$(a) \text{ if } \frac{P_K}{p_K} < \frac{P_H}{p_H},$$

potassium will separate out more readily than hydrogen;

$$(b) \text{ if } \frac{P_K}{p_K} = \frac{P_H}{p_H},$$

potassium and hydrogen will separate out with equal readiness;

$$(c) \text{ if } \frac{P_K}{p_K} > \frac{P_H}{p_H},$$

hydrogen will separate out more readily than potassium.

In the action of barium amalgam on potassium hydroxide,

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[1] In this action mercury does not enter in appreciable amount into the solution. Therefore for mercury, in this case, $P = p$ and $\epsilon = 0$.

the concentration of the solution can probably be regulated to fit all these cases.

(3) Finally, if $\sqrt[\nu]{\frac{P_{Ba}}{p_{Ba}}} < \frac{P_K}{p_K}$, and also $< \frac{P_H}{p_H}$, then neither potassium nor hydrogen will separate out.

This case does not appear to exist in the case of barium, but it is approximated when 1 percent barium amalgam is treated with a saturated solution of potassium chloride; the evolution of hydrogen is extremely slow, and it is very doubtful whether any potassium enters the amalgam.

From the above it is seen that, in order for potassium to replace barium in its amalgam, the concentration of the barium ions, as well as that of the hydrogen ions, in the solution should be made as small as possible. In aqueous solutions the concentration of the hydrogen ions is inversely proportional to that of the hydroxyl ions; therefore the product of the concentrations of the potassium and hydroxyl ions should be chosen as large as possible. This is done in acting on the amalgam with a saturated solution of potassium hydroxide.

It is now easy to understand why Fernekes did not succeed in accomplishing this replacement to a marked degree by acting on barium amalgam with potassium sulphate solution. He reduced the concentration of the barium ions in the solution to a minimum, but he neglected to sufficiently reduce that of the hydrogen ions at the same time.

In the case of any amalgam,[1] if it should be found impossible to replace the metal by potassium from a potassium salt solution, the reason would be to seek in the following relation:

$$\frac{P_M}{p_M} < \frac{P_K}{p_K},$$

in which case no potassium would separate out. Whether hydrogen would be evolved or not would depend on whether

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[1] That is, of any amalgam consisting of mercury and a more electropositive metal. If the amalgam contained a more electro-negative metal than mercury, e. g., platinum, then under ordinary circumstances the mercury would be more readily replaced than the other metal.

$$\frac{P_M}{p_M} > \frac{P_H}{p_H}$$

or

$$\frac{P_M}{p_M} < \frac{P_H}{p_H}.$$

To conclude, it may be added, that, while all the phenomena of solutions may not be capable of explanation by the ionic theory, it is at present nevertheless very rash to claim it to have been shown "conclusively" that this theory has outlived its usefulness.

Further work on the action of metals on solutions will be presented later.

N. C. College of Agriculture and Mechanic Arts,
West Raleigh, Nov. 12, 1904.

VAPOUR-PRESSURE BY AIR-BUBBLING

BY EDGAR PHILIP PERMAN

In a paper by Carveth and Fowler on "Saturation by Air-Bubbling",[1] the authors throw doubt on the accuracy of this method of finding vapour-pressure, and similar doubt is expressed in an abstract[2] of a paper of mine on "Vapour-pressure of Aqueous Ammonia Solutions".[3] I therefore take this opportunity, kindly afforded me by the editors, of defending the method.

In the summer of 1902, I set myself the problem of finding the partial vapour pressures of an aqueous ammonia solution. The air-bubbling method seemed to me to be the most promising for my purpose, and, as a test, I applied it in the first instance to water only, and found that it gave results for the vapour-pressure of water in close accordance with the usually accepted numbers, the *greatest* difference between any two experiments being about one percent of the total pressure, while the difference between the mean vapour-pressure, at any particular temperature, and the true vapour-pressure is much less than this.

I believe that similar results could be obtained by any competent experimenter, if the experiments were carried out in the manner indicated in my paper on "The Evaporation of Water in a Current of Air".[4] Carveth and Fowler do not believe that the air was saturated with the vapour of the liquid through which it passed. My proof that saturation had taken place is based on the following facts:—

(1) That when the rate of the air-current was varied (never, however, exceeding 1 liter per minute) no effect was produced on the amount of water-vapour carried over, e. g., in two experi-

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[1] Jour. Phys. Chem. 8, 313 (1904).

[2] Ibid. 8, 299 (1904).

[3] Jour. Chem. Soc. 83, 1168 (1903).

[4] Proc. Roy. Soc. 72, 72 (1903).

ments (now taken from my note-book) a rate of 5 liters of air in an hour gave a vapour-pressure of 57.33 mm, while 5 liters in one and one-half hours gave 57.34 mm.

(2) That a thermometer reading to 0.01° showed no fall of temperature, such as would be caused by evaporation, with a much more rapid current of air than that actually used, and with only *two* flasks, four (and in some cases five) being the number employed in the vapour-pressure experiments. To these reasons may be added the consistent agreement of the results with the accepted vapour-pressures.

Considering these results satisfactory, I next applied the method to aqueous ammonia solutions of various concentrations, and again obtained consistent results. In this case the method is an approximation only, because the concentration of the solution cannot remain constant as the air passes through it; nevertheless the error can be made as small as we please by using a sufficient number of flasks, and by increasing their size. In my experiments four flasks were used; the concentration of the solution in the last flask was found at the end of each experiment, as well as at the beginning, and if any variation had taken place, the mean concentration was taken as correct. This neglects errors of the *second* order only. The alteration at the lower concentrations was found to be not more than the errors of titration, while at the higher concentrations, the change was about one percent; in a few cases somewhat more. This, however, is no proof that the air, on leaving the last flask, was not saturated with the ammonia and aqueous vapor, for even if it were to pass through the solution with extreme slowness, a change of concentration would take place.

That saturation had occurred, however, is shown by some previous experiments of mine,[1] in which, using only *one* flask, the rate of air-current was varied from 0.14 liter to 1.27 liters per minute, yet without any certain effect on the "rate of escape" of the ammonia. To this may be added the similarity between these experiments and those on water only, and the consistency of the results obtained.

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[1] Jour. Chem. Soc., 73, 511 (1898).

In the most recent experiments the air-current was made very slow (0.05 liter per minute or less) for the concentrated solutions, not so much for fear of non-saturation, as because of the danger of fall of temperature through evaporation.

It is stated by Carveth and Fowler that the errors of the air-bubbling method have not been evaluated even for solvents. I have experimented with only one solvent, water, and can make no statement with regard to others, but I claim that, in the case of water, if the experiments are conducted in the manner described by me, the errors are sufficiently known, and moreover have been separately investigated. The errors most likely to arise are (1) variation of temperature or pressure; (2) non-saturation of the air; (3) loss of water-vapour; (4) variation of vapour-pressure owing to dirt or grease. These have been carefully guarded against, and proved to be absent within narrow limits.

The same remarks apply also to my experiments on ammonia solution, but in this case the accuracy is somewhat diminished owing to the much greater experimental difficulties. From preliminary experiments made by me on the completeness of the absorption of the ammonia and other possible errors, I estimated the value of the partial pressures of the ammonia obtained by this method to be not more than one percent from the truth, except in a few special cases. Since the amount of water drawn off was found by difference, the error in its estimation would very likely reach ten percent at the lower temperatures, when the amount is very small, but would be much less at the higher temperatures, say 30° and upwards.

The air-bubbling method has been applied to the determination of molecular weights, but has not come into general use, and, in my opinion, is not very suitable for this purpose, for the following reasons: (1) Its slowness; (2) the very careful manipulation required; (3) the comparative clumsiness of the apparatus; (4) the want of sufficient accuracy, unless a large number of experiments are made.

I do not think, however, that any conclusions as to the accuracy of the air-bubbling method can be drawn from the experiments of Carveth and Fowler, for they introduced a complication which does not occur as the experiments are usually conducted, *viz.*, the supersaturation of the air, and it is doubtful whether or not the air was given a reasonable opportunity of returning to its former condition. I suggest also that the use of an air-bath is open to grave objection, and that due attention may not have been paid to the connections. If the experiment is prolonged over several hours, rubber joints must be avoided at any cost.

Moreover, the authors do not state how the flasks were cleaned. I found, myself, that frequent steaming out was the most satisfactory method.

In conclusion, I hope that this paper may help to make clear to what uses the air-bubbling method may, or may not, advantageously be put.

University College,
Cardiff.

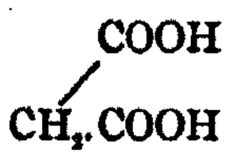
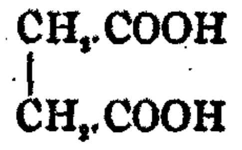
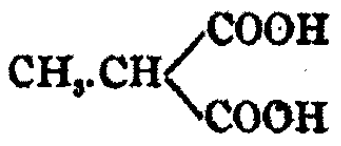
THE HEATS OF COMBUSTION OF ATOMS AND MOLECULES

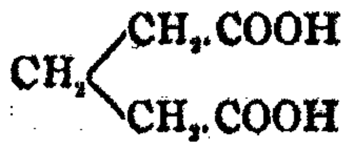
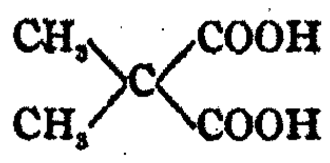
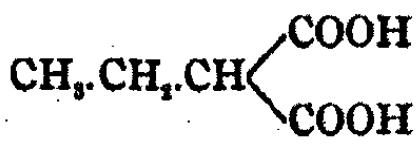
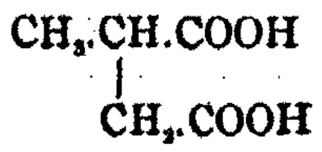
BY LAWRENCE J. HENDERSON

That the heats of combustion of neighboring homologues differ in most cases by a constant value—approximately 157 calories—has long been known, and relatively few exceptions to the rule have been discovered. Such exceptions are, however, to be observed in the following cases,

$$CH_3.COOH, \; - H.COOH, \; 209 - \;\; 62 = 147 \text{ Cal.}$$
$$CH_3.CONH_2, \; - H.CONH_2, \; 283 - 135 = 148$$

and in other similar cases of the difference between the members C_1 and C_2 of an homologous series; further, a few cases of variation from the rule are to be found in higher members of homologous series; as for instance:

			Difference.
C_2	 $\begin{array}{c}COOH\\ \vert\\ COOH\end{array}$	60 Cal	
C_3	 $\begin{array}{l}\quad COOH\\ \;\;/\\ CH_2.COOH\end{array}$	207	147 Cal
C_4	 $\begin{array}{l}CH_2.COOH\\ \vert\\ CH_2.COOH\end{array}$	357	150
	 $CH_3.CH\left\langle\begin{array}{l}COOH\\ COOH\end{array}\right.$	362	155

C_6	 $CH_2\left\langle\begin{array}{l}CH_2.COOH\\CH_2.COOH\end{array}\right.$	515	158 or 153
	 $\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle C\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.$	515	158 or 153
	 $CH_3.CH_2.CH\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.$	518	161 or 156
	 $\begin{array}{l}CH_3.CH.COOH\\\quad\mid\\\quad CH_2.COOH\end{array}$	515	158 or 153

If, however the more general case of the substitution of a hydrogen atom by the methyl group be considered, it becomes at once apparent that such regularity as that above mentioned is confined to special cases of this substitution, and is exceptional. The substitution does not produce a constant change in the energy of the molecule. Thus Stohmann observed a considerable difference between the heats of reaction of the substitution of H by CH_3 on a carbon atom and on a nitrogen atom. The following examples make clear this lack of regularity:

$CH_3.CH_3$	$H.CH_3$	370 — 213 = 157 Cal
$CH_3.OH$	$H.OH$	171 — 0 = 171
$CH_3.NH_2$	$H.NH_2$	258 — 91 = 167
$CH_3.NH.CH_3$	$H.NH.CH_3$	420 — 258 = 162
$CH_3.COOH$	$H.COOH$	209 — 62 = 147
$CH_3.O.CO.C_6H_4OH$	$H.O.CO.C_6H_4OH$	896 — 726 = 170

These remarkable variations in the heats of reaction of apparently identical substitutions are by no means confined to the case $CH_3 \rightarrow H$.

In the following discussion I shall consider the substitution by the groups OH, O, and NH_2 of hydrogen atoms which are directly united to carbon atoms.[1]

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[1] As a basis for the necessary comparisons I use the heats of combustion of the paraffine hydrocarbons as calculated by Stohmann, Jour. prakt. Chem. 49, 122 (1894), and his determinations of the heats of combustion of other hydrocarbons. All data, unless otherwise stated, are to be found in Stohmann's tables. Zeit. phys. Chem. 6, 334 (1890); 10, 410 (1892).

TABLE I.[1]—OH substitution

CH_4	CH_3OH	$210 — 171^{1,l} = 39$ Cal
C_2H_6	C_2H_5OH	$367 — 326^{2,l} = 41$
C_3H_8	$CH_3.CHOH.CH_3$	$524 — 478^{4,l} = 46$
C_3H_8	$CH_3.CH_2.CH_2OH$	$524 — 480^{4,l} = 44$
C_4H_{10}	$CH_3\diagdown$ $CH_3—COH$ $CH_3\diagup$	$680 — 633^{4,l} = 47$
C_4H_{10}	$\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$	$681 — 637^{4,s} = 44$
C_5H_{12}	$CH_3\diagdown$ $CH_3—COH$ $CH_3.CH_2\diagup$	$838 — 788^{4,l} = 50$
C_5H_{12}	$CH_3.CH_2.CH_2.CH_2.CH_2OH$	$838 — 794^{4,l} = 44$
$C_6H_5.CH_3$	$C_6H_5.CH_2OH$	$934 — 895^{1,l} = 39$
$(C_6H_5)_2CH_2$	$(C_6H_5)_2CHOH$	$1656 — 1616^{1,l} = 40$
$(C_6H_5)_3CH$	$(C_6H_5)_3COH$	$2380 — 2342^{1,l} =$
C_6H_6	C_6H_5OH	$780 — 732^{1,s} = 48$
C_2H_6	CH_2OH | CH_2OH	$367 — 282^{1,l} = 85 = 42$ Cal per OH
C_3H_8	CH_2OH | $CHOH$ | CH_2OH	$524 — 397^{1,l} = 127 = 42$
C_4H_{10}	Erythrit, $C_4H_{10}O_4$	$680 — 504^{1,s} = 176 = 44$
C_5H_{12}	Penterythrit, $C_5H_{12}O_4$	$836 — 661^{1,s} = 175 = 44$
C_5H_{12}	Arabit, $C_5H_{12}O_5$	$836 — 612^{1,s} = 224 = 45$
C_6H_{14}	Mannit, $C_6H_{14}O_6$	$993 — 728^{1,s} = 265 = 44$
C_7H_{16}	Perseit, $C_7H_{16}O_7$	$1149 — 836^{1,s} = 313 = 45$
C_6H_6	$C_6H_4(OH)_2$*	$780 — 684^{1,s} = 96 = 48$
C_6H_6	Pyrogallol, $C_6H_3(OH)_3$	$780 — 639^{1,s} = 141 = 47$

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[1] The heats of combustion of the hydrocarbons refer to that state of matter for which the heats of combustion of the substitution-products hold.

1. Stohmann; 2. Berthelot; 3. Thomsen; 4. Louginine; *s.* solid; *l.* liquid; *g.* gaseous.

* Average of the heats of combustion of 1,2, 1,3 and 1,4 dioxybenzol.

If we assume that the value obtained by Louginine, although comparable among themselves, are too low (therefore yielding too great differences) and correct them according to the determinations of Stohmann and Berthelot, we obtain the following average values:

Primary aliphatic alcohols	40 Cal.
Secondary " "	42
Tertiary " "	44
Primary aromatic "	39
Phenols	48
Glycol and glycerine	42
Erythrit and penterythrit	44
Arabit, mannit and perseit	45

TABLE II.

O substitution

C_2H_6	$CH_3.CHO$	$370 - 282^{3,g} = 88$ Cal.
C_3H_8	$C_2H_5.CHO$	$529 - 441^{3,g} = 88$
C_4H_{10}	$(CH_3)_2.CH.CHO$	$687 - 600^{3,g} = 87$
C_3H_8	$CH_3.CO.CH_3$	$529 - 437^{3,g} = 92$
C_5H_{12}	$CH_3.CO.C_3H_7$	$847 - 754^{3,g} = 93$
$C_6H_5.CH_3$	$C_6H_5.CHO$	$934 - 842^{1,l} = 92$
$C_6H_5.CH:CH.CH_3$	$C_6H_5.CH:CH.CHO$	$1202 - 1113^{1,s} = 89$
$2CH_4$	$CH_3.O.CH_3$	$426 - 349^{3,g} = 77$
$2C_2H_6$	$C_2H_5.O.C_2H_5$	$740 - 660^{3,g} = 80$
$2CH_4$	$CH_3.O.CH_3$	$426 - 334^{2,g} = 82$
$C_6H_5.CH_2.CH_3$	$C_6H_5.CO.CH_3$	$1090 - 988^{1,s} = 102$
$(C_6H_5)_2CH_2$	$C_6H_5.CO.C_6H_5$	$1656 - 1558^{1,s} = 98$

Aliphatic ethers	80 Cal.
" aldehydes	88
" ketones	92

TABLE III.

O + OH substitution[1]

CH_4	$H.COOH$	210 — 59 = 151 Cal.
C_2H_6	$CH_3.COOH$	366 — 207 = 159
C_3H_8	$C_2H_5.COOH$	523 — 364 = 159
C_4H_{10}	$C_3H_7.COOH$	680 — 520 = 160
C_5H_{12}	$C_4H_9.COOH$	836 — 677 = 159
C_6H_{14}	$C_5H_{11}.COOH$	993 — 832 = 161
C_7H_{16}	$C_6H_{13}.COOH$	1149 — 989 = 160
C_8H_{18}	$C_7H_{16}.COOH$	1306 — 1145 = 161
C_9H_{20}	$C_8H_{17}.COOH$	1463 — 1302 = 161
$C_{10}H_{22}$	$C_9H_{19}.COOH$	1619 — 1458 = 161
$C_{11}H_{24}$	$C_{10}H_{21}.COOH$	1776 — 1616 = 160
$C_{12}H_{26}$	$C_{11}H_{23}.COOH$	1932 — 1772 = 160
$C_{14}H_{30}$	$C_{13}H_{27}.COOH$	2246 — 2086 = 160
$C_{16}H_{34}$	$C_{15}H_{31}.COOH$	2559 — 2398 = 161
$C_{18}H_{38}$	$C_{17}H_{35}.COOH$	2872 — 2712 = 160
$C_{20}H_{42}$	$C_{19}H_{39}.COOH$	3185 — 3026 = 159
$C_{22}H_{46}$	$C_{21}H_{43}.COOH$	3498 — 3338 = 160

$$CH_4 - H.COOH = 151 \text{ Cal.}$$
$$R.CH_3 - R.COOH = 160$$
$$R.CH_2OH - R.COOH = (R.CH_3 - R.COOH) - (R.CH_3 - R.CH_2OH) = 160 - 40 = 120 \text{ Cal.}$$
$$R.CHO - R.COOH = (R.CH_3 - R.COOH) - (R.CH_3 - R.CHO) = 160 - 88 = 72 \text{ Cal.}$$
$$CH_3OH - H.COOH = (CH_4 - H.COOH) - (CH_4 - CH_3OH) = 151 - 40 = 111 \text{ Cal.}$$

That is to say: the substitution of two hydrogen atoms in a primary alcohol to form an acid reduces the heat of combustion of the molecule by 120 Cal. (The case of formic acid, in which the reduction is 111 Cal, is an exception). In an aldehyde the substitution of a hydrogen atom by hydroxyl (formation of an acid) reduces the heat of combustion of the molecule by 72 Cal.

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[1] Stohmann. Jour. prakt. Chem. 49, 107 (1894).

TABLE IV.

2O + 2 OH substitution[1]

			Per 1 O × 1 OH
C_2H_6	$COOH$ | $COOH$	366 — 60 = 306 Cal.	= 153
C_3H_8	$COOH$ | $CH_2—COOH$	523 — 207 = 316	= 158
C_4H_{10}	$CH_2—COOH$ | $CH_2—COOH$	680 — 357 = 323	= 161
C_5H_{12}	$CH_2—COOH$ | $CH_2—CH_2—COOH$	836 — 515 = 321	= 160
C_6H_{14}	$CH_2—CH_2—COOH$ | $CH_2—CH_2—COOH$	993 — 669 = 324	= 162
C_7H_{16}	$CH_2—CH_2—COOH$ | $CH_2—CH_2—CH_2—COOH$	1149 — 829 = 320	= 160
C_8H_{18}	$CH_2—CH_2—CH_2—COOH$ | $CH_2—CH_2—CH_2—COOH$	1306 — 984 = 322	= 161
C_9H_{20}	$CH_2—CH_2—CH_2—COOH$ | $CH_2—CH_2—CH_2—CH_2—COOH$	1463 — 1141 = 322	= 161
$C_{10}H_{22}$	$CH_2—CH_2—CH_2—CH_2—COOH$ | $CH_2—CH_2—CH_2—CH_2—COOH$	1619 — 1297 = 322	= 161

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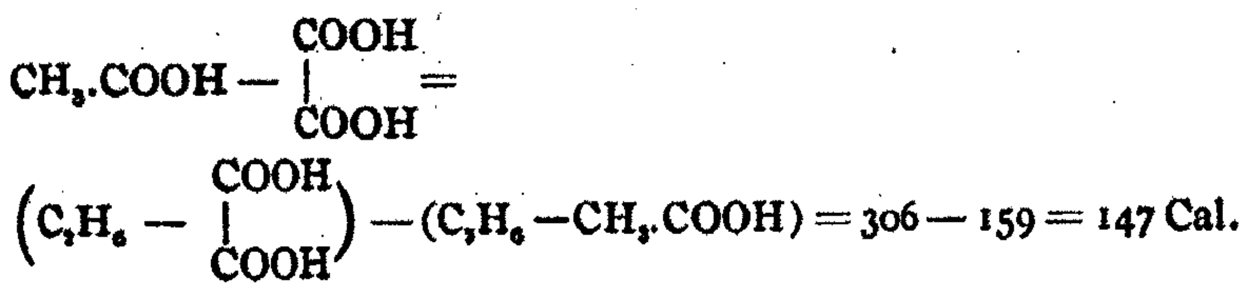
[1] Stohmann, Jour. prakt. Chem., 49, 114 and 116 (1894).

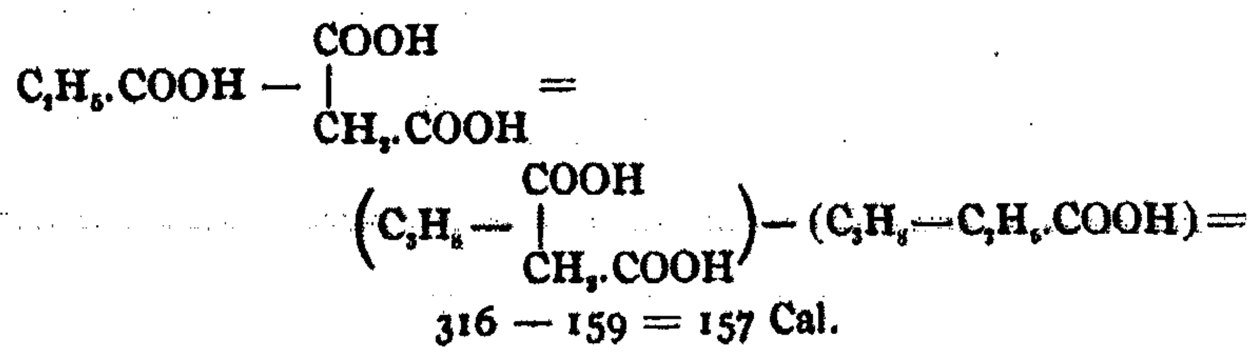
TABLE IV.—(*Continued*).

C_4H_6	$\begin{array}{l} COOH \\ \vert \\ CH_2-COOH \end{array}$	523 — 207 = 316 Cal. = 158
C_4H_{10}	$\begin{array}{l} \quad\;\; COOH \\ \quad\;\; \vert \\ CH_3-CH-COOH \end{array}$	680 — 362 = 318 = 159
C_5H_{12}	$\begin{array}{l} \qquad\qquad\;\; COOH \\ \qquad\qquad\;\; \vert \\ CH_3-CH_2-CH-COOH \end{array}$	836 — 518 = 318 = 159
C_5H_{12}	$\begin{matrix} CH_3 \\ CH_3 \end{matrix}>C<\begin{matrix} COOH \\ COOH \end{matrix}$	836 — 515 = 321 = 160
C_6H_{14}	$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}>C<\begin{matrix} COOH \\ COOH \end{matrix}$	993 — 676 = 317 = 158
C_6H_{14}	$\begin{matrix} CH_3 \\ CH_3 \end{matrix}>CH-CH<\begin{matrix} COOH \\ COOH \end{matrix}$	993 — 675 = 318 = 159
C_6H_{14}	$CH_3-CH_2-CH_2-CH<\begin{matrix} COOH \\ COOH \end{matrix}$	993 — 675 = 318 = 159
C_7H_{16}	$\begin{matrix} CH_3-CH_2 \\ CH_3-CH_2 \end{matrix}>C<\begin{matrix} COOH \\ COOH \end{matrix}$	1149 — 833 = 316 = 158
C_8H_{18}	$\begin{matrix} C_2H_5 \\ C_3H_7 \end{matrix}>C<\begin{matrix} COOH \\ COOH \end{matrix}$	1306 — 990 = 316 = 158
C_9H_{20}	$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix}>C<\begin{matrix} COOH \\ COOH \end{matrix}$	1463 — 1146 = 317 = 158
$C_{10}H_{22}$	$C_7H_{15}-CH<\begin{matrix} COOH \\ COOH \end{matrix}$	1619 — 1303 = 316 = 158
$C_{11}H_{24}$	$C_8H_{17}-CH<\begin{matrix} COOH \\ COOH \end{matrix}$	1776 — 1458 = 318 = 159
$C_{19}H_{40}$	$C_{16}H_{33}-CH<\begin{matrix} COOH \\ COOH \end{matrix}$	3029 — 2708 = 321 = 160

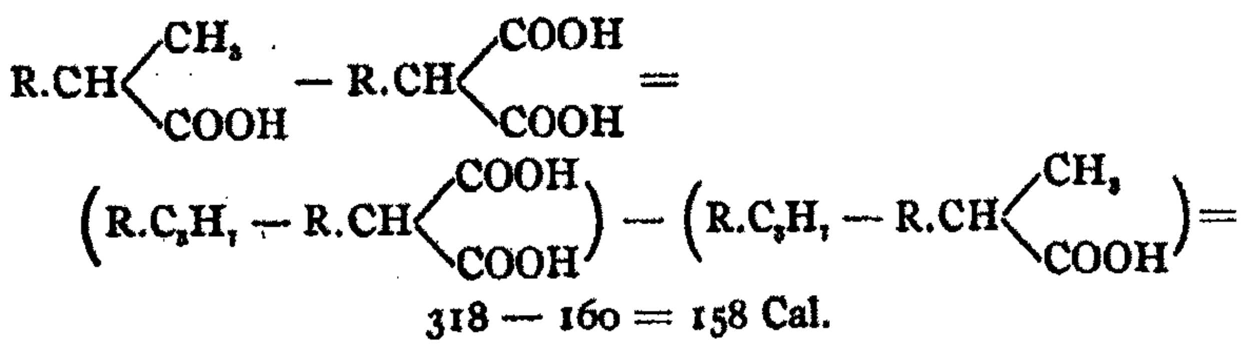
$\begin{array}{l} COOH \\ \vert \\ COOH \end{array}$	306	153
$\begin{array}{l} COOH \\ \vert \\ CH_2-COOH \end{array}$	316	158
Malonic acid series	318	159
Higher normal dicarbonic acids	322	161



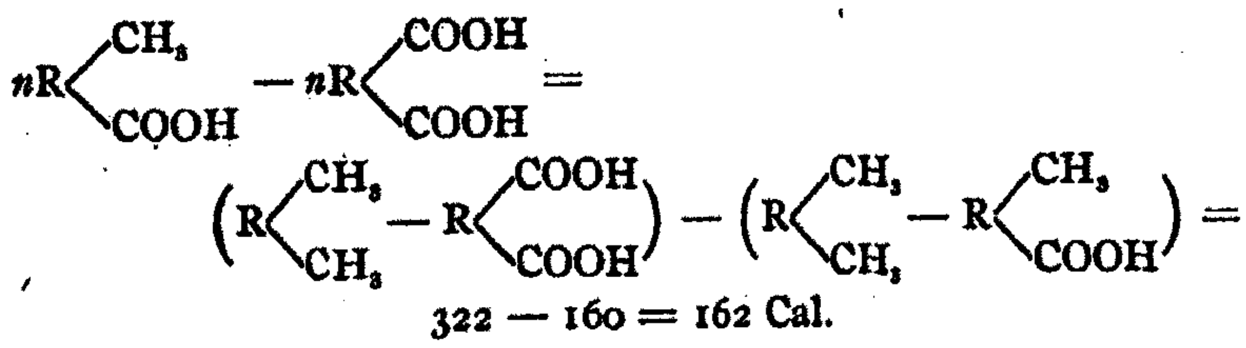
$$CH_3.COOH - \begin{matrix} COOH \\ | \\ COOH \end{matrix} = \left(C_2H_6 - \begin{matrix} COOH \\ | \\ COOH \end{matrix}\right) - (C_2H_6 - CH_3.COOH) = 306 - 159 = 147 \text{ Cal.}$$



$$C_2H_5.COOH - \begin{matrix} COOH \\ | \\ CH_2.COOH \end{matrix} = \left(C_3H_8 - \begin{matrix} COOH \\ | \\ CH_2.COOH \end{matrix}\right) - (C_3H_8 - C_2H_5.COOH) = 316 - 159 = 157 \text{ Cal.}$$



$$R.CH\left\langle\begin{matrix} CH_3 \\ COOH \end{matrix}\right. - R.CH\left\langle\begin{matrix} COOH \\ COOH \end{matrix}\right. = \left(R.C_3H_7 - R.CH\left\langle\begin{matrix} COOH \\ COOH \end{matrix}\right.\right) - \left(R.C_3H_7 - R.CH\left\langle\begin{matrix} CH_3 \\ COOH \end{matrix}\right.\right) = 318 - 160 = 158 \text{ Cal.}$$



$$nR\left\langle\begin{matrix} CH_3 \\ COOH \end{matrix}\right. - nR\left\langle\begin{matrix} COOH \\ COOH \end{matrix}\right. = \left(R\left\langle\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right. - R\left\langle\begin{matrix} COOH \\ COOH \end{matrix}\right.\right) - \left(R\left\langle\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right. - R\left\langle\begin{matrix} CH_3 \\ COOH \end{matrix}\right.\right) = 322 - 160 = 162 \text{ Cal.}$$

TABLE V.

O + OH substitution, aromatic series

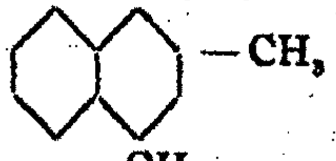
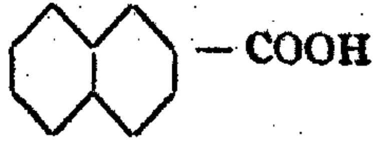
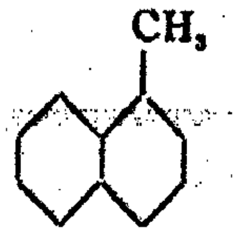
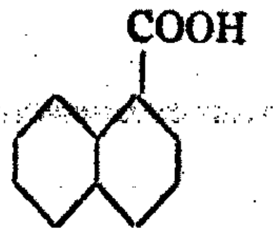
$C_6H_5.CH_3$	$C_6H_5.COOH$	$934 - 772^{1,5} = 162$ Cal.
$C_6H_5.CH_2.CH_3$	$C_6H_5.CH_2.COOH$	$1090 - 933^{1,5} = 157$
$C_6H_4 : \genfrac{}{}{0pt}{}{CH_3\ (1)}{CH_3\ (2)}$	$C_6H_4 : \genfrac{}{}{0pt}{}{CH_3\ (1)}{COOH\ (2)}$	$1084 - 929^{1,5} = 155$
$C_6H_4 : \genfrac{}{}{0pt}{}{CH_3\ (1)}{CH_3\ (3)}$	$C_6H_4 : \genfrac{}{}{0pt}{}{CH_3\ (1)}{COOH\ (3)}$	$1084 - 929^{1,5} = 155$
$C_6H_4 : \genfrac{}{}{0pt}{}{CH_3\ (1)}{CH_3\ (4)}$	$C_6H_4 : \genfrac{}{}{0pt}{}{CH_3\ (1)}{COOH\ (4)}$	$1084 - 927^{1,5} = 157$
		$1388 - 1228^{1,5} = 160$
		$1388 - 1233^{1,5} = 155$
		per 1 O + 1 OH
$C_6H_4 < \genfrac{}{}{0pt}{}{CH_3\ (1)}{CH_3\ (2)}$	$C_6H_4 < \genfrac{}{}{0pt}{}{COOH\ (1)}{COOH\ (2)}$	$1084 - 772^{1,5} = 312 = 156$ Cal.
$C_6H_4 < \genfrac{}{}{0pt}{}{CH_3\ (1)}{CH_3\ (3)}$	$C_6H_4 < \genfrac{}{}{0pt}{}{COOH\ (1)}{COOH\ (3)}$	$1084 - 769^{1,5} = 315 = 157$
$C_6H_4 < \genfrac{}{}{0pt}{}{CH_3\ (1)}{CH_3\ (4)}$	$C_6H_4 < \genfrac{}{}{0pt}{}{COOH\ (1)}{COOH\ (4)}$	$1084 - 771^{1,5} = 313 = 156$

TABLE VI.

O and OH substitution, more complicated cases

$C_6H_5.CH_3 + CH_4$	$C_6H_5.CO.O.CH_3$	$1147 - 944^{1,5} = 203$ Cal.
$C_6H_5.CH_3 + C_2H_6$	$C_6H_5.CO.O.C_2H_5$	$1304 - 1099^{1,5} = 205$
C_2H_6	CH_2OH | $COOH$	$366 - 167^{1,5} = 199$
C_2H_6	CHO | CHO	$366 - 164^{*,5} = 202$
C_2H_6	CHO | $COOH$	$366 - 128^{2,5} = 238$

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* Calculated from de Forcrand. Ann. Chim. Phys. (6) 3, 187 (1884).

$R.CHO + R.H - R.COOR$
$= (R.CH_3 + RH - R.COOR) - (R.CH_3 - R.CHO)$
$= 204 - 88 = 116$ Cal.

$CH_3.COOH - CH_2OH.COOH$
$= (C_2H_6 - CH_2OH.COOH) - (C_2H_6 - CH_3.COOH)$
$= 199 - 159 = 40$ Cal.

$CH_2OH.CH_3 - CH_2OH.COOH$
$= (C_2H_6 - CH_2OH.COOH) - (C_2H_6 - CH_2OH.CH_3)$
$= 199 - 40 = 159$ Cal.

$CH_3.CHO - CHO.CHO$
$= (C_2H_6 - CHO.CHO) - (C_2H_6 - CH_3.CHO)$
$= 202 - 88 = 114$ Cal.

$CH_3.COOH - CHO.COOH$
$= (C_2H_6 - CHO.COOH) - (C_2H_6 - CH_3.COOH)$
$= 238 - 159 = 79$ Cal.

$CH_3.CHO - CHO.COOH$
$= (C_2H_6 - CHO.COOH) - (C_2H_6 - CH_3.CHO)$
$= 238 - 88 = 150$ Cal.

TABLE VII.

NH_2 substitution

CH_4	$CH_3.NH_2$	$210 - 248^{3,l} = - 38$ Cal.
C_2H_6	$C_2H_5.NH_2$	$367 - 401^{3,l} = - 34$
C_6H_6	$C_6H_5.NH_2$	$780 - 813^{1,l} = - 33$
C_2H_6	$CH_2.NH_2.COOH$	$366 - 235^{1,s} = + 131$
C_3H_8	$CH_3.CH.NH_2.COOH$	$523 - 388^{1,s} = + 135$
C_6H_{14}	$C_4H_9.CH.NH_2.COOH$	$993 - 856^{1,s} = + 137$
CH_4	$H.CONH_2$	$210 - 135^{1,l} = + 75$
C_2H_6	$CH_3.CONH_2$	$366 - 283^{1,s} = + 83$
C_3H_8	$C_2H_5.CONH_2$	$523 - 440^{1,s} = + 83$
C_4H_{10}	$C_3H_7.CONH_2$	$680 - 596^{1,s} = + 84$
C_5H_{12}	$C_4H_9.CONH_2$	$836 - 752^{1,s} = + 84$
$C_{12}H_{26}$	$C_{11}H_{23}.CONH_2$	$1932 - 1850^{1,s} = + 82$
$C_{14}H_{30}$	$C_{13}H_{27}.CONH_2$	$2246 - 2161^{1,s} = + 85$
$C_{16}H_{34}$	$C_{15}H_{31}.CONH_2$	$2559 - 2473^{1,s} = + 86$
$C_6H_5.CH_3$	$C_6H_5.CONH_2$	$934 - 848^{1,s} = + 86$

$R.NH_2$	$- 35$ Cal.
$R.CH.NH_2.COOH$	134
$R.CO.NH_2$	84
$H.CO.NH_2$	75

$RH.COOH - R.NH_2.COOH$
$= (RH.CH_3 - R.NH_2.COOH) - (RH.CH_3 - RH.COOH)$
$= 134 - 160 = -26$ Cal.

$RNH_2.CH_3 - R.NH_2.COOH$
$= (RH.CH_3 - R.NH_2.COOH) - (RH.CH_3 - R.NH_2.CH_3)$
$= 134 - (-35) = 169$ Cal.

$RCH_2.NH_2 - R.CO.NH_2$
$= (R.CH_3 - R.CO.NH_2) - (R.CH_3 - R.CH_2.NH_2)$
$= 84 - (-35) = 119$ Cal.

$R.CHO - R.CO.NH_2$
$= (R.CH_3 - R.CO.NH_2) - (R.CH_3 - R.CHO)$
$= 84 - 88 = -4$ Cal.

$H.CH_2.NH_2 - H.CO.NH_2$
$= (CH_4 - H.CO.NH_2) - (CH_4 - H.CH_2.NH_2)$
$= 75 - (-35) = 110$ Cal.

In the following tables the results of the above analysis are summarized:

TABLE 1

$R.CH_3 - R.CH_2OH$	= 40 Cal.
$R_2CH_2 - R_2.CHOH$	= 42
$R_3.CH - R_3.COH$	= 44
$R.CH_3 - R.CH_2OH$ (aromatic series)	= 39
$C_6H_6 - C_6H_5OH$	= 48
$R.CHO - R.COOH$	= 72
$CH_3.COOH - CH_2OH.COOH$	= 40
RH — glycol and glycerine	= 42
RH — erythrit and penterythrit	= 44
RH — arabit, mannit and perseit	= 45

TABLE 2[1]

$2RH - R.O.R$	= 80 Cal.
$R.CH_3 - R.CHO$	= 88
$R_2CH_2 - R.CO$	= 92
$R.CH_2OH - R.COOH$	= 120
$H.CH_2OH - H.COOH$	= 111
$R.CH_2OR - R.COOR$	= 124
$R.CHO + RH - R.COOR$	= 116
$CH_3.CHO - CHO.CHO$	= 114
$CH_3.COOH - CHO.COOH$	= 79
$R.CH_2.NH_2 - R.CO.NH_2$	= 119
$H.CH_2.NH_2 - HCONH_2$	= 110

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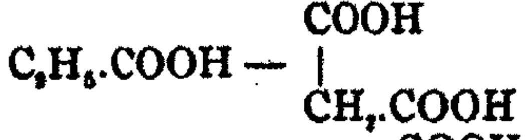
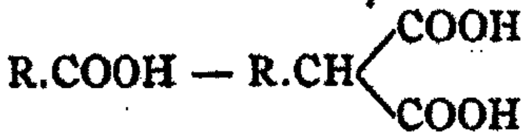
[1] Aromatic compounds will not be considered further; in no series do they constitute exceptions, but to a certain degree they add complexity to the analysis.

TABLE 3

$R.CH_3 - R.CH_2NH_2$	= − 35 Cal.
$RH.COOH - R.NH_2.COOH$	= − 26
$R.CHO - R.CO.NH_2$	= − 4

TABLE 4

$R.CH_3 - R.COOH$	= 160 Cal.
$H.CH_3 - H.COOH$	= 151
$CH_3.COOH - COOH.COOH$	= 147
 $C_2H_5.COOH - \begin{array}{l} COOH \\ \vert \\ CH_2.COOH \end{array}$	= 157
 $R.COOH - R.CH\begin{cases} COOH \\ COOH \end{cases}$	= 158
 $R.COOH - nC_nH_{2n}\begin{cases} COOH \\ COOH \end{cases}$	= 162
$CH_2OH.CH_3 - CH_2OH.COOH$	= 159
$CHO.CH_3 - CHO.COOH$	= 150
$R.NH_2.CH_3 - R.NH_2.COOH$	= 169

From the above summary it is clear that the heat of reaction of a substitution is dependent not alone upon the nature of the atoms or atom groups which take part directly in the reaction, but also in high degree upon the chemical composition of the remainder of the molecule, and upon the arrangement of the atoms therein. Thus the same substitution—H by OH—which leads from paraffine hydrocarbon to primary alcohol with a loss of 40 Cal to the heat of combustion of the molecule, when it converts an aldehyde into an acid diminishes the heat of combustion by 72 Cal. On the other hand marked and parallel differences in the heat of formation from the hydrocarbons of primary, secondary, and tertiary alcohols, and of aldehydes and ketones are to be seen.

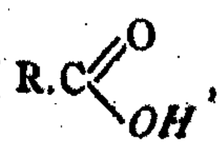
Primary alcohols	40	Aldehydes	88
Secondary "	42	Ketones	92
Tertiary "	44		

Upon closer scrutiny, it is evident that the magnitudes of these differences vary in a regular way; this is shown in the following tables:

SERIES I.[1]

OH

$$\mathrm{R.CH_2\mathit{OH}},\ 40 = \mathrm{CH_2\mathit{OH}.COOH},\ 40 < \mathrm{R_2.CH\mathit{OH}},\ 42 = \mathrm{CH_2\mathit{OH}.CH_2\mathit{OH}},\ 42 < \mathrm{R_3.C\mathit{OH}},\ 44 = \text{erythrit},\ 44 < \text{arabit},\ 45 < \mathrm{R.C}\begin{smallmatrix}\diagup \mathrm{O} \\ \diagdown \mathit{OH}\end{smallmatrix},\ 72.$$



SERIES II.

O

$$\mathrm{CH\mathit{O}.COOH},\ 79 < \mathrm{R}-\mathit{O}-\mathrm{R},\ 80 < \mathrm{R.CH\,\mathit{O}},\ 88 < \mathrm{R_2C\mathit{O}},\ 92 < \mathrm{HC\mathit{O}NH_2},\ 110 < \mathrm{HC\mathit{O}OH},\ 111 < \mathrm{CH\mathit{O}.CHO},\ 114 < \mathrm{R.CO.\mathit{O}.R},\ 116 < \mathrm{R.C\mathit{O}.NH_2},\ 119 < \mathrm{R.C\mathit{O}.OH},\ 120.$$

SERIES III.

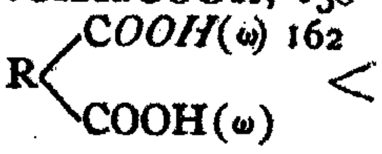
$\mathit{NH_2}$

$$\mathrm{R.\mathit{NH_2}},\ -35 < \mathrm{R.CH\mathit{NH_2}.COOH},\ -26 < \mathrm{R.CO\mathit{NH_2}},\ -4.$$

SERIES IV.

$\mathit{O} + \mathit{OH}$

$$\mathrm{C\mathit{COH}.COOH},\ 147 < \mathrm{CHO.C\mathit{OOH}},\ 150 < \mathrm{H.C\mathit{OOH}},\ 151 < \mathrm{C\mathit{OOH}.CH_2.C\mathit{OOH}},\ 156 < \mathrm{C\mathit{OOH}.CHR.COOH},\ 158 < \mathrm{CH_2OH.C\mathit{OOH}},\ 159 < \mathrm{R.C\mathit{OOH}},\ 160 < \mathrm{R}\begin{smallmatrix}\diagup \mathrm{C\mathit{OOH}}(\omega)\ 162 \\ \diagdown \mathrm{COOH}(\omega)\end{smallmatrix} < \mathrm{R.CHNH_2.C\mathit{OOH}},\ 169.$$



As the amount of oxygen in the molecules increases, the heats of reaction of the above substitutions at first increase, then decrease. This diminished heat of reaction when the molecule contains much oxygen and is to be observed in the following cases: Series I, $\mathrm{CH_2\mathit{OH}.COOH}$, 40; Series II, $\mathrm{CH\mathit{O}.COOH}$, 79, $\mathrm{H.C\mathit{O}.NH_2}$, 110, $\mathrm{H.C\mathit{O}.OH}$, 111; Series IV, $\mathrm{C\mathit{OOH}.COOH}$, 147, $\mathrm{C\mathit{OOH}.CHO}$, 150, $\mathrm{H.C\mathit{OOH}}$, 151, and in the malonic acid series. In all these cases, with the exception of the malonic acid series, the molecule contains at least one doubly bound oxygen atom or two hydroxyl groups per carbon atom; in the cases with the lowest differences the oxygen

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[1] In this table the substituting atom is *underlined*, the difference in heat of combustion between original substance and end product set along side.

content is even greater. We observe on the other hand in the case of the malonic acids variations which, as in the cases of alcohols, aldehydes, and ketones, are to be ascribed to the arrangement of the atoms within the molecule, for the normal dicarbonic acids possess greater heats of formation.

We have seen that the heat of reaction of a substitution is dependent not only upon the nature of the atom groups which directly take part in the reaction, but also upon their position in the molecule and upon the nature of the rest of the molecule. In other words, an atom does exert an influence upon the heat of a reaction of its containing molecule, even when it is not directly concerned in the reaction, in varying degree, however, according to its position in relation to the reacting group. Such an influence, however, upon the heat of a reaction is only possible if this atom affects the heat of combustion of one or more of the atoms directly concerned in the reaction, namely, the substituting and substituted atoms and the atom to which they are united. The following consideration makes this clear:

$CH_3.CH_3$	$CH_3.COOH$	366 − 207 = 159 Cal.
$COOH.CH_3$	$COOH.COOH$	207 − 60 = 147

If we assume that an atom has no effect upon the heats of combustion of atoms with which it is not directly united, we may express the heat of combustion of the group CH_3 in the above substances by K_1, and that of the group COOH by K_2; the heats of combustion of the various substances are then

$$\begin{array}{ll} CH_3.CH_3 & 2K_1 \\ CH_3.COOH & K_1 + K_2 \\ COOH.COOH & 2K_2 \end{array}$$

Substituting these values in the equations we obtain

$$\begin{cases} 2K_1 - (K_1 + K_2) & = 159 \text{ Cal.} \\ K_1 + K_2 - 2K_2 & = 147 \end{cases}$$

$$\begin{cases} K_1 - K_2 & = 159 \\ K_1 - K_2 & = 147 \end{cases}$$

which is absurd.

Accordingly, we come to the conclusion that an atom may affect the heat of combustion of another atom in the same molecule even when it is not directly united with that atom. Such influences are to be observed in all cases which, with the existing data, it is possible to study. Hence it follows that *every atom of a molecule, in a degree dependent upon its position, influences the heat of combustion* (Wärmewert) *of every other atom of the molecule, whether or not it is united to that atom.*[1]

An obvious corollary to this proposition is the following: *Isomers never possess the same heats of combustion unless the sums of the mutual influences of the atoms in the various molecules are equal.*

This general principle of the influence of an atom upon the heats of combustion of the other atoms of the molecule renders more complicated the further analysis of such reactions as have been considered in the course of this paper. Let us consider, for instance, the case:

CH_4	CH_3OH	$210 - 171 = 39$ Cal.

Here 39 Cal expresses the difference between the heat of combustion of H in the molecule CH_4 plus the influence of H upon the heat of combustion of CH_3 on the one hand, and the heat of combustion of OH in the molecule CH_3OH plus the influence of OH upon the heat of combustion of CH_3 on the other hand. If we represent these four values by H, fH, OH, and fOH, we we may write the equation,

$$H + fH - OH - fOH = 39 \text{ Cal.}$$

It is evident that no conclusion can be drawn from this fact with regard to the absolute or relative magnitudes of these four quantities. Thus, for instance, Stohmann's conclusion — "Der Wärmewert einer an Stickstoff gebundenen Methylgruppe liegt bedeutend höher, als wenn die gleiche Gruppe an ein Kohlenstoffatom gebunden ist"[2] is not necessarily correct.

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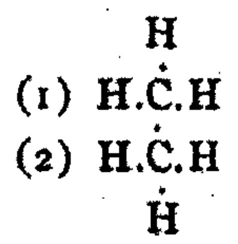
[1] The only other possible conclusion, that certain atoms of a molecule are thus influenced, others not, seems to me untenable.

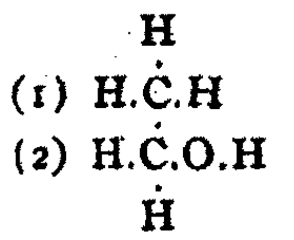
[2] Jour. prakt. Chem. 49, 490 (1894).

For the valence theory there are two possibilities according to the above established facts.

If we assume with Thomsen that the heat of formation of a molecule from the "free atoms" is the sum of the heats of reaction of the various valences, we reach the conclusion that the heats of reaction of the valences are variable, because the heats of combustion of the atoms of the molecule are variable. The following makes this clear:



$$\begin{array}{c} H \\ (1)\ H.\dot{C}.H \\ (2)\ H.\dot{C}.H \\ \dot{H} \end{array}$$



$$\begin{array}{c} H \\ (1)\ H.\dot{C}.H \\ (2)\ H.\dot{C}.O.H \\ \dot{H} \end{array}$$

According to the principle that every atom of a molecule affects the heat of combustion of every other atom of the molecule it follows that the carbon atoms (1) of the methyl groups have different heats of combustion in these two molecules, for the effects on the carbon atoms (1) of the hydrogen atom on the one hand and of the hydroxyl group on the other, borne by the carbon atoms (2), are different. *If the heat of combustion of a bound carbon atom* (apart from its original value as a "free atom") *is dependent only upon the heats of reaction of its valences then the valences must be variable.*

A second possibility is that the heats of reaction of the valences are constant, and that other relationships exist within the molecule which influence in high degree its heat of combustion.

I will make no choice between these two possibilities, but nevertheless point out that at present no facts are known which indicate the existence within the molecule of such considerable relationships of unknown character.

This paper presents the following logical deductions:

The heat of combustion of an atom chemically bound in a molecule is dependent not only upon its nature and the nature of the atoms with which it is directly united, but also upon the nature and position of every other atom of the molecule.

If there are not present within the molecule considerable energy relationships of unknown character, the energy of a valence is variable and a function of all the atoms of the molecule and of their positions.

Prof. T. W. Richards and I are at present engaged in determining accurately, with the aid of Atwater's modification of the Berthelot bomb, the heats of combustion of certain organic substances. With the aid of these figures we shall extend the above analysis, and especially consider quantitatively the various factors which are there involved.

NEW BOOKS

The Phase Rule and Its Applications. *By Alex. Findlay. With an Introduction to the Study of Physical Chemistry by William Ramsay. 13 × 18 cm; pp. lxiv + 313. New York: Longmans, Green, and Co., 1904. Price: $1.60.* — This is the first of a series of volumes on physical chemistry. Each volume is to cover a special field and is to be rewritten at dates depending on the development of the subject and the rate of purchase by the scientific public. It is of course proper that the series should begin with the phase rule, and it is gratifying to see that this fact is now pretty generally recognized. Mr. Findlay has given us a very good book. It is short, it is clearly written, it covers the ground well and it is remarkably free from errors. On the first reading the reviewer noticed only four errors and but one of these is a serious one.

The author has failed to emphasize the fact that an amorphous mass is a supercooled liquid and consequently he quotes van't Hoff's early characterization of glass as a solid solution. This was natural enough at that time but is not justified today. In Figs. 57 and 58 on p. 191, the concentration-temperature curves for two series of solid solutions are made part of the same smooth curve. It is hard to see how these can be other than intersecting curves since one refers to one crystalline form and the other to another. In the discussion of the triangular diagram, p. 228, it is said that there are two methods of representation, one an equilateral triangle of unit height in which the co-ordinates are measured perpendicular to the sides and the other an equilateral triangle of unit side in which the co-ordinates are measured parallel to the sides. If the author had ever used the triangular diagram much, he would have found that these two are the same. [It is only right to state that the reviewer made the same mistake in 1897]. As it is, the author has omitted the rectangular isosceles triangle, which is a different one. The most serious error is in the iron-carbon diagram which has been "simplified" so as to make it thoroughly misleading.

With the exception of these few details, the book is a very satisfactory one. It is also one that the student can read without difficulty and with profit, which is more than can be said for the reviewer's own book on the subject. The book has been tested to a certain extent in the reviewer's laboratory and has been found satisfactory. *Wilder D. Bancroft.*

Laboratory Exercises in Physical Chemistry. *By Frederick H. Getman. 12 × 19 cm; pp. viii + 241. New York: John Wiley and Sons, 1904. Price: $2.00, net.* — Prior to the appearance of this book, no English writer has published a work designed for the laboratory guidance of students of physical chemistry. Regarding the works of Ostwald and Traube as having "too great detail and too many references to the literature," but as having the greatest merit as "standards of reference," the author has endeavored to condense the material and simplify the treatment of the subject.

Under introductory measurements are given weighing, volume and density, surface tension and viscosity, and solubility. The other sections deal with the study of thermometry, melting- and boiling-points and calorimetry; the use of the spectroscope, refractometer, and polarimeter; electrical units, resistance, electromotive force, current and dielectric constant; and, finally, a chapter on chemical dynamics. A set of tables of constants is appended.

Might it not be suggested that the clear statement of some definite problem and references to the original papers are of very decided advantage in laboratory instruction? Does a treatment of chemical dynamics detailed in six pages give the student a sufficient insight into the *chemistry of reactions?* And where is the chemistry of *separations* treated? Is not the subject which is presented chemical physics?

The treatment is in most cases very simple, and the work is well written; it is one which used in conjunction with a good textbook will certainly be of considerable service in laboratory instruction. *H. R. Carveth*

Elektrolytisches Verfahren zur Herstellung parabolischer Spiegel. *By Sherard Cowper-Coles. Ins Deutsche übertragen von Emil Abel. (Monographien über angewandte Elektrochemie. XIV. Band). 16 × 24 cm; pp. 17. Halle: Wilhelm Knapp, 1904. Price: 1 mark.* — Parabolic mirrors are made by depositing silver chemically on a glass form and backing this silver with copper precipitated electrolytically. The mirror is then removed from the glass form and given a facing of platinum or palladium. For the electrolytic precipitation of palladium, an ammonium palladium chloride solution is used; for platinum, a solution containing ammonium platinum chloride and sodium citrate. The copper backing is precipitated with a current density of 1.6 amp/qdm. No data are given for the palladium precipitation.

Wilder D. Bancroft.

Künstlicher Graphit. *By Francis A. J. Fitz-Gerald. Ins Deutsche übertragen von Max Huth. (Monographien über angewandte Elektrochemie. XV. Band). 16 × 24 cm; pp. 60. Halle: Wilhelm Knapp, 1904. Price: 3 marks.* — The subject is treated under the headings: historical sketch; preparation of artificial graphite; appendix. In the chapter on the preparation of graphite, the processes considered are those of Castner, of Girard and Street, of Acheson, and of Rudolph and Harden. The Acheson process is discussed from the following points of view: decomposition of carborundum; preparation of pure carbon; preparation of pure graphite; graphite and anthracite; graphite and coke; preparation of graphite objects; preparation of graphite electrodes; properties of Acheson graphite. In the appendix reference is made to the experiments of Fitz-Gerald and Wilson, of Ludwig and of Borchers.

Wilder D. Bancroft.

Die elektrochemische Reduktion der Nitroderivate organischer Verbindungen in experimenteller und theoretischer Berziehung. *By Joh. Möller. 16 × 24 cm: pp. 113. Halle: Wilhelm Knapp, 1904. Price: paper, 4 marks.* — In the experimental part there is a discussion of the electrolytic reduction of nitro compounds in acid and in alkaline solutions. The theoretical part is devoted to the theories of Haber, Löb and Chilesotti. The monograph was written before the publication of the last paper by Löb, in which the discrepancies in the theoretical conceptions were removed. The experimental part covers nearly eighty pages and appears to be very complete. *Wilder D. Bancroft.*

Kritische Studien über die Vorgänge der Autoxydation. *By C. Engler and J. Weissberg. 15 × 23 cm; pp. xi + 204. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: paper 6 marks.*—In the historical introduction the views of Hoppe-Seyler, van 't Hoff, Traube, Engler, and Haber on active oxygen are outlined briefly. The second chapter deals in detail with the general theory of Engler which is the basis of classification for the whole book. In the third chapter we find the experimental data illustrating direct autoxidation, while indirect autoxidation appears as the heading for chapter four. A chapter on autoxycatalysis comes next and then one on the factors affecting autoxidation. The book closes with a chapter on the part played by oxygen in the living organism. The authors have written an admirable monograph. There are distinctly two opinions as to the merits of their theory; but that is neither here nor there. They have brought together a large mass of interesting data and have presented the results in a clear and intelligent manner. The reviewer has often expressed the opinion that we need all the good monographs on chemical subjects that we can get. This book is one of those that we need.

Wilder D. Bancroft.

Ostwald's Klassiker der exakten Wissenschaften. *No. 145. Über die Konstitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs. Untersuchungen über aromatische Verbindungen von August Kekulé. Herausgegeben von A. Ladenburg. 12 × 18 cm; pp. 89. Leipzig: Wilhelm Engelmann, 1904. Price: 1.40 marks.*—These two classic papers are a welcome addition to the series in which they appear. The first of them contains a good deal of material in its earlier pages which is purely polemical in character, and which, as is pointed out in the editor's notes, will have little interest for any except those thoroughly conversant with the different constitutional formulas in use at the time the paper appeared. The latter part is of more general interest, for it contains the first definite statement of the tetravalence of carbon, an idea which is here enunciated so clearly that it would scarcely be possible in our own day to give it a more concise or complete form.

The second paper is a reprint and an enlargement of the original which appeared in the *Bulletin* in 1865, and constitutes perhaps the most important single contribution that has ever been made to organic chemistry.

Both the papers are models of clear and logical reasoning as applied to scientific work; and for that reason, if for no other, they should be on the shelves of every chemist. *A. P. Saunders.*

Die wissenschaftlichen Grundlagen der analytischen Chemie. *Elementar Dargestellt von W. Ostwald. Vierte, Verbesserte Auflage. 14 × 21 cm; pp. xii + 223. Leipzig: Wilhelm Engelmann, 1904. Price: 7 marks.*—The fourth edition does not differ materially from the third and is issued because the previous edition has been exhausted. It is only necessary to call attention to the fact that an edition lasts but three years and that those who wish to possess a copy of this edition should not wait too long.

Wilder D. Bancroft.

A Text-Book of Quantitative Chemical Analysis *by Gravimetric, Electrolytic, Volumetric and Gasometric Methods. By J. C. Olsen. 16 × 23 cm; pp. xix + 513. New York: D. Van Nostrand Company, 1904. Price: $4.00, net.*—An instructor in quantitative analysis once remarked that the quantitative laboratory was the place for "weeding out" those students who had not the requisite skill and patience to become chemists. It was the custom of this instructor to give the student a substance, a few verbal instructions, and refer him to Fresenius. He would then retire to his private laboratory, leaving the student to shift for himself. All too frequently the student resorted to qualitative analysis and simple arithmetic. Doubtless this is not the case in most laboratories, but it is a regrettable fact that, in many, the instruction is left to assistants who have little appreciation of the importance of the subject and less experience in the details of manipulation. It has long been evident that a *textbook* of quantitative analysis would help compensate for the indifference of the instructor.

A number of books on "technical analysis" have appeared, but they deal with special methods and in no way help the student who is trying to get a comprehensive grasp of the subject.

Of course one compares the book with Fresenius. This we have no right to do for this is a *textbook*. But the comparison, if made, merely emphasizes the excellencies of this book. The book is clearly written, makes interesting reading and is free from the suggestion of 'cribbing' or 'padding'. It contains those suggestions and methods which the author has found successful. The needs of the student are kept constantly in view, but the book's usefulness is not limited to students. There is not space here to adequately review the separate chapters. In brief the book is divided as follows: Introduction; objects of analysis, calculation of results, the limits of accuracy, and the method of keeping notes.

I. The construction and care of the balance (a modern balance); the process of weighing; the determination of the sensitiveness; the ratio of the arms of the balance and the calibration of weights. Then the author departs from the usual custom and explains what use is to be made of the corrections obtained.

II. General operations: The mass law (called the law of ionization of saturated solutions) is introduced briefly to explain the effect of an excess of the reagent, both as to decreasing and increasing the solubility of the precipitate. The occlusion of mother liquor and the digestion of the precipitate to increase the size of the crystals, are explained. Under the preparation of pure salts for standards, the importance of stirring the solution during crystallization in order to obtain small crystals free from mother liquor is pointed out.

III. Determination of water: It is encouraging to find suggested, the dilution of the sulphuric acid of the desiccator for drying efflorescent salts. The relative efficiency of sulphuric acid, phosphorus pentoxide and calcium chloride for drying gases is discussed. The numerical data given bring the discussion down to a practical basis.

In the succeeding chapters, the method is that of a combined textbook and manual. The methods used are discussed and their limitations noted. This is followed by examples for practice. Among the directions for determining aluminum as oxide we find the following: "All of this work should be done during the intervals when the liquid is running through the funnel. It will run just as fast if not watched." Similar comments scattered through the text give it a human interest which in no way detracts from the excellence of the book.

IV.-V. The determination of metals as oxide.

VI. The determination of metals as sulphide and sulphate.

VII. The determination of metals as phosphate, chromate and chloride.

VIII.-IX. The determination of acids.

X.-XII. The analysis of alloys. These chapters devoted to this sadly neglected subject are especially valuable. The limitations of the methods are noted and the examples for practice cover a wide range. The methods are the best now available.

XIII.-XVI. These chapters deal with the analysis of minerals, including all of the more common ones. It is a pleasure to find the methods of Jannasch in such a book.

XVII.-XVIII. The chapters on electrolytic analysis are in some degree less satisfactory. The dissociation theory is confined to three pages, which is good. The manipulation is satisfactorily described. The methods are chiefly Classen's which is not so good, although that is much a matter of taste. The use of rotating electrodes is mentioned but not described. Evidently the author has not tried this method, so that one can pardon its omission. The author has wisely confined himself to those determinations which work.

XIX.-XXVII. Volumetric analysis: The methods of calibration of volumetric apparatus are given. The necessity for this calibration is pointed out. Suitable exercises for practice are given. When we recall that in most courses in quantitative analysis, calibration is not even mentioned, the presence of this chapter is a pleasure. The standard volumetric methods follow.

XXVIII.-XXX. Under the heading of "technical analysis" the author gives the standard methods for iron, steel, coal, water, oils, and fats.

XXXI. Gas analysis: Both the accurate methods of Hempel and the much used Orsat are described.

XXXII. Stoichiometry: This chapter includes the methods for obtaining the necessary factors; the equations, and calculations, for oxidation and reduction reactions; and instructions for the use of logarithms. The chapter will prove useful not only to the student, but also to many teachers.

An appendix including the strength of reagents, the necessary tables, and a good index complete the book. A few misprints were noticed, but none were serious. The book is printed in large type on excellent paper and is well bound. The cuts like the methods are up to date. That the publishers should content themselves with only five pages of advertising matter is a subject for congratulation.

Some may differ as to the value of certain methods used, but all will agree that the author has given us an excellent and much needed book. He has used physical chemistry where it would help, and he has not used it indiscriminately for the sake of impressing the unsophisticated. Throughout he has shown excellent judgment as to what to omit and what to include. Certainly the book will find friends wherever quantitative analysis is taught or studied.

E. S. Shepherd.

An Introduction to the Study of Spectrum Analysis. *By W. Marshall Watts. 14 × 22 cm; pp. vii + 325. New York: Longmans, Green and Co., 1904. Price: bound, $3.20.* — "In the present work the author has sought to explain principles and procedure from the very beginning, as well as to give an account of the refinements and achievements of this method of analysis, which have marked its latest developments. There is a very large amount of work waiting to be done, both by those who have the command of fine instruments and elaborate apparatus, and also by those who have only the simplest means, and it is hoped that to these last, especially, this book may prove a useful guide."

The headings of the chapters are: how to produce a spectrum; flame spectra; spectra produced by means of electricity; absorption spectra — the electric arc; the diffraction spectrum — measurement of wave-lengths; on the production of dark lines by absorption — the Fraunhofer lines of the solar spectrum; spectra of the stars and nebulae; the sun, its protosphere, chromosphere, corona, sun spots and prominences; new stars — double stars — comets; the concave grating — photography of the spectrum; relationships between the different lines of a spectrum, and between lines of the spectra of allied elements; band spectra — spectra of compounds; the spectroheliograph — electromagnetic theory of light — the "Zeeman effect" — the Michelson echelon diffraction grating.

Under self-induction, p. 159, one is surprised to find no reference to Hemsalech. Otherwise the book is admirable, while the illustrations are quite remarkable for their excellence. The author brings out clearly, p. 17, the difference between the flame spectra of cupric chloride and cupric oxide, as well as the action due to hydrochloric acid. The remarks on the spectrum given by a Geissler tube, p. 31, should be read and remembered. The chapter on the regularities in spectrum lines is thoroughly satisfactory and the same may be said of the chapter on the echelon grating. Altogether, this is a very readable book.

Wilder D. Bancroft.

Application of Some General Reactions to Investigations in Organic Chemistry. *By Dr. Lassar-Cohn. Authorized Translation by J. Bishop Tingle. 12 × 18 cm; pp. 101. New York. John Wiley and Sons, 1904. Price: cloth, $1.00.* — The chapters are entitled: fixation of labile hydrogen atoms; modification of reactions; improvement in the conditions of reactions; influence of neighboring atoms and atomic complexes. In the second chapter we find the difference in results produced by potassium and sodium salts; the improvement in the yield of phenylhydroxylamine by using ammonium chloride instead of calcium or sodium chloride; the changes due to substituting sodium methylate for sodium hydroxide. In chapter three we note especially the improvement in the yield of nitramino compounds, of vanilline, of fuchsine and of quinoline.

Wilder D. Bancroft.

A Compendium of Chemistry, *including General, Inorganic, and Organic Chemistry. By Carl Arnold. Authorized Translation from the Eleventh Enlarged and Revised German Edition by John A. Mandel. 14 × 21 cm; pp. xii + 627. New York: John Wiley and Sons, 1904. Price: bound, $3.50.* — One can only stand aghast at the amount of information compressed into these six hundred pages. The work contains a brief statement of the more important theories, and then gives a pretty complete survey of the whole field of both inorganic and organic chemistry. On hastily turning over the pages one is apt to get the impression that here is a book which would be most convenient for reference because it is so comprehensive; but a more careful consideration of the treatment allowed any individual compound or group of compounds is likely to lead to just the opposite impression,—that everything in the book is treated so briefly and so incompletely that as a reference book it would have but little value; and for one who has larger works at hand the latter impression will surely prevail. The fact that the work has gone into its eleventh edition in the original shows, however, that there are a large number of workers who find it useful in spite of its defects. *A. P. Saunders.*

Experiments Arranged for Students in General Chemistry. *By Edgar F. Smith and Harry F. Keller. Fifth Edition. 12 × 18 cm; pp. 94. Philadelphia: P. Blakiston's Son and Co., 1904. Price: bound, $.60.* —This volume contains a large number of experiments following pretty much the conventional plan as regards the order of the elements considered. The experimental directions are evidently worked out with care, and while there are few of them that are new, the course is arranged with judgment, and is well worth the attention of those who have to select a manual for laboratory work. The book would without doubt yield very satisfactory results in the hands of a good instructor.
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

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General

Thorium, carolinium, berzelium. *C. Baskerville. Jour. Am. Chem. Soc.* **26**, *922* (*1904*). — So-called thorium oxide, mixed with carbon in a carbon tube, was placed in a quartz tube and heated in a current of pure chlorine. A volatile chloride distils over, thorium chloride crystallizes on the walls of the quartz tube, while a non-volatile chloride remains behind. The metal of the volatile chloride has been named berzelium and that of the non-volatile chloride carolinium while thorium is retained for the name of the intermediate element. The atomic weights of the three substances in their present degree of purity are carolinium 255, thorium 220 and berzelium 212. The density of the carolinium oxide is 11.26 and that of berzelium oxide 8.45. The chemical properties of the three substances differ somewhat but no difference has yet been found between the spectra of carolinium and of thorium. *W. D. B.*

Eleventh annual report of the committee on atomic weights. *F. W. Clarke. Jour. Am. Chem. Soc.* **26**, *235* (*1904*). — The new determinations during 1903, were caesium 132.879, fluorine 19.036, iron 55.871, cerium 140.25, radium 225. Jones defended his results on lanthanum; Ramsay found 40.81 for the density of krypton, while Adie obtained a preliminary value of 208.8 for bismuth. *W. D. B.*

A revision of the atomic weight of beryllium. *C. L. Parsons. Jour. Am. Chem. Soc.* **26**, *72*; *Zeit. anorg. Chem.* 40, *400* (*1904*). — The salts analyzed were beryllium acetylacetonate and basic beryllium acetate. The value obtained by the author is 9.113. It is shown that the substance obtained by Krüss and Moraht which gave a black sulphide and a white hydroxide was a mixture of zinc and iron salts. *W. D. B.*

The atomic weight of tungsten. *E. F. Smith and F. F. Exner. Jour. Am. Chem. Soc.* **26**, *1082* (*1904*). — Tungsten hexachloride and tungsten metal were converted into oxide. The mean of the two series is 184.05. *W. D. B.*

The atomic weight of indium. *L. M. Dennis and W. C. Geer. Jour. Am. Chem. Soc.* **26**, *437* (*1904*). — A brief account of the general properties of indium and its salts. Indium can easily be precipitated electrolytically in presence of formic acid. No reference is made to the atomic weight. *W. D. B.*

The metric standard of volume. *T. W. Richards. Jour. Am. Chem. Soc.* **26**, *413* (*1904*). — The author wishes to substitute the word milliliter for what seems to him the less exact and more cumbrous phrase cubic centimeter. *W. D. B.*

The continuous advance of electrochemistry. *J. W. Richards. Trans. Am. Electrochem. Soc.* 5, *37* (*1904*). — An address as retiring president. The subject was treated under the headings: The investigation and classification of electrochemical phenomena; the building of a comprehensive electrochemical theory; applications to industrial uses. *W. D. B.*

A criticism of Clarke's new law in thermochemistry. *H. E. Patten and W. R. Mott. Jour. Am. Chem. Soc.* 26, *1446* (*1904*). — The authors give their reasons for believing that Clarke's recent law (7, 307) is not an accurate statement of the facts. *W. D. B.*

Molecular conductivity. *C. J. Reed. Trans. Am. Electrochem. Soc.* 5, *103* (*1904*). — The author makes the point that many people use the word conductivity when they really mean conductance. This confusion does exist and there is also a pretty general failure to distinguish between resistance and resistivity. *W. D. B.*

One-Component Systems

The melting-points of solid chloroform, toluene and ether. *E. H. Archibald and D. McIntosh. Jour. Am. Chem Soc.* 26, *305* (*1904*). — A hydrogen thermometer was used and the following melting-points were obtained: chloroform −63.2°, ether −117.6°, toluene −97°-99°. A well-stirred bath of solid carbon dioxide and ether had a temperature of −79.5° under atmospheric pressure. *W. D. B.*

On fluid crystals. *A. Coehn. Zeit. Elektrochemie,* 10, *656* (*1904*). — If the turbidity of the fluid crystals is due to an emulsion, a separation could be effected by electrical osmose provided the dielectric constants of the hypothetical components are different. No such separation could be detected and consequently no conclusions could be drawn. *W. D. B.*

New method of determining compressibility with application to bromine, iodine, chloroform, bromoform, carbon tetrachloride, phosphorus, water and glass. *T. W. Richards and W. N. Stull. Jour. Am. Chem. Soc.* 26, *399*; *Zeit. phys. Chem.* 49, *1* (*1904*). — The method involves "the comparison of each substance with mercury by noting the pressure needed to compress the whole system, with small added quantities of mercury to a fixed point as determined by electrical indication. Solids attacking mercury were surrounded by water, and liquids attacking mercury were enclosed in very thin compressible glass-bulbs."

"The compressibility of bromine, iodine, chloroform, bromoform, carbon tetrachloride, phosphorus, water and glass were determined by reference to mercury, in most cases as far as 500 or 600 atmospheres." *W. D. B.*

Theory of the critical state. *J. Traube. Zeit. anorg. Chem.* 37, *225* (*1903*). — The author assumes the existence of liquid particles which he calls "liquidons" and of larger gas particles which he calls "gasons". A homogeneous liquid consists mostly of fluidons, a saturated vapor mostly of gasons. At each temperature there is equilibrium both in the liquid and the gaseous phase between the fluidons and the gasons. The author discusses the bearing of this view on the critical phenomena. He considers the critical temperature as analogous to the consolute temperature in binary dineric systems. *W. D. B.*

Theory of the critical state. *J. Traube. Zeit. anorg. Chem.* 38, *399* (*1904*). —The author has not been able to convince Young of the accuracy of the results found by Teichner. A cut is shown in which differences of density are visible above the critical temperature. The experiments themselves rather indicate convection currents. Various reasons are given for not adopting the Andrews point of view. *W. D. B.*

Two-Component Systems

The solidification and inversions of mixtures of silver nitrate and potassium nitrate. *A. Ussow. Zeit. anorg. Chem.* 38, *419* (*1904*).—The solid phases along the silver nitrate and potassium nitrate freezing-point curves are: two modifications of silver nitrate; the compound $AgNO_3.KNO_3$ not stable at its melting point; potassium nitrate. The change to the second modification of potassium nitrate occurs below the eutectic temperature of 131°. *W. D. B.*

The effect of pressure on the inversion temperatures of iron. *G. Tammann. Zeit. anorg. Chem.* 37, *448* (*1903*).—From the data of Roberts-Austen, Le Chatelier and others, the author deduces some of the pressure-temperature curves for iron. He reaches the conclusion that there is a triple point with α, β and γ iron as solid phases at about 770° and a pressure of 12000 kg/qcm. The data for the martensite change are not concordant enough to permit of satisfactory conclusions being drawn. *W. D. B.*

A study of the supercooled fusions and solutions of sodium thiosulphate. *S. W. Young and J. P. Mitchell. Jour. Am. Chem. Soc.* 26, *1389* (*1904*).—There are three different pentahydrates of sodium thiosulphate and four hydrates containing less than five of water. The authors have made a number of experiments on the behavior of supercooled melts. They attempt to account for their results by assuming the existence of several different kinds of nuclei, each kind having the properties necessary to make it fit. It must be admitted that the authors make out a fairly good case and yet one hardly feels as though their explanation was the right one. Since it seems impossible to remove all solid nuclei by filtration, it seems to the reviewer desirable to go to the other extreme temporarily and fill the solutions with dust, etc. While the explanation of the differences is the thing to be desired, this is not the first problem. We should first know the conditions as to time and temperature of heating which make the melts behave most nearly alike. *W. D. B.*

The composition and solubility of the hydrates of sodium thiosulphate. *S. W. Young and W. E. Burke. Jour. Am. Chem. Soc.* 26, *1413* (*1904*).—The authors have determined solubility curves for the α and β pentahydrates, for the monohydrate, the dihydrate and what is thought to be the tetrahydrate. This leaves the curves for the γ pentahydrate and its unknown decomposition product still to be determined. *W. D. B.*

The molecular depression constant of *p*-azoxyanisol. *H. M. Smith and W. H. McClelland. Jour. Am. Chem. Soc.* 26, *1446* (*1904*).—The authors have determined the molecular lowering of the freezing-point of the fluid crystals of *p*-azoxyanisol for twelve different substances. The mean is about 562 for eight substances, four aromatic ketones coming in a class by themselves with lowerings of 720–970. These abnormal values are believed to be due to the solubility of the solutes in the flowing crystals though this should give too small a depression. *W. D. B.*

A modification of the freezing-point method. *S. W. Young and W. H. Sloan. Jour. Am. Chem. Soc.* 26, *913* (*1904*).—The solution to be measured is placed in a vacuum-jacketted vessel which stands in a pail of shaved ice. The solution is stirred with an ice stirrer until equilibrium is reached, when the concentration of the solution is determined by weighing. Very concordant results are obtained with the apparatus but the freezing-point lowerings are uniformly less than those obtained by the usual method. The apparatus is to be improved further. *W. D. B.*

The amount of moisture remaining in a gas after drying with phosphorus pentoxide. *E. W. Morley. Jour. Am. Chem. Soc.* 26, *1171* (*1904*).—A current of gas "passing at the rate of 2 liters an hour through 25 cc of phosphorus pentoxide properly filled into a drying tube, contains much less than 1 mg of water vapor in 40,000 liters; whether a half or a tenth of this quantity no one can now say."

It is very easy to dry a gas and this can be done quickly. The thing that takes time is to dry the glass vessel in which a gas is contained. *W. D. B.*

Acid sulphates of the rare earths. *B. Brauner and J. Picek. Zeit. anorg. Chem.* 38, *322* (*1904*).—When rare earth sulphates and sulphuric acid are heated to 130° under diminished pressure, the free sulphuric acid distils off, leaving acid sulphates behind. At temperatures of 180° and upwards the acid sulphates begin to decompose. After seven hours at 230° the percentage decomposition decreased in the following order: yttrium, lanthanum, praseodymium, cerium, samarium, neodymium. *W. D. B.*

Volatilization of platinum. *G. A. Hulett and H. W. Berger. Jour. Am. Chem. Soc.* 26, *1512* (*1904*).—Platinum begins to volatilize in air at about 800°. With rising temperature the rate of volatilization increases markedly. In an atmosphere free from oxygen no volatilization takes place. The phenomenon is probably due to the formation of volatile oxide. *W. D. B.*

Alcohometric tables, for each integral percentage by weight, and for each degree of the hydrogen thermometer from 15° to 22°. *E. W. Morley. Jour. Am. Chem. Soc.* 26, *1185* (*1904*).—The tables are based on the data of Mendeléeff. The specific gravities given are the weights of 1 cc of aqueous alcohol, the weight being reduced to vacuum. *W. D. B.*

On the non-existence of arsenic pentachloride. *W. R. Smith and J. E. Hora. Jour. Am. Chem. Soc.* 26, *632* (*1904*).—The authors have determined the freezing-point curve for chlorine in arsenic chloride up to a concentration represented by $AsCl_3 + 3Cl_2$. They find no break in the curve, and analysis of the solid phase seems to show that it is the trichloride. The authors therefore conclude that Baskerville's arsenic pentachloride was merely a solution of chlorine in arsenic trichloride. *W. D. B.*

Multi-Component Systems

Equilibrium in the system BeO, SO_3, H_2O. *C. L. Parsons. Jour. Am. Chem. Soc.* 26, *1433 ; Zeit. anorg Chem.* 42, *250* (*1904*).—Beryllium sulphate can occur with two and with four of water but the salt with seven of water is mythical. By an application of the phase rule it is shown that only one phase separates from basic solutions. The experiments are not accurate enough to decide definitely whether this phase is a solid solution of $BeSO_4$ in BeO or whether it is a compound containing about 25 BeO to 1 $BeSO_4$; but this latter hypothesis is improbable. This is a very creditable piece of work; but there are two criticisms which must be made. The concentrations of the solutions should not have been given as volume concentrations and the experiments should have come down to the point at which hydrated beryllium sulphate does separate. This would not have entailed much extra work especially as a number of the solutions are duplicated, apparently unconsciously. Thus 1 and 8, p. 1443, are identical, are also 2 and 10, and these are not the only cases.

W. D. B.

The equilibrium $Mg(OH)_2 + 2NH_4Cl \rightleftarrows MgCl_2 + 2NH_4OH$. *W. Herz and G. Muhs. Zeit. anorg. Chem.* 38, *138* (*1904*).—In 1896 Lovén showed that the action of ammonium salts in preventing the precipitation of magnesia by ammonia could be explained on the basis of the mass law without assuming formation of complex salts. He approached the equilibrium from one side only. The authors have approached equilibrium from the other side, starting with magnesium hydroxide and ammonium chloride. They confirm Lovén's results. There are apparently fewer complications with magnesium hydroxide thanwith the hydroxides of manganese, zinc and cadmium. *W. D. B.*

Thermo-electric determinations of the reduction temperature of zinc[1] *W. McA. Johnson. Trans. Am. Electrochem. Soc.* 5, *211* (*1904*).—The author has heated zinc oxide or zinc ore in a graphite crucible with charcoal, coke or graphite, and has determined the temperature at which the zinc oxide begins to react. This temperature varies with the nature of the reducing agent and with the previous history of the zinc oxide. If 1100° charcoal is used the reduction temperature is about 1025°. *W. D. B.*

The dissociation of lead nitrate. *L. Baekeland. Jour. Am. Chem. Soc.* 26, *391* (*1904*).—The author has determined the dissociation pressures for pure dry lead nitrate from 223° to 448°. The reaction is a reversible one and may be written

$$Pb(NO_3)_2 \rightleftarrows Pb + O + 2NO_2.$$

Addition of oxygen or of nitrogen peroxide forces back the dissociation (Cf. 8, 416). *W. D. B.*

The action of water upon the phosphates of calcium. *F. K. Cameron and A. Seidell. Jour. Am. Chem. Soc.* 26, *1454* (*1904*).—Monocalcium phosphate and tricalcium phosphate are hydrolyzed very perceptibly while dicalcium phosphate is only slightly decomposed by water. With tricalcium phosphate equilibrium apparently was not reached in thirty-five days. The authors make the unfortunate statement "that it is safe to say that with both tri- and monocalcium phosphate the amount of decomposition and the concentration of the resulting solution at the temperature employed is dependent upon the proportion of the mass of the solid phosphate to the mass of water." It would have saved time and have been more satisfactory if the authors had also added an excess of lime to phosphoric acid solutions. *W. D. B.*

Boric and arsenious acids. *F. Auerbach. Zeil. anorg. Chem.* 37, *353* (*1904*). — The author determined the distribution ratio of arsenious acid for amyl alcohol and water, also for amyl alcohol and saturated boric acid solution. The two values were not the same. Equilibrium constants were then calculated for the system amyl alcohol, arsenious acid, borax, water and an excess of boric acid. These constants varied from 0.79 to 0.42, the theoretical value being 0.081. Further experiments convinced the author that the trouble was due to complex sodium arsenites. The rest of the paper is filled with calculations and conclusions based on this assumption. *W. D. B.*

A study of reversible oxidation and reduction reactions in solutions. *E. P. Schoch. Jour. Am. Chem. Soc.* 26, *1422* (*1904*). — The author has studied the reaction between potassium ferrocyanide and iodine in a slightly acid solution. The equilibrium is found to depend on the first power of the free iodine concentrations, on the second power of the iodide and ferricyanide concentrations, and on the fourth power of the ferrocyanide concentration. Since the reaction is believed to be

$$2\mathrm{Fe(CN)_6}'''' + \mathrm{I_2} \rightleftarrows 2\mathrm{Fe(CN)}''' + 2\mathrm{I}'$$

neither the ferricyanide nor the ferrocyanide behaves as it should.

W. D. B.

The densities of fused salts and the chemical equilibrium of their mixtures. *E. Brunner. Zeil. anorg. Chem.* 38, *350* (*1904*). — The author has determined the densities of a number of fused salts and has then determined the equilibria at the same temperature for pairs of salts on the assumption that there is no contraction or expansion beyond that caused by the metathetical reaction. The salts were taken in equivalent quantities. Check experiments were also made with salt pairs having a common ion. At 900° the following equilibria were found: 47.7 percent ($\mathrm{NaCl} + 0.5\ \mathrm{K_2CO_3}$); 47.2 percent ($\mathrm{NaBr} + 0.5\ \mathrm{K_2CO_3}$); 37.5 percent ($\mathrm{LiCl} + 0.5\ \mathrm{K_2CO_3}$); 44.0 percent ($\mathrm{LiCl} + 0.5\ \mathrm{Na_2CO_3}$); 37 percent ($\mathrm{LiCl} + 0.5\ \mathrm{Na_2SO_4}$). Between 800 and 1000 the change of the equilibrium with the temperature is very small. For potassium chloride and sodium bromide the density change is too small to permit of any conclusions as to the equilibrium. The same is true for mixtures of sulphates and carbonates. The experiment with two salts of the same acid showed that the original assumption was not absolutely correct. *W. D. B.*

The water-gas equilibrium in the Bunsen burner. *F. Haber and F. Richardt. Zeit. anorg. Chem.* 38, *5* (*1904*). — The inner and outer flames of the Bunsen burner were separated by Teclu's method. The ratio of the concentrations of carbon dioxide, hydrogen, carbon monoxide and water was determined for the inner flame and for the intermediate zone. The constant thus obtained agreed well with the results of Hahn. Equilibrium is apparently reached practically instantaneously in the inner flame while it is not displaced appreciably in the zone between the two flames. The authors account for this by assuming the existence of some catalytic action in the inner flame. The temperatures were measured by means of two thermocouples of different thickness, by calculation from the composition of the gases, and by calculation from the heats of combustion and the specific heats. *W. D. B.*

Fractional combustion, over heated palladium wire, of gas mixtures containing hydrogen. *F. Richardt. Zeit. anorg. Chem.* 38, *65* (*1904*). — Below 450° methane does not burn in presence of a massive palladium wire. If the methane be passed rapidly over the wire, there is practically no combustion even at 600°–650°. At both temperatures hydrogen is burned completely. While it is possible to separate hydrogen from methane or ethane by fractional combustion, it is not possible to separate ethane from methane in this way. No separation is possible when ethylene is present. *W. D. B.*

The delicacy of tests employed for the detection of metals. *F. Jackson. Jour. Am. Chem. Soc.* 25, *992* (*1903*). — A tabulated statement of the "comparative delicacy of the tests employed in the ordinary methods used in qualitative analysis in detecting metals." The figures given "were chosen as the probable limit of detection, if the element was not known to be present." This sort of work is very desirable. One would have liked to know also what the limits were when the metal was known to be present. *W. D. B.*

On beryllium compounds. *F. Haber and G. van Oordt. Zeit. anorg. Chem.* 38, *377* (*1904*). — When beryllium hydroxide is first precipitated in the cold, it is a voluminous gelatinous mass which takes up carbonic acid readily and which dissolves with ease in potassium or ammonium carbonate, in dilute caustic alkali and in dilute acids. It loses all these properties gradually on standing, more rapidly on heating. It is not known what the change is that takes place. Many of the contradictory statements in regard to beryllium hydroxide are due to people having ignored the change of properties with the time. *W. D. B.*

The action of ozone on hydrogen. *G. Pickel. Zeit. anorg. Chem.* 38, *307* (*1904*). — Contrary to the statement of Berthelot, ozone acts on hydrogen even at 20°. *W. D. B.*

The colors of the allotropic modifications of silver. *J. C. Blake. Am. Jour. Sci.* (*4*) 16, *282*; *Zeit. anorg. Chem.* 37, *243* (*1903*). — The author assumes the existence of four forms of silver: white silver, white by reflected light and practically opaque; blue silver, gold-yellow by reflected light, blue by transmitted; red silver, indigo-blue by reflected light, red by transmitted; yellow silver, indigo-blue by reflected light, yellow by transmitted. The conditions of formation are discussed; but there is not much in the way of theory. *W. D. B.*

Osmotic Pressure and Diffusion

An experiment illustrating osmosis. *H. C. Byers. Jour. Am. Chem. Soc.* 26, *1545* (*1904*). — If an egg is placed in concentrated hydrochloric acid for a few minutes, the shell dissolves and the outer surface of the egg itself is converted into a semi-permeable membrane. If this egg be placed in pure water, it will expand, while it will contract if placed in a saturated calcium chloride solution. *W. D. B.*

The migration of colloids. *W. R. Whitney and J. C. Blake. Jour. Am. Chem. Soc.* **26**, *1339* (*1904*). — "Colloidal gold solutions, prepared by the action of an ethereal solution of gold chloride on an aqueous solution of acetylene, retain, even after prolonged dialysis against conductivity water, a constant conductivity five or six times as great as that of the water outside the dialyzer. This conductivity is almost completely lost by repeatedly migrating the gold downwards with the electric current against a membrane of goldbeaters' skin and redissolving it again in pure water, and is to that extent, at least, attributable to electrolytes associated with or 'adsorbed' by the gold."

The rate of migration was determined for colloidal gold, platinum, silver, Prussian blue, "ferric hydrate", silicic acid and gelatine in vertical tubes. The rate is directly proportional to the potential gradient. The boundary between colloidal solution and pure water is stable when the potential gradient just above the boundary is greater than that just below it.

"The soluble mud obtained by downward migration, when placed under pure water, diffused upward into it at a rate comparable with that of electrolytes diffusing from concentrated solutions into pure water. A reverse effect, consisting either in a sudden retardation of the downward movement of the boundary or in a reversal of its direction, occurs in the migration of colloidal solutions in vertical tubes. This is due, in part, to changes in the potential gradient arising from the decomposition products of electrolysis, and in part to a reverse movement of the colloid itself where precipitation by the current is not complete."

"The 'reversals' obtained by Billitzer were probably due to the effect of the migration of the gelatine, superimposed on that of the metallic colloids present with it.

"The rate of migration of the boundary, independent of gravity, diffusion, and the reverse effect, in the case of colloidal gold, platinum, silver, Prussian blue, 'ferric hydrate' and quartz, is approximately that of the univalent ions of neutral inorganic salts.

"These facts are in agreement with the deductions of Lamb and of Smoluchowski, based on the theory of the electrical double layer, according to which the rate of migration of solid particles suspended in water should be independent of the size and shape of the particles, and should be of the same order of magnitude as the rate of migration of the ions.

"The charge on the colloid particles is probably due to associated ions, which determine the migration, diffusion and permanent suspensibility of the particles." *W. D. B.*

Velocities

The hydration of milk-sugar in solutions. *C. S. Hudson. Jour. Am. Chem. Soc.* **26**, *1065* (*1904*). — The multirotation of milk-sugar is shown to be due to a change in the degree of hydration in solution. The same reaction velocity constant was obtained starting from the two ends. If milk-sugar in large excess is shaken with water, an initial solubility is obtained which gradually increases owing to dehydration in solution. Barium nitrate, potassium sulphate, sodium chloride, iodine and arsenious oxide were tested in water and did not show this phenomenon. Consequently the author concludes that there is no slow chemical change when these substances dissolve. *W. D. B.*

A contact process for the preparation of ammonia-free water. *H. B. Pulsifer. Jour. Am. Chem. Soc.* **26**, *1387* (*1904*). — Steam is passed over a mass of platinized asbestos heated to redness. Any organic or nitrogeneous substance, including ammonia, is completely decomposed and the distillate is entirely free from ammonia. *W. D. B.*

Electromotive Forces

Preparation of materials for standard cells and their construction. *H. S. Carhart and G. A. Hulett. Trans. Am. Electrochem. Soc.* **5**, *59* (*1904*). — The mercury was treated with dilute nitric acid and then distilled in vacuo. The cadmium sulphate was shaken with cadmium oxide and allowed to crystallize very slowly. Cadmium amalgam was prepared electrolytically. Since mercurous sulphate varied in its properties when precipitated chemically, it was prepared by electrolyzing diluted sulphuric acid with a mercury anode and a platinum cathode. To prevent hydrolysis this mercurous sulphate is washed with saturated cadmium sulphate solution. The sulphate should be protected from the light. Very constant readings when cells of the H-form are made up from these materials. These cells do not need to be "aged". *W. D. B.*

The standard cell. *F. A. Wolff, Jr. Trans. Am. Electrochem. Soc.* **5**, *49* (*1904*). — The author maintains that the two units to be defined should be the ohm and the volt and that the ampere should be deduced from these. The standard cell should be the Weston cell and not the Clark. A consideration of the sources of error shows that the mercurous sulphate is the most unreliable of the materials used. This is best prepared electrolytically (Cf. preceding review). The author uses dilute sulphuric acid and mercury electrodes, with an anode density of 0.1 amp/qdm. *W. D. B.*

On normal elements. *N. T. M. Wilsmore. Zeit. Elektrochemie,* **10**, *685* (*1904*). — If the lower parts of the H-form of normal cell be drawn into little tubes and these tubes filled with asbestos, the mercury does not come in contact with the place where the platinum wire passes through the glass and consequently the glass does not break. A modified form of normal electrode is also described. *W. D. B.*

A simple normal electrode. *H. Danneel. Zeit. Elektrochemie,* **10**, *685* (*1904*). — An inverted Y-tube with a stop-cock in one arm connects the normal electrode with the other vessel. The vertical stem can be closed with a cork and is useful for washing out the external arm of the Y. *W. D. B.*

Single potentials of the halogen elements. *W. R. Mott. Trans. Am. Electrochem. Soc.* **5**, *73* (*1904*). — The author states that the observed decomposition voltages rarely differ by more than a tenth of a volt from those calculated from the thermochemical data. Starting from the Ostwald zero he calculates the following single potentials, fluorine — 2.57, chlorine — 2.00, bromine — 1.53, and iodine — 0.87 volts. The thermochemical heats of formation for salts in solution differ from the heats of formation by the heat of solution. This would seem to be self-evident, but it seems not to have been either to the author or to the audience. *W. D. B.*

The composition and resolution of voltages. *J. W. Richards. Trans. Am. Electrochem. Soc.* 5, *89* (*1904*). — The author points out that if a metal such as crude copper contains metals less noble than copper, it will become anode to pure copper in a copper sulphate solution. Starting from this fact, the author deduces that copper could be refined without external current if one were willing to take the time. The weak point in this argument is the assumption that the copper would dissolve under these circumstances. The author also does a mathematical calculation to show that copper and hydrogen can be precipitated simultaneously at the cathode at a voltage lower than that necessary to precipitate hydrogen. This is known not to be true. The real state of things is that no precipitation of hydrogen occurs until the voltage rises above the value for hydrogen. The relative amounts of hydrogen and copper precipitated will then depend on the relative decomposition voltages. The author has averaged the potentials when he should have averaged the masses. If he had not ignored the experimental facts, he would not have fallen into error. *W. D. B.*

The aluminum electrolytic condenser. *C. I. Zimmerman. Trans. Am. Electrochem. Soc.* 5, *147* (*1904*). — The author summarizes his paper as follows: —

"The film coating the aluminum electrode varies from less than 0.000005 centimeter to more than 0.000050 centimeter as estimated by the interference color phenomena observed; this thin film acts as an asymmetrical conductor; a condenser with two of these asymmetrical dielectrics holds a constant coulomb charge when operating upon an alternating current circuit; this constant charge sets up a uniform pressure between the electrolyte and a point in the metallic or external circuit which is neutral to the alternating pressure; the pressures upon the films are unidirectional pressures which pulsate in continuous sinusoidal variations with one-half the amplitude and one-half the frequency of the pulsations of the impressed pressure; with the Graetz rectifier group of cells, uniform pressure of approximately 1.2 times the impressed alternating pressure may be observed; the condenser action of the cell is due to the energy variations accompanying the variations of the distribution of the constant coulomb charge within the cell; the energy variations are one-half the maximum energy held by the cell; the ordinary condenser behavior upon AC circuits is possessed by the aluminum condenser; the losses in the cell are small and consist of film losses, C^2R losses and decomposition losses, the film losses being due to leakage and to a loss directly proportional to the frequency."

W. D. B.

A contribution to the study of the electric arc. *W. S. Weedon. Trans. Am. Electrochem. Soc.* 5, *171* (*1904*). — This paper deals with the so-called flame arcs, which are obtained from most metals and from carbons containing certain metallic salts. In the flame arc most of the light comes from the arc itself, while the light comes chiefly from the glowing electrodes in the crater arcs. Experiments with a 500-volt direct current shows that there is no relation between the amount of current and the change in weight of the electrodes. When the electrodes are water-cooled, there is practically no change in weight at all. When horizontal copper arcs were run in hydrogen, the molten copper suddenly swelled to two or three times its normal size when the circuit was broken. This was apparently due to the absorption of hydrogen. Experiments made with two different electrodes showed that in some cases, the cathode determined the nature of the arc, while in other cases it did not. The author offers no explanation for these apparent contradictions, but it seems probable that it is chiefly a question of the relative volatilities of the two substances at the temperatures of the two electrodes. This is confirmed by the fact that variations in the current with copper magnetite electrodes change the character of the arc. *W. D. B.*

Electric smelting experiments for the manufacture of ferro-nickel from pyrrhotite. *E. A. Sjöstedt. Trans. Am. Electrochem. Soc.* 5, *233* (*1904*). — A 100-kilowatt furnace is described in which a ferronickel containing three percent nickel was made from a poorly roasted ore, containing about three percent sulphur and fifty-three percent iron. It is believed that a 500-horse power furnace would yield about 2.5 tons of ferronickel per hour.

W. D. B.

Electrolysis and Electrolytic Dissociation

Electrolytic iron. *C. F. Burgess and C. Hambuechen. Trans. Am. Electrochem. Soc.* 5, *201* (*1904*). — Wrought iron or steel can be refined satisfactorily in a solution of ferrous and ammonium sulphates (concentration not given) at 30° with a current density of 0.6 to 1.0 amp/qdm. The iron can be deposited to a thickness of about 0.75 inch before the surface becomes too rough. The current efficiency is nearly 100 percent and the deterioration of the electrolyte is slight, the actual amount not being stated. The iron thus obtained is very pure, containing no carbon, silicon or manganese. Hydrogen is present but can be driven out by heating. The difficulty is to melt the iron without introducing impurities. *W. D. B.*

The rapid precipitation of metals in the electrolytic way. *F. F. Exner. Jour. Am. Chem. Soc.* 25, *896* (*1903*).—The solution was stirred by rotating the anode 500-900 times per minute. Data are given for the precipitation of copper, nickel, zinc, silver, bismuth, mercury, cobalt, cadmium, iron, lead, molybdenum, tin, gold and antimony; also for separations of copper from nickel and copper from zinc. *W. D. B.*

Electrolytic determination of nitric acid with a rotating anode. *L. H. Ingham. Jour. Am. Chem. Soc.* 26, *1251* (*1904*). — Using a rotating anode and a current of 4 amperes, the nitrate in 0.5 g KNO_3 can be reduced quantitatively to ammonia in 30 minutes, copper sulphate being added to the solution.

W. D. B.

The use of a rotating anode in the electrolytic estimation of zinc. *L. H. Ingham. Jour. Am. Chem. Soc.*, 26, *1269* (*1904*).—One-quarter to one-half a gram of zinc can be deposited quantitatively from an acetate, hydroxide or formate solution in about fifteen minutes. Valuable measurements were also made on the rate of precipitation. This is a side of electrolytic analysis which has been overlooked in the past. It is a great pleasure to see that this matter is now receiving proper attention. *W. D. B.*

Electrolytic separations possible with a rotating anode. *D. S. Ashbrook. Jour. Am. Chem. Soc.* 26, *1283* (*1904*).—The conditions are given for the rapid separation of copper from aluminum, antimony, arsenic, cadmium, chromium, cobalt, iron, lead, magnesium, manganese, nickel, uranium, and zinc; of cadmium from aluminum, chromium, cobalt, iron, magnesium, manganese, nickel and zinc; of silver from aluminum, cadmium, chromium, cobalt, iron, lead, magnesium, manganese, nickel and zinc. With the exception of the silver from copper in cyanide solution, which apparently was not successful, this paper is practically a condensed manual on electrochemical analysis. The separations all of course come under the head of constant current methods. *W. D. B.*

A rapid and convenient method for the quantitative electrolytic precipitation of copper. *T. W. Richards and H. Bisbee. Jour. Am. Chem. Soc.* 26, *530* (*1904*). — Five cubic centimeters of acidified copper sulphate solution were run into the space between two platinum crucibles, one set within the other. A current density of 2 amp/qdm was employed at first and was gradually decreased. To avoid the trouble of watching the process, a fixed voltage of 1.9 volts from a storage cell was afterwards used. This method is more rapid than the ordinary ones but not so quick as those in which a rotating electrode is used. *W. D. B.*

Determination and separation of gold in the electrolytic way. *S. P. Miller. Jour. Am. Chem. Soc.* 26, *1255* (*1904*). —Starting with 0.1236g gold in a cyanide solution, all the gold was precipitated in less than two hours. In a cyanide solution gold can be separated from iron but not from silver or cadmium. In phosphate solutions gold can be separated from cadmium, iron, zinc, nickel or cobalt but apparently not completely from copper. In sulphide solution, gold may be separated from arsenic, molybdenum and tungsten. From this solution the gold precipitates with a shining yellow color, appearing like polished metal. The diagram showing the rate of precipitation of gold from double cyanide solution is an interesting and a valuable one; but the reviewer has been unable to understand the voltage current diagrams for gold and cadmium. *W. D. B.*

The electrolytic precipitation of nickel from phosphate solutions. *W. T. Taggart. J. Am. Chem. Soc.*, 25, *1039* (*1903*).—Nickel can be precipitated completely by electrolysis of nickel sulphate solution to which disodium phosphate and phosphoric acid have been added. The nickel is free from phosphorus. It is not stated why sodium phosphate should be added. So far as one may judge it is an unnecessary complication. The author did not succeed in effecting a satisfactory separation of nickel from manganese, iron, aluminum or chromium. The chromium salts are oxidized to chromate but we are not told what the difficulties are in the other cases. This seems a pity because now the author's negative results are of no value and some one else will probably have to duplicate the work. *W. D. B.*

The electrolytic determination of manganese and its separation from iron and zinc. *G. P. Scholl. Jour. Am. Chem. Soc.*, 25, *1045* (*1903*).—In a formic acid solution it is easily possible to precipitate manganese quantitatively as peroxide. By observing suitable precautions a separation of manganese from iron and from zinc can be effected. *W. D. B.*

The electrolytic assay of copper containing arsenic, antimony, selenium and tellurium. *G. L. Heath. Jour. Am. Chem. Soc.* 26, *1120* (*1904*). — The author describes four different methods for the electrolytic determination of commercial copper or of low-grade material, the choice depending on the relative amounts of arsenic, antimony, selenium and tellurium in the sample. *W. D. B.*

Results obtained in electrochemical analysis by the use of a mercury cathode. *E. Myers. Jour. Am. Chem. Soc.* 26, *1124* (*1904*). — Using a mercury cathode it is easy to determine chromium electrolytically and to separate chromium from aluminum or beryllium. Molybdenum could also be determined in this way and the separation of this metal from vanadium was also accomplished. Iron can be separated from cerium, lanthanum, praseodymium, neodymium, yttrium, vanadium, beryllium or aluminum. *W. D. B.*

Some phenomena observed in connection with the use of a copper voltameter. *I. Adams and B. MacNutt. Trans. Am. Electrochem. Soc.* 5, *191* (*1904*). — The authors use a copper voltameter with no stirring and obtain polarization phenomena. They also find that copper sulphate dissolves copper. They believe that copper voltameter is accurate to the fourth decimal place; but without referring to the work of anybody else and without giving any data in confirmation of their belief. Reference is made in the text to a cut which does not appear. *W. D. B.*

Experiments on electrolytic separation of the alkaline earth metals. *A. Coehn and W. Kettembeil. Zeit. anorg. Chem.*, 38, *198* (*1904*).—"The electrolytic precipitation of the metals of the alkaline earths at mercury cathodes takes place under voltages varying by several tenths of a volt one from the other.

"If one electrolyzes a mixed chloride solution of the alkaline earth metals at potentials between those for the decomposition of the two salts, a separation of the two metals by electrolysis becomes possible with formation of amalgam.

"The analytical accuracy of this method was tested carefully for the case of barium and strontium." *W. D. B.*

On amalgams. *W. Kettembeil. Zeit. anorg. Chem.*, 38, *213* (*1904*).—Three classes of metals are distinguished: those which form amalgams readily from aqueous solutions; those which form no amalgams from aqueous solutions; the other metals such as iron, cobalt, nickel, platinum, etc. This is really a double classification, depending on the solubility in mercury and the rate of decomposition by water. No amalgams of the rare earths could be obtained by electrolysis with a mercury cathode. When determining decomposition voltages the second break for sodium, barium and magnesium at platinum cathodes is found in the same place with mercury cathodes. The reversible formation of potassium amalgam from sodium amalgam and caustic potash is discussed. *W. D. B.*

The reduction of nitric acid in metallic nitrates to ammonia by the electric current. *W. H. Easton. Jour. Am. Chem. Soc.* 25, *1042* (*1903*). — Practically quantitative reduction of potassium nitrate to ammonia takes place when an equal quantity of crystallized copper sulphate is added to the solution. No attempt is made to account for the results obtained. The amount of reduction, other things being equal, appears to be a function of the ampere-hours and not of the current density. The copper cannot be replaced by silver, cobalt or cadmium. *W. D. B.*

The electrolytic preparation of chloroform from acetone. *J. E. Teeple. Jour. Am. Chem. Soc.* 26, *536* (*1904*). — A solution of salt and acetone was electrolyzed at 20°, hydrochloric acid being added to neutralize the alkali formed. A current efficiency of 80 percent was maintained for eight hours.

W. D. B.

The tungstate compounds. *E. Schaefer. Zeit. anorg. Chem.*, 38, *142* (1904).—In the fourth division of the paper the author discusses the electrolysis of the tungstate solutions. The ions in a sodium tungstate solution are $2Na'$ and WO_4''. At the anode WO_4'' loses oxygen and becomes WO_3. If there is no diaphragm this combines with the alkali from the cathode, forming Na_2WO_4 and water. When a diaphragm is present the following reactions take place at the anode:

$$7WO_3 + 5Na_2WO_4 = 5Na_2O.12WO_3, \text{ paratungstate.}$$
$$8WO_3 + 5Na_4O.12WO_3 = 5Na_2W_4O_{13}, \text{ metatungstate.}$$

In phosphoric acid solutions, complex phosphoric acid tungstates are formed and the electrolysis follows different lines. *W. D. B.*

Observations on the precipitation of electrolytic white lead. *C. F. Carrier, Jr. Trans. Am. Electrochem. Soc.*, 5, *229* (*1904*). — This is a study of the patent of Richards and Roepper according to which a solution of sodium sulphite, sodium acetate and some nitrate is electrolyzed between lead electrodes. This did not work well and the process was varied in a number of ways. None of the experiments gave a white lead which had the right chemical composition, let alone the physical characteristics. *W. D. B.*

The economic balance in electrolytic copper refining. *L. Addicks. Trans. Am. Electrochem. Soc.* 5, *119* (*1904*). — The author discusses the economic balance of copper, considering the variables, tank resistance, age of electrodes and current density. It is stated: "In any given case the multiplicity of relations pointed out above must be solved a pair at a time and a set of final heats run off with the winners." In the discussion of this point Mr. Addicks says: "Of course I do not mean to consider the factors two at a time, without taking into account their relative importance." Without speculating as to the meaning of this last sentence, it may be well to consider a concrete case. Suppose we start with a given copper sulphate solution at 20° and determine the best concentration of sulphuric acid for that temperature. Having done that, suppose we take the best solution and vary the temperature. If we decide on say 45° as the best temperature, it does not by any manner of means follow that the concentration of sulphuric acid is the best for the new temperature. It seems a pity that Mr. Addicks should not have outlined the way in which copper refiners actually reach their final conclusion as to the best conditions.

W. D. B.

The transport number of sulphuric acid. *O. F. Tower. Jour. Am. Chem. Soc.*, 26, *1039* (*1904*).—Experiments on the transference numbers of sulphuric acid solutions at 20° gave the following values: N/1, 0.1877; N/2, 0.1869; N/5, 0.1805; N/10, 0.1964; N/20, 0.1791; N/50, 0.1809. It is believed that the value for the N/10 solution is too low. If we take 70 as the migration velocity of sulphate as ion at 18°, the value for hydrogen as ion becomes 326, corresponding well with the 330 obtained for hydrochloric acid by Noyes and Sammet.

W. D. B.

On the velocities of the ions in liquid ammonia solution. *E. C. Franklin and H. P. Cady. Jour. Am. Chem. Soc.* 26, *499* (*1904*). – The method was a modification of that of Masson. The absolute migration velocities for certain univalent ions in liquid ammonia at —33° are from 2.4 to 2.8 times as great as they are in aqueous solutions at 18°. The values are in agreement with the velocities calculated from conductivity measurements by the method of Kohlrausch.

W. D. B.

On the combination of a solvent with the ions. *J. L. R. Morgan and C. W. Kanolt. Jour. Am. Chem. Soc.*, 26, *632*; *Zeit. phys. Chem.*, 48, *365* (*1904*). — "As a result of the electrolysis of a solution of silver nitrate and pyridine in water, a loss of pyridine has been observed at the anode and a corresponding gain of pyridine at the cathode. By similar experiments with cupric nitrate and water, dissolved in alcohol (which, owing to experimental difficulties, are to be regarded only as preliminary) the quantity of water has been found to decrease at the anode and to increase at the cathode. The authors point out that the van't Hoff form of the dilution law follows from the mass law if we assume that two anions or two cations condense with the solvent to form a complex ion.

W. D. B.

A lecture experiment with an undissociated salt. *D. McIntosh. Jour. Am. Chem. Soc.* 25, *996* (*1903*). — If a solution of ferric sulphocyanate be placed in a U-tube and covered carefully with a less dense solution of hydrochloric acid, a current may be passed through the solutions for several hours without displacing the boundary. This is because the color is due to the undissociated ferric sulphocyanate. With a potassium copper tartrate solution covered with dilute sodium hydroxide, the color boundaries move toward the anode. With ammoniacal copper sulphate covered with dilute ammonia, the color boundaries move to the cathode.

W. D. B.

The theories of indicators. *J. Stieglitz. Jour. Am. Chem. Soc.*, 25, *1112* (*1903*). — The author gives reasons for believing that the color changes with phenolphthaleine or methyl orange are due to the formation and disappearance of chromophoric groups rather than to electrolytic dissociation. As the chromophoric theory would apply to concentrated solutions, one must regret that the author has not discussed the behavior of phenolphthaleine in concentrated solutions of caustic potash and sulphuric acid.

W. D. B.

Dielectricity and Optics

The effect of light and temperature on selenium. *R. Marc. Zeit. anorg. Chem.* 37, *459* (*1903*).—Selenium cells are more sensitive to red light than to violet light. The author finds an alleged inversion point at 70° which is, of course, nothing more than the temperature at which the amorphous selenium changes rapidly to metallic selenium under the conditions of the experiment. Not being familiar with the work of Saunders, the author attributes the light-sensitiveness to selenium itself. His own experiments prove the contrary for he obtains light-sensitiveness both with amorphous and with metallic selenium.
W. D. B.

A new spectrum lamp and a gas collector for lecture purposes. *E. Rupp. Zeit. anorg. Chem.* 38, *107* (*1904*).—A glass burner has a reservoir in the bottom which holds a solution and from which a glass tube rises to the level of the air tube. The gas collector consists of a rotating upright with clamps from which the inverted glass cylinders are suspended. *W. D. B.*

Crystallography, Capillarity and Viscosity

The size of crystal molecules. *R. Wegscheider. Boltzmann's Festschrift,* *367* (*1904*).—The assumption of normal molecular weights in mix-crystals rests on the alleged constancy of the distribution ratio. The author maintains that the distribution ratio is not constant. He believes that a mix-crystal consists of the molecules X_n, $X_{n-1}Y$, …, X_{n-a}, Y_a, …, XY_{n-1}, Y_n in reversible equilibrium.
W. D. B

Theory of capilliarity. *G. Bakker. Zeit. phys. Chem.* 48, *1* (*1904*).—In the interior of a liquid the author postulates the two forces of cohesion and thermal pressure. "The equation of state for a homogeneous phase can be considered as the analytical expression for the equilibrium between these two forces and the external pressure." The same expression is obtained for the rise of a liquid in a capillary tube without having to assume the molecular pressure of Laplace. "The mean of the potential in the capillary film is given by the mean of the density just as the potential of a homogeneous phase is given by its density." *W. D. B.*

Capillary constants and specific gravities of salts at their melting points. *S. Motylewski. Zeit. anorg. Chem.*, 38, *410* (*1904*).—The author has determined the mean weight of drops of fourteen fused sodium and potassium salts, also the specific gravities at the melting-point. Quincke's equation for fused salts is shown not to hold. *W. D. B.*

The effect of viscosity on the capillarity constants in aqueous acetic acid. *L. Grunmach. Boltzmann's Festschrift,* *460* (*1904*).—When surface tensions are measured by the wave method, it seems probable that the results may be affected by the viscosity of the liquid or solution. In the neighborhood of the viscosity maximum for aqueous acetic acid this seems to be true. As we pass the maximum with increasing concentration of acetic acid, the viscosity and the capillarity constant both decrease, which is not what would be expected if the viscosity had a marked effect on the capillary measurements. *W. D. B.*

Determination of viscosity in liquids. *K. Beck. Zeit. phys. Chem.* 48, *641* (*1904*). — By very quick work the author succeeds in measuring the viscosity of blood, by the Ostwald method, before it has time to coagulate. For viscous liquids the author modifies the usual method by working under pressure. It was found that the isomorphous substances, dibenzyl, stilbene, benzylaniline, benzal aniline and azobenzene have very nearly the same viscosity at the melting-points. The viscosity-concentration curve for pairs of these substances runs nearly parallel to the freezing-point curves, being linear when these latter are. A number of experiments were also made with racemic compounds. The two benzaldoximes have very different viscosities. *W. D. B.*

The viscosity of solutions in relation to the constitution of the dissolved substance. *A. A. Blanchard. Jour. Am. Chem. Soc.* 26, *1315* (*1904*). — In a number of the cases studied the change of the viscosity with the concentration is constant. With silver nitrate solution the viscosity is the same as that of an ammonia solution when the ratio of ammonia to silver is 2 : 1. With zinc chloride and copper nitrate the ratio must be 4 : 1. Zinc sulphate and copper sulphate solutions to which ammonia in excess has been added have higher viscosities than solutions of ammonia alone. The author believes that some of the phenomena of negative viscosity are due to compounds of ions with the solvent and he uses the term "solvate" for such complexes. *W. D. B.*

The emulsifying action of soap. *F. G. Donnan. Jour. Am. Chem. Soc.*, 25, *1215* (*1903*).—It is claimed that the results obtained by Hillyer (8, 151) are not new, having been stated years before by Krafft and by the author.

W. D. B.

A method of grading soaps as to their detergent power. *H. W. Hillyer. Jour. Am. Chem. Soc.* 25, *1256* (*1903*).—The formation of drops when a soap solution runs out under oil is taken as a measure of the detergent value of the soap. The author describes the special form of apparatus which he has found serviceable. *W. D. B.*

THE RELATION OF PHYSICAL CHEMISTRY TO PHYSICS AND CHEMISTRY[1]

BY J. H. VAN'T HOFF

According to the programme, I have to consider: "General Principles and Fundamental Conceptions which Connect Physical Chemistry with the Related Sciences, Reviewing in this Way the Development of the Science in Question Itself."

Let me begin by defining physical chemistry as the science devoted to the introduction of physical knowledge into chemistry, with the aim of being useful to the latter. On this basis I can limit my task to the relations of physical chemistry to the two sciences it unites, chemistry and physics.

But even if I limit myself to these relations, which are not the only two,[2] I wish to restrict myself yet more, in order, in the spirit of this Congress, to call your attention to broad views; so I shall follow up only two lines, in answering two questions regarding two fundamental problems in chemistry:

I. What has physical chemistry done for our ideas concerning matter?

II. What has it done for our ideas concerning affinity?

The small table which I have the honor to put before you will enable us to answer these questions by appeal to the scientific development of our science, which also I have to review:

I. Ideas concerning matter.	II. Ideas concerning affinity.
1. Lavoisier, Dalton (1808).	1. Berthollet, Guldberg, Waage (1867).
2. Gay-Lussac, Avogadro (1811).	2. Berzelius, Helmholtz (1887).
3. Dulong, Petit, Mitscherlich (1820).	3. Mitscherlich, Spring (1904).
4. Faraday (1832).	4. Deville, Debray, Berthelot.
5. Bunsen, Kirchhoff (1861).	5. Thomsen, Berthelot (1865).
6. Periodic System (1869).	6. Horstmann, Gibbs, Helmholtz.
7. Pasteur (1853), Stereochemistry (1874).	
8. Raoult, Arrhenius (1886–7).	
9. Radioactivity (Becquerel, Curies).	

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[1] Address delivered before the Section of Physical Chemistry of the International Congress of Arts and Sciences, at St. Louis, September 22, 1904. Published by permission of the Congress.

[2] In Chicago I devoted to this subject eight lectures, which have since appeared in the Decennial Publications, under the title "Physical Chemistry in the Service of the Sciences," Chicago, 1903.

I. Physical Chemistry and Our Ideas Concerning Matter

THE CONCEPTS OF ATOMS AND MOLECULES

Regarded as a whole, we may say that the initial application of physical knowledge for the purpose of developing our ideas of matter consisted chiefly in the employment of physical methods and instruments in the study of the properties of matter. This stood foremost in physical chemistry in the first period of its existence.

Reviewing the history of chemistry, we must acknowledge that one of the first fundamental steps was made by the study of the physical property of weight, and the introduction of a physical instrument, the balance, for this purpose. It was, in large part, on this basis that Lavoisier was the great innovator of chemistry; and it was due solely to the following of chemical change with the balance that chemistry got its fundamental laws of constant weight and of constant and multiple proportions. These were summarized by Dalton in the fruitful though hypothetical conception of atoms, which, as is well known to you all, asserts that every element exists in the form of small unchangeable particles, identical for a given element, but differing with the latter.

As the study of weight led to the idea of atoms, so the study of another physical property, that of volume and density, led to our idea of molecules. These molecules, which might be described as constellations of atoms, were a necessity with Dalton's conception; but, in a binary compound for instance, they might consist of two atoms or of twenty. Now, it hardly needs to be recalled that Gay-Lussac, and especially Avogadro, in following the volume relations of gases in chemical action, drew the conclusion that the molecules of gases occupy equal volumes under identical conditions. Thenceforward, we had a reliable method for determining the relative weights of such molecules.

As the study of the physical properties, weight and volume led to the concepts of atoms and molecules, so sharply defined that the relative weights of these entities form the fundamental constants of chemistry, so a further study of physical properties has led to broad generalizations concerning the nature of atoms and molecules, which we shall now outline.

PROPERTIES OF ATOMS

As to atoms, I would call your attention to four peculiarities which seem to me of fundamental importance. First, Dulong and Petit found that the physical property called heat capacity is nearly the same for different atoms, *i. e.*, that the quantity of heat requisite to produce a given rise of temperature does not vary greatly for atomic quantities, for 7 parts of lithium and for 240 parts of uranium.

Second, Faraday, in studying the electrical conductivity of electrolytes, *e. g.*, of aqueous solutions of salts, found that the quantity of electricity which atoms can transport varies as the whole numbers—from one in potassium to two in zinc. This fundamental property, which gives the sharpest expression to our notion of valency was brought by Helmholtz into a very clear form by the assumption that electricity, as well as matter, consists of atoms, either negative or positive, and that material atoms are able to combine with them—potassium with one of the positive kind, zinc with two, chlorine with a negative one—and so transport them in electrolysis.

The third great step was made by the study of light, a physical property again. Bunsen and Kirchhoff found that, heated in the gaseous state, every atom emits a definite set of light waves, producing a characteristic line-spectrum, which is yet the sharpest test of the kind of atoms one is dealing with, and which so became the most fruitful guide in the detection of new kinds.

The last generalization that I have to mention, and which we owe to Newlands, Mendeléeff, and Lothar Meyer, includes physical properties in general, and asserts that they vary with increasing atomic weight in a periodic way. This shows itself most sharply in the atomic volume, which passes through maximum values in lithium (7), sodium (23), potassium (39), rubidium (85), and caesium (133). A corresponding periodicity is observed in other properties, as for example that of combining with electrical atoms, or valency, which in the said elements passes through unity. Analogous behavior is exhibited by the melting-points and boiling-points, which for these metals are exceptionally low.

If my programme did not, to a certain extent, exclude quite recent investigations, confining me to a view of past history, I should like to consider one more physical property, that of radioactivity, which also seems to be a property of atoms. I can only insist on the fact that it was physical properties again, the making the air conductive for electricity, and the spectrum, which revealed radium.

PROPERTIES OF MOLECULES

Turning to molecules, I have three predominant generalizations to outline. The first is Mitscherlich's discovery of the fact that analogous molecular constitution corresponds to analogous outer crystalline form, to so-called isomorphism. Let me add that there is hardly any more satisfactory proof of the soundness of our concept of the internal structure of matter than, *e. g.*, the identity of the crystalline forms of the alums, which we consider to have corresponding internal structure.

A second step, to a certain extent a similar one, was made by Pasteur, when he deduced disymmetry of molecular constitution from disymmetry in behavior, optically as well as crystallographically. For instance, dextrorotatory ordinary tartaric acid and its laevorotatory antipode showed this disymmetry, both in optical rotation and in the particular so-called enantiomorphous crystalline form. The molecules were supposed to have analogous structure differing from each other as the right hand from the left. As is well known, it was only later that the probable molecular structure was sharply defined, and stereochemistry was founded.

The third great step was the opening of a way to determine the molecular weights of dissolved substances. It was chiefly the application of Avogadro's law to osmotic pressures, in connection with Raoult's measurements of freezing-points and vapor-pressures, that opened the way. We may now assert that the liquid state is not characterized by high molecular complexity.

But the great innovation, introduced by Arrhenius, and immediately brought into relation with the achievement in question, was the admission of the existence of ions in electrolytes, for example, the presence of negatively charged chlorine atoms and positively charged sodium atoms in an ordinary salt solution. Once more it was a physical property, the electrical conductivity, that led to this extremely fruitful supposition.

CONCLUSION

If, after this short summary of its properties, we try to look into the nature of matter, we conclude that matter is not continuous, but that there are centres of action which seem to have an eternal existence, changing only in the place that they occupy,—these are the atoms. They keep together in some way and form the molecule; how, it is pretty hard to say. The planetary constellation, with ordinary attraction and centrifugal force in equilibrium, is excluded by the consideration that at the absolute zero there is no movement at all. The repulsive force that we want might be of electrical nature, and so we come to our combination of material and electrical atoms. There is indeed something fascinating here, and when we admit for carbon that it may unite to four equally charged electrical atoms and hold them by a force of the nature of elasticity, we have at once a possible equilibrium and the tetrahedral grouping. My only difficulty is that an uncharged atom of carbon, coming into contact with the ions just described, would take away half the electric charge, and so the valency of any element might be reduced to unity. The latest supposition, that matter is built up of electricity alone, lies again beyond the scope of this address.

Let me now turn to the second part of my subject, and touch upon the problem of affinity; indeed, the action that keeps atoms together must be closely related to affinity.

II. Physical Chemistry and Our Ideas Concerning Affinity

While physical chemistry, in the first period of its development was chiefly devoted to the study of the physical properties of matter, the second and present period is characterized by the predominant place of the problem of affinity.

This change in the general aspect of our science goes hand in hand with a different way of working: in the development of our ideas of matter, physical chemistry introduced physical methods and instruments for the study of physical properties; in the development of our ideas of affinity, physical chemistry has introduced physical principles.

AFFINITY CONSIDERED AS FORCE

The first line of thought considered affinity as a force, and in this direction it was natural to think of the Newtonian attraction as the chemical agent. So it was that Berthollet, and with far more success Guldberg and Waage, applied the laws of mass action to problems of affinity, formulating a relation still known as the mass law, according to which affinity is proportional to the weight in the unit of volume.

Now, as we all know, affinity is of a specific nature, and does not depend on weight merely; on the contrary the least heavy elements are generally the most active. So Berzelius built up his system founded on the notion that elements have a specific electrical character, either positive or negative, and, in combining, act by electrical attraction. In this direction Helmholtz made a further step in taking into account the quantitative side. Considering the electrical charges involved in Faraday's law, he pointed out as very important that the attraction due, for instance, to the negative charge in chlorine and the positive one in hydrogen far exceeds the gravitational attraction of the masses. Yet a satisfying notion of affinity was not obtained in this way.

AFFINITY MEASURED AS WORK

A second line of thought took into consideration not the force but the work that affinity represents, and it seemed a decisive step when Thomsen and Berthelot declared that the heat developed in chemical change corresponds to the work that affinity can produce. Indeed, it was in this way that in many cases an *a priori* calculation of the heat development of a reaction permitted prediction of the direction in which the process would proceed, the direction being that of the evolution of heat. Yet, this principle, however weighty, is not absolutely reliable. The chemical actions that produce cold, as that of hydrochloric acid on sodium sulphate, are objections not to be overcome.

The step really leading to a clear and unobjectionable notion of affinity was made in the study of the so-called reversible chemical changes. This reversible character perhaps needs some explanation, easily to be provided by an illustration. Kill a chicken and prepare chicken soup; it would then be very difficult to get your chicken again. This is because preparing chicken soup is not reversible. On the contrary, let water evaporate or freeze, it will be easy to reproduce the water.

Now, at first sight, chemical change does not seem reversible; and indeed it often is not, as in the explosion of gunpowder. But the investigations of Berthelot and Péan de St. Gilles on the mutual action of acids and alcohols, and those of Deville and Debray on high temperature action, which even splits up water, have shown that many chemical changes can be reversed. Indeed, we have types corresponding absolutely to evaporation, as the loss of water vapor from hydrates; and others corresponding as well to freezing and melting, as the splitting of double salts into their components at definite temperatures, *e. g.*, copper calcium acetate at 77° C. Also in analogy with physical phenomena, we have in these reversible chemical changes the possibility of equilibrium, the two chemically different forms of matter co-existing, as do water and its vapor at a maximum pressure.

Such a reversal of chemical change can take place under the influence of temperature, of electricity, of light, of pressure. And the easiest way to arrive at a measure of affinity is presented in the last case, as was foreseen by Mitscherlich. Let us take gypsum as an example. Burnt commercial gypsum, mixed with water, will combine with the water. We know that this chemical change can produce pressure, and that it may be prevented by sufficient pressure and be reversed by it, as Spring succeeded in pressing out sulphuric acid from sodium bisulphate. And it is possible in such cases exactly to determine the limiting pressure, such that a higher one presses out the sulphuric acid while a lower one is overpowered by the affinity action. If the chemical change takes place under a pressure only slightly less than that which would prevent it, thus practically taking place under the limiting pressure, we get out of affinity the greatest quantity of work that it can possibly produce, and this quantity is the same whatever the nature of the opposing action, be it electricity, light, or anything else. Therefore, in this maximum work we have a sound measure of affinity.

It was a very happy coincidence indeed, that this conception of affinity made possible the application of a physical principle known as the second law of thermodynamics. This principle may be formulated in different ways. For my purpose let me say that it limits the possibility of natural processes to the occurrence of those in which a difference of intensity is diminished. If there is a difference of pressure in two parts of a gas, a movement will occur, producing equality; if there is a difference of temperature, heat will be transported so as to produce equality once more. It is curious that such simple necessities, which we all feel as such, can be converted into far-reaching, sharply formulated equations, as was done by Carnot and Clausius. These principles were first applied in chemistry by Horstmann. Then, by successive application to chemical problems by Massieu, Gibbs, Helmholtz, and others, was won a system of relations touching the problem of affinity, to which I can give only brief attention:

1. Affinity may be defined as the maximum quantity of work that a chemical change can produce. Equilibrium ensues when this quantity is zero.

2. The mass law can be obtained in a well-founded and somewhat modified form, restricted to dilute gases and solutions.

3. The Thomsen-Berthelot principle assumes a modified form in the rule that a fall of temperature induces the formation of the system which develops heat. It is, for instance, in accordance with this rule that at ordinary temperatures water is stable in comparison with detonating gas, and that at high temperatures this relation is reversed, as it was found by Deville to be.

4. Lastly, we have the phase rule, indicating, for example,

in what cases chemical phenomena will be comparable with melting and freezing, and in what cases they will be comparable with evaporation and condensation.

Most curious of all, we can treat problems of affinity in an absolutely trustworthy way, so that our calculations furnish a check upon experiment, without admitting anything concerning the nature of affinity or of the matter wherein the affinity is supposed to reside.

ON CERTAIN HEATS OF DILUTION

BY J. E. TREVOR

The Potential of a Component

When the form of a Gibbsian 'fundamental equation' of a two-component system in a trivariant state, *i. e.*, in a one-phase state, is once found from experiment, the thermodynamic properties of the system in the state in question can be found by analytical means. The most convenient set of state variables to employ in the search for the form of a fundamental function of such a system is probably that composed of the pressure p, the absolute temperature θ, and the masses M_1, M_2, of the independently variable components of the system. These are the variables of which the thermodynamic potential H of the system is a function. The thermodynamic potential $H(p, \theta, M_1, M_2)$ can be found from the specific thermodynamic potential $h(p, \theta, m_1)$, where m_1 denotes the 'composition' of the phase,

$$m_1 = \frac{M_1}{M_1 + M_2};$$

and the specific thermodynamic potential, because of the general relation

$$h = m_1\mu_1 + (1 - m_1)\mu_2,$$

can be found from the 'potentials' of the components, $\mu_1(p, \theta, m_1)$, $\mu_2(p, \theta, m_1)$; so the determination of the form of any fundamental function of the system can be reduced to the determination of the forms of these two potentials.

To the end of finding expressions for these potentials, suppose the mass dM_j of the j-th component to be added, irreversibly, to the mixture of mass

$$M_1 + M_2,$$

under the conditions of constant pressure, temperature, and mass of the other component. Before the addition, the energy of both masses is

$$E + e_j . dM_j ,$$

where E is the energy $E(p, \theta, M_1, M_2)$, of unknown form, of the system, and $e_j(p, \theta)$ is the specific energy of the j-th component. After the addition, the energy of the system is

$$E + \left\{ e_j + \Delta_j - p\left(\frac{\partial V}{\partial M_j} - v_j\right)\right\} dM_j\,;$$

where $V(p, \theta, M_1, M_2)$ is the volume of the mixture, v_j is the specific volume $v_j(p, \theta)$ of the j-th component, and Δ_j is the irreversible heat absorption accompanying the addition — *i. e.*, Δ_j is the 'heat of dilution' by the j-th component.

In the addition, then, the energy of the mixture has increased by the amount

$$(1) \qquad \left\{ e_j + \Delta_j - p\left(\frac{\partial V}{\partial M_j} - v_j\right)\right\} dM_j = \frac{\partial E}{\partial M_j}\, dM_j\,,$$

the rate of increase being equal to $\partial E/\partial M_j$, since it would have the same value were the addition in any way to be reversibly made. By changing variables in

$$dE = -p\,dV + \theta\, dH + \mu_1 dM_1 + \mu_2 dM_2,$$

where H is the entropy of the system, we obtain for $\partial E/\partial M_j$ the general equation

$$(2) \qquad \frac{\partial E}{\partial M_j} = -p\,\frac{\partial V}{\partial M_j} + \theta\,\frac{\partial H}{\partial M_j} + \mu_j.$$

Elimination of $\partial E/\partial M_j$ between these two equations yields an expression for μ_j,

$$(3) \qquad \mu_j = e_j + p v_j + \left(\Delta_j - \theta\,\frac{\partial H}{\partial M_j}\right).$$

In these equations, e_j, v_j may be regarded as known functions of p, θ; and Δ_j, $\partial V/\partial M_j$ as experimentally determinable functions of p, θ, m_1; but the function $\partial H/\partial M_1$ of the variables p, θ, M_1, M_2 remains of unknown form. In order to obtain a formulation of this function, we must consider the addition of the mass aM_j along a reversible path.

The reversible addition may be imagined to be effected by means of the arrangement described by Fig. 1, which represents the mass $M_1 + M_2$ enclosed in a cylinder and separated from a mass of the *j*-th component S_j by a piston permeable only by this component, the whole standing under the pressure p exerted by an outer solid piston. The 'osmotic pressure' P_j, with reference to the *j*-th component, of the system is balanced by a force applied from without to the semipermeable piston. An infinitesimal decrease of tihs force will result in a reversible addition of the mass dM_j to the mixture, at constant pressure, temperature, and mass of the other component.

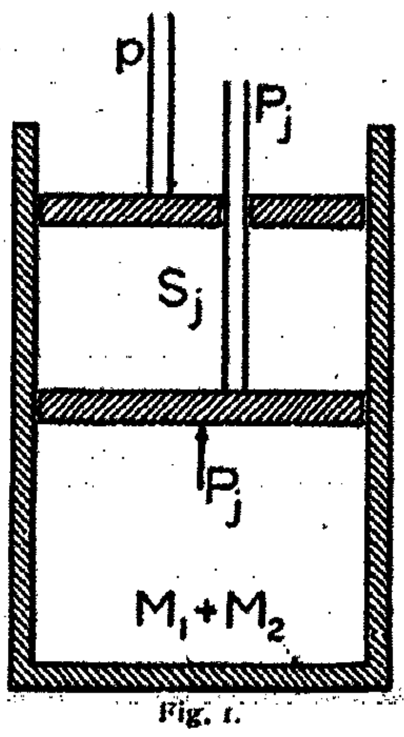

Fig. 1.

Before this reversible addition, the energy of the mass $M_1 + M_2 + dM_j$ is

$$E + e_j . dM_j;$$

after the addition it is

$$E + \left\{ e_j - P_j \frac{\partial V}{\partial M_j} - p\left(\frac{\partial V}{\partial M_j} - v_j\right) + \theta\left(\frac{\partial H}{\partial M_j} - \eta_j\right) \right\} dM_j,$$

where η_j is the specific entropy of the *j*-th component. The rate of increase of the energy of the mixture has therefore been

$$(4) \qquad e_j - P_j \frac{\partial V}{\partial M_j} - p\left(\frac{\partial V}{\partial M_j} - v_j\right) + \theta\left(\frac{\partial H}{\partial M_j} - \eta_j\right) = \frac{\partial E}{\partial M_j}.$$

We accordingly have:

In the irreversible addition,

$$\frac{\partial E}{\partial M_j} = e_j - p\left(\frac{\partial V}{\partial M_j} - v_j\right) + \Delta_j; \qquad (\alpha)$$

in the reversible addition,

$$\frac{\partial E}{\partial M_j} = e_j - p\left(\frac{\partial V}{\partial M_j} - v_j\right) + \theta\left(\frac{\partial H}{\partial M_j} - \eta_j\right) - P_j \frac{\partial V}{\partial M_j}; \qquad (\beta)$$

the general relation,

$$\frac{\partial E}{\partial M_j} = \mu_j - p\frac{\partial V}{\partial M_j} + \theta\frac{\partial H}{\partial M_j}. \qquad (\gamma)$$

Through elimination of common terms between these equations, we find:

From (α) and (β),

$$(5) \qquad \Delta_j = \theta\left(\frac{\partial H}{\partial M_j} - \eta_j\right) - P_j\frac{\partial V}{\partial M_j};$$

From (α) and (γ),

$$(6) \qquad \mu_j = e_j + pv_j + \left(\Delta_j - \theta\frac{\partial H}{\partial M_j}\right);$$

From (β) and (γ),

$$(7) \qquad \mu_j = (e_j + pv_j - \theta\eta_j) - P_j\frac{\partial V}{\partial M_j}.$$

The first of these equations determines $\partial H/\partial M_j$, whereupon the second determines μ_j. The result of both together is given by (7). Since the parenthesized expression in (7) is the specific thermodynamic potential h_j of the j-th component, this expression may be written

$$(8) \qquad \mu_j = h_j - P_j\frac{\partial V}{\partial M_j}, \qquad (j = 1, 2)$$

which is the relation sought. It may be noted here that, when the mass of the other component vanishes, P_j becomes zero and the equation reduces to

$$\mu_j = h_j,$$

as it should.

Another Derivation

In place of successive reversible additions of the masses dM_1, dM_2 to the mixture having the mass $M_1 + M_2$, let us imagine the described osmotic apparatus to be utilized for the reversible addition of the mass M_1 to the mass M_2, and for the addition of M_2 to M_1. In either case, the energy of both masses before the addition of M_j is

$$e_1M_1 + e_2M_2\,;$$

and after the addition it is

$$e_1M_1 + e_2M_2 - \int_0^{M_j} P_j \frac{\partial V}{\partial M_j}\, dM_j - p(V - v_1M_1 - v_2M_2) \\ + \theta(H - \eta_1M_1 - \eta_2M_2).$$

Equating the difference of these quantities with the change

$$E - e_1M_1 - e_2M_2$$

of the energy of the whole affair during the operation, and rearranging, we find

$$E + pV - \theta H = M_1(e_1 + pv_1 - \theta\eta_1) \\ + M_2(e_2 + pv_2 - \theta\eta_2) - \int_0^{M_j} P_j \frac{\partial V}{\partial M_j}\, dM_j\,;$$

which may be written

$$H = M_1h_1 + M_2h_2 - \int_0^{M_j} P_j \frac{\partial V}{\partial M_j}\, dM_j\,;$$

whence, on differentiation with regard to M_j,

$$\mu_j = h_j - P_j \frac{\partial V}{\partial M_j}, \qquad (j = 1, 2)$$

as before.

The First Derivatives of the Thermodynamic Potential

From the general relation

$$V = (M_1 + M_2).v(p,\theta,m_1),$$

where v is the specific volume of the system, we find[1]

$$(9a) \qquad \frac{\partial V}{\partial M_1} = v + (1 - m_1)\frac{\partial v}{\partial m_1} = \phi_1,$$

$$(9b) \qquad \frac{\partial V}{\partial M_2} = v - m_1\,\frac{\partial v}{\partial m_1} = \phi_2.$$

Incidentally it may be noted that ϕ_1, ϕ_2 are obviously equal to $\partial\mu_1/\partial p$ and $\partial\mu_2/\partial p$, respectively. The equations (9*a*), (9*b*) convert the equations (8) for μ_1, μ_2 to

$$(10) \qquad \mu_j = h_j - P_j\phi_j\,; \qquad (j = 1,2)$$

wherefore the general equation

$$H = M_1\mu_1 + M_2\mu_2$$

for the thermodynamic potential of the system in a trivariant state may be written

$$(11) \qquad H = M_1(h_1 - P_1\phi_1) + M_2(h_2 - P_2\phi_2).$$

---

[1] If it should be desired to express ϕ_1, ϕ_2 by means of the specific volumes, or of the densities, of the components as they stand in the mixture, we should have

$$\phi_1 = (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1}\frac{v}{1-m_1}$$

$$\phi_2 = -\, m_1^2 \cdot \frac{\partial}{\partial m_1}\frac{v}{m_1},$$

or

$$\phi_1 = -v^2 \cdot \frac{\partial}{\partial m_1}\frac{1-m_1}{v}$$

$$\phi_2 = +\, v^2 \cdot \frac{\partial}{\partial m_1}\frac{m_1}{v}.$$

Differentiating this equation,

$$(12)\quad dH = \left\{ M_1\left(v_1 - \frac{\partial(P_1\phi_1)}{\partial p}\right) + M_2\left(v_2 - \frac{\partial(P_2\phi_2)}{\partial p}\right) \right\} dp$$

$$- \left\{ M_1\left(\eta_1 + \frac{\partial(P_1\phi_1)}{\partial \theta}\right) + M_2\left(\eta_2 + \frac{\partial(P_2\phi_2)}{\partial \theta}\right) \right\} d\theta$$

$$+ \left\{ h_1 - P_1\phi_1 - M_1 \frac{\partial(P_1\phi_1)}{\partial m_1}\frac{\partial m_1}{\partial M_1} - M_2 \frac{\partial(P_2\phi_2)}{\partial m_1}\frac{\partial m_1}{\partial M_1} \right\} dM_1$$

$$+ \left\{ h_2 - P_2\phi_2 - M_2 \frac{\partial(P_2\phi_2)}{\partial m_1}\frac{\partial m_1}{\partial M_2} - M_1 \frac{\partial(P_1\phi_1)}{\partial m_1}\frac{\partial m_1}{\partial M_2} \right\} dM_2 ;$$

whence we deduce

$$(13)\quad \begin{cases} V = M_1\left(v_1 - \dfrac{\partial(P_1\phi_1)}{\partial p}\right) + M_2\left(v_2 - \dfrac{\partial(P_2\phi_2)}{\partial p}\right), \\ H = M_1\left(\eta_1 + \dfrac{\partial(P_1\phi_1)}{\partial \theta}\right) + M_2\left(\eta_2 + \dfrac{\partial(P_2\phi_2)}{\partial \theta}\right); \end{cases}$$

or, dividing through by $M_1 + M_2$,

$$(13a)\quad \begin{cases} v = m_1\left(v_1 - \dfrac{\partial(P_1\phi_1)}{\partial p}\right) + (1 - m_1)\left(v_2 - \dfrac{\partial(P_2\phi_2)}{\partial p}\right) \\ \eta = m_1\left(\eta_1 + \dfrac{\partial(P_1\phi_1)}{\partial \theta}\right) + (1 - m_1)\left(\eta_2 + \dfrac{\partial(P_2\phi_2)}{\partial \theta}\right). \end{cases}$$

where η is the specific entropy of the system.

Rearranging these equations (13*a*), and appending an equation obtained by comparing the equations $\mu_j = \partial H/\partial M_j$ with the initial equations for μ_j, we find

$$(14)\quad \begin{cases} m_1 \dfrac{\partial(P_1\phi_1)}{\partial p} + (1 - m_1)\dfrac{\partial(P_2\phi_2)}{\partial p} = + m_1 v_1 + (1 - m_1)v_2 - v \\ m_1 \dfrac{\partial(P_1\phi_1)}{\partial \theta} + (1 - m_1)\dfrac{\partial(P_2\phi_2)}{\partial \theta} = - m_1\eta_1 - (1 - m_1)\eta_2 + \eta \\ m_1 \dfrac{\partial(P_1\phi_1)}{\partial m_1} + (1 - m_1)\dfrac{\partial(P_2\phi_2)}{\partial m_1} = 0. \end{cases}$$

These three equations may be regarded as expressing the relations between the slopes of the two osmotic pressure curves in the P,p-, in the P,θ-, and in the P,m_1-diagram, at any assigned p, θ, m_1. The second members of the first two of the equations are, respectively, the decrease of the specific volume and the increase of the specific entropy in the formation of the phase-mixture from its components. Denoting these changes of volume and entropy by $-\Delta v$ and $+\Delta\eta$, multiplying each equation through by the corresponding dp, $d\theta$, or dm_1, and adding, we find

$$(15) \quad m_1.d(P_1\phi_1) + (1 - m_1).d(P_2\phi_2) = -\Delta v.dp + \Delta\eta.d\theta.$$

The first member of this equation is a portion of the differential of the increase Δh of the thermodynamic potential in the formation of the phase-mixture from its components. We have, equation (11),

$$H = M_1(h_1 - P_1\phi_1) + M_2(h_2 - P_2\phi_2);$$

whence, dividing through by $M_1 + M_2$,

$$\begin{aligned} h &= m_1(h_1 - P_1\phi_1) + (1 - m_1)(h_2 - P_2\phi_2) \\ &= \{ m_1h_1 + (1 - m_1)h_2 \} - \{ m_1P_1\phi_1 + (1 - m_1)P_2\phi_2 \}; \end{aligned}$$

whence

$$\begin{aligned} \Delta h &= -m_1P_1\phi_1 - (1 - m_1)P_2\phi_2, \\ -d\Delta h &= m_1d(P_1\phi_1) + (1 - m_1)\,d\,(P_2\phi_2) + (P_1\phi_1 - P_2\phi_2)\,dm_1; \end{aligned}$$

wherefore, on comparison with (15),

$$(16) \quad -d\Delta h = -\Delta v.dp + \Delta\eta.d\theta + (P_1\phi_1 - P_2\phi_2).dm_1.$$

This equation (16) corresponds to the general thermodynamic equation

$$dh = vdp - \eta d\theta + (\mu_1 - \mu_2)dm_1.$$

The quantity Δh is, of course, always negative. The equations

$$\frac{\partial\Delta h}{\partial p} = \Delta v, \quad \frac{\partial\Delta h}{\partial\theta} = -\Delta\eta, \quad \frac{\partial\Delta h}{\partial m_1} = P_2\phi_2 - P_1\phi_1,$$

are identical with the equations (14), and so are equivalent to the 'derived relations'

$$\frac{\partial H}{\partial p} = V, \quad \frac{\partial H}{\partial\theta} = -H, \quad \frac{\partial H}{\partial m_j} = \mu_j. \qquad (j = 1,2)$$

Osmotic Pressures and Heats of Dilution

The 'heats of dilution' Δ_1, Δ_2 of irreversible dilution of the phase-mixture are given by (5) and (6) as

$$(17)\qquad \Delta_j = -P_j \frac{\partial V}{\partial M_j} + \theta\left(\frac{\partial H}{\partial M_j} - \eta_j\right)$$

$$\Delta_j = \mu_j - e_j - pv_j + \theta \frac{\partial H}{\partial M_j}.$$

If Δ_j be expressed with the aid of the osmotic pressures and the specific volume, the second of these formulations yields the same result as the first. We shall, therefore, employ the simpler of the two equations—the first.

As a preliminary, it is necessary to express $\partial H/\partial M_j$ with the aid of the osmotic pressures and the specific volume. We have, equation (13),

$$H = M_1\left(\eta_1 + \frac{\partial(P_1\phi_1)}{\partial\theta}\right) + M_2\left(\eta_2 + \frac{\partial(P_2\phi_2)}{\partial\theta}\right);$$

whence

$$\frac{\partial H}{\partial M_1} = \eta_1 + \frac{\partial(P_1\phi_1)}{\partial\theta} + M_1 \frac{\partial^2(P_1\phi_1)}{\partial\theta\partial m_1}\frac{\partial m_1}{\partial M_1} + M_2 \frac{\partial^2(P_2\phi_2)}{\partial\theta\partial m_1}\frac{\partial m_1}{\partial M_1}$$

$$(18a)\quad = \eta_1 + \frac{\partial(P_1\phi_1)}{\partial\theta} + m_1(1-m_1)\frac{\partial^2(P_1\phi_1)}{\partial\theta\partial m_1} + (1-m_1)^2 \frac{\partial^2(P_2\phi_2)}{\partial\theta\partial m_1}$$

$$\frac{\partial H}{\partial M_2} = \eta_2 + \frac{\partial(P_2\phi_2)}{\partial\theta} + M_2 \frac{\partial^2(P_2\phi_2)}{\partial\theta\partial m_1}\frac{\partial m_1}{\partial M_2} + M_1 \frac{\partial^2(P_1\phi_1)}{\partial\theta\partial m_1}\frac{\partial m_1}{\partial M_2}$$

$$(18b)\quad = \eta_2 + \frac{\partial(P_2\phi_2)}{\partial\theta} - m_1(1-m_1)\frac{\partial^2(P_2\phi_2)}{\partial\theta\partial m_1} - m_1^2 \frac{\partial^2(P_1\phi_1)}{\partial\theta\partial m_1}.$$

The last of equations (14) convert (18*a*) and (18*b*) to

$$(19)\qquad \begin{cases} \dfrac{\partial H}{\partial M_1} = \eta_1 + \dfrac{\partial(P_1\phi_1)}{\partial\theta} \\ \dfrac{\partial H}{\partial M_2} = \eta_2 + \dfrac{\partial(P_2\phi_2)}{\partial\theta}; \end{cases}$$

which convert (17) to

$$(20a)\qquad \Delta_1 = \theta \frac{\partial(P_1\phi_1)}{\partial\theta} - P_1\phi_1$$

$$(20b)\qquad \Delta_2 = \theta \frac{\partial(P_2\phi_2)}{\partial\theta} - P_2\phi_2;$$

which equations may be written

$$\Delta_1 = \theta^2 \cdot \frac{\partial}{\partial\theta}\frac{P_1\phi_1}{\theta}, \qquad \Delta_2 = \theta^2 \cdot \frac{\partial}{\partial\theta}\frac{P_2\phi_2}{\theta}. \tag{21a, 21b}$$

It may be noted also that, because of equations (20), the two heats of dilution are connected by the relation

$$\Delta_2 - \Delta_1 = \theta \cdot \frac{\partial}{\partial\theta}(P_2\phi_2 - P_1\phi_1) - (P_2\phi_2 - P_1\phi_1),$$

which, since

$$P_2\phi_2 - P_1\phi_1 = \frac{\partial \Delta h}{\partial m_1},$$

may be written

$$\Delta_2 - \Delta_1 = \frac{\partial}{\partial m_1}\left(\theta\frac{\partial \Delta h}{\partial\theta} - \Delta h\right)$$

$$= \theta^2 \cdot \frac{\partial}{\partial\theta \partial m_1}\frac{\Delta h}{\theta}, \tag{22}$$

a relation of simple and rather curious form.

The equations

$$P_1 = P_1(p,\theta,m_1), \qquad P_2 = P_2(p,\theta,m_1),$$

for the two osmotic pressures of the phase-mixture are found from equations (21)

$$\frac{\partial}{\partial\theta}\frac{P_1\phi_1}{\theta} = \frac{\Delta_1}{\theta^2}, \qquad \frac{\partial}{\partial\theta}\frac{P_2\phi_2}{\theta} = \frac{\Delta_2}{\theta^2},$$

by integration with regard to θ; which yields

$$P_1\phi_1 = \theta\int\frac{\Delta_1}{\theta^2}d\theta, \qquad P_2\phi_2 = \theta\int\frac{\Delta_2}{\theta^2}d\theta. \tag{23a}$$

Substituting for ϕ_1, ϕ_2 their values, as expressed by equations (9), we find

$$\begin{cases} P_1\left(v + (1 - m_1)\dfrac{\partial v}{\partial m_1}\right) = \theta\displaystyle\int\frac{\Delta_1}{\theta^2}d\theta \\ P_2\left(v - m_1\dfrac{\partial v}{\partial m_1}\right) = \theta\displaystyle\int\frac{\Delta_2}{\theta^2}d\theta. \end{cases} \tag{23b}$$

Evaluation of the second members of these equations depends upon the formulation, from experiment, of the functions $\Delta_j(p, \theta, m_1)$.

When the equations (23*a*),

$$P_j\phi_j = \theta\int\frac{\Delta_j}{\theta^2}\,d\theta$$

$$= \theta\cdot D_1(p,\theta,m_1),$$

representing the osmotic pressures by means of the heats of dilution, are combined with the equations (10) for the component potentials,

$$\mu_j = h_j - P_j\phi_j,$$

and the resulting expressions for the potentials are substituted in the equation

$$H = M_1\mu_1 + M_2\mu_2,$$

for the thermodynamic potential of the phase-mixture, we obtain

$$(24) \qquad H = M_1(h_1 - \theta D_1) + M_2(h_2 - \theta D_2).$$

From this equation it appears that appeal to experiment for the forms of the two functions Δ_j suffices for determination of the forms of the fundamental functions of a two-component phase-mixture, when the fundamental functions of the separate components are known. This is a very interesting general result.

Let us now return to consideration of the equations for the two osmotic pressures P_j. If throughout any region of p,θ,m_1-values it may be assumed that $\Delta_1 = 0$, or that $\Delta_2 = 0$, the equations (21) become

$$(25) \qquad \frac{\partial}{\partial\theta}\frac{P_1\phi_1}{\theta} = 0, \qquad \frac{\partial}{\partial\theta}\frac{P_2\phi_2}{\theta} = 0,$$

whence

$$(26) \qquad P_1\phi_1 = r_1(p,m_1).\theta. \qquad P_2\phi_2 = r_2(p,m_2).\theta.$$

It thus appears that, when $\Delta_j = 0$,

$$\int\frac{\Delta_j}{\theta^2}\,d\theta = r_j.$$

When the phase-mixture is a 'dilute solution,' m_1 is small in comparison with unity, and $\partial v/\partial m_1$ is small in comparison with v, wherefore the first of equations (26) sensibly reduces to the van't Hoff equation,

$$P_1 v = r_1\theta,$$

in which the function r_1, as was discovered by van 't Hoff from experimental evidence, is approximately equal to the ideal-gas constant r. The *general* form of the relation is, of course, that of the first equation (23*b*). Van 't Hoff's theory omits all consideration of the simultaneous value of the complementary osmotic pressure P_2.

If the assumption of a vanishing heat of dilution may be replaced by the assumption that, in any region of p,θ,m_1-values, Δ_1 or Δ_2 is independent of θ, how will the osmotic pressures in this region depend upon the temperature? From the equations (20),

$$\Delta_j = \theta\frac{\partial(P_j\phi_j)}{\partial\theta} - P_j\phi_j,$$

the rates of change of the heats of dilution with changing temperature are found to be

$$\frac{\partial\Delta_j}{\partial\theta} = \theta\frac{\partial^2(P_j\phi_j)}{\partial\theta^2}\,;$$

wherefore, in the region in question,

$$\frac{\partial^2(P_j\phi_j)}{\partial\theta^2} = 0,$$

$$\frac{\partial(P_j\phi_j)}{\partial\theta} = f_j,$$

$$P_j\phi_j = f_j\theta + g_j, \qquad (j = 1,2) \tag{27}$$

where the f's and g's are independent of θ. These equations differ in form from the equations (26) by an additive term.

The Locus $P_1 = P_2$

Let the plane diagram of Fig. 2 represent the osmotic pressures P_1, P_2 of a phase-mixture, in their dependence on the composition m_1 at any assigned values of p, θ. Since both curves rise from zero values, they will intersect at a point a. The equation $P_1 = P_2$ is the locus $R(p, \theta, m_1) = 0$ of the points a.

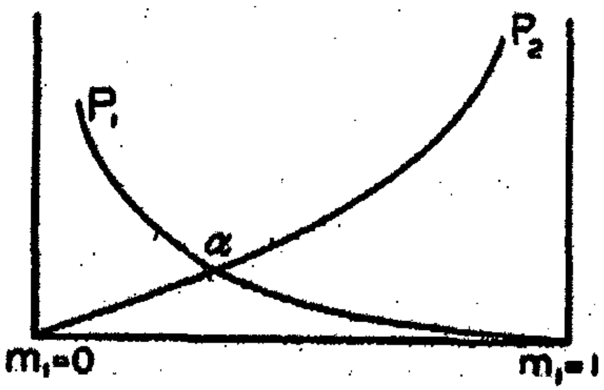

Fig. 2

If the variables p, θ, m_1 be represented by rectangular coordinates in space, to every point of the space in which the variables have possible values will correspond a pair of values of P_1, P_2; and the equation $R = 0$ will represent a surface that is the locus of the points at which P_1, P_2 are equal. Let us seek to connect the common value P_0 of the osmotic pressures at this locus with the specific thermodynamic potential $h\,(p, \theta, m_1)$ of the system.

A general thermodynamic relation that will be of service in this task is

$$\frac{\partial V}{\partial M_j} = \frac{\partial}{\partial p}\mu_j(p, \theta, M_1, M_2),$$

$$(a) \qquad = \frac{\partial}{\partial p}\,\mu_j(p, \theta, m_1),$$

which is one of the conditions of integrability of the differential of the thermodynamic potential H,

$$Vdp - Hd\theta + \mu_1 dM_1 + \mu_2 dM_2.$$

Further requisite general relations are obtained from

$$H = (M_1 + M_2).h,$$

whence follows

$$\frac{\partial H}{\partial M_j} = h + (M_1 + M_2)\,\frac{\partial h}{\partial m_1}\frac{\partial m_1}{\partial M_j},$$

wherefore

$$(b) \qquad \begin{cases} \mu_1 = h + (1 - m_1)\dfrac{\partial h}{\partial m_1}, \\ \mu_2 = h - m_1\dfrac{\partial h}{\partial m_1}, \end{cases}$$

which are the equations in question.

Now, from the equations (8)

$$P_j = \frac{h_j - \mu_j}{\dfrac{\partial V}{\partial M_j}},$$

the equation $P_1 = P_2$ of the locus may be written

$$(h_1 - \mu_1)\frac{\partial V}{\partial M_2} = (h_2 - \mu_2)\frac{\partial V}{\partial M_1},$$

which is converted by (*a*) and (*b*) to

$$\left(h_2 - h_1 + \frac{\partial h}{\partial m_1}\right)\frac{\partial h}{\partial p} = \left(h - m_1h_1 - (1 - m_1)h_2\right)\frac{\partial^2 h}{\partial p\partial m_1},$$

which, because of

$$h - m_1h_1 - (1 - m_1)h_2 = \Delta h,$$

becomes

$$(28) \qquad \begin{vmatrix} \Delta h & \dfrac{\partial h}{\partial p} \\ \dfrac{\partial \Delta h}{\partial m_1} & \dfrac{\partial^2 h}{\partial p\partial m_1} \end{vmatrix} = 0,$$

which is the equation of the locus. The vanishing of this Wronskian of Δh and $\partial h/\partial p$ requires that these functions shall be connected by a linear relation

$$-\Delta h = z(p,\theta)\cdot\frac{\partial h}{\partial p}.$$

We shall shortly see that the coefficient z of this relation is equal to the common value P_0 of the two osmotic pressures.

Let us now seek to express P_0. From (16) we have

$$\frac{\partial \Delta h}{\partial m_1} = P_2\phi_2 - P_1\phi_1,$$

which equation connecting P_1, P_2 becomes, for $P_1 = P_2 = P_0$,

$$P_0(\phi_2 - \phi_1) = \frac{\partial \Delta h}{\partial m_1}.$$

Now, by (*a*) and (*b*),

$$\phi_2 = \frac{\partial V}{\partial M_2} = \frac{\partial \mu_2}{\partial p} = \frac{\partial h}{\partial p} - m_1 \frac{\partial^2 h}{\partial p \partial m_1},$$

$$\phi_1 = \frac{\partial V}{\partial M_1} = \frac{\partial \mu_1}{\partial p} = \frac{\partial h}{\partial p} + (1 - m_1)\frac{\partial^2 h}{\partial p \partial m},$$

whence

$$\phi_2 - \phi_1 = -\frac{\partial^2 h}{\partial p \partial m_1},$$

which converts the above equation for P_0 to

$$(29) \qquad P_0 = -\frac{\partial \Delta h}{\partial m_1} : \frac{\partial^2 h}{\partial p \partial m_1},$$

the equation for the osmotic pressure at the locus. Elimination of

$$\frac{\partial \Delta h}{\partial m_1} : \frac{\partial^2 h}{\partial p \partial m_1}$$

between (28) and (29) yields a second equation for P_0,

$$(30) \qquad -P_0 = \Delta h : \frac{\partial h}{\partial p}.$$

Starting with the equation (29) for P_0, we can obtain a succession of expressions for the locus $P_1 = P_2$ and also for the osmotic pressure there. Since the second member of this equation must be a function of p, θ only, we have, equating its m_1-derivative to zero,

$$\left(\frac{\partial^2 h}{\partial p \partial m_1}\frac{\partial^2 \Delta h}{\partial m_1^2} - \frac{\partial \Delta h}{\partial m_1}\frac{\partial^3 h}{\partial p \partial m_1^2}\right) : \left(\frac{\partial^2 h}{\partial p \partial m_1}\right)^2 = 0.$$

The denominator of the fraction here, which is equal to $(\partial v/\partial m_1)^2$, presumably does not vanish; so we have

$$(31)\qquad \begin{vmatrix} \dfrac{\partial \Delta h}{\partial m_1} & \dfrac{\partial^2 h}{\partial p \partial m_1} \\ \dfrac{\partial^2 \Delta h}{\partial m_1^2} & \dfrac{\partial^3 h}{\partial p \partial m_1^2} \end{vmatrix} = 0.$$

Eliminating

$$\frac{\partial \Delta h}{\partial m_1} : \frac{\partial^2 h}{\partial p \partial m_1}$$

between (31) and (29), and noting that $\partial^2 \Delta h/\partial m_1^2 = \partial^2 h/\partial m_1^2$, we find a corresponding third expression for the osmotic pressure at the locus,

$$(32)\qquad P_0 = -\frac{\partial^2 h}{\partial m_1^2} : \frac{\partial^3 h}{\partial p \partial m_1^2}.$$

The second member of (32) is, in its turn, a function of p, θ; wherefore we can proceed as above, obtaining another pair of equations analogous to (31) and (32), and continue the process *ad infinitum.*

We thus have, collecting the equations (28) to (32), the successive equations

$$(33)\qquad P_0 = -\frac{\Delta h}{\dfrac{\partial h}{\partial p}} = -\frac{\dfrac{\partial \Delta h}{\partial m_1}}{\dfrac{\partial^2 h}{\partial p \partial m_1}} = -\frac{\dfrac{\partial^2 h}{\partial m_1^2}}{\dfrac{\partial^3 h}{\partial p \partial m_1^2}} = \ldots,$$

and the zero Wronskian matrix

$$(34)\qquad \left\| \begin{matrix} \Delta h & \dfrac{\partial h}{\partial p} \\ \dfrac{\partial \Delta h}{\partial m_1} & \dfrac{\partial^2 h}{\partial p \partial m_1} \\ \dfrac{\partial^2 h}{\partial m_1^2} & \dfrac{\partial^3 h}{\partial p \partial m_1^2} \\ \ldots & \ldots \end{matrix} \right\| = 0.$$

The vanishing of this matrix, being the condition that the functions constituting each of its rows shall be connected by a linear relation whose coefficient is independent of m_1, is the condition for the existence of the equations (33). When the first column is replaced by the values derived from the first of equations (33)

$$\Delta h = -P_0 \frac{\partial h}{\partial p},$$

the matrix becomes

$$\left\| \begin{matrix} -P_0 \dfrac{\partial h}{\partial p} & \dfrac{\partial h}{\partial p} \\ -P_0 \dfrac{\partial^2 h}{\partial p \partial m_1} & \dfrac{\partial^2 h}{\partial p \partial m_1} \\ -P_0 \dfrac{\partial^3 h}{\partial p \partial m_1^2} & \dfrac{\partial^3 h}{\partial p \partial m_1^2} \\ \cdots & \cdots \end{matrix} \right\| = 0,$$

which is obviously identically satisfied. It is, finally, not without interest to note that the equations (33) may be given the forms

$$-\Delta h = P_0 v, \qquad -\frac{\partial \Delta h}{\partial m_1} = P_0 \frac{\partial v}{\partial m_1}, \qquad \text{etc.}$$

From this equation we may obtain some curious information concerning the form of the thermodynamic potential, and the forms of the component-potentials, of the phase-mixture. From the equation

$$\Delta h = h - m_1 h_1 - (1-m_1) h_2,$$

we find

$$h = \Delta h + (h_1 - h_2) m_1 + h_2;$$

whence, from (33), at the locus,*

(35) $$h = -P_0 \frac{\partial h}{\partial p} + (h_1 - h_2) m_1 + h_2.$$

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* Note that this equation is

$$h = -P_0 v + (h_1 - h_2) m_1 + h_2.$$

Further, from the general equations (*b*),

$$\mu_1 = h + (1 - m_1)\frac{\partial h}{\partial m_1},$$

$$\mu_2 = h - m_1\frac{\partial h}{\partial m_1},$$

substituting for *h* from (35)

$$\mu_1 = -P_0\left(\frac{\partial h}{\partial p} + (1 - m_1)\frac{\partial^2 h}{\partial p \partial m_1}\right) + h_1,$$

$$\mu_2 = -P_0\left(\frac{\partial h}{\partial p} - m_1\frac{\partial^2 h}{\partial p \partial m_1}\right) + h_2,$$

and replacing $\partial h/\partial p$ by the specific volume *v* of the mixture, we find that, at the locus,

(36)
$$\mu_1 - h_1 = P_0 v^2 . \frac{\partial}{\partial m_1}\frac{1 - m_1}{v}$$

$$\mu_2 - h_2 = -P_0 v^2 . \frac{\partial}{\partial m_1}\frac{m_1}{v}.$$

The quantities whose composition-derivatives appear in these equations are successively the densities, in the mixture, of the first and of the second components.

Formulation of Heats of Dilution

In conclusion, let us now formulate the heats of dilution Δ_1, Δ_2, of irreversible dilution of a two-component phase-mixture, by means of the specific thermodynamic potential of the mixture. For these heats of dilution we have the equations (20),

$$\Delta_1 = \theta\frac{\partial(P_1\phi_1)}{\partial\theta} - P_1\phi_1. \qquad \Delta_2 = \theta\frac{\partial(P_2\phi_2)}{\partial\theta} - P_2\phi_2.$$

By equations (10) and (*b*) we have, respectively,

$$P_1\phi_1 = h_1 - \mu_1, \qquad P_2\phi_2 = h_2 - \mu_2,$$

$$\mu_1 = h + (1 - m_1)\frac{\partial h}{\partial m_1}, \qquad \mu_2 = h - m_1\frac{\partial h}{\partial m_1},$$

wherefore

$$P_1\phi_1 = h_1 - h - (1 - m_1)\frac{\partial h}{\partial m_1}; \qquad P_2\phi_2 = h_2 - h + m_1\frac{\partial h}{\partial m_1};$$

which values serve to convert the above equations for Δ_1, Δ_2 to

$$(37a)\quad \Delta_1 = -\left(h_1 - \theta\frac{\partial h_1}{\partial \theta}\right) + \left(h - \theta\frac{\partial h}{\partial \theta}\right) + (1 - m_1)\cdot\frac{\partial}{\partial m_1}\left(h - \theta\frac{\partial h}{\partial \theta}\right)$$

$$(37b)\quad \Delta_2 = -\left(h_2 - \theta\frac{\partial h_2}{\partial \theta}\right) + \left(h - \theta\frac{\partial h}{\partial \theta}\right) - m_1\cdot\frac{\partial}{\partial m_1}\left(h - \theta\frac{\partial h}{\partial \theta}\right).$$

The expression $h - \theta\cdot\partial h/\partial\theta$ is the specific Gibbsian heat-function, defined by the equation

$$g = e + pv;$$

wherefore the equations (37) may be expressed in the compact form

$$(38a)\qquad \Delta_1 = (g - g_1) + (1 - m_1)\frac{\partial g}{\partial m_1}$$

$$(38b)\qquad \Delta_2 = (g - g_2) - m_1\frac{\partial g}{\partial m_1}.$$

Expressing the second member of each of these equations by means of a derivative of a single function, we find

$$(39a)\qquad \Delta_1 = (1 - m_1)^2\cdot\frac{\partial}{\partial m_1}\frac{g - g_1}{1 - m_1}$$

$$(39b)\qquad \Delta_2 = -m_1^2\cdot\frac{\partial}{\partial m_1}\frac{g - g_2}{m_1}.$$

Finally, by subtraction, the equations (38) yield

$$\Delta_1 - \Delta_2 = g_2 - g_1 + \frac{\partial g}{\partial m_1}$$

$$(40)\qquad = \frac{\partial \Delta g}{\partial m_1},$$

when Δg is written for the increase

$$g - m_1 g_1 - (1 - m_1)g_2$$

of the heat-function in the formation of unit mass of the phase-mixture from its components.

If the formulas for the heats of dilution be assembled, for comparison, we shall have :

$$\left\{\begin{aligned} \Delta_1 &= \theta^2 \cdot \frac{\partial}{\partial\theta}\frac{P_1\phi_1}{\theta} \quad (21a) \\ \Delta_2 &= \theta^2 \cdot \frac{\partial}{\partial\theta}\frac{P_2\phi_2}{\theta} \quad (21b) \\ \Delta_1 - \Delta_2 &= \theta^2 \cdot \frac{\partial}{\partial\theta}\frac{P_1\phi_1 - P_2\phi_2}{\theta} \end{aligned}\right.$$

$$\left|\begin{aligned} \Delta_1 &= (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1}\frac{\left(h - \theta\frac{\partial h}{\partial\theta}\right) - \left(h_1 - \theta\frac{\partial h_1}{\partial\theta}\right)}{1 - m_1} \quad (37a) \\ \Delta_2 &= -m_1^2 \cdot \frac{\partial}{\partial m_1}\frac{\left(h - \theta\frac{\partial h}{\partial\theta}\right) - \left(h_2 - \theta\frac{\partial h_2}{\partial\theta}\right)}{m_1} \quad (37b) \\ \Delta_1 - \Delta_2 &= -\theta^2 \cdot \frac{\partial^2}{\partial\theta\partial m_1}\frac{\Delta h}{\theta} \quad (22) \end{aligned}\right.$$

$$\left|\begin{aligned} \Delta_1 &= (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1}\frac{g - g_1}{1 - m_1} \quad (39a) \\ \Delta_2 &= -m_1^2 \cdot \frac{\partial}{\partial m_1}\frac{g - g_2}{m_1} \quad (39b) \\ \Delta_1 - \Delta_2 &= \frac{\partial \Delta g}{\partial m_1}. \quad (40) \end{aligned}\right.$$

Cornell University. November, 1904.

THE ALUMINUM RECTIFIER[1]

BY S. BARCLAY CHARTERS

The most satisfactory theory of the aluminum rectifier is that given by Taylor and Inglis.[2] They found the same results with a platinum anode covered with a film of aluminum hydroxide as with an aluminum anode. This apparently eliminates from consideration any effect due to the metal as such. Measurements made with an aluminum anode in sulphuric acid solution led to the following statements:

"These experiments show that the presence of certain ions, even in small concentration, enables a large current to pass through the cell. It seems probable, therefore, that the reason for the peculiar action of the aluminum is that the film of hydroxide with which the ánode is covered is permeable to certain ions, but impermeable to others.[3] If this is so, any anion which can readily pass through the film will enable a current to pass, while anions which cannot readily pass through will not enable it to do so. The anomalous behavior in H_2SO_4 would then be due to the impermeability of the film to SO_4'' ions, and also to $Al^{\cdots}$ ions. This explanation is also in accord with the fact that reversal of the current immediately causes current to pass through the cell, this being due to the permeability of the film to $H^{\cdot}$ ions, for it is difficult to suppose that reversal of the current immediately removes the film, and subsequent reversal immediately restores it.

"The surface of the aluminum electrode, when formed, is covered with a film of hydroxide which preserves it from further action of the air or the electrolyte. If, therefore, a piece of aluminum be made the anode in dilute H_2SO_4, the SO_4'' ions are unable to pass through the film to the anode, and the $Al^{\cdots}$ ions cannot pass from the anode into the solution. Hence there are

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[1] Part of a thesis presented to the Faculty of Sibley College for the degree of Electrical Engineer in June, 1904.

[2] Phil. Mag. [6], 5, 301 (1903).

[3] Cf. Ostwald: Zeit. phys. Chem. 6, 71 (1890).

no ions to carry electricity through the film, and no current can pass. A very small current does pass, and this may be due to $Al^{\cdot\cdot\cdot}$ ions being formed at the anode, and $H^{\cdot}$ ions of water passing at the same time through the film, and leaving OH' ions, which form $Al(OH)_3$ with the $Al^{\cdot\cdot\cdot}$ ions just formed. This aluminum hydroxide replaces that which may be removed by solution in the acid, and in this way the continuity of the film is maintained.

"If Cl', Br', or NO_3' ions are present, they can migrate through the film, thus carrying electricity to the anode where they unite with $Al^{\cdot\cdot\cdot}$ and form neutral salts, and this formation of salt behind the film will break it loose in spots and so enable the current to pass easily."

A rise of temperature is recognized as being fatal to the working of the aluminum rectifier when aqueous solutions are used. The temperature at the surface of the electrode is the important factor and not the mean temperature of the solution. These two are by no means the same.[1] It is more rational to apply the cooling where it is needed,[2] and it was therefore decided to make a series of tests on the behavior of water-cooled electrodes. The work was divided into two parts. In the first part measurements were made on the behavior of different electrolytes when using a direct current. The object of this was to determine the minimum leakage current at different voltages, since it is known that an alternating current always gives a higher leakage than does a direct current. In the second part of the work a number of efficiency runs were made with a single electrolyte.

STUDY OF ELECTROLYTES

Description of Apparatus and Instruments

In order to study the action of various electrolytes, a series of runs were made to determine the voltage required to rupture the films; the amount of leakage current and the point at which

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[1] Richarz and Ziegler, Wied. Ann. 63, 261 (1897).

[2] Fischer, Zeit. Elektrochemie, 10, 543 (1904).

it began to increase rapidly; the rise in temperature of the electrolyte during a run, and other points of a similar nature.

The electrolytes studied were disodium phosphate, sulphuric acid, and citric acid. Phosphoric acid, which acts like disodium phosphate, and which was used in the efficiency runs later, was not studied very fully, because of the similarity of action between an acid and its salts under these circumstances.

These substances were all used in succession in the same cell, and under as nearly similar conditions as could be obtained. The tank used was a small rectangular vessel, about 6 × 10 × 6 inches in size, with rather thick walls. Glass was used rather than another material because it allowed a clear view of the aluminum anode, so that all changes in the appearance of the film could be observed.

The aluminum anode was a seamless tube, supplied to us very courteously by the Pittsburgh Reduction Company, and was coiled up into two complete turns, with the two ends extending out of the electrolyte. To the two free ends short lengths of rubber tubing were attached, so that a stream of water could be allowed to flow through the tube, serving to keep the tube and the surrounding electrolyte cool. In this manner the temperature could be kept fairly constant during a run.

By bending the tube into a coil, a much larger surface of aluminum was exposed to the electrolyte than would otherwise have been possible. This larger surface kept the leakage current density at a low value, and this also assisted in keeping the tube itself cool. The coils were made as small as possible, care being taken to avoid rupture. In bending the tubes, which had comparatively thin walls, they were first filled with sand, and the ends tightly corked. They were then coiled by hand around a smooth cylinder, the sand with which they were filled preventing their being crushed during the process. Care was taken to avoid cutting or damaging the surface, as it is difficult to get the film to form over a rough or broken surface.

The temperature was measured by a thermometer suspended in the electrolyte, close to the aluminum, so as to get the temperature *at the film* as nearly as possible.

The second electrode was formed of a lead plate, which had a large surface exposed to the electrolyte, so that it was easily able to collect all the current which might flow, without heating to any perceptible degree.

The tank was cleaned by washing first with concentrated nitric acid, and then with water. A weak solution of ammonium hydroxide was then poured in, and finally the tank was thoroughly washed out and rinsed in distilled water. The lead electrode was treated in the same way.

The aluminum tube was cleaned by immersing it in a very dilute solution of sodium hydroxide, and allowing it to remain only until minute bubbles were seen to form on the surface, when it was removed and thoroughly washed in distilled water.

When the apparatus was cleaned and ready to use, it was assembled by placing the lead plate in one end of the tank, and the coiled aluminum in the other. These were suspended so as to rest a short distance from the bottom, and were then secured in position. The electrodes were about five inches apart at their nearest parts.

Connections were made to a steady supply of cool water, and arrangements made to allow a constant stream to flow through the tube during the test.

The direct current in the mains was at a pressure of 500 volts, and as it was necessary to begin at a very low pressure and come up to the full potential by small increments, without sudden jumps, some method of adjusting the voltage was necessary. To do this a lamp rheostat was used. Eighteen 16-c. p. lamps were connected in two sets of nine each in parallel, each set of nine being in series. Cross connections were also made so that pressures of from 0 volt to 500 volts could be obtained in nine steps of about 50 volts each. As it was desired to use still smaller increments of pressure, the current after passing the first rheostat was led through a second in series. This second rheostat consisted of several U-tubes connected in series to form a liquid resistance, each leg being fitted with an adjustable electrode.

By combining these two rheostats in series, it was possible to go from 0 volt to 500 volts in steps of about 5 volts each. The use of two lamps in parallel enabled about an ampere to be drawn without endangering the lamps. In some cases where more current was required, 32-c. p. lamps were used.

The direct current used was applied in such a manner that the aluminum was always the anode, and the lead the cathode.

An ammeter was used to measure the current, and a voltmeter placed so as to measure the pressure applied across the cell. The ammeter had been carefully calibrated and was quite accurate. It was provided with two scales, one reading from 0.0 to 0.5 ampere and the other from 0.00 to 0.01 ampere. By starting on the lower scale and then changing over to the higher one, it was possible to read small values of current very accurately.

The voltmeter had three scales—from 0 to 15, from 0 to 150, and from 0 to 600 volts respectively. It was also calibrated and found to be quite accurate.

As the voltmeter was connected inside the ammeter, a small current flowed through the latter all the time. This was 0.005 ampere, approximately, and was deducted from the ammeter readings before they were recorded.

In order to protect the sensitive ammeter from a sudden rush of current through it, it was put in shunt by a single-pole switch, which was closed except when readings were being taken.

METHODS OF MAKING TESTS

When all the apparatus was in order and all the electrical connections had been made, the switches were closed and the lowest value of pressure applied. At first the current rose to a considerable value, and then slowly died away until it became constant. These permanent values are the ones recorded in the result sheets.

The reason for the sudden flow of current at first is that the aluminum is clean, and has no surface film. As the current passes, a film of aluminum hydroxide is formed on the surface of the aluminum anode while hydrogen is set free at the cathode.

As the film grows thicker, it opposes more and more effectively the passage of current, until finally a point is reached where only a very small leakage current passes, just sufficient to retain the film. This leakage current gives the permanent values recorded.

Each time the voltage is raised, a similar operation occurs, the leakage current increasing slowly in value as the voltage rises.

So long as the voltage is below a certain critical value, this increase is very gradual. After this critical point is reached, the current increases very rapidly with a small increase in pressure, and soon reaches a point where the film is ruptured. Sometimes after the critical point is reached, the current continues to increase without any increase in the pressure whatever.

The point of rupture is known as the break-down point. It varies widely, depending upon the electrolyte used, the temperature in the film, the state of the film, and other conditions.

The thickness of the film varies directly with the pressure, and the higher the pressure, the thicker the film. When the film is first formed it is so thin that interference colors are produced when light falls on it in the proper direction. As the pressure increases, these colors pass from one to another, running through the spectrum in covering a range of about 125 volts. This can be shown by placing a strip of aluminum in the tank, and then raising it up out of the electrolyte for each step up in pressure, when the colors will appear in their order in bands, the width of which varies with the distance the aluminum is raised each time. The colors are very faint on low pressures and more intense on the higher values. The lower the break-down pressure, the smaller the variation in pressures required to run through the spectrum. Thus it is easily seen that each particular pressure has a certain value of film thickness. When, therefore, we do not increase the pressure gradually, but throw it on all at once, we are quite likely to rupture some weak point in the film before the current has had time to build the film up to the proper thickness required for the new and higher pressure. This is true even after the film has been worked at the lower voltage for a considerable time, and has had time to become comparatively thick.

After the film has once been formed, as this process of producing a film by applying to it increasing values of pressure is termed, the film is not so sensitive to changes and we can come up to the critical pressure by much longer steps than otherwise, though we cannot, in any case, apply the full pressure immediately without drawing excessive currents for an instant. If the film does not rupture, this current is only momentary.

This is not, however, the point of greatest importance, since we never run very near the critical point in using the electrolyte in a rectifier, as the leakage current is entirely too great. Still, it is of some importance in showing the behavior of the film under these higher pressures.

If we allow the current to flow when the pressure is above the critical point, we get something analogous to the disruptive discharge. Furious sparking takes place all over the tube, but more especially just at the surface line of the liquid. The tube is rapidly destroyed, holes being torn clear through it in a few moments. The action occurs much more readily with certain electrodes than with others.

Even though the tube may not be punctured, we can never form a good film over any spot where this disruptive sparking has taken place. Excessive current will flow before the pressure is near the critical value, and will flow at lower and lower pressures as the tube continues in use. The spot where a discharge has occurred is rough, as though the particles of the metal had been torn out of place. There is also some blackening caused, a hard, grayish substance somewhat resembling corundum being formed. This was noted by Cook.[1]

By moving the tube so that the damaged spot is out of contact with the electrolyte, the use of the tube may be continued. Wrapping insulating tape over the spot has no effect whatever.

The effect of sparking on the break-down pressure can be shown by a direct comparison of results obtained before and after such sparking.

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[1] Phys. Rev. 18, 23 (1904).

	Volts	Ampere
Before disruptive sparking	238	0.18
	288	0.20
After disruptive sparking	180	0.25
	140	0.30

The conditions were exactly similar in all four cases.

Several runs were made in which no cooling water was used. If the pressure was maintained all the time and the tube given no chance to cool off, the temperature of the electrolyte rose, especially when the runs were long, and the break-down occurred at a much earlier point. If the run was short, or the pressure was applied intermittently, the results obtained were much the same as in the cases where cooling water was used. These results will be discussed in the various sets of runs, as they were made.

As soon as any considerable leakage current flows, the temperature of the electrolyte rises, as its resistance is considerable. This heating tends to lower the break-down point and to increase the leakage current, and is to be avoided when possible. The rise in temperature as the leakage current increases is quite clearly shown in some of the runs.

Test of Di-sodium Phosphate

The first electrolyte to be studied was di-sodium phosphate (Na_2HPO_4). A saturated solution of the salt was used in the tank. The film was slowly formed, the pressure first applied being 5 volts. It was then worked up by equal increments of 5 volts each to 165 volts, and was then considered to be formed sufficiently to permit making a run.

At first nothing could be seen. Then, as the pressure increased, gas began to be given off at both electrodes, in quantities small at first but increasing with the pressure, until it was quite noticeable.

Run 1.—This was begun at 38 volts and carried up by easy stages. Gas was given off in small quantities, increasing up to 175 volts when, by watching the cell with the room darkened, minute sparks could be seen at intervals, here and there over the tube. This sparking gradually increased until the end of the run, when 242 volts were applied, and the run was stopped in order not to spoil the film.

RUN 1

Temp.	Volts	Amperes	Temp.	Volts	Amperes
15°	0	0.0	14°	174	0.038
15	38	0.0042	14	178[1]	0.040
15	54	0.0053	14	188	0.057
15	65	0.0068	14	196	0.0735
15	75	0.0072	14	206	0.089
14.75	83	0.0088	14	209	0.092
14.75	105	0.0128	14	212	0.095
14.5	115	0.0144	14	216	0.125
14.25	120	0.0147	14	224	0.143
14.25	130	0.020	14	230	0.170
14.25	148	0.021	14	234	0.180
14.25	156	0.023	14	238[2]	0.190
14	160	0.028	14	242	0.250
14	170	0.032			

The current increased very gradually from zero up to about 200 volts, when it began to increase more and more rapidly as the pressure rose. As can be seen from the curve (Fig. 1), the critical point occurs somewhere between 175 and 200 volts. The temperature fell during the first of the run, due to the cooling water being very cold, and then remained constant.

The amount of gas given off increased with the current, until at the end of the run the electrolyte was made to look slightly whitish, due to the number of gas bubbles contained in it.

Run 2.—The second run was begun at 48 volts and carried on by increasing the pressure more rapidly than in Run 1. At

RUN 2

Temp.	Volts	Amperes	Temp.	Volts	Amperes
12.0°	48	0.0025	11.75°	284	0.100
12.0	100	0.006	11.75	300	0.200
12.0	160	0.011	11.75	304	0.220
12.0	176	0.015	11.75	308	0.250
12.0	208	0.018	12.0	320[3]	0.500
12.0	240[1]	0.020			

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[1] Visible sparking began.

[3] Film ruptured.

[2] Sparking badly.

240 volts the first visible sparking appeared. The current increased very slowly up to this point. Somewhere between 240 and 284 volts the critical point was passed. As the pressure rose, the current and the sparking increased rapidly until at 320 volts disruptive sparking occurred at one point just at the surface of the liquid, and ended the run. The bad spot on the tube was moved up out of the electrolyte, and the next run then taken.

Run 3.—This was very much the same as Run 2. Visible sparking began at 264 volts, corresponding to a sudden increase in current. The current continued to increase and at 325 volts the film was again ruptured. The critical point seems to have been somewhere between 200 and 264 volts.

RUN 3

Temp.	Volts	Ampere	Temp.	Volts	Ampere
11.5°	80	0.00265	10.0°	264[1]	0.065
11.0	140	0.00565	10.0	280	0.150
10.5	160	0.00625	9.5	288	0.200
10.25	180	0.0080	9.0	294	0.270
10.0	200	0.010	9.0	325[2]	Off scale

These three runs were all taken, using cooling water in the tube. In most cases the temperature in the cell fell. This was because the cooling water was very much colder than the electrolyte at the beginning of the run, and also to the fact that the runs were begun before the cell had reached its lower temperature limit.

Run 4.—This run was taken without using cooling water. The values of the current were much larger than those in the previous runs, and sparking began at 140 volts. The temperature of the electrolyte rose steadily. After reaching 160 volts the run was stopped and the cell allowed to cool down. When the temperature had fallen to what it had been at the start the run was resumed, and it was found that although the pressure had raised to 176 volts, the current had fallen to one-fourth of

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[1] Visible sparking began.

[2] Film ruptured.

RUN 4

Temp.	Volts	Ampere	Temp.	Volts	Ampere
15°	0	0.0	17.0°	100	0.034
15	15	0.00265	17.5	110	0.055
15	27.5	0.0048	18.0	140[1]	0.080
15	40.0	0.010	18.7	160	0.10
15.2	50	0.013	—	—[2]	—
15.6	52	0.015	15	176	0.025
16.0	55	0.017	15.5	232	0.04
16.25	70	0.025	16.0	252	0.065
16.5	75	0.0251	16.1	292[3]	0.250
16.7	85	0.029			

its value at 160 volts. Both current and temperature rapidly rose, the film being ruptured at 292 volts.

From these runs it seems that where cooling water is used it should be possible to work without difficulty up to 220 volts, after the film has been properly formed. The results of these runs are shown graphically in Fig. 1.

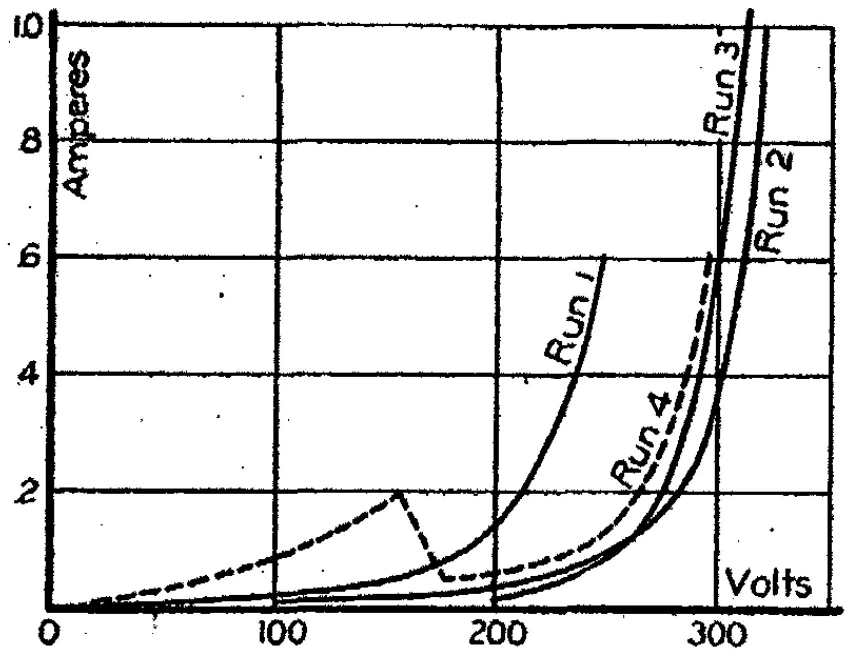

Fig. 1

TEST OF SULPHURIC ACID

After completing the test of the di-sodium phosphate solution, the apparatus was taken apart and cleaned before beginning the runs. The old aluminum tube was discarded, as the

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[1] Sparking. [2] Stopped to let cell cool. [3] Film ruptured.

disruptive sparking to which it had been exposed had practically destroyed its further usefulness, and a new tube was substituted. This tube was as nearly like the old one as was possible, both in size and form.

The new electrolyte was sulphuric acid. This was as pure as possible, being known as storage battery acid, and had a specific gravity of 1.2. While this density does not correspond to the maximum conductivity, yet it is quite near to it and answers very well for the purposes of the test. Electrical connections and the arrangement of the cell and apparatus remained as in the previous test.

Run 5.—This run was begun applying a pressure of 5 volts across the cell. The pressure was then increased by easy stages up to 103 volts, when the film broke down, though it was not destroyed in spots, as in the previous case. Instead there seemed to be a general giving way of the film all over the tube, so that the current was able to pass without doing much damage.

RUN 5

Temp.	Volts	Ampere	Temp.	Volts	Amperes
13.5°	5	0.0035	12.25°	62	0.2150
13.25	10	0.0045	12.25	67	0.300
13.0	15	0.0074	12.25	73.5	0.400
12.75	25	0.0140	12.0	76.0	0.950
12.75	40	0.0650	12.0	103.0[1]	1.350
12.5	48	0.110			

The critical region is not so clearly defined as in the previous cases. The leakage current rises rather rapidly after passing about 40 volts, and while the film is not actually broken down at 103 volts, it permits of so great a leakage current as to render the operation of the apparatus as a rectifier impossible.

Run 6.—This run was the same in all particulars except that no cooling water was used. The values of the current lie below those obtained in Run 5, partly because of the fact that the film had already been formed by the previous run, and partly because of the lower temperature obtained in the tank in that run.

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[1] Film ruptured.

RUN 6

Temp.	Volts	Ampere	Temp.	Volts	Ampere
9.5°	5	0.005	10.0°	40	0.025
9.5	10	0.010	10.0	53.5	0.130
9.5	20	0.012	10.1	64	0.1550
9.5	26	0.015	10.2	70	0.250
9.5	30	0.018	10.5	78[1]	0.850

As before, the current rises rapidly after about 40 volts has been applied, but the curve bends upward much more sharply, showing that the critical point lies somewhere between 65 and 75 volts. The run was stopped before the film was damaged.

There was no noticeable sparking in either of these runs, probably because the pressure was not sufficiently high. Quantities of gas were given off, however, increasing as the current rose, so that toward the end of the run the electrolyte was so filled with bubbles of gas as to be whitish in color and almost opaque.

While no test was made of the gas given off, it seems probable that it was mostly hydrogen and oxygen together with a little sulphur dioxide or other impurities which gave it a penetrating odor and made it very disagreeable to breathe, as it irritated the air passages and produced coughing and soreness.

Test of Citric Acid

It was now decided to try some organic acid as the electrolyte, in order to find out the possibilities in that direction. Accordingly, citric acid was chosen as being convenient, cheap, and readily obtainable.

The apparatus was cleaned and arranged as before, and as the tube had not been damaged, it was decided to use the same one over again. Before putting in the new electrolyte, however, it was thoroughly scrubbed in running water to free it from all traces of sulphuric acid. While it is not advisable to use the same tube in more than one solution, it was done here to economize on material and time. The electrolyte was a solution of

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[1] Film breaking.

citric acid in water, 100 grams of the crystallized acid being dissolved in 1.5 liters of water.

The effect of the use of the tube in another solution is clearly shown in Runs 7, 8, 9, and 10. As the impurities were eliminated and a new film formed, we can reach successively higher and higher pressures without increasing the current leakage.

In making these runs the pressure was run up until the critical point was reached, when the pressure was taken off for a few moments and then applied again at a very much lower value. On running up a second time it was found possible to reach a very much higher pressure than before, without damaging the film. This process is beautifully shown by the curves in Fig. 2. The last curve, No. 10, seemed to represent nearly standard results with this tube.

Run 7.—In this run the pressure first applied was 10 volts, and it was then run up by small increments to 156 volts, where

RUN 7

Temp.	Volts	Ampere	Temp.	Volts	Ampere
14.0°	10	0.0016	12.50°	105	0.022
14.0	20	0.0025	12.25	110	0.030
14.0	40	0.0046	12.20	120	0.077
13.5	60	0.0073	12.0	135	0.210
13.0	80	0.0120	11.5	150	0.300
12.75	93	0.0180	11.5	156[1]	0.320

the run was stopped. The current rose very gradually until 100 volts was reached, and then increased very rapidly until the end of the run.

Run 8.—After the end of Run 7 the cell was allowed to rest for a few moments, and the pressure was again applied, starting this time at 56 volts and running up to 102 volts, when the run was stopped. The current began at a very low value and in-

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[1] Film weakening.

RUN 8

Temp.	Volts	Ampere	Temp.	Volts	Ampere
11.0°	56	0.002	10.75°	166	0.190
10.75	108	0.005	10.50	180[1]	0.290
10.75	140	0.075	10.50	202	0.340
10.75	150	0.170			

creased slowly up to about 140 volts, then increasing rapidly to the end of the run.

Run 9.—The cell was given a few moments to recover; the pressure was again applied, starting at 68 volts and running up to 412 volts. The current increased very slowly at first, giving a critical value of about 225 volts. From there it increased quite rapidly until 310 volts was reached. The film then broke down, the value of current obtained at 412 volts being so large as to show this clearly.

RUN 9

Temp.	Volts	Ampere	Temp.	Volts	Amperes
10°	68	0.002	10.1°	310	0.80
10	132	0.005	10.25	400[2]	2.00
10	200	0.009	10.4	408	2.10
10	240	0.080	10.5	412	2.20
10	260	0.260			

Run 10.—After the cell had been restored to normal conditions a pressure of 60 volts was applied and another run started. The pressure was run up to 424 volts, when the film was seen to be breaking and the run was stopped.

RUN 10

Temp.	Volts	Ampere	Temp.	Volts	Ampere
13.25°	60	0.002	12.0°	318	0.125
13.25	112	0.003	11.5	352	0.630
13.0	140	0.005	11.5	356	0.650
13.0	208	0.0065	11.25	360	0.670
12.5	264	0.010	11.0	364	0.700
12.0	288	0.025	11.6	424[2]	1.80

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[1] Film weakening.

[2] Film breaking.

The current increased slowly at first, giving a critical point of from 300 to 325 volts. A rapid increase up to 364 volts followed where the film was still good. The next step in pressure produced such a large increase in current that the film was known to be giving way, and the run was at once stopped.

The data for Runs 7-10 are represented graphically in Fig. 2.

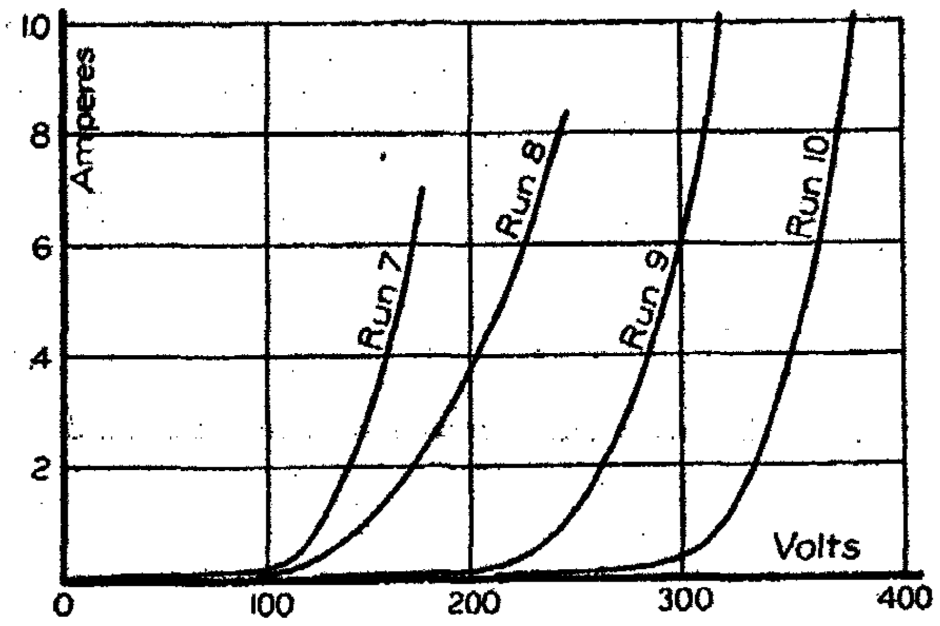

Fig 2

Test of Dilute Solution of Citric Acid

After completing these runs it was thought desirable to see if the concentration of the solution made any difference in the action. The electrolyte was diluted to one-tenth of its former strength, and a new aluminum tube was prepared and placed in position. Everything else was as in previous runs.

Run 11.—The run was begun at a very low pressure, and carried up to the highest voltage obtainable from the line (508 volts). The current increased very gradually, and the form of the curve shows that the critical pressure lies somewhere at about 500 volts. It was impossible to determine the breaking pressure for the reasons stated above.

RUN 11

Temp.	Volts	Ampere	Temp.	Volts	Ampere
10°	80	0.005	10.25°	332	0.0450
10	104	0.0055	10.0	420	0.110
10	160	0.010	10.0	492	0.260
10	196	0.0110	10.0	500	0.290
10	234	0.0125	10.0	508[1]	0.320
10	284	0.0150			

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[1] Film still good.

In the first four runs there was no visible sparking, although some sparking occurred, as the tube was slightly blackened and pitted near the surface line of the liquid. Gas was given off much as in the runs taken with sulphuric acid, although the amount was not quite so great.

In the run with the dilute acid there was no sparking, and little gas was given off, as the pressure at no time rose above the critical value.

RESULTS OF TESTS OF ELECTROLYTE

As a final step a representative run was selected from each of the four sets of runs, and these were all plotted on one sheet to the same scale (Fig. 3). The ones selected were:

From Set 1—Run 2.
" " 2— " 5.
" " 3— " 10.
" " 4— " 11.

The runs selected were all ones in which cooling water had been used, so that it was possible to compare the action of the film in different electrolytes under similar conditions.

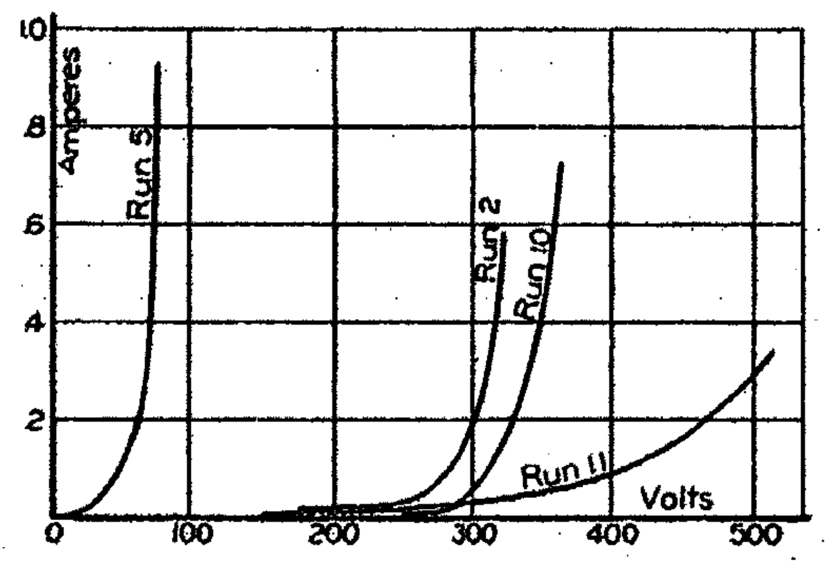

Fig. 3.

As can be seen from the curves, the sulphuric acid has the lowest critical value. If it is desired to use it as the electrolyte in a cell, the pressure should not exceed 55 volts; if excessive leakage is to be avoided. The di-sodium phosphate comes next, but has a very much higher critical value. It should permit the pressure to be worked up to 220 volts without allowing any onsiderable leakage. The critical value of the concentrated citric acid lies somewhere about 300 volts. It can be seen from the curves that it follows the di-sodium phosphate quite closely. The dilute citric acid has the highest critical value of all, as the current is just beginning to increase rapidly at that point. It has, however, a more steady rise than the others, and to correspond to the others in the amount of leakage current allowed, it should not be worked above 325 volts.

While these curves show which electrolyte has the highest critical value and breaking point, they do not show which ones will work the best in a rectifier, as other considerations then enter in. As it is, however, they indicate which ones will probably give the best results, and thus are quite useful as far as they go.

THE ALUMINIUM RECTIFIER

Choice of Electrolyte.

Citric acid solutions are of no value for a rectifier because the conductivity is too low. It is also a question whether any organic acid would withstand oxidation for any length of time. Sulphuric acid is out of the question because it attacks the film too readily. This leaves phosphate or phosphoric acid solutions as the only ones available. Sodium phosphate was rejected because of the possible disadvantage of a formation of caustic soda at the cathode. While admirable results have been obtained with ammonium phosphate solutions, it was thought best to start with a simpler electrolyte, with phosphoric acid.

The electrolyte accordingly was phosphoric acid diluted with water to that concentration which produced maximum conductivity. This was a 45 percent solution of the syrupy acid in water. The solution would have much the same critical and breaking points as the di-sodium phosphate. As the critical value with this solution lies at about 300 volts, no trouble was to be expected on a 110-volt circuit.

The conductivity of sulphuric acid is very much greater than any of the other electrolytes used, but the fact that it must not be worked at above 55 volts prevented its use in this case, although a run was made later on, using it in combination with phosphoric acid.

DESCRIPTION OF THE RECTIFIER

The rectifier consisted of four cells so arranged as to secure all the current. Each cell contained one aluminum electrode and a pair of graphite or lead electrodes. The cells themselves were made of beakers, as these were convenient in form and size and well adapted to the purpose.

The aluminum electrodes each consisted of a piece of aluminum tubing about nine inches long and three-eighths of an inch in diameter, bent into the form of a U, so that they could be placed inside of the beakers. The length of tube in the electrolyte was the same in all cases, approximately six and three-eighths inches, and the area of aluminum exposed to the electrolyte was, therefore, 2.82 square inches per cell. It is necessary that the aluminum should have very nearly the same area exposed to the electrolyte in each cell, as otherwise there would be a greater leakage than there is when the cells are evenly balanced. Care must be taken to avoid cutting or marring the surface of the tube, owing to the difficulty of forming a film over a roughened spot.

The electrodes should be placed as close together as possible without forming short circuits, in order to reduce the resistance of the cell to as low a figure as possible, because such resistance in the cell cuts down the available voltage very seriously on heavy loads. In these cells the electrodes were approximately three-eighths of an inch apart at the bottom, and one-half an inch at the top.

The aluminum electrodes were connected by rubber tubing so that cooling water could flow in at one end of the system and out at the other, keeping the tubes and electrolyte cool. The temperature was measured by two thermometers, one in the cell through which the water entered and the other in the cell at which it left. Under ordinary circumstances these read the same, and only one reading was recorded.

The electrical connections were made as shown in Fig. 4. The alternating current from the mains, 60 cycles and 110 volts, was led through an ammeter and a wattmeter to the rectifier. Here each side of the circuit was divided into two branches, one of which went to an aluminum electrode, and the other to a graphite or lead electrode. On the other side two aluminum electrodes were connected together to form one side of the direct current circuit, and two graphite or lead electrodes were joined to form the other side. The current, after passing through the ammeter, was led to the load. It was regulated by the amount of resistance in the direct current side. When this was on open circuit, only the leakage current flowed, and under these circumstances it was comparatively small. Unfortunately, this leakage current increased with the load, though not in direct proportion to the current flowing. With no load, this leakage current amounted to between 0.3 and 0.5 ampere.

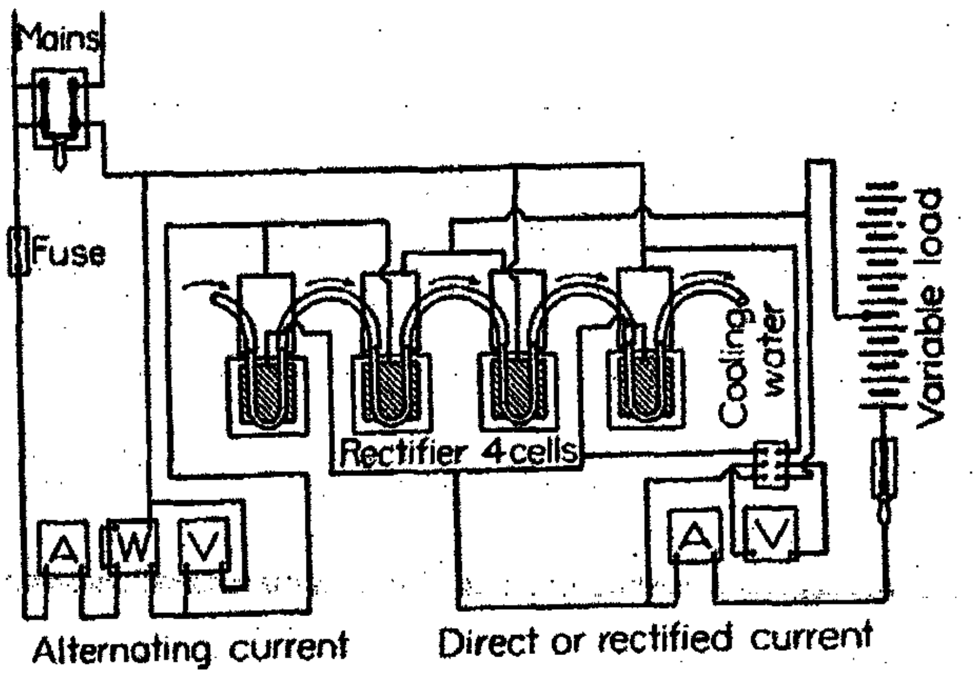

Fig. 4.

A voltmeter placed across the mains measured the pressure of the incoming alternating current. It was arranged with a double throw switch so that the drop in voltage across a cell could be obtained, and the resistance of the cell thus obtained.

Two ammeters were used on the alternating current side, one in reading from 0.0 to 2.0 amperes, and the other from 0.0 to 25.0 amperes. These were accurately calibrated with the Thomson balance in the laboratory. The direct current ammeter was supplied with a shunt, so that it read from 0 to 10 amperes. This was also calibrated on the Thomson balance.

The A. C. voltmeter read to 130 volts, and the D. C. to 150 volts on two scales. These were carefully calibrated by a Weston voltmeter reading to 0.05 volt, belonging to the Department of Physics. The wattmeter was calibrated by means of the ammeter and voltmeter, incandescent lamps being used as a load.

It is claimed that a direct current wattmeter should be used in the direct current side, as, owing to the distorted wave form, the ammeter readings are likely to be in error. Unfortunately, one of these was not available for the test. The ammeter can, however, be checked by inserting a copper voltameter in series with it. This was done here, and the ammeter was found to be approximately correct. In case the needle was swinging at the time when a reading was to be taken, the limits of the swing were observed and the average taken as expressing as nearly as might be the correct reading.

Each cell when assembled was "formed" by applying a direct current to it, with the aluminum as the anode. The pressure was run up in one or two steps to a pressure corresponding to the alternating current pressure which the cell was to rectify. Had an "auto" transformer been available, the aluminum could have been "formed" direct by applying a low value of alternating pressure at first, and gradually raising it to the working pressure. The aluminum having been formed and the cells arranged and all connections made, the current was turned on and a run started.

The current flowing through the rectifier was small at first and was increased step by step until the capacity of the cells was reached. During the run, readings of all the electrical instruments, as well as the temperature of the electrolyte near the aluminum tubes, were taken simultaneously every five minutes.

Each value of current was maintained for half an hour by adjusting the resistance in the direct current circuit. After changing to the next succeeding value of current, some time was allowed to pass before readings were taken in order to permit everything to settle to a state of equilibrium under the new conditions.

Each run was once repeated under exactly similar conditions, as a check on the results. The second run was usually made with a fewer number of current values to cover the range, as it was made merely as a check to the first, and the form of the curves was sure to be closely the same.

When the rectifier was in operation, gas was given off continuously in quantities sufficient to make the electrolyte almost opaque. A little water was added every day or two to compensate for that lost as gas. Otherwise the electrolyte remained unchanged, as there was no perceptible electrolytic action on the phosphoric acid. The quantity of gas given off appeared to vary directly as the current though no quantitative measurements were made.

The current taken by the rectifier was not very steady, partly owing to the variations in voltage and to changes in the cell. At times the current would run up to half again its steady value, when there would be a sharp crackling in the cell, and the current would then subside. This action occurred especially toward the end of a run when the cell was carrying a comparatively heavy current, and was sometimes so frequent as to render it very difficult to get satisfactory electrical readings.

After the end of a run, if the circuit was opened suddenly or the load removed so that the cell was relieved at once, a sharp crackling could be heard in the cells for a moment after the current had ceased. These crackling noises are probably due to some molecular change going on in the aluminum or in the electrolyte, or both, as the tension under which they had been working was suddenly removed.

It was found advisable to remove the aluminum tubes from the electrolyte when not in use, for there seemed to be some dissolving action in the cell, or at the surface line of the electrolyte, so that the aluminum drew an excess of current for a few moments after the circuit was closed, unless this was done. This trouble can be obviated by starting through a resistance. A small inductive resistance in the A. C. side answers quite well, as it has to carry a current for a short time only. This is advisable even when the tubes are removed from the electrolyte. In case the tubes are left in, it sometimes requires quite a little time for the excess current to subside.

The current drawn is not at unity power factor, but leads considerably. Thus the wattmeter reading is always less than the product of the volts and amperes. As the output, however, is in direct current, this power factor is not of so much importance. The power factor varies directly as the current, and approaches unity as the current approaches the capacity of the cell.

The direct current voltage obtained when the direct current end was on open circuit was much higher than when any load, however small, was put on the rectifier. A short table of results shows this clearly:

A. C. Voltmeter	A. C. Ammeter	A. C. Wattmeter	D. C. Volts
103.0	0.50	30	70
107.5	0.44	20	76
106.0	0.32	10	74
106.5	0.36	15	73
110.0	0.30	10	73

The highest voltage obtained under load seldom exceeded 50 volts, the applied pressure being the same.

COMPUTATION OF RESULTS

The results were computed from the readings taken, in the manner shown below. The electrical quantities observed were alternating current amperes, volts, watts, and direct current volts and amperes. The direct current amperes were obtained as the product of the direct current volts and amperes. The power factor was obtained from the alternating current values by substituting in the equation

$$ECP_f = W$$
$$P_f = W/(EC),$$

in which E = voltage, C = current, P_f = power factor, and W = watts.

The current efficiency was obtained by dividing the direct current output by the alternating current input, and the same applies to energy efficiency as well.

The voltage efficiency was computed in a similar manner for each reading, but is not the true efficiency, which was found as follows: The effective value of the alternating current electromotive force is divided into the direct current voltage. The effective e. m. f. = voltmeter reading $\times \sqrt{2} \times 2/\pi$.

The average of the alternating current voltages during half an hour was found and reduced to its effective value. The average of the direct current voltmeter reading for the same period of the run, was also found. This latter, then, divided by the effective e. m. f. gives the true voltage efficiency, as recorded in the average of results, and shown in the voltage efficiency curves.

Efficiency Run I.

In the first efficiency run the arrangement of cells and apparatus previously described was used. One electrode was of aluminum, of course, and the other was formed by two strips of Acheson graphite placed one on each side of the aluminum and electrically connected so as to form one electrode. The electrolyte used was a 45 percent solution of phosphoric acid.

The run began with 0.25 ampere of current flowing on the direct current side. The current was raised by steps up to over 3 amperes on the direct current side, and as the readings were very irregular and the temperature of the electrolyte had begun to rise, the run was discontinued.

The readings obtained are recorded (corrected) on the data sheet under Table I, P_f standing for power factor, V. E. for voltage efficiency, C. E. for current efficiency, and E. E. for energy efficiency. The values under "Average" are the mean of the set except for the voltage efficiency where the mean true efficiency is put down.

TABLE I.

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P_f	V. E.	C. E.	E. E.
12.0°	102.0	0.62	25.0	35.0	0.26	9.10	39.5	34.3	42.0	35.4
12.0	103.5	0.72	26.3	32.5	0.28	9.11	35.4	31.4	38.9	34.7
12.0	105.5	0.70	26.0	34.0	0.26	8.85	36.2	32.3	37.2	34.1
12.0	109.5	0.70	27.0	36.0	0.29	10.45	35.3	32.9	41.5	38.7
11.7	108.0	0.78	27.0	34.5	0.28	9.75	32.1	31.9	35.9	36.1
11.5	108.5	0.70	27.0	35.0	0.28	9.80	35.5	32.3	40.0	36.3
11.5	108.5	0.68	25.0	34.0	0.27	9.18	33.9	31.3	39.7	36.7
Average,		0.70					35.4	36.1	39.5	36.3

TABLE I.—(*Continued*).

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P/	V. E.	C. E.	E. E.
11.7°	105.5	0.64	30	38.0	0.25	9.50	44.5	36.0	39.1	31.7
11.5	109.0	0.59	21	41.5	0.27	11.20	32.7	38.0	45.8	53.4
11.5	107.5	0.59	25	39.0	0.25	9.75	38.4	36.3	42.4	39.9
11.2	108.5	0.60	25	41.0	0.26	10.65	38.4	37.8	43.3	42.6
11.2	108.5	0.59	20	43.0	0.27	11.61	31.4	39.7	45.8	58.1
11.2	109.5	0.58	23	42.5	0.25	10.62	36.3	38.8	43.1	46.2
11.2	110.5	0.61	22	43.0	0.26	11.18	32.7	38.9	42.7	50.8
Average,		0.60					36.5	42.3	43.2	46.1
11.5	110.0	0.85	50	31.0	0.55	17.10	53.5	28.2	64.7	33.2
12.0	108.5	0.98	82	31.0	0.55	17.10	77.2	28.5	55.2	20.9
12.0	110.5	0.92	60	33.0	0.55	18.30	59.0	29.9	59.8	30.5
12.0	108.5	0.97	60	32.0	0.56	17.92	57.0	29.6	57.8	29.9
12.0	110.5	0.92	55	34.0	0.57	19.38	54.0	31.7	62.0	35.3
12.0	108.5	0.97	60	34.0	0.60	21.00	59.0	31.3	61.8	35.1
12.0	109 5	0.92	55	32.0	0.57	18.21	54.5	29.3	62.0	33.2
Average,		0.933					59.1	33.2	60.47	31.1
12.0	110.0	1.05	82	33.0	0.85	28.62	71.0	30.0	81.0	34.4
12.0	108.0	1.08	80	31.0	0.82	25.4	70.4	28.7	75.9	31.7
11.7	108.5	1.08	75	33.0	0.85	28 02	64.0	30.5	78.7	37.7
12.0	105.5	1.08	80	30.0	0.82	24.6	70.2	28.4	75.9	30.7
12.0	107.5	0.98	65	34.0	0.82	27.85	61.7	31.7	83.7	42.9
12.0	107.0	0.95	70	32.5	0.85	27.6	68.8	30.4	89.5	39.4
12.0	107.5	1.03	70	33.0	0.80	26.4	68.2	30.7	74.4	37.7
Average,		1.035					67.7	33.8	79.87	36.35
12.0	106.5	1.45	115	29.5	1.15	33.9	97.2	27.7	79.3	29.5
12.0	107.5	1.45	115	32.0	1.18	37.8	96.5	29.7	81.4	32.1
12.0	104.0	1.35	100	29.0	1.18	34.2	71.3	27.9	87.5	34.2
12.0	104.0	1.35	105	29.5	1.20	35.4	74.9	28.3	88.9	33.7
12.0	106.5	1.50	120	31.0	1.25	38.8	75.2	29.1	83.3	32.3
12.0	105.5	1.45	115	30.5	1.20	36.6	75.2	28.7	82.8	31.8
12.0	106.5	1.50	125	30.5	1.25	38.2	78.3	28.7	83.3	30.5
Average,		1.435					81.2	31.9	83.8	32.01

TABLE I.—(*Continued*).

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	Pf	V. E.	C. E.	E. E.
12.0°	104.5	2.2	190	26.0	1.65	42.9	82.5	24.9	78.6	22.6
12.2	105.5	2.4	175	27.0	1.70	45.9	69.0	25.6	70.8	26.3
12.5	105.5	2.3	175	27.0	1.70	45.9	72.2	25.6	73.9	26.3
13.0	103.5	2.4	200	26.5	1.82	48.2	80.6	25.6	75.8	24.1
13.0	107.0	2.5	190	29.0	1.80	52.2	71.0	27.1	72.0	27.5
13.0	109.0	2.4	185	31.0	1.70	52.7	70.7	28.4	70.8	28.5
13.0	108.0	2.5	180	30.5	1.80	54.9	66.7	28.2	72.1	30.5
Average,		2.385					73.2	29.5	73.42	26.54
13.0	109.5	3.4	305	29.0	2.55	74.0	82.0	26.5	75.0	24.3
13.5	104.0	3.4	305	26.0	2.50	65.0	86.5	25.0	73.6	20.9
13.5	104.0	3.2	305	26.0	2.60	67.6	91.7	25.0	81.1	21.9
13.3	108.5	3.5	295	29.0	2.45	71.1	77.8	25.8	70.1	20.3
13.3	103.5	3.2	275	25.0	2.40	60.0	83.0	24.1	75.0	21.9
13.3	104.5	3.2	275	26.0	2.35	61.1	83.2	24.9	73.5	22.2
13.5	106.5	3.3	280	25.0	2.45	61.2	79.7	23.7	74.3	21.9
Average,		3.31					83.4	28.1	74.35	21.91
14.5	106.5	3.6	350	27.0	3.05	82.2	91.2	25.3	84.9	23.5
15.0	102.5	4.0	360	24.5	3.05	74.8	88.0	24.9	76.3	20.9
15.6	106.5	4.2	380	26.0	3.30	85.7	85.0	24.4	78.6	22.5
15.5	111.5	4.3	390	27.0	3.25	87.7	81.5	24.2	75.2	22.5
15.5	109.5	4.5	400	26.5	3.40	90.1	81.3	24.2	75.7	22.5
15.0	110.5	4.4	390	27.0	3.25	87.7	80.3	24.5	73.8	22.6
15.0	108.5	4.4	395	27.0	3.30	89.1	82.7	24.9	75.1	22.5
Average,		4.2					84.3	27.6	77.1	22.43

The power factor began at an extremely low value of 36 percent, but rose very rapidly at first until a little over 1.5 amperes A. C. had been reached, when it increased very slowly from then on, reaching 85 percent at the end. The current efficiency also began at a low value and rose quite rapidly, reaching a maximum of 84 percent at about 1.5 amperes A. C., a little less than half the load. From this point it decreased very slowly to full load. The efficiency during the greater part of the run was quite good.

The voltage efficiency was highest at the beginning of the run, and fell off very slightly as the current increased in value, dropping to 28 percent. The energy efficiency was also highest at the start and fell off slowly as the current rose. The energy efficiency is quite low because of the poor voltage efficiency. The variation of temperature during the run was slight, a rise of four degrees occurring. This was partly due to changes in the temperature of the cooling water.

Efficiency Run 2

The conditions under which this run was taken were the same as those in the preceding run, except that the electrolyte had become contaminated with carbon. No carbon is able to withstand, for any length of time, the attack of any solution giving off oxygen, and while graphite will resist much longer than carbon, its life in such solutions is short. Before beginning the run, therefore, the electrolyte was removed and filtered so that most of the carbon particles were gotten rid of. The data are given in Table II.

TABLE II.

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	Pf	V.E.	C.E.	E.E.
14.5°	102.0	0.73	39	50.0	0.16	8.0	52.4	49.0	21.9	20.5
14.0	100.5	0.65	25	49.5	0.18	8.92	38.3	49.2	27.7	35.7
13.5	101.0	0.73	30	48.5	0.18	8.74	40.7	48.0	24.6	29.1
13.5	99.5	0.73	30	48.0	0.18	8.65	41.3	48.2	24.6	24.8
13.2	101.5	0.68	25	48.5	0.17	8.25	36.3	47.7	25.0	32.9
13.1	100.5	0.72	26	48.5	0.18	8.74	35.9	48.2	25.0	33.6
13.1	101.5	0.74	29	49.5	0.19	9.4	38.6	48.7	25.7	32.4
Average,		0.711					33.3	55.1	24.35	29.85
13.2	105.5	1.08	80	42.0	0.62	26.1	70.2	39.8	57.4	32.6
13.0	103.7	1.08	82	41.0	0.70	28.7	72.3	39.5	64.7	35.0
13.0	105.5	1.08	83	42.0	0.70	29.4	72.9	39.8	64.7	35.5
13.0	105.5	1.08	85	43.0	0.72	30.9	74.6	40.8	66.6	36.4
13.0	104.5	1.20	100	42.5	0.72	30.6	79.8	40.7	60.0	30.6
13.0	100.0	1.08	85	43.0	0.71	30.5	78.7	43.0	65.7	36.0
13.0	106.5	1.15	90	44.0	1.08	47.5	73.5	41.2	94.0	52.8
Average,		1.107					74.5	45.4	67.58	36.98

TABLE II.—(*Continued*).

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	Pf	V. E.	C. E.	E. E.
13.0°	105.0	1.40	110	41.0	0.96	39.3	74.9	39.1	68.6	35.7
13.0	106.0	1.40	110	41.0	0.96	39.3	74.2	38.7	68.6	35.7
13.0	105.5	1.62	130	40.5	1.00	40.5	76.0	38.4	61.7	31.1
13.0	104.0	1.55	125	40.0	0.96	38.4	77.6	38.5	62.0	30.7
13.0	106.5	1.56	130	40.5	0.96	38.9	78.3	38.1	61.5	29.9
13.0	106.0	1.56	130	40.0	0.97	38.8	78.3	37.7	62.2	29.8
13.0	105.5	1.62	129	40.0	0.95	38.0	75.5	38.0	58.7	29.4
Average,		1.53					76.4	42.6	63.33	31.75
13.0	105.5	2.4	200	36.0	1.70	61.2	79.0	34.1	70.8	30.6
13.5	107.0	2.3	195	37.0	1.65	72.2	79.2	34.6	71.8	37.0
13.5	106.5	2.2	170	35.0	1.60	56.0	72.5	32.9	72.8	32.1
13.5	106.0	2.3	180	35.0	1.60	56.0	74.0	33.0	69.7	31.1
13.5	106.0	2.2	180	35.0	1.60	56.0	77.2	33.0	72.8	31.2
13.5	105.5	2.2	175	35.5	1.58	56.2	75.4	33.4	71.7	32.1
13.5	105.5	2.1	170	35.0	1.55	54.2	76.5	33.2	73.8	31.9
Average,		2.213					76.2	36.8	71.77	32.28
13.5	106.0	3.0	250	33.0	2.23	73.7	78.6	31.1	74.4	29.5
14.0	103.5	3.0	245	32.5	2.25	73.0	78.8	31.5	75.0	29.7
14.0	107.0	3.2	298	34.0	2.35	80.0	87.2	31.8	73.5	26.8
14.0	107.0	3.1	300	34.0	2.30	78.2	90.5	31.8	74.1	26.1
14.0	104.0	2.8	250	32.0	2.20	70.5	86.0	30.8	78.5	28.1
14.0	107.0	3.2	280	35.0	2.28	79.4	81.9	32.7	71.3	28.3
14.0	106.5	3.0	275	34.0	2.28	77.5	86.2	31.9	76.0	28.2
Average,		3.042					84.1	35.3	74.7	28.1
13.0	103.5	3.6	320	32.0	2.85	91.2	85.7	30.9	79.2	28.5
14.2	99.5	3.4	276	30.0	2.72	81.6	81.6	30.2	80.0	29.6
14.7	104.0	3.7	320	32.0	2.85	91.2	83.2	30.7	77.1	28.5
14.8	105.5	3.5	280	30.5	2.70	82.3	75.9	28.9	77.2	29.4
14.8	104.5	3.5	320	30.0	2.82	84.5	87.5	28.7	80.7	26.4
14.9	107.5	3.4	305	33.0	2.70	89.2	83.5	30.7	79.5	29.2
15.0	108.5	3.7	350	34.0	2.92	99.2	94.5	31.3	79.0	28.3
Average,		3.642					84.5	33.6	76.1	28.55

TABLE II.—(*Continued*).

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P_f	V. E.	C. E.	E. E.
14.0	105.5	5.2	510	30.0	4.10	123	93.0	28.4	79.0	24.2
15.8	104.5	5.5	535	30.0	4.30	129	93.4	28.7	80.4	23.5
17.0	105.5	7.40	710	31.0	5.90	183	92.2	29.4	79.8	25.7
18.0	104.0	8.0	—	30.5	6.85	209	—	29.3	85.6	—
Average,		6.7					92.8	32.3	81.2	24.48

The run was begun with a direct current output of about 0.18 ampere, and run up to about 5 amperes, when heating developed to such an extent and the fluctuations in current were so great that the run was cut short a little in order to avoid trouble.

The power factor begins at a very low value, but rises very quickly to about 80 percent and then continues to rise slowly to the end of the run, when its value is almost 93 percent. The current efficiency begins low and rises quickly to 70 percent, when it also increases slowly, reaching a value of a little over 81 percent at the end of the run. The voltage efficiency falls off rather rapidly until about half load when it is a little over 34 percent, and then falls slowly to the end of the run, reaching a value of a little over 32 percent. The energy efficiency falls off steadily during the run, ending at about 24.5 percent. The efficiencies obtained in Run 2 are higher than those in Run 1, though the curves are quite alike in form. The temperature rose about 5° from its lowest point, 4° of this rise occurring in the last twenty minutes of this run.

Efficiency Run 3

By the time Run 2 was ended, the graphite electrodes had disintegrated to such an extent that it was impossible to use them any longer. Consequently, they were replaced by lead electrodes which occupied the same positions in the cell. The electrolyte was again filtered to remove the carbon particles, and when clean was put back into the cells. Everything else remained as before. The data are given in Table III.

TABLE III.

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P*f*	V. E.	C. E.	E. E.
17.0°	104.5	1.07	60	45.5	0.45	20.5	53.7	43.5	42.1	34.2
16.5	102.5	0.97	35	45.0	0.44	19.8	35.5	43.8	45.4	56.6
15.8	105.5	0.88	20	45.0	0.50	22.5	21.6	42.7	56.8	—
15.5	105.5	0.92	20	45.0	0.50	22.5	20.6	42.7	54.4	—
15.0	102.5	0.97	35	44.0	0.54	23.8	35.3	42.9	58.8	68.0
15.0	106.6	1.02	40	46.5	0.57	26.5	36.8	43.7	55.8	66,2
15.0	103.5	0.92	50	45.5	0.48	21.8	52.5	44.0	54.4	43.6
Average,		0.964					36.5	48.3	52.1	53.7
15.5	105.5	1.52	70	40.0	1.15	46.0	43.7	38.0	75.7	65.7
15.5	102.5	1.38	80	38.5	1.15	44.3	56.5	37.7	83.4	55.5
15.5	104.0	1.42	90	39.5	1.25	49.3	60.9	38.0	88.1	54.8
15.2	104.0	1.46	70	39.5	1.15	49.5	46.1	38.0	79.8	65.2
15.0	108.0	1.42	80	41.0	1.25	51.2	52.1	38.0	88.1	64.0
15.0	105.5	1.50	85	40.5	1.15	41.6	53.6	38.4	76.7	48.9
15.0	100.0	1.46	85	38.0	1.15	43.7	58.2	38.0	79.8	51.4
Average,		1.451					53.0	42.2	81.5	57.93
15.0	105.5	2.30	185	38.5	1.70	65.5	76.2	36.5	73.9	35.4
15.0	105.5	2.20	180	37.0	1.65	61.1	77.6	35.5	75.0	33.9
15.1	108.5	2.40	210	38.0	1.74	66.2	80.6	35.0	72.5	31.5
15.0	107.0	2.20	190	38.0	1.74	66.2	80.6	35.5	79.2	34.8
15.0	102.5	2.40	210	37.0	1.74	64.4	85.5	36.1	72.5	30.7
15.0	102.5	2.20	185	35.0	1,67	58.5	82.0	34.2	76.0	31.6
15.0	103.5	2.30	190	36.0	1.60	57.5	80.0	34.8	69.7	30.3
Average,		2.285					80.3	39.4	74.1	32.6
15.0	101.5	3.10	260	33.0	2.35	77.6	82.6	32.5	75.8	29.9
15.0	105.0	3.05	265	35.0	2.40	84.0	82.8	33.3	78.8	31.7
15.0	103.5	3.30	300	34.0	2.50	85.0	87.6	32.9	75.4	28.3
15.0	106.0	3.40	315	34.5	2.50	86.2	87.2	32.5	73.6	27.4
15.0	106.5	3.20	325	35.0	2.45	85.8	95.5	32.9	76.7	26.4
15.0	107.5	3.20	285	35.5	2.45	87.0	82.8	33.1	76.7	30.5
15.0	105.5	3.10	280	33.5	2.35	78.8	85.6	31.8	75.8	30.6
Average,		3.193					86.3	36.3	76.1	29.25

Table III.—(*Continued*).

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	Pf	V. E.	C. E.	E. E.
15.8	101.0	4.00	340	32.5	3.20	104.0	84.2	32.2	80.0	30.6
16.0	103.5	4.00	350	32.0	3.05	97.5	84.5	30.9	76.3	27.9
16.0	105.0	4.00	360	32.0	3.10	99.2	85.8	30.5	77.6	27.5
16.0	103.5	4.10	380	31.5	3.20	100.7	89.5	30.4	78.0	26.7
16.0	99.5	4.05	380	30.0	3.20	64.0	94.4	30.2	77.1	24.1
16.0	104.5	4.20	390	31.5	3.30	104.0	88.9	30.1	78.6	26.7
16.0	107.5	4.20	385	32.5	3.25	105.5	91.5	30.2	77.4	27.4
Average,		4.078					88.4	33.5	77.85	27.27
16.0	106.5	5.60	550	30.5	4.25	127.5	92.2	28.9	75.9	23.2
16.8	106.0	5.70	525	31.0	4.30	133.2	87.0	29.3	75.5	25.4
17.0	102.5	6.10	560	30.0	4.40	132.0	89.8	29.3	72.2	23.6
17.0	106.0	5.90	565	31.0	4.30	133.2	90.4	29.3	72.9	23.6
17.2	104.5	5.30	510	30.5	4.15	126.5	92.1	29.2	78.3	24.8
17.0	105.5	4.80	435	30.5	3.65	111.5	85.0	28.9	76.1	25.6
16.0	98.0	5.10	480	28.5	4.00	114.0	96.0	29.1	78.5	23.8
Average,		5.50					90.3	32.4	75.63	24.25
16.0	100.5	6.60	590	28.0	5.00	140.0	88.9	27.9	75.8	23.8
16.2	102.5	6.70	630	30.0	5.05	151.5	91.7	29.3	75.4	24.1
16.0	102.5	5.70	520	30.0	5.00	150.0	89.0	29.3	87.8	28.9
16.0	105.5	6.80	660	30.0	5.50	165.0	92.0	28.4	80.9	25.0
16.0	100.5	7.10	695	29.5	5.65	166.8	97.5	29.3	79.6	24.0
16.0	103.0	6.90	660	30.0	5.32	159.6	92.9	29.1	77.2	24.2
16.0	103.0	6.80	635	29.5	5.05	149.0	90.6	28.7	74.4	23.5
Average,		6.65					91.8	32.2	78.7	24.8
17.0	102.5	8.30	790	29.0	6.70	194.1	93.0	28.3	80.8	24.6
17.0	102.5	8.30	800	29.0	6.50	188.5	94.0	28.3	78.4	23.6
17.0	103.5	7.70	725	29.3	6.00	175.8	91.0	28.3	78.1	24.3
17.0	102.5	8.00	750	28.5	6.25	178.0	91.5	27.8	78.1	23.7
17.0	100.0	8.00	760	27.0	6.40	173.0	95.0	27.0	80.0	22.8
Average,		8.06					92.9	31.1	79.1	23.8

The run was begun with a direct current output of about 0.5 ampere and carried up to 6.4 amperes. The curves obtained begin at higher values and, in general, lie higher than those in Runs 1 and 2.

The power factor rises gradually from 36 percent at the start to 88 per cent at about half load, and then increases very slowly to full load reaching a value of nearly 93 per cent. The current efficiency rises from 52.1 percent at the lowest load to about 78 percent at half load, and then remains constant until the end of the run. The voltage efficiency, starting at 49 percent, fell off to 34 percent at half load, and then dropped off very slowly to the end of the run. The energy efficiency fell off fairly rapidly up to half load and then decreased slightly to full load. In this run the current carried was somewhat in excess of that in either of the two previous runs. The temperature changed very gradually and finally reached a point at the end of the run only two degrees above the lowest point.

Efficiency Run 4.

The conditions in this run were exactly the same as in Run 3; the current, however, reached a much larger value, Table IV.

TABLE IV.

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P/	V. E.	C. E.	E. E.
16.0°	109.0	0.98	65	49.0	0.55	26.9	60.8	44.9	56.1	41.5
15.5	110.5	1.00	70	50.0	0.55	27.5	63.4	45.2	55.0	39.3
15.0	108.0	1.04	75	49.0	0.56	27.4	66.6	45.4	53.8	36.5
15.0	108.5	1.08	80	50.0	0.57	28.5	68.3	46.1	52.7	35.7
15.0	107.5	1.04	75	49.0	0.56	27.4	67.0	45.6	53.8	36.5
15.0	108.5	0.98	68	49.0	0.55	26.9	64.0	45.2	56.1	39.6
15.0	107.5	1.04	68	47.5	0.55	26.1	60.8	44.2	52.9	38.4
Average,		1.02					64.4	50.4	54.2	38.2
16.0	108.5	3.0	265	41.0	2.20	90.2	81.5	37.8	73.3	34.1
15.8	105.5	2.7	230	39.0	2.15	84.0	87.2	37.0	79.7	36.5
15.8	106.0	2.8	265	39.5	2.20	87.0	89.0	37.3	78.6	32.8
16.0	105.5	3.0	275	39.0	2.40	93.6	87.0	37.0	80.0	34.1
16.0	107.5	2.7	230	39.0	2.15	84.0	79.2	36.3	79.7	36.8
15.5	105.5	2.8	275	37.5	2.15	80.7	93.1	35.5	76.7	29.4
15.5	105.5	2.7	235	37.0	2.10	77.9	82.5	35.1	77.8	33.1
Average,		2.81					85.3	40.8	78.0	33.3

TABLE IV.—(*Continued*).

	Alternating			Direct			Percent efficiency			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P*f*	V. E.	C. E.	E. E.
16.0	107.5	4.5	450	36.5	3.70	135	93.2	34.0	82.2	30.0
16.2	107.0	4.0	380	36.5	3.40	124	88.5	34.1	85.0	32.7
16.2	108.5	4.4	430	36.5	3.35	122	90.1	33.7	76.1	28.5
16.1	107.5	4.4	440	36.0	3.40	123	93.0	33.5	77.3	27.9
16.1	105.5	4.2	380	35.0	3.23	113	85.8	33.2	76.9	29.8
16.0	107.5	4.3	400	35.5	3.30	117	86.5	33.0	76.7	29.3
16.0	106.5	4.2	370	35.5	3.25	116	82.6	33.3	77.5	31.2
Average,		4.3					88.5	38.7	78.8	29.9
15.0	104.5	5.8	560	31.5	4.45	140	92.5	30.1	76.7	25.0
16.0	103.5	5.4	510	31.5	4.30	136	91.2	30.4	79.7	26.6
16.0	104.5	5.5	550	31.5	4.45	140	95.8	30.1	81.0	25.5
16.0	103.5	5.3	505	30.5	4.25	130	92.0	29.5	80.3	25.7
16.0	103.0	5.2	495	29.5	4.15	122	92.4	28.7	79.8	24.7
16.0	104.5	5.7	465	28.5	4.40	126	78.1	27.3	77.2	27.0
16.0	105.5	5.7	495	31.0	4.39	136	82.3	29.3	77.1	27.7
Average,		5.5					89.4	34.3	77.7	26.0
17.0	101.5	7.5	700	27.5	6.05	167	92.0	27.1	80.7	23.8
17.5	105.5	8.3	830	29.5	6.40	189	94.7	27.9	77.3	22.7
18.0	106.0	8.3	850	30.0	6.50	195	96.7	28.3	78.5	22.9
18.0	103.5	8.1	815	28.0	6.50	182	97.1	27.1	80.3	22.3
18.0	106.0	8.0	800	30.5	6.35	194	94.3	28.3	79.5	24.2
18.0	105.5	8.3	815	30.0	6.40	192	93.0	28.4	77.2	23.5
18.0	105.5	8.1	800	30.0	6.25	188	94.3	28.4	77.7	23.5
Average,		8.1					94.5	31.2	78.7	23.3
19.0	103.5	11.9	1190	27.5	9.20	253	96.6	26.6	77.3	21.3
20.0	104.0	11.8	1180	27.5	9.35	277	96.0	26.4	79.3	23.5
20.0	102.5	12.4	1230	27.5	9.65	265	96.9	26.8	77.8	21.5
20.5	103.0	12.0	1160	27.0	9.35	253	93.8	26.2	77.9	21.9
20.5	101.5	11.8	1150	27.0	9.35	253	96.0	26.6	79.2	22.1
21.0	101.5	12.3	1230	27.0	9.60	259	98.5	26.6	78.0	21.0
21.5	104.0	12.3	1240	27.5	9.50	261	97.0	26.4	77.3	20.9
Average,		12.1					96.4	29.9	78.1	21.7

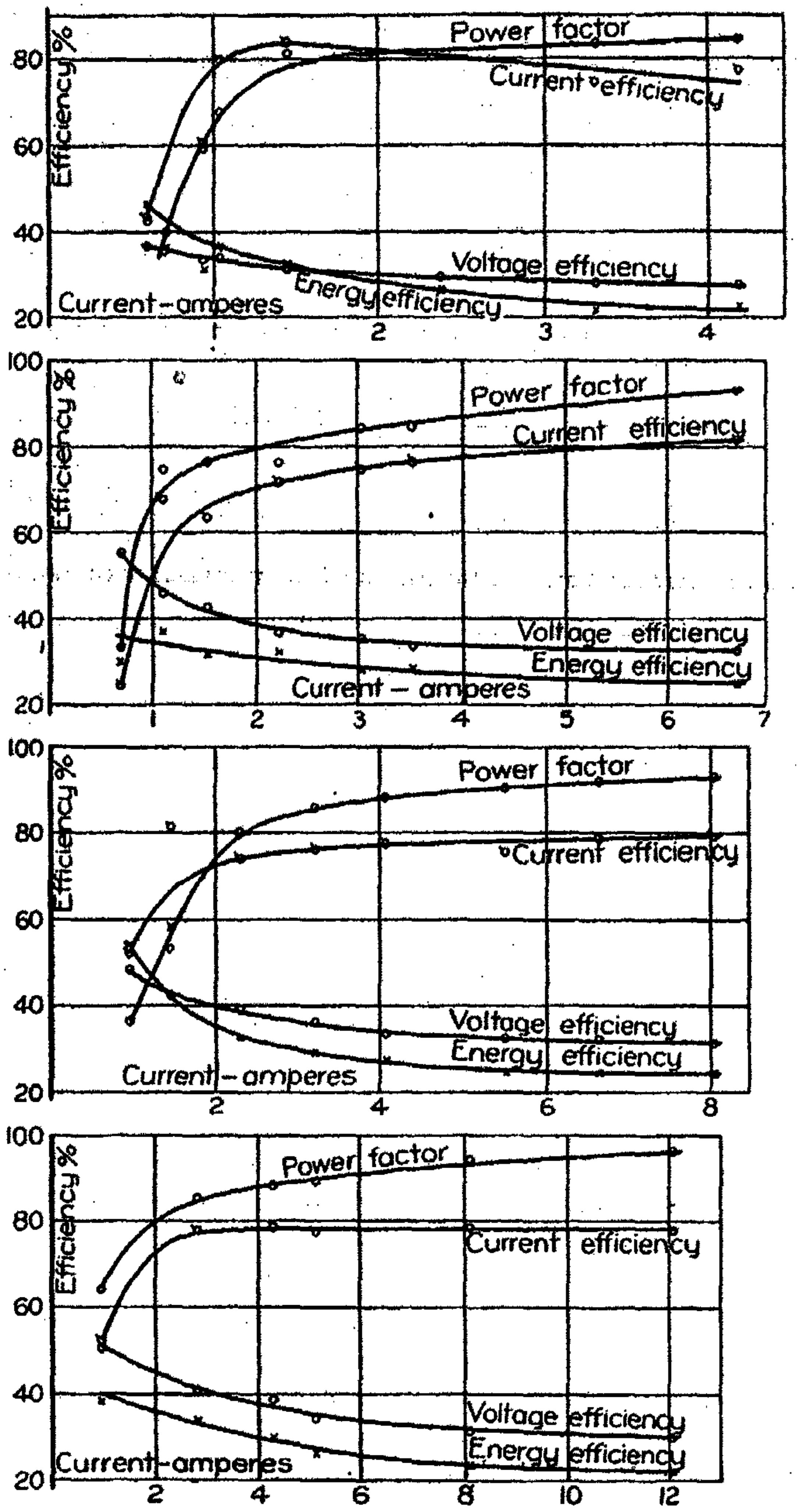
Efficiency %
Power factor
Current efficiency
Voltage efficiency
Energy efficiency
Current-amperes
20
40
60
80
100
1
2
3
4
5
6
7
8
10
12

Fig. 5.

The power factor rose rapidly at first from its starting point at 64 percent, and then increased more slowly toward the end, reaching a value of 96.4 percent. The current rose rapidly just at the start, and then, as in the previous run, remained constant during the greater part of the run, at 79 percent. The voltage efficiency fell off in the usual way from 51 percent at the start to 30 percent at the end.

The current carried in this run was quite heavy, over 12 amperes on the alternating current side. In spite of this, the tubes, when examined, showed no signs of wear whatever, and were apparently in as good condition as when they were first put into operation, indicating that the life of the tube under ordinary conditions would be quite long. The results of the four runs are shown graphically in Fig. 5, the abscissas being amperes on the alternating current side.

Efficiency Runs 5 and 6.

After making the runs already discussed, it was decided to try an experiment. Half the electrolyte was removed, and its place was taken by sulphuric acid of sp. gr. 1.2. As the critical pressure of sulphuric acid is about 65 volts, the run was made on 55 volts.

All the previous runs had been made on 110 volts, and to obtain 55 volts it was necessary to put in another transformer. This was done and the runs were taken as before, except that their duration was somewhat shorter.

Run 5. This run was begun at a direct current output of 0.5 ampere, and carried to an output of 5 amperes. The data are given in Table V. The power factor rose steadily from 66 percent to 93 per cent. The current efficiency rose from 55 percent at the start to 80 percent at about half load, and then fell off slightly to the end of the run. The voltage efficiency ran down steadily from 32 percent to 23 percent. The energy efficiency fell off to 17 percent at the end of the run, the lowest value yet reached.

Run 6. This was similar in all respects to Run 5, but was carried a trifle further. The data are given in Table VI.

TABLE V

	Alternating			Direct			Percent efficiency				
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts.	P*f*	V. E.	C. E.	E. E.	Drop
17.0°	53.5	1.54	65	16.5	0.95	15.7	78.8	34.3	61.7	24.4	6.0
17.0	54.0	1.08	30	18.0	0.56	10.1	51.4	36.3	51.9	33.7	6.5
17.0	53.5	1.08	45	15.5	0.61	9.45	78.0	32.3	56.5	21.0	6.5
16.5	53.5	1.05	40	13.0	0.55	5.2	69.3	27.1	52.4	13.0	7.0
16.5	52.5	0.97	25	16.5	0.50	8.25	49.5	34.9	51.6	33.0	9.0
16.5	53.5	1.08	40	15.5	0.60	9.30	69.4	32.2	55.5	23.3	8.0
Average,		1.13					66.06	32.85	54.93	24.73	7.16
17.0	52.5	2.5	100	12.0	1.9	23.8	76.2	25.4	76.0	23.8	5.5
17.0	52.5	2.9	110	13.0	2.1	27.3	72.4	27.5	72.5	24.8	6.0
17.0	51.5	3.0	108	12.5	2.0	25.0	70.0	27.0	66.8	22.2	6.0
17.0	53.5	2.8	105	13.0	2.0	26.0	70.1	27.0	71.5	24.7	5.5
17.2	54.5	3.0	120	13.0	2.2	28.6	73.4	26.6	73.4	23.8	6.0
18.0	53.0	2.5	95	12.0	1.9	23.8	71.6	25.2	76.1	25.1	7.0
Average,		2.783					72.3	26.45	72.71	24.06	6.0
18.0	52.0	3.4	150	12.0	2.75	33.0	85.0	25.5	80.8	22.0	6.5
18.2	51.5	3.5	145	12.0	2.90	34.8	80.5	25.9	82.8	24.0	6.5
18.0	52.5	3.6	155	13.0	3.00	39.0	82.0	27.5	83.3	25.1	6.2
18.0	51.5	4.0	170	14.0	3.1	43.4	82.5	32.0	77.5	25.5	6.5
18.0	51.5	4.0	155	13.5	3.1	41.9	75.5	29.2	77.5	27.1	6.5
18.2	51.5	3.7	140	13.0	2.95	38.4	78.5	28.1	79.7	27.4	6.5
Average,		3.7					80.66	28.03	80.26	26.2	6.44
18.2	50.5	6.9	320	10.5	5.50	57.7	89.0	23.1	79.8	18.05	5.0
20.2	48.5	6.7	312	10.0	5.25	52.5	96.0	22.9	78.3	16.85	5.0
20.0	50.5	6.5	310	10.9	5.10	55.5	94.5	24.9	78.5	17.9	5.0
20.0	49.5	5.8	360	9.5	4.70	44.5	—	21.3	81.1	12.4	5.0
19.0	48.5	6.0	250	10.0	4.85	48.5	86.0	22.9	80.8	19.4	5.0
19.0	50.5	6.4	285	10.5	5.00	52.5	96.0	23.1	78.1	18.4	5.0
19.0	50.0	6.3	310	10.5	4.90	51.5	98.5	23.3	77.8	16.6	5.9
Average,		6.37					93.3	23.07	79.2	17.08	5.0

TABLE VI

	Alternating			Direct			Percent efficiency				
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P_f	V. E.	C. E.	E. E.	Drop
17.0°	53.5	0.55	15	18.0	0.35	6.3	51.0	37.5	63.6	42.0	8.5
17.0	51.5	0.45	10	15.0	0.28	4.2	43.5	31.7	62.3	42.0	8.2
16.5	53.5	0.50	15	16.0	0.30	4.8	56.5	33.3	60.0	32.0	8.5
16.0	53.5	0.55	20	16.5	0.38	6.3	67.8	34.3	69.1	31.3	8.0
Average,		0.487					54.7	34.2	63.75	38.82	8.3
17.0	51.5	1.5	55	13.0	1.2	15.6	71.2	28.1	80.0	28.4	6.0
17.0	51.5	1.6	60	12.5	1.3	16.25	72.5	27.5	81.2	27.1	5.5
17.0	51.0	1.7	60	12.5	1.3	16.25	69.5	27.3	76.5	27.1	6.0
17.0	52.5	1.9	70	13.0	1.45	18.85	70.4	27.5	76.3	22.0	6.0
Average,		1.675					70.9	27.6	78.5	26.15	5.875
17.0	52.5	2.7	100	13.0	2.0	26.0	70.5	27.5	74.0	26.0	6.0
17.2	51.5	3.0	120	11.5	2.4	27.6	78.7	25.4	80.0	26.0	6.0
17.6	51.5	3.1	110	13.0	2.35	30.6	69.0	28.1	75.9	27.8	5.5
18.0	51.5	3.0	105	13.0	2.2	28.6	68.0	28.1	73.3	27.2	5.5
Average,		2.95					71.55	27.27	75.8	26.75	5.75
18.0	48.5	7.5	295	8.0	6.2	49.6	81.2	18.4	82.8	16.8	4.5
18.5	50.0	6.0	270	9.0	4.7	42.3	90.0	20.0	78.4	15.65	5.5
19.0	51.5	5.9	265	9.5	4.6	43.7	87.2	20.5	78.0	16.5	5.0
20.0	48.5	8.4	380	10.0	6.8	68.0	93.5	22.9	81.0	17.8	5.0
Average,		6.95					88.9	20.45	80.05	16.68	5.0
Run at very low pressure											
16.0	29.5	0.88	18	8.5	0.38	3.23	69.3	30.5	43.2	18.0	
16.0	31.5	0.88	10	9.0	0.35	3.15	36.1	31.8	39.9	31.5	
16.0	32.5	0.75	11	9.7	0.39	3.78	45.1	33.05	32.0	35.5	
Average,		0.836					50.1	31.78	38.36	28.3	

The power factor is lower, reaching only 89 percent. The current efficiency rose from 63 percent to 78 percent and then very slowly to 80 percent. The voltage efficiency fell off steadily from the start, and the energy efficiency dropped to 16.7 percent, the lowest obtained.

The last run was very short, owing to the fact that the temperature began to rise very rapidly toward the end.

In both runs the efficiencies obtained were, in general, lower than those obtained in the first four runs. It was further found, on examining the tubes, that the sulphuric acid had corroded the tubes so much that they were practically useless for further work. It was found on trial with the pressure at 110 volts and the electrolyte phosphoric acid, that the tubes could not be made to work, and so the investigation was stopped at this point.

Some of these results were quite unexpected. A leakage current would of course account for a low current efficiency at low current; but it is very surprising to find the current efficiency rising rapidly to about 80 percent in all the runs and then remaining practically constant. So long as one assumes the existence of mechanical valves a heavy leakage current is not unreasonable; but we do not believe in valves any more. We have not yet had time to make tests on the influence of depolarizers on the current efficiency, but we hope to do this before long and also to determine the wave forms of the current entering and leaving the rectifier.

The low energy efficiency is due to the low voltage efficiency. The internal resistance of the rectifier was not determined. An examination of the current-voltage curve shows that this is not a straight line. We have therefore a changing resistance, a changing electromotive force or both. The loss in voltage cannot be due solely to the internal resistance of the rectifier, this being not over a few ohms. There is apparently a counterelectromotive force which increases with increasing current and which has a value of 50-60 volts[1].

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[1] Cf. Isenburg: Zeit. Elektrochemie, 9, 278 (1903).

The general results of this paper are:

1. Water-cooled aluminum electrodes in a phosphoric acid solution are satisfactory mechanically.

2. A current efficiency of 75-80 percent can easily be obtained over a fairly wide range of current.

3. Under the conditions of the tests, the voltage efficiency of the aluminum rectifier may be taken as 30-35 percent and the energy efficiency as 20-30 percent.

4. With increasing load the power factor rises rapidly to above 90 percent.

5. The chief cause of the voltage loss is not the internal resistance of the rectifier. The results can be explained by assuming a counterelectromotive force increasing with the current and having a value of 50-60 volts over part of the range studied.

This work has been carried out under the supervision of Prof. Bancroft. My thanks are also due to Messrs. Carveth and Mott for suggestions and to the Department of Electrical Engineering for the loan of instruments.

Cornell University.

A CONTRIBUTION TO THE THEORY OF SOLUTION

BY GEOFFREY MARTIN

1. Sphere of Molecular Activity

Consider any one molecule *m* inside a fluid. It is surrounded by a group of molecules. If we take all these molecules which lie within a sphere of extremely small radius whose centre is *m*, there is a special action exerted on *m* by each molecule within this sphere, those molecules nearest to *m* exerting a more powerful action than those near the surface of the sphere. Beyond a certain distance ϵ from *m* these special actions are assumed to be insensible. This length ϵ is the radius of the aforesaid sphere, called the *sphere of molecular activity.*

ϵ is an arbitrary distance, which *decreases* as we increase the motion of the molecules; for the molecules of a fluid are in incessant motion and in consequence of this motion are in a state of incessant flux to and fro about every point in the liquid so that every molecule remains on an average under the influence of another for a short time *t*, as they pass each other in the liquid, —*t* depending on the velocity of the molecule, and the greater is the velocity the smaller is *t*. If, now, in the time *t*, during which the molecule A is under the influence of the molecule B, the distance ϵ which separates them is so wide that the force which A exerts has in this time no appreciable influence in curving the path of B, we assume that this distance ϵ is the required limit of the sphere of molecular activity.

If, now, the velocity of the molecules be increased, the average time *t*, during which one molecule is under the action of another, will *diminish;* and therefore, in order that the *force* F which the one molecule must exert on the other in order to produce an appreciable curvature in this shorter time *t*, the molecules must now *approach* each other *closer* than previously, for this will make the attractive force stronger, and so neutralize the smaller *time* for which the forces act. It is clear, therefore, that ϵ *decreases*, and F *increases* as the velocities of the molecules *increase;* and vice-versa.

That is to say, ϵ *decreases* and F *increases* as the temperature increases; and conversely ϵ *increases* and F *decreases* as the temperature of the liquid falls.

It is owing to this fact (as we shall prove later) that the solubility *increases* with the temperature and *decreases* with *fall* of temperature.

2. Every Dissolved Molecule in a Liquid is Surrounded by a Vacuum

Consider now a liquid whose molecules are all of the same kind. Then the molecules will on the average be arranged symmetrically about every point within it. If, however, we introduce into the liquid a foreign molecule m (see Fig. 1), the foreign molecule will form a centre of disturbance and destroy the symmetrical structure of the liquid about it. For, consider any molecule M_1 of the liquid. Describe about M_1 the sphere of molecular activity ABC of radius ϵ. Now take any other molecule M_2 of the liquid which lies on this sphere of molecular activity, and describe about M_2 its sphere of molecular activity ABD. Then M_2 and every molecule beyond M_2 is unaffected by M_1 and vice versa. Let now the molecule M_1 be replaced by a foreign molecule which is different in nature from the other surrounding molecules of the liquid. Two cases must be considered:

Case I. When the molecules of the liquid attract each other more strongly than they attract M_1.

Case II. When the molecules of the liquid attract each other less strongly than they attract M_1.

Case I.—Consider any molecule m (see Fig. 1) in the interval between M_1 and M_2. Describe about m its sphere of molecular activity A′B′C′. Then m is pulled in the direction mB′ by the

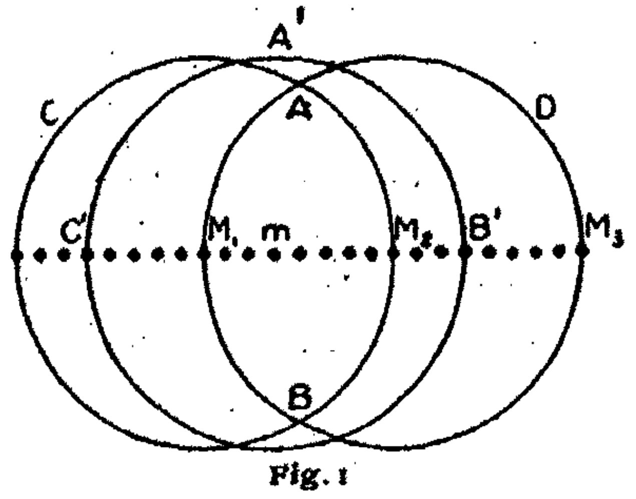

Fig. 1

united action of the molecules which lie in the line mB'. Similarly m is pulled in the contrary direction by the action of the molecules which lie in the line mC'. But since the molecule M_1 exerts a *weaker* pull on m than it could exert were it the molecule of the liquid it has displaced, it is clear that there will be a resultant force exerted on m in the direction mB'; and so m will tend to move away from M_1 until it passes beyond the sphere of molecular activity ABC. Every molecule of the liquid within the sphere of molecular activity of M_1 will be acted upon by a resultant force tending to direct it away from M_1. A sort of vacuum bubble will therefore form around M_1, and M_1 will continually travel about the liquid in this vacuum bubble; for as it moves forward the molecules of the liquid will be drawn away from before it, so that the dissolved molecule will possess great freedom of movement, behaving, in fact, as if it were in a vacuum.

This puts us in a position to understand why van 't Hoff's law of osmotic pressure should hold true. Van 't Hoff believes that a substance dissolved in a liquid exerts the same pressure on the walls of the vessel as were the solvent imagined removed and the dissolved substance existed in a gaseous state in the space occupied by the liquid. This view has been seriously questioned by many authors of great mathematical repute. For example, Prof. Oskar Meyer remarks regarding this point[1]: " . . . Osmotic pressure is not one of the phenomena which the kinetic theory of gases has to explain. I will also not conceal that I do not think van't Hoff's views of the kinetic nature of osmotic pressure to be correct. For osmose does not arise from the kinetic pressure of the dissolved substance, but from quite different forces. . . . "

These authors have, however, entirely neglected the fact that all kinds of molecules do not exert attractive forces of the same intensity. For example, the molecules of carbon exert an enormous attractive force on each other, as is shown by the extraordinary hardness and involatility of certain forms of carbon. Oxygen, helium, nitrogen molecules, however, exert but a feeble attractive force on each other.

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[1] Kinetic Theory of Gases, English Translation (1899), p. 367.

Case II.—Here the molecules of the liquid attract M_1 more strongly than they attract themselves. In this case the molecules of the liquid combine with M_1, and the combination will proceed until the molecules of the liquid attract each other more strongly than they attract the new compound, so that the case reduces to Case I, but with this difference—the new unit is not the original molecule M_1 but the compound formed between M_1 and the liquid molecules. Traces of such compounds are very often met with in solution.

In this connection it should be observed that when a molecule adds on atoms or molecules to *itself*, the *intensity* of the external molecular attraction it exerts usually *diminishes*. For example in organic chemistry saturated compounds are more volatile than unsaturated compounds of the same molecular weight. In inorganic chemistry, compounds of a high valency grade are *more* volatile than compounds of the same molecular weight but of a lower valency grade. Unstable compounds are, in general, more volatile and fusible than stable compounds of the same molecular weight, and the addition of atoms to a molecule decreases its stability. This matter is fully discussed in an earlier paper[1], to which the reader is referred.

3. Magnitude of the Repulsive Force R Exerted on m at any Distance d from M_1

The repulsive force R exerted on *m* (see Fig. 1) at a distance *d* from M_1 is clearly the difference in the intensity of the force which a *molecule of the liquid* if *at* M_1 would exert on *m*, and the force which the foreign molecule M actually exerts. (Compare Archimedes Principle in Hydrostatics.)

If at a distance *d* a *liquid molecule* exerts a force F (*d*), and if at a distance *d* a *foreign molecule* exerts a force *f*(*d*), then the repulsive force R acting on *m* at a distance *d* is

$$R = F(d) - f(d). \qquad (1)$$

If we assume (as is always done by writers on molecular physics—principally, by the way, because it is *convenient*) that the law with which the force *decays* with the distance is the *same* for all kinds of molecules, the equation (1) assumes a

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[1] Chem. News, 89, 241 (1904).

much simpler form; for $f(d)$ now becomes $k.F(d)$, where k is a constant *less* than unity. Hence

$$R = (1 - k).F(d). \qquad (2)$$

If the foreign molecules exert forces of the *same intensity* as the liquid molecules, then in (1) $f(d) = F(d)$ and $R = 0$; and in (2), $k = 1$ and $R = 0$. This is the case when the compounds are *chemically similar*, as I will show in a paper which will be published later.

4. *Limit of Solubility*

Consider the molecule B of the foreign substance traveling in the middle of a "vacuum bubble" in the interior of the liquid. Suppose now a molecule A of the liquid to move towards B. Then as it approaches the surface of the bubble it will begin to be acted upon by a force tending to pull it backwards into the liquids. Consider now the two foreign molecules B,B′ to be close together, and consider a molecule A of the liquid situated as in the figure. Then A will be attracted *away* from B in the direction AF; and away from B′ in the direction AF′. Consequently, there will be a resultant force R acting on A tending to drive it *away* from the line B,B′ joining the molecules

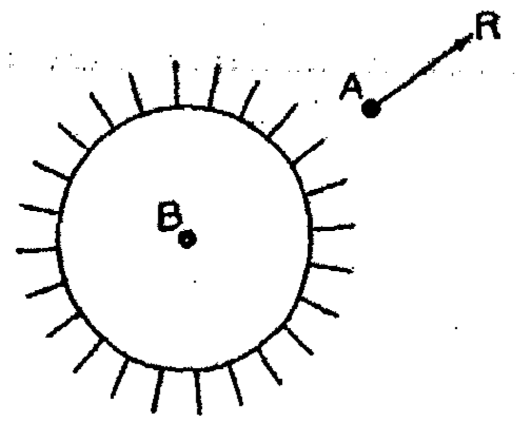

Fig. 2.

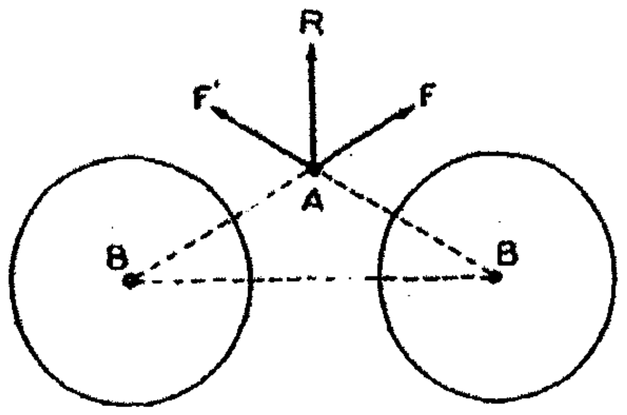

Fig. 3.

B,B′. Consequently, the two molecules B,B′ will tend to draw together in the liquid as soon as B comes within the sphere of attraction of B′.

Now before the molecule A of the liquid will be repelled away from the line BB′, the force exerted on A must be of an appreciable magnitude F (see Section 1). Consequently, so long as the molecules B,B′ are at such a distance *apart* that the force exerted on A is smaller than F, A will not tend to move away from the line BB′, and so B and B′ will not tend to draw together.

Whence we arrive at the cause of the limited solubility of one body in another. *A liquid can only dissolve so many molecules that the average distance between any two of these molecules is greater than the critical distance, whereat the repulsive force R reaches a certain minimum value F depending upon the temperature, molecular weight, and nature of the liquid.* If a greater number of molecules B,B′ are dissolved in the liquid, the molecules will *draw* together, and separate *out* until the average distance between the dissolved molecules becomes greater than this *critical* distance.

5. *Reason why the Solubility Increases with the Temperature*

The minimum repulsive force F (see Section 1) *increases* as the kinetic energy of the molecules of the liquid increases; and conversely diminishes as the kinetic energy of the molecules diminishes. Consequently the molecules of the liquid can approach *nearer* at high temperatures than at low temperatures without being repelled; so that B and B′ can approach *nearer* together without being drawn together when the liquid is hot than when it is cold; so that in general the *solubility* of the molecules of B in the liquid A must *increase* or *decrease* as the temperature *increases* or *decreases*.

6. *The Cause why Chemically Similar Substances are Miscible in all Proportions, and Chemically Unlike Substances usually Unmiscible*

The repulsive force (see Section 3) exerted on a molecule is

$$R = F(d) - f(d) \quad \text{or} \quad R = (1 - k).F(d).$$

If the two compounds are *chemically similar*, in general $f(d) = F(d)$; or $k = 1$. Then in this case $R = 0$, and the *minimum* repulsive force F is never attained, no matter how closely A approaches to B. Consequently, the two molecules B and B′ do not tend to draw together and separate out. Hence the molecules B are in this case miscible in all proportions among the molecules of A. If, however, the two substances are not chemically similar, then in general R has always a finite magnitude greater than F and so the two liquids will separate out into two layers when the molecules of B assume more than a definite average distance apart in the manner previously described.

In hydrostatics a cork tends to be expelled out of the water *because* the water it displaces weighs *more* than the cork; whereas a body of the same density as water does not tend to separate out from water. Similarly, a *chemically dissimilar* molecule tends to be expelled from among the intermolecular interstices of a liquid because the force it exerts on the surrounding molecules is *less* than the force which the molecule of the liquid it *displaces* exerts, and a *chemically similar* molecule does not tend to be expelled out of the molecular interstices of the liquid because the forces it exerts are of the same magnitude as those of the liquid molecule it has displaced.

7. *Why Molecules so often Dissociate when they Pass into Solution*

A molecule A in the interior of a liquid is surrounded equally on every side by other molecules, each of which exert an attractive force on A. The molecule of A, then is subjected to an outward tension directed equally in all directions. This tension has been called by Lord Rayleigh[1] the intrinsic pressure of the liquid. If the molecule A is not of a rigid enough constitution, it would tend to expand out in every direction under the action of these attractive forces. This is the reason why so many molecular systems, when they pass into solution, decompose under this strain into their constituent atoms or ions. It is only when the internal attractive force holding the constituent parts of the molecule together is greater than the "internal tension" of the liquid that the molecule holds together undissociated in the liquid.

University of Kiel
Oct. 19, 1904.

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[1] Phil. Mag. October, 1890.

NEW BOOKS

High-Temperature Measurements. *By H. Le Chatelier and O. Boudouard. Authorized Translations and Additions by G. K. Burgess. Second edition, revised and enlarged. 12 × 18 cm; pp. xv + 341. New York: John Wiley and Sons, 1904. Price: $3.00.*—The appearance of the second edition of the translation of this book gives some idea of the interest in high temperature measurements. The text has been increased by one hundred pages, the new matter being chiefly in the division on heat radiation and optical pyrometry.

The chapter on electrical resistance pyrometry has been amplified but is still much too brief. A few indefinite statements occur. Thus (p. 86) "The vapor density of this substance (iodine) decreases with rise of temperature, this effect being attributed to a doubling of the iodine molecule." Failure to letter the cut (p. 38) makes the text difficult reading. Following the French edition, many of the cuts are unlettered and a few are not even described. Descriptions of the Féry and Wanner pyrometers have been included.

The chapter on recording pyrometry has been brought up to date by including Saladin's ingenious, but not very useful instrument. The fact that no accurate calibration of this instrument is possible, limits its usefulness to relative determinations of the critical points of steel.

In the chapter on standardization one meets the old error, of assuming that the temperature to which a substance rises, after surfusion, is the freezing-point. However, this chapter collects all of the most reliable information as to fixed points and in this respect will prove very useful to users of pyrometers.

Throughout, the translator has kept the limitations of the instruments well in mind, but he could have placed more emphasis on the relation between the resistance and thermoelectric pyrometers. Every year sees students trying to measure temperatures of one or two hundred degrees with a platinum-rhodium thermocouple.

This revision is a great improvement over the French edition but one is tempted to quarrel with the translator for not giving us a new book instead. It is not the history but the practice of pyrometry that needs elucidation; we need instructions in the actual making of these measurements. Until such a book is forthcoming, the translation will serve as our most complete source of information on high temperature measurements. *E. S. Shepherd*

The Electric Furnace. *By Henri Moissan. Authorized Translation by Victor Lenher. 15 × 23 cm; pp. ix + 302. Easton: The Chemical Publishing Company, 1904.*

The Electric Furnace. *By Henri Moissan. Translated by A. T. de Mouilpied. 14 × 23 cm; pp. x + 307. London: Edward Arnold, 1904. Price: $2.75.*

While a translation of Moissan's book is much to be desired, it seems a pity to overload the market with two. The same thing was done in the case of van't Hoff's lectures. Apparently both translations are authorized since the American edition contains a special preface by Moissan of date May 10, 1903, and the English edition one dated July, 1904. Both editions contain a great deal that was not in the French original. The pages on the carbides of potassium, sodium, neodymium, praseodymium, magnesium, beryllium and iron are new, and there are a number of extra pages on calcium carbide. The silicides of manganese, nickel, cobalt, copper and platinum were *not* mentioned in the French edition and neither were the borides of calcium, strontium and barium. The chapter on the phosphides, sulphides and arsenides is also new. The English edition, being of later date, contains an account of some compounds not to be found in the American edition, such as samarium and vanadium carbides, and the silicides of vanadium, cerium and tungsten. It must be admitted that the American translation is inferior in point of style to the other, and the absence of an index is very annoying. One translation or the other should be found in every chemical laboratory. *Wilder D. Bancroft*

Recherches sur l'Hydrodynamique. *By P. Duhem. Deuxième serie. 22 × 28 cm; pp. 153. Paris: Gauthier-Villars, 1904.* — Sometime ago (7, 592) we called attention to the *première série* of Duhem's revision of the theory of hydrodynamics, in which the thermal phenomena that hydrodynamic processes involve are brought into the account. A *deuxième série* of these researches has since been issued, treating of limiting conditions, the theorem of Lagrange and viscosity, coefficients of viscosity and viscosity in the neighborhood of the critical state. *J. E. Trevor*

Die Darstellung des Zinks auf elektrolytischen Wege. *By Emil Günther. (Monographien über angewandte Elektrochemie. XVI. Band.) 16 × 24 cm; pp. xii + 241. Halle: Wilhelm Knapp, 1904. Price: paper, 10 marks.* — Three-quarters of the book is devoted to the electrolysis of aqueous solutions of zinc salts. The material is classified primarily as to the solubility or insolubility of the anodes. The Roessler-Edelmann process for refining zinc rich in silver comes under the first head as does also Rontchewsky's laboratory method for getting lead peroxide at the anode and zinc at the cathode. When an insoluble anode is used, the only solutions which need be considered are sodium zincate and zinc chloride. Of the two the latter is the only one which has proved much of a success commercially. The Hoepfner process was worked for a while at Fürfurt and a special form of it is a commercial success in England. As the author worked under Hoepfner at one time, the account of Hoepfner's difficulties and his successes is quite full.

Thirty pages near the end of the book deal with the electrolysis of fused zinc chloride, including the Swinburne-Ashcroft process while another thirty pages are given up to a general statement of costs.

One of the great difficulties in the electrolytic extraction of zinc is the tendency of the zinc to precipitate in an unsatisfactory manner at the cathode. Under these circumstances one would suppose that the first thing to do would be to study systematically the conditions affecting the electrolytic precipitation of zinc. As a matter of fact this apparently has never been done. The work of Mylius and Fromm and of Foerster and Günther is good as far as it goes but it does not begin to cover the ground. It is an open question whether the evil effects of a low current density, p. 145, are not imaginary. No explanation is offered for the beneficial effect, p. 146, of chilling the solutions. Amberg's experiments on the electrolysis of zincate solutions, p. 61, were made for analytical purposes and do not touch the main question at all. The author evidently does not see the bearing of Nahnsen's experiments, p. 65, on the effect of other metals. While Foerster and Günther did not get the 150 percent yield of zinc which Ashcroft is said to have obtained by electrolyzing basic zinc chloride, p. 139, there is no certainty that Ashcroft's conditions were duplicated.

Among the interesting minor points brought out are the deleterious action of pitch, p. 110; the formation of an organic acid, p. 143; and the unexplained difficulty with chlorine in cold weather, p. 163. The book is valuable for what it brings and also because it calls our attention indirectly to what has not been done.

Wilder D. Bancroft

Electric Furnaces and Their Industrial Applications. *By J. Wright. 14 × 22 cm; pp. viii + 288. New York: The Norman W. Henley Publishing Co., 1905.*—This book is an admirable compilation and will be of distinct value in the laboratory. The headings to the chapters are: Historical and general; arc furnaces; resistance furnaces and typical processes; calcium carbide manufacture; iron and steel production in the electric furnace; phosphorus manufacture in the electric furnace; glass manufacture in the electric furnace; electrolytic furnaces and processes; miscellaneous electric furnace processes; laboratory furnaces and experimental research; tube furnaces; terminal connections and electrodes; efficiency and theoretical considerations; measurement of furnace temperatures.

There is a certain lack of proportion in devoting six pages to the Swinburne-Ashcroft zinc process and about half a page, with no cut, to the Castner sodium process. The cut for the Acker process does not represent the furnace as it is. One is also a little inclined to doubt the absolute accuracy of the statement that a temperature of 3867° C is obtained in the Machalske phosphorus furnace five minutes after starting.

A great deal of miscellaneous information has been gathered together and much of this will prove useful to the student. Thus there are descriptions of the furnaces of Hutton and Petavel, Howe, Potter and Heraeus. The kryptol furnace is not mentioned but that is because the book appeared in 1904 though the publishers have seen fit to put 1905 on the title-page. The chapter on temperature measurement is valuable though one should not use a platinum resistance thermometer for temperatures above 500°.

Wilder D. Bancroft

Grundriss der Stereochemie. *By A. Hantzsch. Second enlarged and improved edition. pp. viii + 188. Leipzig: John Ambrosius Barth, 1904. Price: paper, 5.60; bound, 6.40 marks.*—The book begins with a short historical account of the evolution of stereochemistry, followed by 53 pages on isomerism due to asymmetric carbon and 5 on optically active derivatives of nitrogen, sulphur, and tin. The next 48 pages are devoted to the geometrical isomerism of optically inactive carbon compounds, and the remaining 70 to organic compounds containing nitrogen, ammonio-cobalt and platinum derivatives, and Bischoff's *Sterische Hinderungen*.

The stereochemistry of the "ten years" is thus compressed into one-third of the work, the remaining space being reserved for the newer and consequently more interesting developments of the subject.

The readers of this Journal will be specially interested in the numerous cases in which physico-chemical measurements have been used to settle questions of configuration, in the grouping of the bases according to their action on chlorsuccinic acid, in the equilibrium between syndiazo and diazonium compounds, and in the references to problems of chemical kinetics scattered through the book.

There are numerous, though not exhaustive, references to the literature, and a five page index. *W. Lash Miller*

Elektrizität und Materie. *By J. J. Thomson. (Die Wissenschaft, Heft 3). Autorisierte Ubersetzung von G. Siebert. 14 × 22 cm; pp. vi + 100. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: paper, 3; bound, 3.60 marks.*—The current third volume of the promising series of monographs issued under the general title *Die Wissenschaft* is a German translation of J. J. Thomson's Silliman Lectures on Electricity and Matter. The very considerable interest of these lectures has already been pointed out in this Journal (8, 507), in an appreciative review of the original text as published by the Mrs. Hepsa Ely Silliman Foundation. The promptness of the issue of this German version is extremely praiseworthy. *J. E. Trevor*

Abriss der allgemeinen oder physikalischen Chemie. *By Carl Arnold. 13 × 20 cm; pp. viii + 123. Hamburg: Leopold Voss, 1903. Price: bound, 2 marks.*—This book is an example of marvelous condensation, and should be of value to students preparing for an examination. It seems doubtful whether it would be especially valuable to any one just taking up the subject. Ostwald's little book on introductory physical chemistry is condensed to a point that gives the ordinary student mental indigestion and it is a mammoth volume in comparison with this one. *Wilder D. Bancroft*

Grundzüge der Kristallographie. *By C. M. Viola. 16 × 26 cm.; pp. x + 389. Leipzig: Wilhelm Engelmann, 1904. Price: paper, 11; bound, 12 marks.*—This is an elementary text-book by one of the foremost crystallographers of the day, treating the subject in the light of the most recent contributions to the science. The nine chapters after the introduction are devoted to the following topics: Derivation of the fundamental law, crystal drawing, fundamental forms, harmony, shape, intergrowths (*Verwachsungen*), symmetry, chemico-physical relations, and, finally, geometrical structure. The prominence given to the conceptions *cohesion* and *harmony* constitutes, perhaps, the most characteristic distinction from other elementary crystallographies. *A. C. Gill*

Annuaire pour l'An 1905. *Publié par le Bureau des Longitudes. 10 × 15 cm. Paris: Gauthier-Villars. Price, paper, 1.50; post-paid, 1.85 francs.*—The *Annuaire* of the Bureau of Longitudes appears promptly, with its usual extensive tabulations of astronomical, physical, and chemical data. The special feature of the issue is the continuation, from the preceding volume, of the article by M. P. Hatt, giving an elementary account of the tides.

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.

Studies on indium. I. *A. Thiel. Zeit. anorg. Chem.* 40, *280* (*1904*).—When indium is converted into the oxide, its apparent atomic weight varies between 113.4 and 113.9. The conversion of indium into the dichloride, trichloride and tri-iodide did not give satisfactory results. The analysis of indium trichloride gave a value of 115.03 ± 0.02 for the atomic weight of indium, while the analysis of the tribromide gave 114.81 ± 0.07. The value from the oxide is certainly wrong. The author believes that the trichloride results are the most accurate. Provisionally we may consider the atomic weight of indium as 115.

The true melting-point of the metal is 155° instead of 176° as found by Winkler. Indium crystallizes in the regular system. It is very soft and the crystals weld under slight pressure. The hydroxide forms colloidal solutions readily. The oxide is distinctly volatile above 1000°. Conductivity measurements show that the trichloride is about fifty percent hydrolyzed in a M/10000 solution. When the potential difference of the tenth-normal calomel electrode is taken as —0.620 volt, the potential difference between iridium and M/10 indium trichloride solution is + 0.108 volt. In a "second preliminary" paper, Zeit. anorg. Chem. 39, 119 (1904) it is stated that indium can easily be determined quantitatively when a silver cathode is used. *W. D. B.*

Determination of the atomic weight of nitrogen by volumetric analysis of nitrous oxide. *A. Jaquerod and S. Bogdan. Comptes rendus*, 139, *49* (*1904*).—Nitrous oxide is burned at constant volume to nitrogen by means of an electrically-heated iron wire. Knowing the initial and final pressure as well as the densities it is possible to calculate the atomic weight of nitrogen by means of the ratio N_2/N_2O. The result is 14.019 and the authors express their belief that Stas's value of 14.04 is certainly too high. *W. D. B.*

The densities of sulphur dioxide and of oxygen. *A Jaquerod and A. Pintza. Comptes rendus*, 139, *129* (*1904*).—The authors weigh liquid sulphur dioxide before and after filling a known volume with this gas. The weight of a liter under normal conditions is 2.92664g. From data for 760 mm, 570 mm and 380 mm pressure they extrapolate to the density at zero pressure. This limiting density corresponds to an atomic weight for sulphur of 32.01.

W. D. B.

Valency and the periodic system. *R. Abegg. Zeit. anorg. Chem.* 39, *290* (*1904*).—The assumptions made are the following: Each element possesses both a positive and a negative maximum valence, the arithmetical sum of the two always being eight and the value of the positive valence being the same as the number of the group in the periodic system. The negative valences are called contravalences. Whether an element makes use of its positive or negative valences depends on the popularity of the other elements in the compound. When one kind of valence is in use, the other kind is much weakened though not entirely destroyed.

The author discusses the applications of this hypothesis at length. Since ICl reacts with water to form hydrochloric and hypo-iodous acids, the chlorine must be negative and the iodine positive. Since caustic potash converts carborundum into silicates and carbon, the silicon must be positive and the carbon negative. A natural corollary of this would be that since chlorine is certainly negative in chloroform, caustic potash should form chloride and formate with no setting free of carbon.

The author lays special stress on the fact that no distinction can or should be drawn between true compounds and molecular compounds. This is good but it may overlook certain facts. When we are merely considering the heating of calcium carbonate, we may treat it as a system made up of CaO and CO_2. When we are considering the reaction between calcium carbonate and barium chloride, we take $Ca^{\cdot\cdot}$ and CO_3'' as the constituents. In many cases at any rate we call a substance a molecular compound when we can get along with one set of constituents in all ordinary reactions. When we have to make use of at least two sets we call the substance a molecular compound. The first of these two statements is not universally true because such a definition would force us to call silver chloride a molecular compound. On the other hand something of this sort has been an unconscious factor in many cases and it is a pity to have it ignored completely. *W. D. B.*

The atomic volumes of the rare earths and their bearing on the periodic system. *C. Benedicks. Zeit. anorg. Chem.*, 39, *41* (*1904*).—The author favors the suggestion made by Retgers in 1895 to put the rare earths La–Yb in a single place in the periodic table between barium and tantalum. It is pointed out that the curve representing the atomic volumes is improved in general appearance by such an action. *W. D. B.*

The properties of substances as functions of atomic and molecular spaces. *J. Traube. Zeit. anorg. Chem.*, 40, *372* (*1904*).—The author believes that a classification according to atomic volumes or co-volumes is more rational than one according to atomic weights. The atomic volume of metallic silver is nearly the same as that of gold and very different from that of sodium. Metallic silver is also more like metallic gold than like sodium. On the other hand, silver and sodium compounds are often isomorphous and the molecular volumes are also nearly equal. *W. D. B.*

Chemical equilibrium and temperature gradient. *W. Nernst. Boltzmann's Festschrift*, 904 (*1904*).—A discussion of the equilibrium relations for cases in which the heat conduction is so intense as to cause a serious temperature gradient inside the gas mass. *W. D. B.*

The free energy of some technically important reactions. *H. v. Jüptner. Zeit. anorg. Chem.*, 39, *49*; 40, *61* (*1904*).—The author calculates the free energy for the systems: hydrogen and oxygen from Bose's data; carbon monoxide and oxygen from the data of Hahn and of Le Chatelier; carbon and oxygen from the data of Boudouard and of Le Chatelier. From these reactions he deduces the change of the free energy when carbonic acid is formed from carbon and oxygen, also when carbon monoxide is formed from carbon and carbonic acid. Since the available data are really insufficient, the results are merely first approximations. Curves are given showing the change of the free energy with the temperature. *W. D. B.*

The significance of the coefficient B in the expression for the change of the free energy. *H. v. Jüptner. Zeit. anorg. Chem.* 40, *65* (*1904*).—When the van't Hoff equation for the displacement of the equilibrium with the temperature is integrated, it becomes:

$$\int \frac{Q_T\,dT}{RT^2} + \log K = const.$$

"This constant determines, however, the relation between the temperature and the equilibria of the reactions in question and is therefore of importance in physical chemistry." The value of this constant is determined for several reactions (preceding review) on the assumption that in the author's interpolation formula we have B = R × *const* where R is the gas constant. *W. D. B.*

Bibliography of colloids. *A. Müller. Zeit. anorg. Chem.* 39, *121* (*1904*).—A bibliography of colloids containing three hundred and fifty-six references. There is also an appendix in which the articles are grouped according to their subjects. This last is an admirable feature. *W. D. B*

The heats of combustion of organic compounds. *J. Thomsen. Zeit. anorg. Chem.*, 40, *185* (*1904*).—The author gives his reasons for believing that Lemoult's work (8, 294, 361, 513) is unsound theoretically and experimentally. *W. D. B.*

Heats of combustion of organic sulphur compounds. *P. Lemoult. Comptes rendus*, 139, *131* (*1904*).—Thermochemical data. *W. D. B.*

One-Component Systems.

The inversion point for the two forms of thallous iodide. *D. Gernez. Comptes rendus*, 138, *1695* (*1904*).—Yellow thallous iodide is stable below 168° and the red form above this temperature. Hebberling's determination, 190°, is 22° too high. *W. D. B.*

The effect of pressure on the melting-point of tin and bismuth. *G. Tammann. Zeit. anorg. Chem.* 40, *54* (*1904*).—A pressure of 3000 kg/qcm raises the freezing-point of tin 6.5° and lowers that of bismuth 11.4°. These values do not agree well with those calculated from the formula, but it is believed that the discrepancy is due chiefly to an inaccuracy in the volume change. *W. D. B.*

The van der Waals "a" for alcohol and ether. *E. H. Hall. Boltzmann's Festschrift, 899* (*1904*).—From Amagat's experiments on alcohol and ether the author deduces that the *a* of the van der Waals equation is a function of pressure and temperature if we may make the assumption that isothermal change of volume is not accompanied by change of the internal energy, aside from the potential energy due to molecular attraction, the rate of this change with change of volume being a function of both volume and temperature. If we assume "that the pressure due to molecular attraction within a fluid is a/v^2, where v is the specific volume and a is some constant," the data show that the preceding assumption cannot be correct. The author comes to no final decision.

W. D. B.

The coefficient a of the rectilinear diameter. *E. Mathias. Comples rendus*, 139, *359* (*1904*).—In the formula $a = -\alpha\Theta/\Delta$, Θ is the critical temperature, Δ the critical pressure and α the angular coefficient of the rectilinear diameter, and a is a constant. The author finds the following values for a, nitrogen 0.685, oxygen 0.713, hydrogen 0.24. Since a must be constant for the law of corresponding states to hold, it is evident that it cannot apply to hydrogen. The author therefore divides substances into two classes, those with a value of a approximating unity and those with a low value of a. In the second class come the substances like hydrogen and helium which have very low critical temperatures.

From experiments by Young it is shown that in many cases a is proportional to the square root of the critical temperature. *W. D. B.*

Allotropic forms of antimony sulphide. *J. Guinchant and P. Chrétien. Comptes rendus*, 139, *51* (*1904*).—Black antimony sulphide has a specific gravity of 4.659; the precipitated red sulphide a value of 4.120, while a specific gravity of 4.278 is found for the lilac form obtained by heating and quenching the black modification. There is quite a difference between the heat of change of the damp, precipitated red sulphide and that of the same powder after being dried. The determination of the heats of change from the heats of solution gave values differing markedly from those previously deduced by Berthelot.

W. D. B.

Heat of change of black crystallized antimony sulphide into precipitated orange sulphide. *M. Berthelot. Comptes rendus*, 139, *97* (*1904*).—The author believes that his thermochemical data are more accurate than those of Guinchant and Chrétien (preceding review). Berthelot dissolved the black antimony sulphide in sodium sulphide solution and precipitated as the red sulphide by means of hydrochloric acid. As the values varied with the temperature and the strength of the solution, it is certain that they must have been wrong. The method of Guinchant and Chrétien is much more accurate.

W. D. B.

New method for preparing phosphorus tribromide. *A. C. Christomanos. Zeit. anorg. Chem.*, 41, *276* (*1904*).—Phosphorus is dropped into a flask containing benzene, the requisite amount of bromine added and the phosphorus tribromide distilled off. Phosphorus tribromide melts at −41.5° and boils at 171°; its density is 2.88467 at 0°. The vapor density corresponds to the formula PBr_3. *W. D. B.*

Two-Component Systems

The hydrates of nitric acid. *F. W. Küster and R. Kremann. Zeit. phys. Chem.* 41, *1* (*1904*).—A scarifying criticism of Erdmann's views and experiments on nitric acid. A calmer statement of the facts would probably have had quite as much effect. The authors have made distillation experiments at —15°; they have measured viscosity coefficients; and they have determined the complete freezing-point curve for nitric acid and water. There are two maxima in the freezing-point curve, one corresponding to $HNO_3.3H_2O$ and the other to $HNO_3.H_2O$. There is a special discussion as to the relation between the form of the freezing-point curve and the percentage dissociation of a compound in the melt. The authors conclude that the two hydrates of nitric acid exist to quite an extent in the melt. They determine the change of the density with the temperature and find a strongly marked minimum change for 15° fall of temperature in the case of solutions having concentrations corresponding to $HNO_3.3H_2O$ and $HNO_3.H_2O$. This is very interesting, but unfortunately the authors spoil the effect by jeering at people who detect hydrates by "breaks" in the density-concentration curve. Even if we postulate a perfectly smooth curve at any one temperature, it seems to the reviewer that sharply-marked minimum changes with the temperature at particular points must necessarily give curves at any other temperatures which will not be smooth curves. It is very probable that the recognition of the "breaks" is less arbitrary by the method of the authors than by the usual method; but it is difficult to see how the difference can be anything more than a difference in relative experimental error. If one method is sound theoretically, the other must be also.

W. D. B.

The freezing-point curve for N_2O_4 and NO. *N. v. Wittorf. Zeit. anorg. Chem.*, 41, *85* (*1904*).—On adding NO to NO_2, the freezing-point of the latter is lowered. The eutectic temperature is —112° and the solution contains about 65 per cent by weight of N_2O_4. From there the freezing-point curve rises to the freezing-point of N_2O_3 at —103°. Beyond this point two liquid layers appear.

W. D. B.

The melting-points of mixtures of alkaline earths with boric anhydride. *W. Guertler. Zeit. anorg. Chem.*, 40, *337* (*1904*).—A study of the freezing-point curves shows that the pyroborates, metaborates and biborates of calcium, strontium and barium are definite compounds stable at their melting-points. The same is true of magnesium orthoborate, magnesium pyroborate and barium orthoborates, while the orthoborates of calcium and strontium probably come under the same head, though the author did not succeed in getting the melt to crystallize as it cooled.

W. D. B.

The limits of miscibility of fused boric anhydride and borates. *W. Guertler. Zeit. anorg. Chem.*, 40, *225* (*1904*).—The borates of lithium, potassium, sodium, rubidium, caesium, thallium and silver do not form two liquid layers when fused with an excess of boric anhydride. The borates of copper, lead, bismuth, antimony, arsenic, titanium, molybdenum, tungsten and vanadium form two liquid layers with boric anhydride over certain ranges of concentration, but the consolute temperatures are below 1400°. None of these solutions crystallize on cooling if they contain more boric anhydride than the metaborate. They give either a clear glass or an emulsion. The borates of calcium, strontium, barium, magnesium, zinc, cadmium, manganese, iron, cobalt, nickel, cerium, lanthanum, neodymium, praseodymium, samarium and gadolinium form two liquid layers with boric anhydride and the consolute temperatures lie above 1400° and were not reached. The composition of the lower layer was determined in each case. *W. D. B.*

Sodium amalgams. *A. Schuller. Zeit. anorg. Chem.*, 40, *385* (*1904*).—The author believes that the following solid phases occur in the system, sodium and mercury: Hg, $NaHg_4$, $NaHg_2$, $NaHg_2$, $Na_{12}Hg_{13}$, NaHg, Na_3Hg_2, Na_5Hg_2, solid solution, Na_3Hg, Na. These results depend solely on the cooling curves and were not checked in any other way. Under the circumstances it seems quite possible that some of the conclusions may need revision. *W. D. B.*

Aluminum alloys. *W. Campbell. Jour. Am. Chem. Soc.*, 26, *1290* (*1904*).—The author has examined the copper-aluminum series of alloys microscopically. From 0–32 per cent copper, the alloy consists of two kinds of crystals, aluminum and a eutectic of $Al + Al_2Cu$. The 32 per cent Cu alloy being the eutectic composition, the alloys containing 32–52 per cent Cu consist of Al_2Cu in the above-mentioned eutectic. The 53–78 per cent Cu alloys consist of Al_2Cu and a solid solution containing from 78–83 per cent copper. At high temperatures the 83–92 per cent alloys present a homogeneous structure similar to martensite, while with 92–100 per cent Cu we have a homogeneous solid solution. The author observed that between 83 and 92 per cent the constitution of the alloy depended on the temperature and suspects the existence of a eutectoid. The evidence is not yet complete and the promised pyrometric data will be awaited with interest.

The method of superposition was used in studying these changes in the solid and in that respect the work needs repeating under conditions which do give equilibrium. The microscopic evidence leads the author to abandon the conception of a minimum in the freezing-point curve at 92 per cent Cu. The paper is illustrated by thirty-six photomicrographs. These are among the most beautiful photomicrographs that have appeared and testify to the author's unusual technique as a metallographist *E. S. S.*

Properties of the alloys of silver and cadmium. *T. Kirke Rose. Proc. Roy. Soc.*, 74, *218* (*1904*).—The author of this paper was seeking a substitute for copper in the alloy from which trial plates are cast, and in some manner tried cadmium. He found that perfectly uniform trial plates could be made when this metal was used to alloy with the silver. One practical difficulty was met. The cadmium being volatile below the melting-point of silver, there is a certain difficulty in obtaining exactly the composition sought but the plate produced is uniform, and that is a distinct advantange. The author attributes the homogeneity to the fact that the silver forms a solid solution with the cadmium with a limiting concentration of 80 per cent silver. Since the trial plates contain 92.5 per cent of silver there is no eutectic to cause segregation, and the plates made from this alloy are satisfactory. In this paper the author has extended his observations to the entire series of alloys, and some of his deductions are quite unwarranted either by theory or from his experiments. He believes he has established the existence of some five compounds between silver and cadmium. The equilibrium diagram submitted can only be explained as due to

experimental error. There are two horizontal branches to the supposed liquidus, and the fact that the observed eutectic temperature is not constant but rises at an angle of about 7° does not seem to have indicated to the author that his measurements were inaccurate.
E. S. S.

Alloys of zinc and magnesium. *O. Boudouard. Comptes rendus*, 139, *424* (*1904*).—The freezing-point curve for zinc and magnesium is said to have a maximum for the composition Zn_7Mg with a minimum on either side of this concentration, but this does not appear from the published data. When an alloy containing 80 per cent zinc is acted on by 0.3 per cent HCl, the compound Zn_2Mg is said to be left behind. When an alloy containing 70 per cent zinc is acted on by a hot 5 per cent ammonium chloride solution, the residue is said to correspond to the compound $ZnMg_4$. No secondary breaks were determined in the freezing-point curve and the microscopic examination was carried out in an equally unsatisfactory manner. While the author may be right as to the existence of Zn_3Mg and $ZnMg_4$ the work will have to be repeated before one can have any confidence in the results.
W. D. B.

Copper and oxygen. *E. Heyn. Zeit. anorg. Chem.*, 39, *1* (*1904*).—The author has determined the freezing-point curve for copper and cuprous oxide from pure copper up to solutions containing nine per cent cuprous oxide. The measurements make it probable that the solid phases are pure copper and cuprous oxide. The eutectic contains about 3.5 percent cuprous oxide, perhaps a little more. It appears probable that 19° should be subtracted from all the readings. It is suggested that the cuprous oxide in copper can be estimated quantitatively by the eye, using a microscope.
W. D. B.

The density of gold-copper and gold-silver alloys. *C. Hoitsema. Zeit. anorg. Chem.*, 41, *63* (*1904*).—Determinations were made of the densities of cast gold-copper and gold-silver alloys. Assuming 19.26, 8.7 and 10.4 as the specific gravities of gold, copper and silver at 15°, it is found that there is a slight expansion for the gold-copper alloys and a slight contraction for the gold-silver alloys No reference is made to the actual phases occurring in the alloys.
W. D. B.

Equilibrium and solubility relations of hydrated cerium sulphates. *J. Koppel. Zeit. anorg. Chem.*, 41, *377* (*1904*).—Muthmann and Rölig published some years ago (3, *116*) solubility determinations for cerium sulphate which were in flat contradiction with the form of solubility curves required by theory. This work has now been repeated and has been shown to be wrong in every detail. Solubility curves are given for the salts with four, five, eight, nine and twelve of water. The salt with twelve of water is stable up to +3°; from +3° to 33° we have the octahydrate. The salt with nine of water, curiously enough, is stable from 33° to 40°, while the tetrahydrate is stable above this temperature. The pentahydrate is not really stable at any temperature; but its solubility can easily be determined.
W. D. B.

Scientific phenomena connected with polishing. *F. Osmond and G. Cartaud. Comptes rendus*, 139, *289* (*1904*).—The authors look upon the substance to be polished and the substance polishing it as two substances, A and B, whose superficial layers interpenetrate under pressure. If each substance penetrates readily into the other, each will become encrusted with the other. If A penetrates into B and B does not penetrate readily into A, then B is the polisher and A the substance polished. It follows from this that slight changes in the degree of penetration might reverse the situation. When one rubs iron with moistened alumina, the iron is polished; if the alumina be dry, the iron is encrusted. A similar phenomenon can be obtained with iron and rouge. This can sometimes be of value in metallographic work. When steel is treated with dry rouge, the cementite is polished and the ferrite encrusted. By careful work one can even bring out differences between different crystals or crystal surfaces of the same phase. *W. D. B.*

The distillation of a mixture of two metals. *H. Moissan and O'Farrelley. Comptes rendus,* 138, *1659* (*1904*).—Copper and zinc give a boiling-point curve with neither maximum nor minimum. Copper and lead behave in the same way while the curve for copper and tin shows a maximum for a mixture containing about 60–61 percent. There is evidently a mistake in one determination. While a mixture containing 60 per cent tin distilled practically unchanged one containing 66 percent tin is said to have given residues varying from 79.9 percent tin down to 76.3 percent. This must be an error of observation, since such a result is absolutely impossible. Lead and tin give neither maximum nor minimum. In the system copper and lead, the authors state that the two liquid layers remain even at the boiling-point. *W. D. B.*

Theory of dilute solutions, based on the law of van 't Hoff. *E. Ariès. Comptes rendus,* 139, *401* (*1904*).—The author adds another to the many deductions of the van 't Hoff-Raoult formula. To the reviewer the original deduction by van't Hoff is still the best because the assumptions involved were stated clearly and explicitly. *W. D. B.*

New studies on the liquefaction of helium. *J. Dewar. Comptes rendus,* 139, *421* (*1904*).—Side-arms containing wood charcoal were fastened to tubes and these tubes filled, some with hydrogen and others with helium. When these tubes were plunged into liquid hydrogen, the vacuum became so high that a coil giving a 40 cm spark in air merely caused an intermittent phosphorescent discharge showing only the continuous spectrum of the glass. From the comparative experiments with hydrogen and helium the author is confirmed in his belief that the boiling-point of helium lies between 5° and 6° abs. Using wood charcoal as a condensing agent, the author was able to show the presence of helium in the gases dissolved in rain water, in sea water, and even in water from the Thames. *W. D. B.*

The absorption of gases by wood charcoal at low temperatures. *J. Dewar. Comptes rendus,* 139, *261* (*1904*).—The author has determined the number of volumes of hydrogen, nitrogen, oxygen, argon, helium, $2H_2 + O_2$, $CO + O_2$, and carbon monoxide absorbed by wood charcoal at 0° C and at −185° C. In all cases there is much more gas absorbed at the lower temperature, the absolute increase being by far the least for helium. Quite an effective fractional separation of oxygen and nitrogen can be made by condensing and distilling between these two temperatures. *W. D. B.*

The oxides of platinum. *L. Wöhler. Zeit. anorg. Chem.*, 40, *423* (*1904*).—There are only two oxides of platinum, PtO_2 and PtO. The hydrates of PtO_2 are: $Pt(OH)_6H_2$ white, $PtO(OH)_4H_2$ yellow, $PtO_2(OH)_2H_2$ brown, and PtO_3H_2 black. Complete dehydration cannot be effected without partial decomposition of the platinic oxide even in an atmosphere of oxygen. Platinic oxide dissolves but slowly in hydrochloric acid but the rate increases rapidly owing to the accelerating effect of the chlorplatinic acid.

The color of the PtO and also of its hydrate $PtO.2H_2O$ is black. Platinous oxide is a stronger oxidizing agent than the platinic oxide and a stronger reducing agent than metallic platinum. All the other alleged oxides of platinum were shown to be mixtures.

W. D. B.

Multi-Component Systems

Some ternary alloys of tin and antimony. *W. Campbell. Jour. Am. Chem. Soc.*, 26, *1306* (*1904*).—Assuming Reinders' guess at the constitution of the tin-antimony alloys, the author studies the microstructure of alloys to which 10 per cent of a third metal has been added. Only one composition of each ternary alloy was examined. The following quotation shows the method of attack: "Bismuth and antimony *are said* to form a series of isomorphous solid solutions like gold and silver. Bismuth and tin form a simple series of alloys with a eutectic at 58 percent Bi melting at 133° C. The dendrites of tin which separate out contain about 10 percent bismuth in solid solution, however. (This last statement has been shown to be untrue, both by analytical and microscopic determinations.) *If*, as before, *the antimony and tin combined to form SbSn*, we should have a ground mass of 18 percent bismuth and 82 percent tin, which would be formed of grains and dendrites of tin (10 per cent bismuth in solid solution) surrounded by an envelope of the eutectic of *Bi-Sn*". The italics are ours. This would seem to mean that the eutectic of this ternary alloy is binary, a condition which could exist only if all of the antimony combined to form SbSn (following the author) and this compound were *absolutely* insoluble in the melt. In a similar manner the combinations Pb-Sb-Sn, Ag-Sb-Sn, Cu-Sb-Sn, Cd-Sb-Sn as SbSn were examined.

The author assumes the existence of Ag_3Sn and Ag_3Sb, neither of which compounds has been shown to exist. He assumes Gautier's freezing-point curves to be accurate when they have been repeatedly shown to be hopelessly inaccurate. Le Chatelier's curve for CuSb is taken, when Baikoff has shown what the real curve is; and thus having assumed the existence of certain combinations of tin and antimony with each other and with the third metal, the author tries to deduce what happens in the ternary alloy. As he examines only one composition by one method (microscopic) his deductions are hopelessly uncertain. If all of the assumptions were correct even those familiar with the complexity of ternary systems would hesitate to guess, from one composition chosen at random, what phases were present. In his conclusion the author admits that the eutectic *may* not be binary, promises us the cooling curves of the alloys studied, and is going to isolate (?) and analyze the phases present. The work is unsystematic and the conditions of experiment unknown. About the only thing which can be said is that we now know what certain particular composition of some ternary alloys look like under the microscope. What they mean, how they change, in other words the essential information is wanting. Students of the phase rule will do well to read this paper. *E. S. S.*

New studies on vanadium steels. *L. Guillet. Comptes rendus*, 139, *407* (*1904*).—Vanadium steels show marked changes of properties when the heat treatment is varied. Steels containing more than 0.7 percent vanadium (not 7.0 per cent as previously reported) are of no value commercially.

W. D. B.

Properties and constitution of chromium steels. *L. Guillet. Comptes rendus*, 139, *426* (*1904*).—Steels containing 0.2 per cent carbon give a "pearlite structure" for 0–7 per cent chromium, a "martensite or trootsite structure" for 7–15 per cent chromium, a "martensite and carbide structure" for 15–20 percent chromium, and a "carbide structure" for more than 20 percent chromium. For steels richer in carbon, the changes take place with less chromium.

W. D. B.

Acid nitrates. *E. Groschuff. Zeit. anorg. Chem.*, 40, *1* (*1904*).—Reviewed (8, 443) from Ber. chem. Ges. Berlin, 37, 1486 (1904).

Solubility in mixed solvents. *W. Herz and M. Knoch. Zeit. anorg. Chem.*, 41, *315* (*1904*).—Potassium permanganate is more soluble in water than in acetone but has a maximum solubility in a mixture containing about 70 percent of acetone by volume. The solubility of potassium chloride in aqueous acetone decreases with increasing percentage of acetone. Sodium chloride and sugar cause the formation of two liquid layers at 20°. Boric acid and succinic acid behave like potassium permanganate and barium hydroxide like potassium chloride. Bodländer's formula holds approximately for the solubility of sugar in aqueous acetone but not for that of barium hydroxide. *W. D. B.*

Method of splitting lactic acid into its active components. *E. Jungfleisch. Comptes rendus*, 139, *56* (*1904*).—The quinine salt of the optically inactive lactic acid obtained by fermentation can easily be split up by crystallization into the quinine salts of laevorotary and dextrorotary lactic acids. *W. D. B.*

Some salts of the complex cerisulphuric acid with the elements of the rare earths. *B. Brauner. Zeit. anorg. Chem.*, 39, *261* (*1904*).—From a solution of cerium oxide in aqueous sulphuric acid there crystallize a "yellow" salt $Ce(SO_4)_2.4H_2O$ and a "red" salt $CeHCe(SO_4)_4.12H_2O$. The red salt can be prepared synthetically from a solution of cerous sulphate and ceric sulphate in dilute sulphuric acid. If the amount of sulphuric acid is reduced to the minimum required to prevent hydrolysis, a neutral salt separates, having the formula $Ce_4[Ce(SO_4)_4]_3$. In these two complex salts the trivalent cerium can be replaced by lanthanum. In the "red" salt the trivalent cerium can also be replaced by praseodymium or neodymium. The cerium, lanthanum, praseodymium and neodymium acid salts of the cerisulphuric acid are isomorphous.

W. D. B.

Basic mercury salts. *A. J. Cox. Zeit. anorg. Chem.*, 40, *146* (*1904*).—A phase rule study of the basic salts of mercuric chromate, nitrate and sulphate; also of mercurous nitrate and sulphate. At 25° the basic salts are $HgCrO_4.2HgO$,

$Hg(NO_3)_2.2HgO$, $HgSO_4.2HgO$, $3Hg_2(NO_3)_2.2Hg_2O.2H_2O$, $Hg_2(NO_3)_2 2Hg_2O$ (doubtful), $Hg_2(NO_3)_4.2Hg_2O.2H_2O$, $Hg_2SO_4.Hg_2O.H_2O$. Mercuric fluoride forms no basic salts. The value of this paper would be greater, were it not that no reference is made to Hoitsema's work on the basic mercuric sulphates. Hoitsema found the basic salts $HgSO_4.2HgO$, and $2HgSO_4.HgO.2H_2O$ while the author only found one. Hoitsema also obtained mercuric sulphate at 25° as $HgSO_4.H_2O$ and as $HgSO_4$ while the author only records $HgSO_4$. These discrepancies need explanation and leave it doubtful whether basic salts may not have been overlooked in the other solutions. *W. D. B.*

On ferriacetate compounds. *A. Rosenheim and P. Muller. Zeit. anorg. Chem.* 39, *75* (*1904*).—By the action of glacial acetic acid on ferric hydroxide there is formed the crystallized compound $Fe_2(C_2H_3O_2)_5OH$. In aqueous solution this compound hydrolyzes gradually, quantitatively on heating, into colloidal ferric hydroxide and acetic acid. From solutions of ferric chloride or bromide in glacial acetic acid there crystallizes the salt $Fe(C_2H_3O_2)_2R$. These salts have $Fe(C_2H_3O_2)_2$ as complex cation. The course of the hydrolysis has been followed with these salts and with the preceding one by means of freezing-point and conductivity measurements. The ferroacetate nitrate behaves like the corresponding halides and it is probable that the ferroformate chloride also forms a complex cation. *W. D. B.*

The reaction between bismuth oxyhalides and caustic potash. *W. Herz and G. Muhs. Zeit. anorg. Chem.*, 39, *114* (*1904*).—The authors have attempted to determine what solid phases are formed when bismuth oxychloride or oxybromide is treated with caustic potash of varying concentrations. Not being familiar with the phase rule, this simple problem has been rather too much for them. *W. D. B.*

The action of silica on fused alkali carbonates. *N. M. v. Wittorf. Zeit. anorg. Chem.* 39, *187* (*1904*).—It is shown that the decomposition of sodium carbonate by silica at different temperatures depends on the partial pressure of carbon dioxide. *W. D. B.*

Chlorine in the barium sulphate precipitated by barium chloride. *G. A. Hulett and L. H. Duschak. Zeit. anorg. Chem.*, 40, *196* (*1904*).—The chlorine carried down by barium sulphate from a chloride solution can easily be determined by dissolving the barium sulphate in concentrated sulphuric acid and sweeping the hydrochloric acid over into a silver nitrate solution by means of an air current. With increasing concentration of barium chloride there is increasing occlusion of chloride, the chloride running as high as 0.67 percent in some cases. Acidifying the barium chloride with increasing amounts of hydrochloric acid first decreased and then increased the percentage of occluded chlorine. When a barium sulphate is dried and ignited, it loses both water and hydrochloric acid between 300° and red heat, but the residue is neutral and not alkaline. The authors conclude that the occluded salt is made from the two ions $BaCl^{\cdot}$ and HSO_4'. In confirmation of this view they find that pure barium sulphate is precipitated when solutions of $BaPt(CN)_4$ and Na_2SO_4 are mixed. A coarse barium sulphate precipitate takes up practically no chloride on long boiling with a chloride solution. A very fine barium sulphate precipitate under the same conditions takes up chloride while the crystals are increasing in size. *W. D. B.*

Double decomposition of fused halide salts. *N. Békétoff. Zeit. anorg. Chem.* 40, *355* (*1904*).—The author brings forward evidence to show that when double decomposition takes place between two fused halide salts, the basic radical with the higher atomic weight combines chiefly with the halogen having the higher atomic weight. Thus the predominating pair of salts would be KI and NaBr, KBr and NaCl, etc. Attention is called again to the fact that a freshly-cooled melt of sodium and potassium chlorides has a different heat of solution in water from a solidified melt that has stood for six months. This implies the existence of an unstable state in the freshly-cast salts. Since no compound of sodium and potassium chlorides is known, this calls for investigation. The most plausible hypothesis (not suggested by the author) is that the two salts may form two series of solid solutions at higher temperatures. If so, the densities should show it. *W. D. B.*

The preparation of pure sodium hydroxide for laboratory use. *F. W. Küster. Zeit. anorg. Chem.* 41, *474* (*1904*).—It is believed not to be safe to bring large amounts of sodium in direct contact with liquid water under any conditions. The author places several hundred grams of sodium on a wire gauze above the mouth of a flask. The whole is placed in a bell jar together with a beaker of water. The water vapor condenses on the sodium and the caustic soda drips into the flask. *W. D. B.*

The application of physical chemistry to serum therapy. *S. Arrhenius. Boltzmann's Festschrift, 860* (*1904*).—It is found that a mass law equation holds for haemolysine and that the anti-complement should be called anti-haemolysine. *W. D. B.*

Some complex compounds of molybdic and tungstic acids with organic acids. *H. Grossmann and H. Krämer. Zeit. anorg. Chem.*, 41, *43* (*1904*).—Neutral salts of complex dibasic acid appear to exist in solutions containing one of oxalic, tartaric or citric acid to one of Na_2MoO_4 or Na_2WO_4. In dilute solutions there is much hydrolysis and this is more marked with the molybdates than with the tungstates. *W. D. B.*

Hydrate of alumina. *F. Russ. Zeit. anorg. Chem.*, 41, *216* (*1904*).—The solubility of alumina in caustic soda of varying concentrations has been determined and also the rate of precipitation. This gives the data for an intelligent understanding of the Bayer process for purifying bauxite. The so-called "crystalline" alumina is really a sandy deposit. It is formed rapidly in presence of free alkali. *W. D. B.*

Studies on metal hydroxides. I. *H. W. Fischer. Zeit. anorg. Chem.*, 40, *39* (*1904*).—When chromium hydroxide is made from the green chromium chloride, the solution in alkali is colloidal and does not dialyze. Cupric hydroxide appears to form a colloidal solution with pure caustic soda but to form a real solution to a certain extent when carbonate is also present. Chromium hydroxide dissolves in chromic chloride solution partly as solute and partly as colloid. Aluminum hydroxide dissolves in caustic soda chiefly as colloid.

These colloidal solutions differ from the colloidal solutions of the metals in that they are more stable the greater the concentration of acid or alkali.

W. D. B.

The liquid hydrosol of gold. *II. A. Gutbier and F. Resenscheck. Zeit. anorg. Chem.* 39, *112* (*1904*).—When a very dilute solution of phenylhydrazine hydrate is added gradually to a dilute solution of gold trichloride, the hydrosol is first red, then violet (purple ?) and lastly blue. *W. D. B.*

The preparation of colloidal metals. *N. Castoro. Zeit. anorg. Chem.*, 41, *126* (*1904*).—By adding acroleine to hot, slightly alkaline solutions of the chlorides of gold, platinum, palladium, osmium and ruthenium, the author has obtained colloidal solutions of all these metals. It is stated that colloidal solutions of osmium and ruthenium had not been made before. The gold solutions can be obtained varying from blue to purple and red by changing the conditions of formation. *W. D. B.*

Note on the composition of Bredig's silver hydrosol. *J. C. Blake. Zeit. anorg. Chem.*, 39, *69* (*1904*).—When a silver hydrosol is prepared by arcing under water between silver electrodes, both electrodes lose weight and the precipitated silver also loses weight when ignited. This makes it seem probable that this silver hydrosol contains some silver hydroxide. Some experiments without an arc showed the formation of silver hydroxide. *W. D. B.*

Investigations on cyanogen. *M. Berthelot. Comptes rendus*, 138, *1649*, *1653*; 139, *193* (*1904*).—Cyanogen changes gradually when dissolved in water or alcohol and it is therefore impossible to determine a true solubility coefficient. In chloroform there is distinct polymerization but an equilibrium appears to be reached. In acetic acid and benzene there is a slight polymerization or decomposition while there appears to be practically none in turpentine. When cyanogen is brought in contact with aqueous or alcoholic solution of potassium cyanide, there is a change in the cyanogen and in the cyanide. Similar reactions are caused by potassium ferrocyanide. In the last paper there are thermochemical data for some of the changes described in the first two articles.

W. D. B.

The amounts of chlorine precipitated by silver salts from hydrated chromium chloride. *R. F. Weinland and A. Koch. Zeit. anorg Chem.*, 39, *296* (*1904*).—Solutions of different salts have been added to solutions of chromium chloride or bromide and the precipitated silver halide filtered at once. It appears that the percentage of the total halide precipitated immediately may vary from 100 to 35, depending on the nature of the silver salt added and the nature and amount of the free acid. The silver salts of strong acids precipitate less halide than the silver salts of weak acids. Addition of a strong acid also checks the precipitation of halide, the percentage precipitation passing through a minimum, however, for high concentrations of the acid. The statements, that one-third of the total chlorine is precipitated or two-thirds, rest on experimental evidence which is merely the result of a coincidence. *W. D. B.*

Osmotic Pressure and Diffusion.

The fundamental law of osmotic phenomena. *E. Ariès. Comptes rendus*, 139, *196* (*1904*).—The author starts out to prove that the thermodynamic potential of the solvent is the same on the two sides of a semipermeable membrane. His enthusiasm carries him away and he reaches the obviously false conclusion that the potential of any constituent will be the same on both sides of the diaphragm. A little thermodynamics is a very dangerous thing. *W. D. B.*

Action of salts of the alkalies on living matter. *N. C. Paulesco. Comptes rendus*, 138, *1728* (*1904*).—The author has determined the smallest amounts of different salts of the alkalies which will prevent the evolution of carbon dioxide by beer wort. The concentrations are found to be proportional to the molecular weights. *W. D. B.*

Action of salts of the earths on living matter. *N. C. Paulesco. Comptes rendus*, 139, *158* (*1904*).—The results with chlorides, bromides and nitrates of the alkaline earths on beer wort are similar to those obtained with the corresponding salts of the alkali metals. The comparable quantities for the two groups are equivalent weights and not molecular weights. *W. D. B.*

Transference of ultra-microscopic particles by the current. *A. Cotton and H. Mouton. Comptes rendus*, 138, *1692* (*1904*).—Ultra-microscopic particles move under electrical stress at approximately the same speed as larger particles. In some cases it was noticed that the direction of the movement was reversed for particles very close to the walls of the vessel. *W. D. B.*

Action of electric current and of electrolytes on red colloidal gold solutions. *J. C. Blake. Zeit. anorg. Chem.*, 39, *72* (*1904*).—When a red colloidal solution of gold is electrolyzed in a U-tube, the gold collects at the bend of the tube. When a porous asbestos plug is placed at some point in the tube, it appears to act like an intermediate diaphragm. The current by itself will not change the red solution to blue. When the current passes, less potash alum is needed to cause the change than is otherwise necessary. Presence of ether in the solution makes it necessary to add more potash alum in order to bring the change from red to blue. *W. D. B.*

Velocities

The least film thickness for mercury as catalytic agent. *G. Bredig and F. Weinmayr. Boltzmann's Festschrift*, 839 (*1904*). Under otherwise equal conditions the time necessary for the decomposition of dilute aqueous solutions of hydrogen peroxide by metallic mercury is inversely proportional to the wetted mercury surface. A 56 cm^2 surface of ordinary mercury catalyzes at the same rate as 2×10^{-5} g mercury precipitated by alkaline hydrogen peroxide on the gold of a colloidal gold solution containing 3×10^{-5} g gold in 30 cc water. The authors deduce a thickness of the mercury film as about 3×10^{-8} cm. No catalytic action could be detected when less than 2×10^{-6} g mercury were taken. From this the authors deduce 1.5×10^{-7} as upper limit of the thickness of the thinnest film of colloidal mercury which can show catalytic action. *W. D. B.*

On precipitates in colloids. *J. Hausmann. Zeit. anorg. Chem.* 40, *110* (*1904*).—The author has made an elaborate qualitative study of Liesegang's experiment (Cf. 8, 520) using a large number of different salts. While most precipitates were colloidal and in layers, those of barium sulphate, strontium sulphate, calcium sulphate, barium oxalate, silver oxalate, thallous chloride, thallous bromide and thallous iodide were neither.

Experiments on the rate of formation of the colloidal precipitates appeared to show that this is a function of the migration velocity of the ion which precipitates and that it is independent of the nature of the other diffusing ion. For any particular case, the square of the height of the column is proportional to the elapsed time. *W. D. B.*

The mechanism of the catalytic action of platinum black. *R. Vondracek. Zeit. anorg. Chem.*, 39, *24* (*1904*).—Platinum black containing oxygen oxidizes solutions of ammonia or of ammonium salts, nitrogen being set free. If the platinum black be free from oxygen, it can reduce solutions of nitrous and nitric acid. Either in this way or by contact with oxygen from the air, the platinum black regains its oxidizing power. In ammonia solutions platinum black becomes saturated with nitrogen which can be driven out by caustic potash. It seems probable that the oxidation of ammonium nitrite by platinum black takes place in two stages:

$$2NH_4NO_2 + xPtO_n + yH_2O = N_2 + 2HNO_2 + zPt + (y + 3)H_2O$$
$$2HNO_2 + xPt = N_2 + H_2O + xPtO_n\,.$$

W. D. B.

On devitrification. *W. Guertler. Zeit. anorg. Chem.*, 40, *268* (*1904*).—When glasses are heated slowly in presence of crystals, there comes a point at which the rate of crystallization becomes distinctly marked. These temperatures were found to be 550° for sodium metasilicate, 646° for cobalt pyroborate, 670° for manganese biborate and 675° for copper metaborate. These temperatures are accurate to ±20° for very considerable differences in the rates of heating. There is a difference of 505° between the melting-point of sodium metasilicate and its devitrification temperature, while the corresponding difference for manganese biborate is only 225°. These differences vary with the rates of crystallization and the heats of fusion. *W. D. B.*

The crystallization of thallous iodide from solution. *D. Gernez. Comptes rendus*, 139, *278* (*1904*).—When an excess of yellow thallous iodide is heated with water to 168° and allowed to cool slowly, only the yellow form separates. If the tube containing the solution be cooled rapidly the red modification separates from the body of the liquid. The same result can be obtained when the thallous iodide is dissolved in certain salt solutions or fused salts. When the red iodide is precipitated together with a lot of other salts years may elapse before it changes back into the stable, yellow modification. *W. D. B.*

Readiness of reaction of calcium sulphate in colloidal media. *P. Rohland. Zeit. anorg. Chem.*, 40, *182* (*1904*).—In a gelatine solution the hemihydrate of calcium sulphate changes over into the dihydrate more slowly than in pure water. The hardening process does not take place at all and is therefore not a necessary consequence of the formation of the dihydrate. *W. D. B.*

Slow oxidation of cyanogen and cyanides by free oxygen. *M. Berthelot. Comptes rendus*, 139, *169* (*1904*).—The author has made qualitative experiments on the catalytic effect of heat and light on the reaction between oxygen and dissolved cyanogen or cyanides. In all cases there is a slow absorption of oxygen and the rate is increased by light or heat. *W. D. B.*

Electromotive Forces

The electric potentials of nickel and tellurium. *H. Euler. Zeit. anorg. Chem.*, 41, *93* (*1904*).—If rough nickel electrodes are made alternately anode and cathode in a nickel sulphate solution and are then allowed to stand four to six days in an air-free nickel sulphate solution, they give as good results as zinc electrodes. In half-molar nickel sulphate the potential is —0.094 volt (Ostwald zero). Tellurium in a saturated solution of telluric acid probably just balances the calomel electrode, the electromotive force of the cell being zero. These measurements are difficult to make and the results are not final. *W. D. B.*

The electromotive behavior of vanadium. *L. Marino. Zeit. anorg. Chem.*, 39, *152* (*1904*).—In acid or neutral solutions vanadium as anode goes into solution as a quadrivalent ion; in alkaline solutions as a pentavalent ion. The electromotive forces corresponding to these two reactions differ by 0.7 volt, the potential difference for the quadrivalent vanadium being about —0.5 volt while that for the pentavalent vanadium is about +0.2 volt. Vanadium shows no signs of becoming passive and does not behave in any respect like chromium. *W. D. B.*

Some complex silver salts. *G. Bodländer and W. Eberlein. Zeit. anorg. Chem.* 39, *197* (*1904*).—The authors decide that there exist in sulphocyanate and cyanide solutions the salts $KAg(CNS)_2$, $K_3Ag(CNS)_4$, $KAg(CN)_2$ and $K_3Ag(CN)_4$. In iodide solutions they find evidence of $K_2Ag_2I_4$, $K_3Ag_2I_5$, $K_4Ag_2I_6$ and $K_5Ag_2I_7$. This is very interesting and may be all right but one cannot help feeling that the deductions rest on an insecure basis. It is assumed throughout that the dilution law holds for all the salts, whereas the work of Noyes and others makes it probable that the law does not hold even approximately for any of them. *W. D. B.*

Equilibria between silver salts. *R. Lucas. Zeit. anorg. Chem.*, 41, *193* (*1904*).—The author has studied the equilibrium relations for potassium chloride, bromide or sulphocyanate with silver cyanide; also the solubility of silver cyanide in aqueous ammonia, and of silver sulphide in aqueous potassium cyanide. From the sulphide data the author calculates the electrolytic potential of sulphur as —0.59 volt (hydrogen zero). *W. D. B.*

The complex ammonia hydroxides of copper, nickel, cadmium, zinc and silver. *W. Bonsdorff. Zeit. anorg. Chem.*, 41, *132* (*1904*).—Electromotive force measurements showed that in ammoniacal solutions there existed the complex cations $Cd_m(NH_3)_{4m}$ and $Zn_m(NH_3)_{3m}$, while no definite results could be obtained for copper and nickel. Conductivity measurements showed that nickel, cadmium and silver formed strong bases in ammoniacal solutions; that zinc forms a weak base; and that copper probably forms several bases, some weak and one strong. In spite of difficulties with the solubility determinations it was decided that when ammonia was present in slight excess we have cations containing two of ammonia to one of copper and four of ammonia to one of cadmium or nickel. *W. D. B.*

Complex zinc salts. *F. Kunschert. Zeit. anorg. Chem.* 41, *337* (*1904*).—A study was made of zinc in oxalate, alkaline and cyanide solutions. In concentrated oxalate solutions zinc is present as $Zn(C_2O_4)_3''''$; in dilute solutions as $Zn(C_2O_4)_2''$. In alkaline solutions zinc is present chiefly as ZnO_2'' but partly as $HZnO_2'$. In cyanide solutions the complex ions are believed to be $Zn(CN)_4''$ and $Zn(CN)_3'$. The potential difference at zinc electrodes varies as the first power of the concentration of the zinc, the third power of the concentration of oxalate or cyanide as ion, and the fourth power of the concentration of hydroxyl as ion. *W. D. B.*

Solutions of copper in potassium cyanide. *F. Kunschert. Zeit. phys. Chem.*, 41, *359* (*1904*).—In potassium cyanide solution copper is believed to exist chiefly as $Cu(CN)_4'''$ and only to a slight extent as $Cu(CN)_3''$. The potential difference between copper and a cyanide solution varies as the first power of the copper concentration and as the fourth power of the concentration of cyanogen as ion. *W. D. B.*

Electrolysis and Electrolytic Dissociation.

Preparation and electrolysis of pure fused zinc chloride. *S. Grünauer. Zeil. anorg. Chem.* 39, *389* (*1904*)—Fused zinc chloride containing traces of water practically never becomes clear on electrolysis. If the zinc chloride be dehydrated by adding ammonium chloride, the melt remains clear but zinc does not precipitate readily until the whole of the ammonium chloride is electrolyzed out. The same is true when the zinc chloride is treated with concentrated hydrochloric acid. If dry hydrochloric acid gas be passed through zinc chloride, the melting-point of the latter may be raised to 365°. The resulting zinc chloride can be electrolyzed satisfactorily at once. It takes about seventy minutes to dehydrate forty grams of so-called pure zinc chloride in this way. At 600° the current efficiency increased from twenty-three to seventy-six percent as the current increased from 0.5 to 3.0 amp.

From a mixture of the fused chlorides of zinc and iron, iron precipitates pure at first; then comes fused zinc containing less and less iron. The author does not seem to be very clear as to the theory of this. From mixtures of zinc and potassium chlorides, the yield is better than from zinc chloride alone, 59.3-94.7 percent instead of 22.9-76.0 percent. Sodium chloride also increases the current efficiency but not to the same extent as does potassium chloride. Raising the temperature of a zinc chloride melt decreases the current efficiency, it dropping to 8 percent at 732° under a current of 2 amperes.

There is no danger of arsenic in the electrolytic zinc because this substance is completely volatilized by the hydrochloric acid gas during the drying process. Incidentally the author determined the freezing-point curves for zinc chloride and ammonium chloride up to a concentration of 75 molecular percents of ammonium chloride. *W. D. B.*

Electrolytic precipitation from salt solutions of metals which decompose water. *A. Siemens. Zeit. anorg. Chem.*, 41, *249* (*1904*).—If a solution is concentrated with respect to a magnesium salt magnesium can readily be precipitated as an alloy with nickel or cobalt; less readily with iron and only in traces with zinc. It was not possible to precipitate aluminum in this way or the metals of the alkaline earths. The alkali metals precipitate to a measurable extent with nickel or tin but not with iron or silver. In acetone solution it was possible to precipitate the metals of the alkalies and of the alkaline earths at the cathode but not magnesium, aluminum or beryllium. In aqueous solution nickel magnesium sulphate forms no complex ions. The presence of traces of the less noble metals can easily be shown by measurement of electromotive force. *W. D. B.*

The electrolysis of some potassium double cyanides. *H. v. Hayek. Zeit. anorg. Chem.*, 39, *240* (*1904*).—The author first studies the conditions affecting the electrolytic oxidation of potassium ferrocyanide to ferricyanide. The anode solution must be stirred and must be kept alkaline. The anode current density should be low. If these conditions are observed, a current efficiency of 100 percent can be obtained. As long as the concentration of ferrocyanide in the anode solution exceeds 1.75 g/cc. the current efficiency does not depend on the absolute or relative concentration. The permissible current increases with increasing concentration, but no experiments were made to find out whether the maximum may not depend entirely on the rate of stirring.

Potassium nickelous cyanide is partially reduced at the cathode, an instable red solution being formed. Cyanogen is set free at the anode and reacts to a certain extent with water, giving ammonium formate and carbon dioxide. With potassium cobalt cyanide, cobaltic oxide is formed at the anode, some ozone and oxides of nitrogen being also formed. Potassium manganicyanide is first reduced at the cathode to potassium manganocyanide $K_4Mn(CN)_6$ and this decomposes, precipitating $KMn(CN)_3$ which changes in presence of caustic potash into manganous hydroxide. *W. D. B.*

The reduction of combined solid carbonic acid to carbon, and electrochemical changes with solids. *F. Haber and S. Tolloczko. Zeil. anorg. Chem.* 41, *407*, (*1904*).—When fused caustic soda is cooled to 240° and electrolyzed, a current passes, apparently through channels in the solidified mass. It was possible to obtain 40 percent current efficiencies, making metallic sodium at this temperature. When a solidified mixture of fused barium carbonate and chloride is electrolyzed, the barium reduces the carbonate and carbon is set free. Even when barium chloride alone was used, some carbon was formed. It was shown that the carbon dioxide of the air will displace chlorine from heated barium or calcium chloride. When this reaction is prevented, barium subchloride is obtained with a current efficiency of 95 percent.

After determining the polarization in these cases, some experiments were made with solid cells of the Daniell type, using the chlorides of lead, silver and copper. *W. D. B.*

Electrolytic determination of bismuth. *A. Hollard and L. Bertiaux. Comptes rendus*, 139, *366* (*1904*).—Bismuth is separated from copper or lead by chemical methods and then the bismuth is determined electrolytically either in a pyrophosphate or in a sulphate solution. *W. D. B.*

A new modification of colloidal tellurium. *A. Gutbier and F. Resenscheck. Zeit. anorg. Chem.*, 40, *264* (*1904*).—When a potassium cyanide solution of telluric acid is electrolyzed, the solution becomes a brown-violet. On dialyzing this solution a brown-violet colored solution of colloidal tellurium was obtained which has now kept six months without decomposition in a closed flask.

When an ammonium oxalate solution of telluric acid is electrolyzed there is formed a steel-blue solution of colloidal tellurium. In both these cases tellurium separates in a flocculent form if the electrolysis is continued too long. When an ammoniacal solution of telluric acid is electrolyzed there is no precipitation of tellurium and no formation of a colloidal solution. *W. D. B.*

The thermal mercury ammeter. *C. Camichel. Comptes rendus*, 139, *363* (*1904*).—A description of the final form of thermal mercury ammeter (2, 73; 3, 185). *W. D. B.*

Effect of current density on electrolysis with an alternating current. *A. Brochet and J. Petit. Comptes rendus*, 139, *193* (*1904*).—With nickel anodes in a potassium cyanide solution the current efficiency for an alternating current increases with increasing current density up to a current density of about 4-7 amp/qdm and then falls off, the more rapidly the fewer the alternations. From these experiments one would deduce a current efficiency approximating zero for high current density and zero alternations. With a direct current however, an 80 percent current efficiency seems to be the limiting value for high current densities. Since the authors look upon an alternating current, which does not alternate, as a direct current, there is a discrepancy here. This point is to be studied further. *W. D. B.*

On organic solvents and ionizing media. *P. Walden. Zeit. phys. Chem.*, 46, *103* (*1903*).—An excellent résumé of work previously done on the subject by others is given. As solvents typical alcohols, aldehydes, acids, acid anhydrides, acid chlorides and bromides, esters, acid amides, nitriles, sulphocyanates, mustard oils, aldoximes, ketones, and nitro and nitroso compounds were used. These were carefully purified and the electrical conductivity was measured. A goodly number of dielectric constants was also determined by the method of Drude. The conductivity of the pure solvents is explained by assuming "self-dissociation" and considerable space is devoted to mere speculation as to what the composition of the ions might be in the various individual cases. It is proposed to dissolve one solute, tetramethyl ammonium iodide, as "normal electrolyte" in each solvent and from the conductivity of the solutions so obtained to deduce conclusions as to the relative "dissociating power" of the solvents employed. That the author should make the error to regard this as possible is simply a natural consequence of his adherence to the theory of electrolytic dissociation which practically suggests such a procedure. The "dissociative power" of solvents, or, more correctly, the fact whether solutions in certain solvents are electrolytic conductors and to what extent, cannot be determined as readily as this, for the conclusion reached by the proposed method would depend entirely upon the solute chosen. So, for example, if to compare the relative "dissociating power" of water and liquid HCN the solute employed be KI, the conclusion would be that water has less "dissociating power" than liquid HCN, for the solution of KI in water is a poorer conductor than that in liquid HCN; on the other hand, if trichloracetic acid, or any other acid, be chosen as solute, exactly the opposite conclusion would be reached, for aqueous acid solutions are among the best electrolytes known, whereas solutions of acids in liquid HCN are poorer conductors. The original article must be consulted for the many valuable experimental data which it contains. *L. K.*

THE FUNDAMENTAL FUNCTIONS OF ONE-COMPONENT IDEAL-CONSTITUENT GASES

BY J. M. BELL AND J. E. TREVOR

CONTENTS

The Gibbsian Theory. The Pressure and the Molecular Volume. Fundamental Functions. Derivatives of the Fundamental Functions h, f. The Energy and the Heat Function. Functions of α,θ. Functions of α,v. Derivatives. Heat Capacity at Constant Pressure. Heat Capacity at Constant Volume. Work-Integrals. Heat-Integrals. Comparison with Experiment.

Introduction

The assumption of a reversibly displaceable dissociation-equilibrium between unimolecular and bimolecular forms of certain one-component substances in aeriform states was suggested by observation of the 'abnormal vapor densities' exhibited by these substances, especially by nitrogen peroxide, acetic acid, and formic acid. In the case of nitrogen peroxide, this interpretation,

$$N_2O_4 \rightleftarrows 2NO_2,$$

of the phenomena was supported by the agreement of the values of the degree of dissociation at given pressures and temperatures, as deduced from the density of the gas and from the intensity of its color. Gibbs's formulation of the proposed interpretation yielded a very satisfactory formulation of the relation between the pressure, the specific volume, and the temperature of such systems, and thus provided a striking demonstration of the suitability of the interpretation. The interest of Gibbs's theory as an illustrative application of the theory of the thermodynamic equilibria of one-component systems has led us to formulate two of the 'fundamental functions', the thermodynamic potential and the free energy, of one-component ideal-constituent gases, and to deduce some of the more immediate consequences of the forms of these functions. We shall preface our account of this work by an outline of the essential features of Gibbs's theory. The notation that shall be employed is as follows:

p, pressure.
θ, absolute temperature.
μ_j, molecular potential of j-th component.
λ_j, molecular potential of j-th constituent.
V, total volume.
v, molecular volume.
H, total entropy.
η, molecular entropy.
η_{oj}, molecular entropy of the j-th constituent at $v = 1$, $\theta = 1$.
n_j, number of molecular weights of j-th constituent.
N_1, number of molecular weights if the mass were wholly in form of the first constituent.

e_{oj}, molecular energy of the j-th constituent at $\theta = 0$.
e, molecular energy.
f, molecular free energy.
g, molecular heat-function.
h, molecular thermodynamic potential.
H, total thermodynamic potential.
α, degree of dissociation.
c_p, molecular heat at constant pressure.
c_v, molecular heat at constant volume.
Q_v, molecular heat of dissociation at constant volume (for $N_1 = 1$).
t, s, auxiliary functions.

The Gibbsian Theory

In the state variables p, θ, the molecular potential

$$\mu_j = e_j + p_j v_j - \theta\eta_j$$

of a one-constituent ideal gas G_j is

$$(1) \qquad \mu_j = -r.\theta \log\frac{r}{p_j} - c_{pj}\,\theta.\log\theta - \theta(\eta_{oj} - c_{pj}) + e_{oj}.$$

Solving this equation for p_j,

$$p_j = p_j(\mu_j, \theta),$$

and assuming Dalton's law

$$p = p_1 + p_2$$

for a mixture of two non-reacting ideal gases, we obtain an equation

$$(2) \qquad p = p\,(\theta, \mu_1, \mu_2).$$

Now, for a mixture of n_1 molecular weights of the first gas and n_2 of the second, we have

$$0 = -Vdp + Hd\theta + n_1 d\mu_1 + n_2 d\mu_2;$$

whence

$$(3) \qquad \frac{\partial p}{\partial \mu_j} = \frac{n_j}{V}; \qquad (j = 1, 2)$$

whereupon, by differentiating (2) with regard to μ_j and comparing with (3), we find an equation

$$n_j/V = \phi\,(\mu_j, \theta),$$

or, solving for μ_j,

$$(4) \qquad \mu_j = r\theta.\log\frac{n_j}{V} - c_{vj}\theta.\log\theta - \theta(\eta_{oj} - c_{pj}) + e_{oj}.$$

This equation is identical in form with the relation between the potential, the molecular volume, and the temperature of a one-constituent ideal gas; so we find that, in consequence of Dalton's law, the potential of a component of a mixture of two ideal gases is not altered by the presence of the other component. Assuming this to remain true even though the gases participate in a dissociation-equilibrium, we find from (1) and (4), for the molecular potentials λ_1, λ_2 of the constituents of a one-component ideal-constituent gas,

$$(5)\ \lambda_j = -r\theta.\log\frac{r}{p_j} - c_{pj}\theta.\log\theta - \theta(\eta_{oj} - c_{pj}) + e_{oj} \quad (j = 1,2)$$

$$(6a) \quad = \quad r\theta.\log\frac{n_j}{V} - c_{vj}\theta.\log\theta - \theta\,(\eta_{oj} - c_{pj}) + e_{oj}.$$

In order to find λ_j in terms of p, θ, it is necessary to eliminate from (5) the 'partial pressure' p_j of the j-th constituent. We have

$$p_j = n_j\,\frac{r\theta}{V};$$

wherefore, by Dalton's law,

$$(7) \qquad p = (n_1 + n_2)\frac{r\theta}{V};$$

and, so,

$$\frac{p_j}{p} = \frac{n_j}{n_1 + n_2}.$$

Elimination of p_j between this and (5) yields

$$(6b) \ \lambda_j = r\theta.\log\frac{n_j}{n_1 + n_2} - r\theta.\log\frac{r}{p} - c_{pj}\theta.\log\theta$$
$$- \theta(\eta_{oj} - c_{pj}) + e_{oj}.$$

By means of (6*a*), we shall now express the 'dissociation-equilibrium equation' (for equilibria of the nitrogen peroxide type),

$$\lambda_1 = 2\lambda_2,$$

as a relation between the (molecular) partial densities of the constituents and the temperature. We find

$$(8) \ \log\frac{(n_2/V)^2}{n_1/V} = \frac{2c_{v2} - c_{v1}}{r}\log\theta$$
$$+ \frac{(2\eta_{o2} - \eta_{o1}) - (2c_{p2} - c_{p1})}{r} - \frac{2e_{o2} - e_{o1}}{r\theta}.$$

To the end of simplifying the form of this equation, we assume the additivity of the molecular heat of a compound,

$$(9) \qquad 2c_{v2} - c_{v1} = 0,$$

wherefore, since

$$2c_{p2} = 2c_{v2} + 2r$$
$$c_{p1} = c_{v1} + r,$$

we find, by subtraction,

$$(10) \qquad 2c_{p2} - c_{p1} = r.$$

Further, the integration-constants e_{01} and $2e_{02}$ are the energies at $\theta = 0$ of the same mass of the component, first in the form of the first constituent, S_1, and then in that of the second, S_2. These energies will remain unchanged if the two forms be supposed brought to the same volume; so their difference,

$$(11) \qquad 2e_{02} - e_{01} = Q_v(0),$$

is the quantity of heat $Q_v(0)$ that would be absorbed in the complete isometric dissociation of one molecular weight of S_1 at $\theta = 0$, — it is the molecular 'heat of dissociation' of S_1 at constant volume, at the temperature-zero. The heat of dissociation at constant volume is, moreover, independent of the temperature; for

$$Q_v(\theta) = Q_v(0) + (2c_{v_2} - c_{v_1})\theta$$
$$= Q_v(0).$$

If we, finally, put

(12) $$\log a = \frac{2\eta_{02} - \eta_{01}}{r} - 1,$$

the equations (9), (10), (11), (12) enable us to write (8) in the form

$$\log \frac{(n_2/V)^2}{n_1/V} = \log a - \frac{Q_v}{r\theta},$$

or, setting

(13) $$a.\epsilon^{-\frac{Q_v}{r\theta}} = 4.l(\theta),$$

we have

(14) $$\frac{(n_2/V)^2}{n_1/V} = 4.l(\theta).$$

The 'characteristic equation'

$$\phi\left(\frac{V}{N_1}, p, \theta\right) = 0$$

of our ideal-constituent gas contains the mass N_1 of the gas, which is most conveniently expressed as the number of molecular weights that would be present were the mass wholly in the form of the first constituent. This quantity satisfies the relation

(15) $$2N_1 = 2n_1 + n_2.$$

The form of the characteristic equation may be found by eliminating n_1/V and n_2/V between (15) and the equations (7) and (14),

$$\frac{p}{r\theta} = \frac{n_1}{V} + \frac{n_2}{V} .$$

$$\frac{(n_2/V)^2}{n_1/V} = 4.t(\theta).$$

This may be done, after dividing (15) through by V, by eliminating n_2/V between (7) and (15) and between (7) and (14), and thereupon eliminating n_1/V between the resulting equations. We thus find

$$\text{(16)} \qquad \frac{\left(\frac{p}{r\theta} - \frac{N_1}{V}\right)^2}{2\frac{N_1}{V} - \frac{p}{r\theta}} = t,$$

which is the characteristic equation. It is identical with Gibbs's equation (349), in his paper in the third volume of the Transactions of the Connecticut Academy. By (13), the temperature-function t is defined by the equation

$$t = \frac{a}{4} \epsilon^{-\frac{Qv}{r\theta}}.$$

The pressure and the molecular volume

Our first step consists in solving the characteristic equation (16) for the pressure and for the molecular volume. Clearing of fractions, and solving successively for $p/r\theta$ and N_1/V, we find

$$\text{(17)} \qquad \frac{p}{r\theta} = \left(\frac{N_1}{V} - \frac{t}{2}\right) \pm \left(\frac{N_1}{V} t + \frac{t^2}{4}\right)^{½} .$$

$$\text{(18)} \qquad \frac{N_1}{V} = \left(\frac{p}{r\theta} + t\right) \pm \left(\frac{p}{r\theta} t + t^2\right)^{½}.$$

Let us now determine the sign of the square root in each of these equations. From (15), we have

$$n_1 + n_2 = 2N_1 - n_1.$$

Now n_1 varies between N_1 and 0, which causes the second member of this equation to vary between $2N_1$ and N_1. Consequently,

$$n_1 + n_2 \geqq N_1.$$

Again, by (7),

$$\frac{p}{r\theta} V = n_1 + n_2$$

$$\geqq N_1$$

$$\frac{p}{r\theta} \geqq \frac{N_1}{V};$$

which converts (17) and (18) to

$$-\frac{t}{2} \pm \left(\frac{N_1}{V} t + \frac{t^2}{4}\right)^{\frac{1}{2}} \geqq 0,$$

$$+ t \pm \left(\frac{p}{r\theta} t + t^2\right)^{\frac{1}{2}} \leqq 0.$$

The quantities N_1, V, t, p, r, θ, all being positive, the indicated square root must be positive in the first case and negative in the second. We accordingly have, from (17) and (18),

$$(19) \qquad p = r\theta\left(\frac{N_1}{V} - \frac{t}{2}\right) + r\theta\left(\frac{N_1}{V} t + \frac{t^2}{4}\right)^{\frac{1}{2}}$$

$$(20) \qquad \frac{N_1}{V} = \left(\frac{p}{r\theta} + t\right) - \left(\frac{p}{r\theta} t + t^2\right)^{\frac{1}{2}}.$$

For convenience in subsequent work, we shall now introduce the 'molecular volume' v, defined by the equation[1]

$$v = V/N_1,$$

and an auxiliary function s defined by

$$(21) \qquad s = + \left(\frac{p}{r\theta} t + t^2\right)^{\frac{1}{2}}.$$

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[1] Note that, on this substitution, the characteristic equation (16) may be written in the form

$$\frac{\left(1 - \frac{pv}{r\theta}\right)^2}{\left(2 - \frac{pv}{r\theta}\right)} = vt.$$

The form of this function s in the variables v, θ may be found from (21), by substituting $p\,(v, \theta)$ from (19), whereby

$$s = \left\{ \frac{t}{v} + \frac{t^2}{2} + t\left(\frac{t}{v} + \frac{t^2}{4}\right)^{1/2} \right\}^{1/2}$$

$$(22) \qquad = \frac{t}{2} + \left(\frac{t}{v} + \frac{t^2}{4}\right)^{1/2}.$$

With the aid of (21) and (22), the equations (19) and (20),

$$p = p(v,\theta)$$

$$v = v(p,\theta),$$

may be written

$$(19a) \qquad p = \frac{r\theta}{v} + (s - t)r\theta$$

$$(20a) \qquad \frac{1}{v} = \frac{s}{t}\,(s - t).$$

Fundamental Functions

The thermodynamic potential of a mass of a one-component two-constituent gas may be expressed as a function

$$H(p,\theta,N_1).$$

The 'molecular thermodynamic potential' of the gas is then

$$h = \partial H/\partial N_1.$$

The relation

$$2N_1 = 2n_1 + n_2$$

converts the thermodynamic potential into a function

$$H\Big(p,\theta,N_1(n_1,n_2)\Big),$$

whereupon by differentiation with regard to n_2 and comparison with the general equation

$$\partial H/\partial n_2 = \lambda_2$$

we find

$$\lambda_2 = \frac{\partial H}{\partial N_1}\,\frac{\partial N_1}{\partial n_2}$$

$$= h/2.$$

We shall now seek the form of the 'fundamental equation'

$$h = 2\lambda_2(p,\theta)$$

of an ideal-constituent gas.

In equation (6*b*), λ_2 is expressed in terms of p,θ, and the function $n_2/(n_1+n_2)$. It remains to express $n_2/(n_1+n_2)$ in terms of p,θ. Solving equations (7) and (15),

$$pV = (n_1 + n_2).r\theta$$

$$2N_1 = 2n_1 + n_2,$$

for n_1 and n_2, we find

$$\frac{n_2}{n_1+n_2} = 2 - 2\frac{r\theta}{p}\frac{N_1}{V};$$

whence, on replacing N_1/V by its value as a function of p,θ, from (20),

$$\frac{n_2}{n_1+n_2} = 2\frac{r\theta}{p}\left\{\left(\frac{p}{r\theta}t + t^2\right)^{\frac{1}{2}} - t\right\}$$

(23) $$= 2\frac{r\theta}{p}(s-t).$$

Substituting this value in the equation (6*b*) for λ_2, we obtain

$$h = 2\lambda_2$$

(24) $$= 2r\theta.\log 2(s-t) - 2c_{v2}\theta.\log\theta + 2(c_{p2} - \eta_{02})\theta + 2\epsilon_{02}.$$

Since s can be expressed as a function of p,θ, by (21), or as a function of v,θ, by (22), this equation expresses the molecular thermodynamic potential of the gas in either of these pairs of variables.

In order to find the form of the fundamental function

$$f = f(v,\theta),$$

where f is the molecular free energy of the system, we require merely to express the second member of

(25) $$f = h - pv$$

by means of (24) and the equations (19*a*), (20*a*),

$$p = \frac{r\theta}{v} + r\theta(s - t)$$

$$v = \frac{t}{s(s - t)}.$$

We find

$$(26) \qquad f = 2r\theta.\log 2(s - t) - 2c_{v_2}\,\theta.\log \theta + 2(c_{p_2} - \eta_{o_2})\theta$$
$$- r\theta\left(1 + \frac{t}{s}\right) + 2e_{o_2}.$$

The second member of this equation, again, may be regarded as being in v,θ, or in p,θ.

Either of the fundamental equations (24) or (26) may be regarded as the *definition* of a one-component ideal-constituent gas. And it appears, from the close accord between observed densities and the requirements of the characteristic equation, that the thermodynamic behavior of such a gas is quite closely approximated by the behavior of certain actual gases and vapors throughout extensive regions of their possible states. The definition of a one-component ideal-constituent gas, as is evident from the derivation of the fundamental equations (24) and (26), involves the assumptions : *a*, that the interconvertible constituents of the system are ideal gases; *b*, that the pressure of the system is determined by Dalton's law ; *c*, that the potential of neither constituent is altered by the presence of the other ; *d*, that $2c_{v_2} - c_{v_1} = 0$.

Derivatives of the fundamental functions h, f

From (24) and (26), by differentiation, we find the 'derived relations,'

$$(27a) \qquad v = + \frac{\partial h}{\partial p},$$

$$(27b) \qquad p = - \frac{\partial f}{\partial v},$$

$$(28) \qquad \eta = - \frac{\partial h}{\partial \theta} = - \frac{\partial f}{\partial \theta},$$

where η is the molecular entropy of the gas, in the forms

$$v = \frac{t/s}{s - t} \tag{29}$$

$$p = \frac{r\theta}{v} + (s - t)r\theta \tag{30}$$

$$\eta = -2r.\log 2(s - t) - \left(1 - \frac{t}{s}\right)\left(\frac{Q_v}{\theta} + r\right) + 2c_{v2}.\log\theta + 2\eta_{02}. \tag{31}$$

These are the equations

$$\begin{array}{r|l} v = v(p,\theta) & \eta = \eta_a(p,\theta) \\ p = p(v,\theta) & \quad = \eta_b(v,\theta). \end{array}$$

The equations (29) and (30) are, of course, identical with the forms (20*a*) and (19*a*) of the characteristic equation. The equation (30), when v is replaced by its value as expressed by (29), becomes

$$\frac{p}{r\theta} = \frac{s^2 - t^2}{t}.$$

Regarded as expressing the quantity $p/r\theta$ as a function of t,s, this form of the characteristic equation is the equation of the asymptotic cone of the hyperboloid of one sheet. The slopes of this surface are[1]

$$-\frac{\partial}{\partial t}\frac{p}{r\theta} = \frac{s^2}{t^2} + 1, \qquad \frac{\partial}{\partial s}\frac{p}{r\theta} = 2\frac{s}{t}.$$

The energy and the heat-function

From the foregoing equations it is not possible to find the forms of the fundamental equations

$$e = e(v,\eta)$$
$$g = g(p,\eta),$$

where e is the molecular energy of the two-constituent gas, and g is the molecular heat-function defined by the equation

$$g = e + pv.$$

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[1] By equation (35), these slopes are $\alpha^2 + 1$, and 2α, where α is the percentage dissociation.

It is readily possible, however, to find e and g in terms of the pairs of state variables already employed. For e and g we have the general equations

$$e = h - pv + \theta\eta$$

$$g = h + \theta\eta.$$

Substituting for h,p,η from (24), (30), (31), and reducing, noting that $c_{p2} - r = c_{v2}$

$$e = 2c_{v2}\theta - \left(1 - \frac{t}{s}\right)Q_v + 2e_0, \tag{32}$$

$$g = 2c_{p2}\theta - \left(1 - \frac{t}{s}\right)(Q_v + r\theta) + 2e_0. \tag{33}$$

Since s can be expressed as a function of p,θ, or as a function of v,θ, these equations are either

$$e = e_a(p,\theta), \qquad g = g_a(p,\theta),$$

or

$$e = e_b(v,\theta), \qquad g = g_b(v,\theta).$$

The symmetry of (32) and (33) becomes more obvious when it is noted that the quantity $Q_v + r\theta$ is the heat of dissociation at constant pressure, Q_p.

Functions of α,θ

Let us now formulate the foregoing fundamental and derived functions in terms of the temperature of the gas and the degree α of its dissociation. To this end we require to find the form of the function

$$s(\alpha,\theta).$$

Comparison of the equations (7)[1] and (30),

$$pv = (1 + \alpha)r\theta$$

$$p = \frac{r\theta}{v} + (s - t)r\theta$$

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[1] The formulation (7) of Dalton's law is

$$p = (n_1 + n_2)\frac{r\theta}{V}.$$

When $V = v$, we have $n_1 + n_2 = 1 + \alpha$; wherefore

$$pv = (1 + \alpha)r\theta.$$

shows that

$$(34) \qquad s - t = \frac{\alpha}{v};$$

whereupon elimination of v between this equation and (29),

$$\frac{1}{v} = \frac{s}{t}(s - t),$$

yields the desired form,

$$(35) \qquad s = \frac{t}{\alpha}.$$

The simplicity of the physical significance of the ratio and of the difference of our two auxiliary functions s and t, as expressed by the equations

$$\frac{s}{t} = \alpha, \qquad s - t = \frac{\alpha}{v},$$

is very gratifying.

The equation (35) now enables us to express the fundamental and derived functions

$$h, \quad f, \quad e, \quad g, \quad v, \quad p, \quad \eta,$$

in terms of the state-variables α,θ. Substitution of (35) in (24) yields for the molecular thermodynamic potential $h(\alpha,\theta)$,

$$(36) \quad h = 2r\theta.\log 2\frac{1-\alpha}{\alpha}t - 2c_{v2}\theta.\log\theta + 2(c_{p2} - \eta_{o2})\theta + 2e_{o2}.$$

Substitution in (26) yields for the molecular free energy $f(\alpha,\theta)$,

$$(37) \quad f = 2r\theta.\log 2\frac{1-\alpha}{\alpha}t - 2c_{v2}\theta.\log\theta$$

$$+\Big(2(c_{p2} - \eta_{o2}) - (1 + \alpha)r\Big)\theta + 2e_{o2}.$$

Substitution in (32) yields for the molecular energy $e(\alpha,\theta)$,

$$(38) \qquad e = 2c_{v2}\theta - (1 - \alpha)Q_v + 2e_{o2}.$$

Substitution in (33) yields for the molecular heat-function $g(\alpha,\theta)$,

$$(39) \qquad g = 2c_{p2}\theta - (1 - \alpha)(Q_v + r\theta) + 2e_{o2}.$$

Substitution in (29) yields for the molecular volume $v(\alpha,\theta)$,

$$(40) \qquad v = \frac{\alpha^2}{1-\alpha}\,\frac{1}{t}.$$

Substitution of (35) and (40) in (30) yields for the equilibrium pressure $p(\alpha,\theta)$,

$$(41) \qquad p = \frac{1-\alpha^2}{\alpha^2}\, r\theta t.$$

Substitution of (35) in (31) yields for the molecular entropy $\eta(\alpha,\theta)$,

$$(42) \quad \eta = -2r.\log 2\,\frac{1-\alpha}{\alpha}\,t - (1-\alpha)\left(\frac{Q_v}{\theta} + r\right) + 2c_{v2}.\log\theta + 2\eta_{02}.$$

In equation (38),

$$e = 2c_{v2}\theta + 2e_{02} - (1-\alpha)Q_v,$$

the terms $2(c_{v2}\theta + e_{01})$ represent the energy of two molecular weights of the 'ideal' second constituent. But the gas contains $(1-\alpha)$ molecular weights of the undissociated constituent, the formation of which evolves the heat $(1-\alpha)Q_v$; so the energy of the gas is less than $2(c_{v2}\theta + e_{02})$ by this amount.

It is worthy of note that the degree of dissociation $\alpha(v,\theta)$ is a function of the quantity vt. This readily appears on elimination of s between

$$\alpha = t/s, \qquad s - t = \alpha/v,$$

whereby we obtain

$$\alpha^2 + vt.\alpha = vt,$$

which yields

$$(43) \qquad \alpha = +\left(vt + \tfrac{1}{4}(vt)^2\right)^{\frac{1}{2}} - \tfrac{1}{2}\,vt.$$

Since α is positive, the positive root must be taken.

The explicit formulation of $\alpha(p,\theta)$ is more readily obtained from (41),

$$p = \frac{1-\alpha^2}{\alpha^2}\, r\theta t,$$

which yields

$$\alpha^2 = \frac{r\theta t}{p + r\theta t}. \tag{44}$$

Functions of α, v

Omitting consideration of the fundamental functions, let us now formulate the functions under consideration, namely,

$$t, \quad s, \quad \theta, \quad p, \quad \eta,$$

in terms of the molecular volume v of the gas and the degree α of its dissociation.

The equation (40) gives t in terms of these state-variables,

$$t = \frac{\alpha^2}{1 - \alpha} \frac{1}{v}. \tag{45}$$

For s, we have

$$s = t/\alpha;$$

whence, by (45),

$$s = \frac{\alpha}{1 - \alpha} \frac{1}{v}. \tag{46}$$

To find θ, we replace t in (45) by its value (13),

$$\frac{a}{4} \epsilon^{-\frac{Q_v}{r\theta}},$$

whereupon solution for θ yields

$$\theta = \frac{Q_v}{r} : \log\left(\frac{a}{4} \frac{1 - \alpha}{\alpha} \frac{v}{\alpha}\right). \tag{47}$$

Introducing p by means of (7),

$$p = (1 + \alpha) \frac{r\theta}{v};$$

elimination of θ between this and (47) yields

$$p = (1 + \alpha) \frac{Q_v}{v} : \log\left(\frac{a}{4} \frac{1 - \alpha}{\alpha} \frac{v}{\alpha}\right). \tag{48}$$

The molecular entropy $\eta(\alpha, \theta)$ is, by (42),

$$\eta = -2r.\log 2\frac{1-\alpha}{\alpha}t + 2c_{v_2}.\log\theta - (1-\alpha)\left(\frac{Q_v}{\theta}+r\right)+2\eta_{o_2}.$$

Replacing t by (45), and θ by (47), we find the form of $\eta(\alpha, v)$ to be that given by the equation

$$(49)\quad \eta = -2r.\log 2\frac{\alpha}{v} + 2c_{v_2}.\log\frac{\dfrac{Q_v}{r}}{\log\left(\dfrac{a}{4}\,\dfrac{1-\alpha}{\alpha}\,\dfrac{v}{\alpha}\right)}$$
$$-(1-\alpha)r.\log\left(\frac{a\epsilon}{4}\,\frac{1-\alpha}{\alpha}\,\frac{v}{\alpha}\right)+2\eta_{o_2}.$$

To facilitate reference, the numbers of the equations in which the fundamental functions e, f, g, h are expressed in terms of the successive sets of variables p,θ, v,θ, α,θ are exhibited in the accompanying table.

	e	f	g	h
In p,θ or v,θ	32	26	33	24
In α,θ	38	37	39	36

Further to facilitate reference, the numbers of the equations presenting the derived and auxiliary functions whose forms have been found are arranged in the following table. When a letter denotes an independent variable, it is entered in the table in place of the number of an equation. It was not found possible to express any of the functions in question in terms of p,v or of α,p or of any pair of variables including η.

In:	p,θ	v,θ	α,θ	α,v
t	13	13	13	45
s	21	22	35	46
θ	θ	θ	θ	47
v	29	v	40	v
p	p	30	41	48
η	31	31	42	49
α	44	43	α	α

Derivatives

Now that each of the quantities

$$t,\quad s,\quad p,\quad v,\quad \theta,\quad \alpha,\quad \eta,$$

is expressed in terms of each of the pairs

$$p,\theta, \qquad v,\theta, \qquad \alpha,\theta \qquad \alpha,v,$$

of state-variables, the derivatives of each of these quantities with regard to the variables of any pair, and expressed in terms of any of the pairs, can be readily found. The following list of the first derivatives permits comparison of these functions with one another. All are expressed in terms of the same pair, α,θ, of variables. The function

$$\frac{a}{4}\epsilon^{-\frac{Q_v}{r\theta}}$$

whenever it appears is, as hitherto, represented by t. Reciprocal formulas are omitted; for example, having

$$\left(\frac{\partial p}{\partial \alpha}\right)_\theta = -\frac{2r\theta t}{\alpha^3},$$

we omit to write

$$\left(\frac{\partial \alpha}{\partial p}\right)_\theta = -\frac{\alpha^3}{2r\theta t}.$$

To the list have been added the further derivatives obtainable only by means of the relation

$$\left(\frac{\partial y}{\partial x}\right)_u = -\left(\frac{\partial u}{\partial x}\right)_y : \left(\frac{\partial u}{\partial y}\right)_x.$$

The forms of four derivatives, obtainable in this way, relating to adiabatic expansion are so complicated that they are only indicated in the list.

Derivatives of t

$$\frac{dt}{d\theta} = \frac{Q_v t}{r\theta^2}$$

$$\frac{1}{t}\frac{dt}{d\theta} = \frac{Q_v}{r\theta^2}$$

$$\left(\frac{\partial t}{\partial \alpha}\right)_v = \frac{2-\alpha}{\alpha(1-\alpha)}t$$

$$\left(\frac{\partial t}{\partial v}\right)_\alpha = -\frac{1-\alpha}{\alpha^3}t^2$$

Derivatives of s'

$$\left\{\begin{aligned}\left(\frac{\partial s}{\partial p}\right)_\theta &= +\frac{1}{2r}\frac{\alpha}{\theta}\\ \left(\frac{\partial s}{\partial \theta}\right)_p &= +\left(\frac{1+\alpha^2}{2\alpha}\frac{Q_v}{r\theta}-\frac{1-\alpha^2}{2\alpha}\right)\frac{t}{\theta}\end{aligned}\right. \qquad \left\{\begin{aligned}\left(\frac{\partial s}{\partial \theta}\right)_\alpha &= +\frac{1}{\alpha}\frac{Q_v t}{r\theta^2}\\ \left(\frac{\partial s}{\partial \alpha}\right)_\theta &= -\frac{t}{\alpha^2}\end{aligned}\right.$$

$$\left\{\begin{aligned}\left(\frac{\partial s}{\partial v}\right)_\theta &= -\frac{(1-\alpha)^2}{\alpha^3(2-\alpha)}t^2\\ \left(\frac{\partial s}{\partial \theta}\right)_v &= +\frac{1}{\alpha(2-\alpha)}\frac{Q_v t}{r\theta^2}\end{aligned}\right. \qquad \left\{\begin{aligned}\left(\frac{\partial s}{\partial v}\right)_\alpha &= -\frac{1-\alpha}{\alpha^3}t^2\\ \left(\frac{\partial s}{\partial \alpha}\right)_v &= +\frac{t}{\alpha^2(1-\alpha)}\end{aligned}\right.$$

Derivatives of p, v, θ, α, η

$$\left(\frac{\partial p}{\partial \theta}\right)_v = +\frac{1-\alpha^2}{\alpha^2}rt+\frac{(1-\alpha)^2}{\alpha(2-\alpha)}\frac{Q_v t}{\theta}$$

$$\left(\frac{\partial p}{\partial \theta}\right)_\eta = -\left(\frac{\partial \eta}{\partial \theta}\right)_p : \left(\frac{\partial \eta}{\partial p}\right)_\theta$$

$$\left(\frac{\partial p}{\partial \theta}\right)_\alpha = +\frac{1-\alpha^2}{\alpha^2}\left(\frac{Q_v}{\theta}+r\right)t$$

$$\left(\frac{\partial v}{\partial \theta}\right)_p = +\frac{\alpha^3}{2}\frac{Q_v}{r\theta^2 t}+\frac{\alpha^2(2-\alpha)(1+\alpha)}{2(1-\alpha)}\frac{1}{\theta t}$$

$$\left(\frac{\partial v}{\partial \theta}\right)_\eta = -\left(\frac{\partial \eta}{\partial \theta}\right)_v : \left(\frac{\partial \eta}{\partial v}\right)_\theta$$

$$\left(\frac{\partial v}{\partial \theta}\right)_\alpha = -\frac{\alpha^2}{1-\alpha}\frac{Q_v}{r\theta^2 t}$$

$$\left(\frac{\partial v}{\partial p}\right)_\theta = -\frac{\alpha^4(2-\alpha)}{2(1-\alpha)^2}\frac{1}{r\theta t^2}$$

$$\left(\frac{\partial v}{\partial p}\right)_\alpha = -\frac{\alpha^4}{(1-\alpha)^2(1+\alpha)}\frac{Q_v}{Q_v+r\theta}\frac{1}{r\theta t^2}$$

$$\left(\frac{\partial \alpha}{\partial \theta}\right)_p = \frac{\alpha(1-\alpha^2)}{2r\theta}\left(\frac{Q_v}{\theta}+r\right)$$

$$\left(\frac{\partial \alpha}{\partial \theta}\right)_v = +\frac{\alpha(1-\alpha)}{2-\alpha}\frac{Q_v}{r\theta^2}$$

$$\left(\frac{\partial \alpha}{\partial \theta}\right)_\eta = -\left(\frac{\partial \eta}{\partial \theta}\right)_\alpha : \left(\frac{\partial \eta}{\partial \alpha}\right)_\theta$$

$$\left(\frac{\partial\alpha}{\partial p}\right)_\theta = -\frac{\alpha^3}{2r\theta t}$$

$$\left(\frac{\partial\alpha}{\partial p}\right)_v = +\frac{1-\alpha}{\alpha^2}r\theta t + \frac{(1+\alpha)(2-\alpha)}{\alpha^3}\frac{r^2\theta^3}{Q_v}t$$

$$\left(\frac{\partial\alpha}{\partial v}\right)_\theta = +\frac{(1-\alpha)^2}{\alpha(2-\alpha)}t$$

$$\left(\frac{\partial\alpha}{\partial v}\right)_p = +\frac{(Q_v/\theta+r)t}{\alpha}:\left(\frac{\alpha}{1-\alpha^2}\frac{Q_v}{\theta}+\frac{2-\alpha}{(1-\alpha)^2}r\right)$$

$$\left(\frac{\partial\alpha}{\partial v}\right)_\eta = -\left(\frac{\partial\eta}{\partial v}\right)_\alpha : \left(\frac{\partial\eta}{\partial\alpha}\right)_v$$

$$\left(\frac{\partial\eta}{\partial\theta}\right)_p = +\frac{2c_{v2}}{\theta} + \frac{\alpha(1-\alpha^2)}{2r\theta}\left(\frac{Q_v}{\theta}+r\right)^2 + (1+\alpha)\frac{r}{\theta}$$

$$\left(\frac{\partial\eta}{\partial\theta}\right)_v = +\frac{2c_{v2}}{\theta} + \frac{\alpha(1-\alpha)}{2-\alpha}\frac{Q_v^2}{r\theta^3}$$

$$\left(\frac{\partial\eta}{\partial\theta}\right)_\alpha = +\frac{2c_{v2}}{\theta} - (1+\alpha)\frac{Q_v}{\theta^2}$$

$$\left(\frac{\partial\eta}{\partial p}\right)_\alpha = -\frac{\alpha^3}{2\theta t}\left(\frac{(2-\alpha)(1+\alpha)}{\alpha(1-\alpha)}+\frac{Q_v}{r\theta}\right)$$

$$\left(\frac{\partial\eta}{\partial v}\right)_\theta = +\frac{1-\alpha}{\alpha}\left(\frac{1+\alpha}{\alpha}+\frac{1-\alpha}{2-\alpha}\frac{Q_v}{r\theta}\right)rt$$

$$\left(\frac{\partial\eta}{\partial v}\right)_\alpha = +\frac{1-\alpha}{\alpha}\left(\frac{1+\alpha}{\alpha}+\frac{2c_{v2}}{\alpha}\frac{\theta}{Q_v}\right)rt$$

$$\left(\frac{\partial\eta}{\partial\alpha}\right)_\theta = +\frac{Q_v}{\theta} + r\frac{(2-\alpha)(1+\alpha)}{\alpha(1-\alpha)}$$

$$\left(\frac{\partial\eta}{\partial\alpha}\right)_v = +\frac{Q_v}{\theta} + \frac{2-\alpha}{\alpha(1-\alpha)}\frac{r\theta}{Q_v}2c_{v2}$$

Among the results expressed by these equations the following may be especially noted. The increase of the dissociation per degree at constant pressure is proportional to Q_p/θ^2, and the increase per degree at constant volume is proportional to Q_v/θ^2; while the increase of the dissociation per unit isothermal fall of the pressure is proportional to the *cube* of the degree of dissociation and inversely proportional to θt, and the increase per unit isothermal increase of volume depends on the degree of dissociation and is proportional to t. It may also be noted that every derivative at constant volume depends on the heat of dissociation at constant volume. The bearing of the hessians of the fundamental functions on the values of the second derivatives of the 'derived functions' make these hessians of interest. The hessian of the molecular thermodynamic potential is the function

$$(50) \qquad \frac{\alpha^3}{1-\alpha}\left(\frac{2-\alpha}{\alpha(1-\alpha)}c_{v2}+\frac{Q_v^2}{\theta^2}\right)\frac{1}{2r\theta^2t^2}.$$

The hessian of the free energy is yet more complicated than this.

From the equation (38), $e = e(\alpha,\theta)$, it follows that

$$\frac{\partial e}{\partial \alpha} = Q_v, \qquad \frac{\partial e}{\partial \theta} = 2c_{v2}, \qquad \left(\frac{\partial \alpha}{\partial \theta}\right)_e = -\frac{2c_{v2}}{Q_v}.$$

Less obvious than these constant rates is the deduction, from (36) and (37),

$$-\frac{\partial h}{\partial \alpha} = \frac{2}{\alpha(1-\alpha)}r\theta,$$

$$-\frac{\partial f}{\partial \alpha} = \frac{2}{\alpha(1-\alpha)}r\theta - r\theta,$$

that the rates of increase of h and of f with decreasing dissociation are proportional to θ and dependent on the product $\alpha.(1-\alpha)$.

Heat capacity at constant pressure

The molecular heat capacity of a one-component ideal-constituent gas, at constant pressure, is defined by the equation

$$c_p = \theta\left(\frac{\partial \eta}{\partial \theta}\right)_p.$$

From equation (31),

$$\eta = 2c_{v2}.\log\theta - 2r.\log 2(s-t) - \left(1-\frac{t}{s}\right)\left(\frac{Q_v}{\theta}+r\right) + 2\eta_{01},$$

we find

$$(51a) \quad c_p = 2c_{p2} - \left(1-\frac{t}{s}\right)r + \frac{1}{2r}\left(\frac{t}{s}-\frac{t^2}{s^2}\right)\left(\frac{Q_v}{\theta}+r\right)^2.$$

This may be regarded as expressing c_p in p,θ, and in v,θ. In the variables α,θ, and in α,v, the equation becomes

$$(51b)\qquad c_p = 2c_{p2} - (1-\alpha)r + \frac{\alpha - \alpha^3}{2r}\left(\frac{Q_v}{\theta} + r\right)^2$$

$$(51c)\quad c_p = 2c_{p2} - (1-\alpha)r + (\alpha - \alpha^3)\,\frac{r}{2}\,.\log^2\!\left(\frac{a\epsilon}{4}\,\frac{1-\alpha}{\alpha}\,\frac{v}{\alpha}\right).$$

The accompanying Fig. 1 exhibits the course of the func-

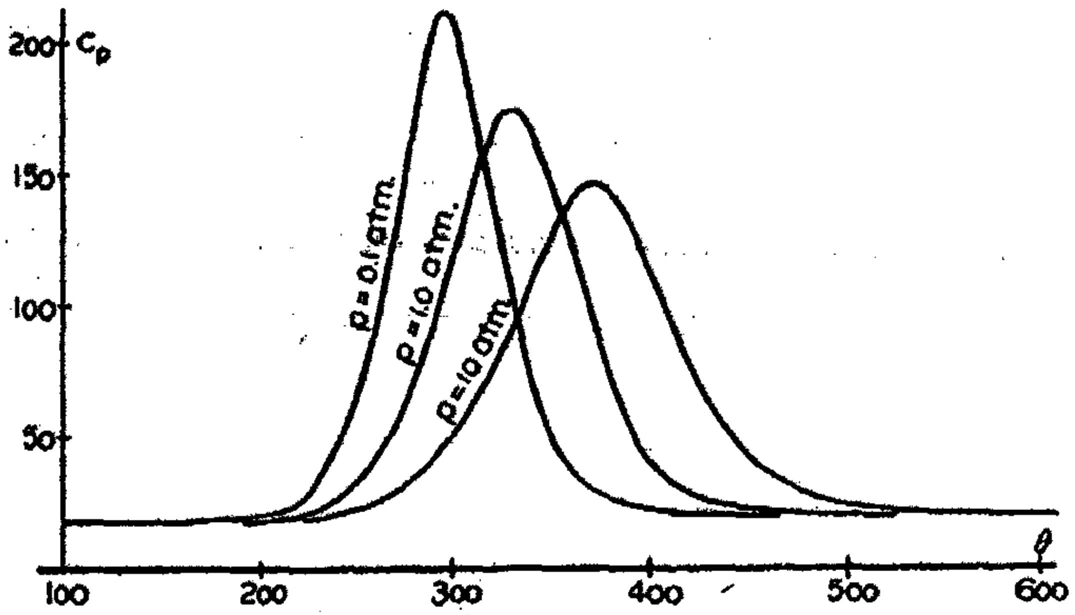

Fig. 1

tion $c_p(p,\theta)$, for nitrogen peroxide, for the successive values 0.1 atm., 1.0 atm., and 10 atm., of the parameter p. In the computation of points on these curves, the constants of the function were assigned the values.

$$c_{p2} = 10\,\frac{\text{cal}}{\text{deg}}$$
$$r = 2\,\frac{\text{cal}}{\text{deg}}$$
$$Q_v = 12900\ \text{cal}$$
$$a = 10^{7.252}\,\frac{1}{\text{lit}}$$

For Q_v was chosen the value given by Ostwald.[1] To find a, the molecular volume corresponding to the set of observations,

$$\alpha = 0.504, \qquad \theta = 273 + 21.7, \qquad p = 59.7\ \text{mm.},$$

cited by Swart[2] from the density determinations of E. and L.

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[1] Lehrbuch: "Thermochemie", 147.

[2] Zeit. phys. chem. 7, 135 (1891).

Natanson, was computed; whereupon a was obtained by substituting the simultaneous values of p, θ, v in the characteristic equation, and solving this for a. This set of results was given the preference because it corresponds to a dissociation of almost exactly fifty percent. From the formulation of the function $c_p(\alpha, \theta)$ it will be noted that

$$\text{when } \alpha = 1, \qquad c_p = 2c_{p_1}$$

$$\text{when } \alpha = 0, \qquad c_p = 2c_{p_2} - r.$$

So, at high temperatures the line $c_p = 20$, and at low temperatures the line $c_p = 18$, is the asymptote of the curves of the family.

An incorrect formulation of the function $c_p(\alpha,\theta)$ has been given by Swart.[1] In his deduction, Swart says : "Bei konstantem Druck ergiebt sich die spezifische Wärme (C_p) ebenfalls als Summe, jetzt von C'_p und der Dissociationswärme. Letztere stellt sich heraus auf $(\partial x/\partial T)_p$, multipliziert mit innerer Dissociationswärme q und äusserer Arbeitsleistung, welche sich in Kalorien nach (2) als T ergiebt; also :

$$C_p = C'_p + \left(\frac{\partial x}{\partial T}\right)_p (q + T)."$$

So Swart obtains C_p, the molecular heat capacity of NO_2 at constant pressure, as the sum of three terms,

$$C'_p + \frac{\partial x}{\partial T} q + \frac{\partial x}{\partial T} T,$$

where x is the degree of dissociation. The first of these terms, the heat absorbed per degree at constant pressure without change of the degree of dissociation, less the work-development of the process, is

$$\begin{aligned} C_{v2} &= C_{p2} - r \\ &= C_{p2} - 2. \end{aligned}$$

The last term, the work-development $p(\partial v/\partial T)_p$, Swart obtains from his equation (2),

$$Ap v = T;$$

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[1] Zeit phys. chem. 7, 120 (1891).

while it should be obtained from his equation (3),

$$Apv = (1 + x)T;$$

as

$$p\left(\frac{\partial v}{\partial T}\right)_p = 1 + x + T\left(\frac{\partial x}{\partial T}\right)_p.$$

So Swart's equation should be written

$$C_p = C_{p2} - 1 + x + \frac{\partial x}{\partial T}(q + T);$$

wherefore, by Swart's transformations,

$$C_p = C_{p2} - 1 + x + \frac{x - x^3}{2}\left(\frac{q}{T} + 1\right)^2,$$

which is identical with our equation (51*b*). Swart's result omits the terms $-1 + x$.

Heat capacity at constant volume

From (31),

$$\eta = 2c_{v2}.\log\theta - 2r.\log 2(s - t) - \left(1 - \frac{t}{s}\right)\left(\frac{Q_v}{\theta} + r\right) + 2\eta_{o2},$$

the molecular heat capacity at constant volume, which is defined by the equation

$$c_v = \theta\left(\frac{\partial\eta}{\partial\theta}\right)_v,$$

is found to be

$$(52a) \qquad c_v = 2c_{v2} + \frac{t(s - t)}{s(2s - t)}\frac{Q_v^2}{r\theta^2}.$$

This equation may be regarded as expressing c_v in p,θ, and in v,θ. In the variables α,θ, and in α,v, it becomes

$$c_v = 2c_{v2} + \frac{\frac{t}{s}\left(1 - \frac{t}{s}\right)}{2 - \frac{t}{s}}\frac{Q^2}{r\theta^2}$$

$$(52b) \qquad = 2c_{v2} + \frac{\alpha(1 - \alpha)}{2 - \alpha}\frac{Q_v^2}{r\theta^2}.$$

$$(52c) \qquad c_v = 2c_{v_2} + \frac{\alpha(1-\alpha)}{2-\alpha} r.\log^2\left(\frac{a}{4}\,\frac{1-\alpha}{\alpha}\,\frac{v}{a}\right).$$

The equation (52*b*) was found by Swart.[1] The course of the function $c_v(v,\theta)$, for nitrogen peroxide, for the successive values 222 liters, 22.2 liters, and 2.22 liters, of the parameter v is exhibited by Fig. 2. Since c_v reduces to $2c_{v_2}$ for $\alpha = 1$ and for $\alpha = 0$, the line $c_v = 16$ is the asymptote, both at high and at low temperatures, of the curves of the family.

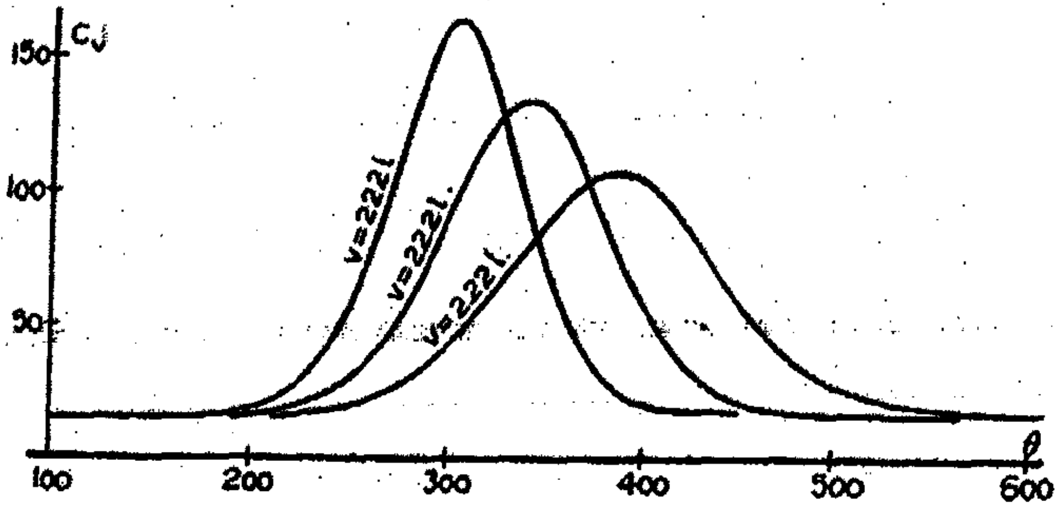

Fig. 2.

It may be added that, from (51*b*) and (52*b*), the difference of the heat capacities at constant pressure and at constant volume is found to be

$$(53) \qquad c_p - c_v = \frac{2-\alpha}{2r}\left(\frac{\alpha-\alpha^2}{2-\alpha}\,\frac{Q_v}{\theta} + (1+\alpha)r\right)^2,$$

which accords with the general thermodynamic equation

$$c_p - c_v = \theta\left(\frac{\partial p}{\partial \theta}\right)_v\left(\frac{\partial v}{\partial \theta}\right)_p.$$

Work Integrals

The expressions that have been obtained for the pressure and the molecular volume of a one-component ideal-constituent gas make possible the calculation of the work absorbed by the molecular quantity of the gas during reversible expansion along any path defined by a relation between the variables. We shall now execute this calculation for paths defined by the constancy

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[1] Zeit. phys. chem. 7, 131 (1891).

of one or the other of the quantities that may be employed as state-variables. The notation

$$\mathrm{W}_{\Delta x,y}$$

shall denote the work absorbed in an expansion between assigned x-limits at constant y.

Isothermal paths

For isothermal expansions, we have:

$$\mathrm{W}_{\Delta p,\theta} = -\int_{p_1}^{p_2} p\frac{\partial v}{\partial p}\,dp = f(p,\theta)\Big|_{p_1}^{p_2}$$

$$\mathrm{W}_{\Delta v,\theta} = -\int_{v_1}^{v_2} p\,dv \quad = f(v,\theta)\Big|_{v_1}^{v_2}$$

$$\mathrm{W}_{\Delta \alpha,\theta} = -\int_{\alpha_1}^{\alpha_2} p\frac{\partial v}{\partial \alpha}\,d\alpha = f(\alpha,\theta)\Big|_{\alpha_1}^{\alpha_2}$$

From equation (26) for f, we find

$$(54a) \qquad (\mathrm{W}_{12})_{\theta} = 2r\theta.\log\frac{s_2 - t}{s_1 - t} - r\theta\left(\frac{t}{s_2} - \frac{t}{s_1}\right);$$

where t is $t(\theta)$, where s denotes successively the functions

$$s(p,\theta), \qquad s(v,\theta), \qquad s(\alpha,\theta),$$

as given by equations (21), (22), (35), and the subscripts distinguish functions of the end values of p, v, or θ. The result obtained by the substitution of $s(\alpha, \theta)$,

$$(54b) \qquad \mathrm{W}_{\Delta\alpha,\theta} = 2r\theta.\log\frac{\alpha_1}{\alpha_2}\frac{1-\alpha_2}{1-\alpha_1} - r\theta(\alpha_2 - \alpha_1),$$

which is more directly obtained from the equation (37) for $f(\alpha,\theta)$, has been deduced by Nernst and Schoenflies from the characteristic equation[1].

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[1] Einführung in die mathematische Behandlung der Naturwissenschaften, 135 (1895).

Isopiestic paths

For isopiestic expansions, we have:

$$W_{\Delta v,p} = -p(v_2 - v_1) \tag{55a}$$

$$W_{\Delta\theta,p} = -p.v(p,\theta)\Big|_{\theta_1}^{\theta_2}$$

$$= -p\,\frac{t}{s(s-t)}\Big|_{\theta_1}^{\theta_2} \tag{55b}$$

The first of these is perfectly obvious. In the second, t and s are the functions of p,θ given by (13) and (21).

Paths at constant degree of dissociation

In expansions at constant degree of dissociation:

$$W_{\Delta v,\alpha} = -\int_{v_1}^{v_2} p\,dv$$

$$= -(1+\alpha)Q_v\int_{v_1}^{v_2}\frac{dv}{v\log\left(\frac{a}{4}\,\frac{1-\alpha}{\alpha}\,\frac{v}{\alpha}\right)}$$

$$= -(1+\alpha)Q_v.\log\left\{\log\left(\frac{a}{4}\,\frac{1-\alpha}{\alpha}\,\frac{v}{\alpha}\right)\right\}_{v_1}^{v_2} \tag{56}$$

Again,

$$W_{\Delta\theta,\alpha} = -\int_{\theta_1}^{\theta_2} p\,\frac{\partial v}{\partial\theta}\,d\theta.$$

From (41) and our tabulation of derivatives,

$$p = \frac{1-\alpha^2}{\alpha^2}\,r\theta t, \qquad \left(\frac{\partial v}{\partial\theta}\right)_\alpha = -\frac{\alpha^2}{1-\alpha}\,\frac{Q_v}{r\theta^2 t};$$

substitution of which yields[1]

$$W_{\Delta\theta,\alpha} = (1+\alpha)Q_v\,.\log\frac{\theta_2}{\theta_1}. \tag{57}$$

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[1] This result has already been obtained by one of us. Boltzmann's "Festschrift," 496 (1904).

Heat Integrals

By means of the expressions that have been obtained for the temperature and the molecular entropy of an ideal-constituent gas, we shall now calculate the reversible heat-absorption of the molecular quantity of gas along paths defined by the constancy of one or the other state-variable of any pair.

Isothermal paths

For isothermal expansions, we have:

$$Q_{\Delta p,\theta} = \theta.\eta(p.\theta)\Big|_{p_1}^{p_2}$$

$$Q_{\Delta v,\theta} = \theta.\eta(v,\theta)\Big|_{v_1}^{v_2}$$

$$Q_{\Delta \alpha,\theta} = \theta.\eta(\alpha,\theta)\Big|_{\alpha_1}^{\alpha_2}$$

$$Q_{\Delta \eta,\theta} = \theta(\eta_2 - \eta_1).$$

From equation (31) for η, we find

$$(Q_{12})_\theta = 2r\theta.\log\frac{s_1 - t}{s_2 - t} + \left(\frac{t}{s_2} - \frac{t}{s_1}\right)(Q_v + r\theta)\,; \tag{58a}$$

where t is $t(\theta)$, where s denotes successively the functions

$$s(p,\theta), \qquad s(v,\theta), \qquad s(\alpha,\theta),$$

as given by equations (21), (22), (35), and the subscripts distinguish functions of the end-values of p, v, or α. The result obtained by the substitution of $s\,(\alpha,\theta)$ is

$$Q_{\Delta\alpha,\theta} = 2r\theta.\log\frac{\alpha_2}{\alpha_1}\,\frac{1 - \alpha_1}{1 - \alpha_2} + (\alpha_2 - \alpha_1)(Q_v + r\theta). \tag{58b}$$

Isopiestic paths

For isopiestic expansions, we have:

$$Q_{\Delta\theta,p} = g(p,\theta)\Big|_{\theta_1}^{\theta_2} \quad ,$$

$$= \left\{2c_{p_2}\theta - \left(1 - \frac{t}{s}\right)r\theta + \frac{t}{s}\,Q_v\right\}_{\theta_1}^{\theta_2}. \tag{59}$$

It will be noted that this formulation is identical with

$$Q_{\Delta\theta,p} = \int_{\theta_1}^{\theta_2} \theta \frac{\partial\eta}{\partial\theta}\, d\theta$$

$$= \int_{\theta_1}^{\theta_2} c_p(p,\theta) d\theta.$$

Isometric paths

For isometric expansions, we have :

$$(a) \qquad Q_{\Delta\theta,v} = e(v,\theta) \Big|_{\theta_1}^{\theta_2}$$

$$Q_{\Delta\alpha,v} = e(\alpha,v) \Big|_{\alpha_1}^{\alpha_2}.$$

In the first of these, we have (32)

$$e = 2c_{v2}\theta - (1 - \alpha)Q_v + 2e_{02},$$

in which, by (43),

$$\alpha = +\left(vt + \tfrac{1}{4}(vt)^2\right)^{\frac{1}{2}} - \tfrac{1}{2}vt ;$$

wherefore (*a*) becomes

$$(60) \qquad Q_{\Delta\theta,v} = 2c_{v2}(\theta_2 - \theta_1) - \frac{Q_v}{2}\left(vt - \sqrt{vt}\sqrt{4 + vt}\right)_{\theta_1}^{\theta_2}.$$

This formula is identical with

$$Q_{\Delta\theta,v} = \int_{\theta_1}^{\theta_2} \theta \frac{\partial\eta}{\partial\theta}\, d\theta$$

$$= \int_{\theta_1}^{\theta_2} c_v(v,\theta) d\theta.$$

In the second case above, replacing θ by $\theta(\alpha, v)$ by means of (47), we find

$$(61) \qquad Q_{\Delta\alpha,v} = \frac{\dfrac{2c_{v2}Q_v}{r} \cdot \log \dfrac{\alpha_2^2}{\alpha_1^2} \dfrac{1 - \alpha_1}{1 - \alpha_2}}{\log\left(\dfrac{a}{4} \dfrac{1 - \alpha_2}{\alpha_2} \dfrac{v}{\alpha_2}\right) \cdot \log\left(\dfrac{a}{4} \dfrac{1 - \alpha_1}{\alpha_1} \dfrac{v}{\alpha_1}\right)} + (\alpha_2 - \alpha_1) Q_v.$$

Paths at constant degree of dissociation

For expansions at constant degree of dissociation, we have, first,

$$Q_{\Delta\theta,\alpha} = \int_{\theta_1}^{\theta_2} \theta \frac{\partial\eta}{\partial\theta}\, d\theta = \int_{\theta_1}^{\theta_2} c_{\alpha} d\theta.$$

Here

$$c_\alpha = 2c_{v2} - (1+\alpha)\frac{Q_v}{\theta};$$

$$Q_{\Delta\theta,\alpha} = 2c_{v2}(\theta_2 - \theta_1) - (1+\alpha)Q_v \,.\, \log\frac{\theta_2}{\theta_1}\,. \tag{62}$$

Again, the heat-absorption of an expansion between *volume* limits,

$$Q_{\Delta v,\alpha} = \int_{v_1}^{v_2} \theta \frac{\partial\eta}{\partial v}\, dv,$$

may be found without integration, by noting in (62) that

$$(Q_{12})_\alpha = \Big\{ 2c_{v2}\theta - (1-\alpha)Q_v \,.\, \log\theta \Big\}_1^2.$$

Replacing θ by $\theta(\alpha,v)$, and taking the integral between v_1 and v_2, we find

$$Q_{\Delta v,\alpha} = Q_v \left\{ \frac{\dfrac{2c_{v2}}{r}}{\log\left(\dfrac{a}{4}\dfrac{1-\alpha}{\alpha}\dfrac{v}{\alpha}\right)} - (1-\alpha)\,.\log\frac{\dfrac{Q_v}{r}}{\log\left(\dfrac{a}{4}\dfrac{1-\alpha}{\alpha}\dfrac{v}{\alpha}\right)} \right\}_{v_1}^{v_2}. \tag{63}$$

Work-functions and heat functions

In addition to the familiar theorems that:

e is the work-function for constant η
f " " " " " " θ
$-pv$ " " " " " " p,

e is the heat-function for constant v
$\theta\eta$ " " " " " " θ
g " " " " " " p,

it appears from the foregoing results that, for thermodynamic systems of the type here considered,

$(1 + \alpha)Q_v . \log \theta$ is the work-function for constant α.

$2c_{v2}\theta - (1 + \alpha)Q_v . \log \theta$ is the heat-function for constant α.

As confirmation of this, it may be noted that, just as

$$(W_{12} + Q_{12})_\theta = (f_2 - f_1)_\theta + (\theta\eta_2 - \theta\eta_1)_\theta = (e_2 - e_1)_\theta \, ,$$
$$(W_{12} + Q_{12})_p = (g_2 - g_1)_p - (pv_2 - pv_1)_p = (e_2 - e_1)_p \, ,$$

so do we have

$$(W_{12} + Q_{12})\alpha = (2c_{v2}\theta_2 - 2c_{v2}\theta_1)\alpha = (e_2 - e_1)\alpha.$$

Comparison with experiment

Equation (59) for $Q_{\Delta\theta,p}$ enables us to compute the data obtained by Berthelot and Ogier[1] in their determinations of the heat developed in the cooling of given masses of nitrogen peroxide between given temperature limits at constant pressure. These data correspond to the integrals (59),

$$\int_{\theta_1}^{\theta_2} c_p \, d\theta = \left\{ 2c_{p2}\theta - \left(1 - \frac{t}{s}\right) r\theta + \frac{t}{s} Q_v \right\}_{\theta_1}^{\theta_2} .$$

Computation by means of this formula, using $p = 1$ atm. and the above specified values of the constants, yields the results exhibited in the accompanying table. The experimental results are entered in the last column of the table.

Values of $Q_{\Delta\theta,p}$

θ_1	θ_2	Q_{12}, calc.	Q_{12}, obsd.
26.5°C.	66.7°C.	65 kg-cal	60 kg-cal
27.7	103.1	108	108
28.9	150.6	126	126
29.0	198.6	138	135
29.2	253.1	148	144
27.6	289.5	157	156

Fig. 3 exhibits the course of the function

$$\int_0^\theta c_p(1, \theta) . d\theta .$$

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[1] Ann. chim. phys. (5) 30, 382 (1883).

Each experimental result is represented by a cross at the upper temperature limit of the definite integral. The accord of the observed data with the form of the theoretical curve is as good as could be expected; as is also the numerical agreement of the data with the values calculated from constants obtained from density determinations and the theory of ideal gases. The slopes of the upper and lower branches of the curve are, of course, equal to $2c_{p_2}$ and $2c_{p_1} - r$ respectively. It will be noted that the curve is parallel to the curve giving the heat function g as a function of the temperature; the curve may, in fact, be formed from the plot of

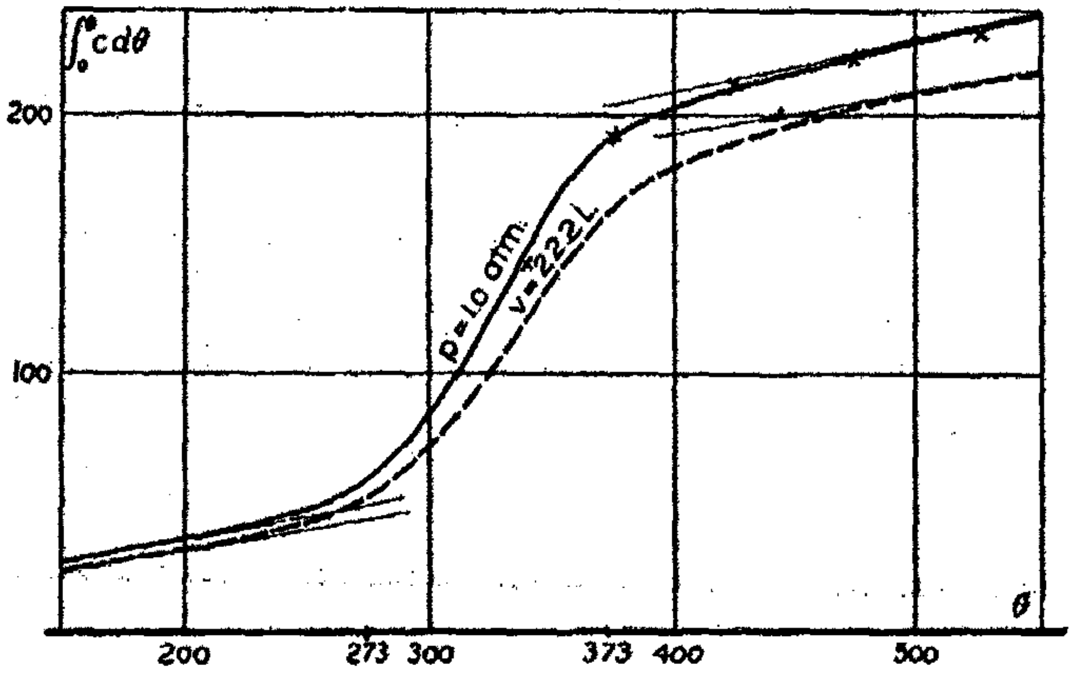

Fig. 3

$$g = g(1,\theta)$$

by displacing the horizontal axis by the amount $2e_{0_2} - Q_v$. Fig. 3 presents also, as a dash curve, the plot of the integral

$$\int_0^\theta c_v d\theta,$$

as a function of θ and the value 22.2 liters of the parameter v. Its course closely resembles that of $\int c_p d\theta$, save that both extremities of the curve have the same slope, $2c_{v_2}$.

Cornell University, December, 1904.

210

THE SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF OTHER SALTS[1]

BY F. K. CAMERON AND B. E. BROWN

The effect of different electrolytes upon the solubility of calcium sulphate has already received considerable attention in this laboratory.[2]

This paper records some results which have been obtained with solutions of ammonium chloride and ammonium nitrate of various concentrations, and with saturated solutions of certain other salts. The solutions employed in the work here described were contained in 8-ounce bottles provided with tightly fitting rubber stoppers, an excess of solid calcium sulphate being present in each bottle. Kahlbaum's chemicals were used. The bottles were kept in a constant temperature bath at 25° C., being temporarily withdrawn from time to time to thoroughly shake the contents. After remaining in the bath for several weeks portions of the solutions were carefully withdrawn for analysis. Determinations on duplicate series made at different times yielded results in very close agreement, and therefore, the averages only are being considered. Where ammonium salts were used the solutions were analyzed for ammonia rather than for acid radicals, but in the case of the other salts the amount present was calculated from the amount of acid radical found in the solutions.

Solubility of Calcium Sulphate in Solutions of Ammonium Chloride

Tilden and Shenstone[3] determined the solubility of calcium sulphate in ammonium chloride solution at different temperatures, but only one concentration of ammonium chloride was considered by these investigators.

Fassbender,[4] in 1876, published some results upon the solubility of calcium sulphate in solutions of both the chloride

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[1] Published by permission of the Secretary of Agriculture.

[2] Jour. Phys. Chem. 5, 556, 643, (1901); 7, 571 (1903); 8, 335, 493 (1904).

[3] Proc. Royal Soc. 38, 333 (1885).

[4] Ber. chem. Ges. Berlin, 9, 1360 (1876).

and nitrate of ammonium respectively, but his figures can only be regarded as approximations.

Cohn[1] and Ditte[2] have also studied the solubility of calcium sulphate in solutions of ammonium chloride, their results presenting discrepancies which can hardly be explained as due to analytical errors.

In the following table are given the results obtained in terms of grams per liter of solution. For comparative purposes the earlier results of Ditte and also of Cohn are given.

TABLE I.—SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF AMMONIUM CHLORIDE AT 25° C.

	Grams $CaSO_4$ per liter		
Grams NH_4Cl per liter	C. and B.	Ditte	Cohn
10.8	3.90	—	—
20.0	—	5.38	—
24.4	5.38	—	—
26.0	—	—	5.71
40.0	—	6.94	—
46.7	7.07	—	—
67.0	—	—	7.30
80.0	—	8.91	—
94.5	8.80	—	—
105.0	—	—	8.28
120.0	—	9.13	—
126.0	—	—	8.62
149.7	10.30	—	—
170.0	—	—	8.81
198.6	10.85	—	—
200.0	—	9.71	—
202.0	—	—	8.67
210.0	10.88	—	—
228.0	—	—	8.32
270.0	—	—	8.07
275.0	10.60	—	—
280.0	—	10.25	—
325.0	9.40	—	—
333.0	—	10.69	—
375.3 (saturated)	7.38	—	—

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[1] Jour. prakt. Chem. (2), 35, 43 (1887).

[2] Compt. rend. 126, 694 (1898); Ann. Chim. Phys. (7) 14, 294 (1898).

The solubility of calcium sulphate in ammonium chloride solutions, as shown by the graphical representation, steadily increases with increasing concentration of ammonium chloride until a concentration of 210 grams of ammonium chloride is reached, at which point approximately 10.9 grams of calcium sulphate are dissolved. With a further increase of the concentration of ammonium chloride the solubility of calcium sulphate decreases until at the point where both salts are present as solid phases the amount dissolved is 7.38 grams per liter.

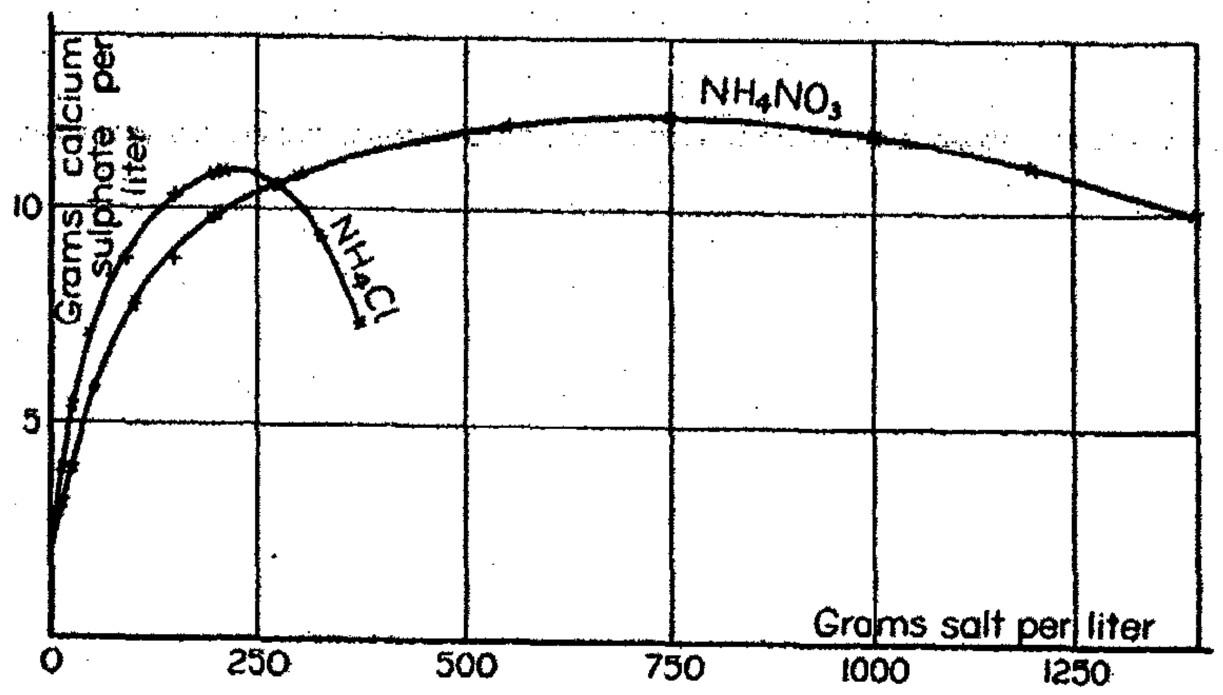

Fig. 1.

From the results given in Table I it will be seen that Ditte observed no maximum point. Cohn, on the other hand, observed a maximum point, but his determinationsare throughout lower than those given in this paper.

Solubility of Calcium Sulphate in Solutions of Ammonium Nitrate

The solubility of calcium sulphate in solutions of ammonium nitrate has been determined by Fassbender[1], Droeze[2] and Cohn[3].

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[1] l. c.

[2] Ber. chem. Ges. 10, 330 (1877).

[3] l. c.

Fassbender's results have but a qualitative value, and, unfortunately, Droeze's results must be regarded as of the same character for the reason that it does not appear from his papers how much ammonium nitrate was actually present in the various solutions, since he expresses their strength in terms of a saturated solution. Cohn's results, when plotted on a chart, agree fairly well with those obtained in the present investigation, in that they show that the maximum amount of calcium sulphate dissolved by ammonium nitrate, at a temperature of 25° C., was approximately the same as that obtained in this laboratory, but the concentration of ammonium nitrate which gives this maximum solubility of calcium sulphate was found to be greater by Cohn than is here shown.

In the following table are given the results obtained with solutions of ammonium nitrate, and they are also shown in the accompanying chart.

TABLE II.—SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF AMMONIUM NITRATE AT 25° C.

Grams NH_4NO_3 per liter	Grams $CaSO_4$ per liter
10	3.18
25	3.93
55	5.80
100	7.65
150	8.88
200	9.85
300	10.80
400	11.40
550	12.02
750	12.20
1000	11.81
1200	11.10
1400	10.02
Saturated	7.55

It will be observed that the solubility of calcium sulphate in ammonium nitrate solutions increases at first with increasing concentration of the more soluble salt, as in the case of the ammonium chloride series. The maximum solubility of calcium sulphate is approximately 12.2 grams in a solution containing 750 grams of ammonium nitrate per liter. From this point, with increasing concentration of ammonium nitrate the solubility of calcium sulphate decreases until both salts exist as solid phases, in which case the amount disolved is 7.55 grams per liter.

Solubility of Calcium Sulphate in Saturated Solutions of Certain Salts.

In order to make more complete our knowledge of the effect of other electrolytes upon the solubility of calcium sulphate, it has been deemed advisable to obtain the solubility of this salt in solutions of other salts when they also were in contact with the solution as a solid phase. This work was also done at 25° C., and the results are given in the following table. In all cases duplicate series were prepared at intervals of several weeks, the results of both series being given in Table III.

TABLE III.—SOLUBILITY OF CALCIUM SULPHATE IN SATURATED SOLUTIONS OF CERTAIN SALTS.

Salt	Grams of salt per liter in saturated solution			Grams $CaSO_4$ per liter		
	I	II	Average	I	II	Average
NaCl	318.1	318.5	318.3	5.51	5.53	5.52
$NaNO_3$	667.9	668.9	668.4	7.12	7.20	7.16
Na_2SO_4	254.3	254.9	254.6	2.58	2.58	2.58
$MgCl_2$	477.1	476.9	476.5	1.10	1.08	1.09
$Mg(NO_3)_2$	615.3	614.9	615.1	15.30	15.22	15.26
NH_4Cl	374.6	380.0	375.3	7.31	7.45	7.38
NH_4NO_3	—	—	—	7.47	7.63	7.55

In previous work in this laboratory on the solubility of calcium sulphate in saturated solution of sodium chloride[1] at 23° the following figures were obtained: NaCl = 315.55 grams per liter of solution, and $CaSO_4$ = 5.37 grams per liter of solution which are in fair agreement with those tabulated above. It was also found for solutions saturated with respect to both calcium sulphate and sodium sulphate[2] at 25°, Na_2SO_4 = 257.1

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[1] Jour. Phys. Chem. 5, 556 (1901).

[2] Ibid., 8, 335 (1904).

grams per liter of solution, and $CaSO_4$ = 2.65 grams per liter of solution, which is in fair agreement with the figures tabulated above. The results given in the above table for solutions of sodium nitrate and magnesium nitrate respectively are in good agreement with values obtained by extrapolating the results formerly obtained.[1] It is interesting further to note the widely different effects of saturated solutions of magnesium chloride and nitrate respectively upon the solubility of calcium sulphate. No calcium sulphate could be determined in saturated solutions of calcium nitrate or calcium chloride.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

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[1] Jour. Phys. Chem. 8, 493 (1904).

FUTURE DEVELOPMENTS IN PHYSICAL CHEMISTRY[1]

BY WILDER D. BANCROFT

It has been the custom of the retiring officers to discuss the development of some portion of that field of chemistry in which they were most interested. Since the president of the American Chemical Society will speak on physical chemistry tomorrow night, it has seemed to me that I might break with tradition and might talk to you about the future of physical chemistry rather than its present or its past.

We have reached a critical stage in the development of the electrolytic dissociation theory. The work of Kahlenberg has shown that there are a number of facts which we did not anticipate and which we cannot explain satisfactorily at the present time. The recent experiments of Noyes show that the dilution law does not hold for any strong electrolyte and that the same empirical equation describes the behavior of binary and of ternary electrolytes. This last fact appears to be fatal to all explanations based on the assumption that electrostatic effects are the disturbing factors. While the mutual attraction or repulsion of two or of three ions may easily change the dissociation formula for a binary or a ternary electrolyte, it is very improbable that the changes will be such as to make two radically different formulas identical. Of course, the hypothesis of hydrated ions gives us some leeway but the outlook is not what it was five years ago. It is too soon yet to say whether we are merely to remodel the electrolytic dissociation theory or whether we are to replace it by something else. My own opinion is that reform is what is needed and not revolution. It is evident, however, that we have gone ahead too fast and that we must test more thoroughly the premises on which our conclusions are based. We know of one error. The proportionality between molecular weight and osmotic pressure holds only for the cases in which the heat of dilution is zero. This is stated clearly in van't

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[1] Address of the retiring Vice-President of Section C—Chemistry, Philadelphia, 1904.

Hoff's original deduction of the van 't Hoff-Raoult formula $n/N = \log p/p_1$ but has been pretty generally overlooked. Since the heat of dilution is rarely zero in any actual case, our deductions as to the molecular weights of solutes are always somewhat in error. In the case of the metals of the alkalies and the alkaline earths dissolved in mercury, the lowering of the vapor-pressure due to the heat of dilution is practically equal to that due to the molecular weight, and we therefore have the surprising result that the apparent molecular weight is only about one-half the atomic weight. One of the first things we have to do is to eliminate this source of error in all cases.

Another distressing feature in the quantitative physical chemistry of today is that the field which it covers is daily growing less. A tenth-normal solution is now considered a concentrated one and some people are so extreme as to maintain that we can not expect agreement between theory and experiment for anything except infinitely dilute solutions. To my mind a theory which holds only for infinite dilution is necessarily wrong. Here again one probable source of error is easy to find. The van 't Hoff-Raoult formula is deduced on the explicit assumption that there is no specific attraction between solvent and solute. If this assumption is wrong, it is reasonable to suppose that the error thus introduced would become less as the concentration approaches zero. Under these circumstances the van't Hoff-Raoult formula might represent the facts at infinite dilution without being a true formulation. This is the case with another well-known and important formula. The Helmholtz and the Nernst equations for the electromotive force of concentration cells are identical for infinitely dilute solutions and for these only. The Nernst equation ignores the concentration of the undissociated salt while the Helmholtz formulation does not. The two equations therefore become identical at the moment when the concentration of the undissociated salt and the disturbing factor due to it become zero, that is, at infinite dilution. Since the Helmholtz formula applies to all concentrations, the Nernst formula is necessarily only approximately accurate. This has been recognized explicitly by Planck, though the point is often overlooked. It is quite conceivable that the shortcomings of the van't Hoff-Raoult formula may be due in part to theoretical inaccuracies and that we have laid too much stress on 'variations from the gas laws.'

If we introduce the conception of a specific affinity between solvent and solute in certain cases, notably those in which the heat of dilution is marked, we combine all of what has stood the test with what is good in Kahlenberg's conceptions and I believe that we are nearly ready to take a long step forward. One point must be kept in mind, however. Raoult's experiments preceded his formula. Before we can hope to work out a satisfactory theory of concentrated solutions, we must have accurate measurements on concentrated solutions and at present we have practically none. We need experiments at constant temperature on the compositions of coexistent liquid and vapor phases for binary systems with one volatile component and with two volatile components. These measurements are not easy to make and that is one reason why they have not been made. We have measured boiling-points and freezing-points because they are easy to measure, but for a theory of concentrated solutions the value of such measurements is very small. This is because we are then measuring the combined effect of the change of the pressure with concentration and with temperature, whereas we ought to study the two separately. Further, if we are to express our results in volume concentrations, we must give the volume concentrations of both components. It would be absurd to pass from dilute to syrupy solutions of sugar for instance, and to treat the concentration of the water as constant. Personally, I believe that the theory of concentrated solutions is relatively simple and that the difficulties have been chiefly of our own making. My own experience with ternary mixtures confirms me in this view. In developing a theory of concentrated solutions we must also keep in mind the actual properties of the components, a thing which we have not done in the past. Thus the dissociation equation for liquid chloral hydrate cannot be the same as that for liquid chloral alcoholate because chloral is miscible in all proportions with alcohol and forms two liquid layers with water. This is a perfectly obvious fact, yet no reference to it is to be found in any text-book on physical chemistry.

In the last ten years the work of Roozeboom and others has brought the phase rule to the front as a basis of classification and as an instrument of research. The importance of the phase rule is going to increase very rapidly in the next decade. The study of alloys has really only just begun. Our knowledge of the carbon steels is still very incomplete and unsatisfactory. In fact, we know the constitution only of a very limited number of binary alloys. Nothing systematic is yet known about the chemical properties of alloys or about the conditions for electrolytic precipitation. The variation of the engineering properties, such as tensile strength, torsional resistance, ductility, etc., with varying concentration and varying heat treatment is a subject which can only be worked out satisfactorily with the phase rule as a guide. On the basis of what has been done it appears quite safe to predict that we do not yet know one-half the possibilities of our structural metals.

Quite recently the constitution of Portland cement has been established and we owe this result to an application of the phase rule. It will not be long now before we get much clearer ideas on the causes of the strength of cements and of the plasticity of the clays. The time will soon come in our engineering schools when the subject known as 'Materials of Engineering' will have to be taught by the chemist rather than by the engineer.

The applications of the phase rule to petrography will be numerous and will come soon. It is evident that no rational classification of minerals can be possible until the constitution of the minerals has been determined. The situation in regard to petrography is much the same to-day as it was in regard to alloys a few years ago and we may reasonably expect as satisfactory results from rocks as from metals. More and more people are experimenting with fused salts, and the new geophysical laboratory at Washington is planning to study igneous rocks in the same thorough way that van't Hoff studied the Stassfurt deposits. The problem is a difficult one experimentally but it can and will be solved.

The classification of electrochemistry under the phase rule is a problem of the immediate future. Some work has been done already, but it is confined to the discussion of the electromotive forces of certain reversible cells. What I mean is something vastly wider than this, the application of the phase rule to all electrolytic and electrothermal processes. Since electrochemistry is essentially chemistry, a classification which is of fundamental importance in chemistry must be equally necessary in electrochemistry.

The extension of the phase rule to organic chemistry is an achievement about which we like to dream but the realization of it seems far off. To treat a large portion of organic chemistry as a system made up of carbon, hydrogen and oxygen will some day be possible; but at present we are balked by so-called 'passive resistances to change.' Theoretically, methyl ether, $(CH_3)_2O$, and ethyl alcohol, C_2H_5OH, are two modifications of the substance C_2H_6O, and they should be mutually convertible. Practically they are not. Only one of the three dibrombenzenes can theoretically be the stable form. Actually, we can not convert any one of them directly into either of the other two.

In spite of all this there is really quite a mass of material waiting to be worked up. Reversible equilibrium between hydrogen and oxygen can be realized at all temperatures. Reversible equilibrium between carbon, carbon monoxide and carbon dioxide is possible above 200° while reversible equilibrium between carbon, methane, acetylene, ethane and hydrogen can be observed above 1200° without catalytic agents. Carbon monoxide and water react at 430° in presence of copper. Methane can be made from carbon monoxide and hydrogen at 250° in presence of nickel, while methyl alcohol can be changed to carbon monoxide and hydrogen by zinc dust. The decomposition of alcohols into aldehydes, or ketones, and hydrogen is reversible. Aldehydes can be changed into carbon monoxide and paraffines, though the reverse reaction has not been accomplished satisfactorily. Methylal and acetal are formed by a reversible reaction, while the ester formation has been studied for years. Formic acid decomposes into carbon monoxide and water when heated by itself and into carbon dioxide and hydrogen when heated in presence of rhodium. Starting from carbon monoxide and caustic soda we can make sodium formate, carbonate and oxalate.

As yet only a few of these reactions have been studied with care and we do not know how many of them are reversible or what are the temperature limits. We do not even know whether colloidal metals act more effectively than the purverulent metals although it is very probable that they do. While we cannot yet tell how far we may be able to go, it is clear that the attempt to apply the phase rule to organic chemistry opens up a most interesting field of research both as regards organic chemistry and as regards the theory of catalytic agents.

The usefulness of the phase rule in studying basic and double salts is being realized more and more by our friends, the inorganic chemists. The recent work on the changing solubility of the hydroxides of many of the metals calls attention to a possibility of error which must not be overlooked. In all cases of hydrolysis there is always a possibility that equilibrium may not be reached in weeks or months. The only safe way is to reach the equilibrium from both sides. In this way and only in this way do we get any clue to the magnitude of the error involved and it is only after we have done this that we are justified in assuming that a reaction is irreversible.

The application of the phase rule to the fractional crystallization of rare earths would certainly lead to marked improvements. There are few people who could separate potassium and sodium chlorides by fractional crystallization, getting out all of each salt entirely pure. Even fewer would be able to separate potassium sulphate and copper sulphate. In spite of this, we start in cheerfully on the fractional crystallization of an unknown number of elements having unknown properties. The result of all this is that we reach a point where further separation is impossible and yet we do not know why. This state of things is really the fault of the physical chemist and not of the inorganic chemist. It is not to be expected that the inorganic chemist can start in off-hand and apply the phase rule to the study of basic and double salts or of rare earths. Before this can be done the physical chemist must work out the methods and must be prepared to give explicit working directions, possibly in the form of recipes.

It must also be clear to you that a study of the conditions of existence of compounds, atomic and molecular, is a prerequisite to any theory of valency.

In the past, reactions in organic chemistry have been studied by physical chemists chiefly as examples of reaction velocity. There are two other fields which will receive more attention in the near future, namely, yields and irreversible reactions. The question of yields is in a very bad way. In Lassar-Cohn's admirable book on laboratory methods in organic chemistry there is an enormous amount of valuable material; but there is really very little in the way of theory. Although we know that a reversible reaction will run to an end if the concentration of one of the reacting substances be kept practically zero, surprisingly little use has been made of this principle. We know that certain reactions take place better in dilute solutions or at low temperatures or in certain solvents but in most cases we cannot tell why. In the pyridine method for introducing acetyl or benzoyl groups the pyridine is said to be effective because it is a weak base, but it is much more probable that it acts as a catalytic agent. We do not know how far the dehydrating action of certain reagents is simply a question of vapor-pressure or how far there is a specific effect due to the particular reagent. The action of sulphuric acid in the formation of ether is something more than a dehydrating effect and the same is true of the effect of zinc chloride in the synthesis of ethyl chloride.

A single instance will be sufficient to show the state of confusion that exists. Anschütz's method of preparing certain esters was to saturate the solution with hydrochloric acid gas and to allow the solution to stand over night. Fischer improved on this by adding less acid and by raising the temperature. He boiled for two hours and found that the hydrochloric acid concentration could be reduced to three percent without affecting the yield. There the matter is left and we are led to look upon a three percent concentration as having special merits, whereas this is undoubtedly merely a result of boiling for the arbitrary period of two hours. If Fischer had boiled for one hour only he would have had to use a stronger acid to have reached equilibrium in the allotted time. If he had boiled three hours, the lowest permissible concentration of hydrochloric acid would undoubtedly have been less than three percent. Anschütz, on the other hand, worked at ordinary temperature and his solutions consequently needed more acid and more time to approximate to equilibrium. All of this is really first principles and it is only one case out of many. If any one will try to classify and explain the results given in Lassar-Cohn's book, he will find himself provided with enough interesting research to last him the rest of his natural life.

The second field for research to which I have alluded is that of irreversible reactions. In inorganic chemistry there are as yet no well-authenticated cases where a reaction starts and then stops short of equilibrium. The results of Pélabon on hydrogen and selenium, and of Hélier on hydrogen and oxygen have been disputed by Bodenstein and must for the present be considered as wrong. In organic chemistry we appear to have many such reactions, typical instances being the formation of nitrobenzene and the decomposition of aldehyde into methane and carbon monoxide. While it is possible that these and other reactions run to an end in infinite time, we have not infinite time at our disposal and it may, therefore, prove profitable to find out whether and how the apparent end-point varies with varying initial conditions. This work is desirable now and will become necessary if we should ever revise our opinions as to the theoretical possibility of an irreversible equilibrium. By definition we cannot determine the existence of an irreversible equilibrium by approaching the end-point from the two sides. It seems to me probable, however, that we can draw conclusions from the reaction velocity. If we are dealing with a case of a theoretically reversible reaction running practically to an end, I can see no reason why the concentration of the decomposition products should have any effect on the reaction velocity, so long as we confine ourselves to gaseous systems. If, however, we are dealing with a theoretically irreversible reaction which does not run to an end, the reaction velocity would vary with the concentration of the decomposition products.

It should be noticed that it will not do to reason from the behavior of a system in presence of a catalytic agent to that of a system without a catalytic agent, since the catalytic agent may displace the equilibrium. Thus ethyl alcohol is decomposed by heated copper into aldehyde and hydrogen while heated alumina changes it chiefly into ethylene and water. It was the study of organic solutes in organic solvents which led Raoult to the formulation of his law. It seems probable that a study of organic reactions may lead to an entirely new class of equilibria. If this happens it will throw much light on the preceding problem because it is very difficult to explain some of the peculiarities in regard to yields in organic chemistry so long as we are obliged to postulate reversible reactions only.

The theorem of Le Chatelier has been applied chiefly to heat and work effects, but this is by no means the extent of its usefulness. Wherever we get a reversible displacement of equilibrium by light, it must be possible to make use of this theorem. The change of color of the silver photochlorides is in accordance with the theorem; but there seems to be no reverse change in the dark. The simplest case with which to begin would appear to be the formation of ozone. There seems to be a contradiction here. Ozone is known to absorb ultra-violet light and yet it is believed to be formed by the action of ultra-violet light. Whether we are dealing with the same sets of rays in the two cases is a point that has not been settled. In fact we do not know definitely whether ozone is formed by the action of ultra-violet light in the absence of electrical waves, though this is a matter easily settled by experiment. We know that ozone gives out light on decomposing, but we do not know anything about the spectrum of this light. It is quite probable also that we must formulate the theorem of Le Chatelier more exactly than we have hitherto done before we can apply it succesfully to the phenomena of light. An instance based on electrical phenomena will show what I mean. If a voltaic cell be short-circuited, the chemical change will be such as to decrease the electromotive force of the cell. If we do not keep the cell at constant temperature the Joule heat will cause the temperature to rise and this may either raise or lower the electromotive force of the cell. We are then really considering two phenomena, the electrical and the heat effects. One may mask the other completely.

In one case, at any rate, we know that we can apply the theorem of Le Chatelier to light phenomena. Suppose we have a gas enclosed in a transparent adiabatic vessel and concentrate upon it light of a wave-length that is absorbed by the gas. The temperature of the gas will rise and equilibrium will be reached when the gas has changed so that it no longer absorbs light of that particular wave-length or when the gas emits light of the same wave-length and intensity as that which is acting upon it. This emission by a gas at some temperature of the light which it absorbs at the same temperature is Kirchhoff's law which thus appears as a special case of what the chemists call the theorem of Le Chatelier. To be frank, I do not now see how we are to apply this theorem to the phenomenon of phosphorescence, and yet we are dealing with an absorption and an emission of light. I venture to suggest that it is to the application of the theorem of Le Chatelier that we must look for a rational treatment of phosphorescence, fluorescence, chemiluminescence, etc., rather than to a theory of vibrating molecules. It will be time enough to discuss the application to radiations when we have solved the simpler problem of the theory of cold light.

A discussion of equilibrium relations would not be complete without some reference to the future of thermodynamics in chemistry. There are two radically distinct ways of considering the relation of thermodynamics to chemistry. One is to look upon thermodynamics as a mathematical shorthand. The aim of thermodynamics is then to present a consistent and formal treatment of the known energy relations. In this case thermodynamics deals with the past and not with the future; with the classification of knowledge and not with the discovery of new laws. This is the point of view of most mathematical chemists and it is because of this that we do not turn to the mathematical chemist for new ideas. There is another way of considering thermodynamics, namely, as an instrument of research. It is not too much to say that the mathematical chemist can work out in a few hours or days results which would take his less fortunate colleague months or even years to obtain. At present the race is to the tortoise and not to the hare; but I cannot believe that this will always be so. Other things being equal, the man who can handle his thermodynamics will beat the man who cannot; but in order to have that take place thermodynamics must be considered as an instrument of research and not as a branch of metaphysics. We must confess that the mathematical chemistry of the past decade has not done what it should have done and that there is no immediate prospect of any improvement. In the meantime we do not despair. There are great possibilities in the application of mathematics to chemistry and some day they will be developed.

So far, we have considered problems involving equilibrium only. When we begin to study the conditions which make a reaction possible and which govern its rate, we are brought face to face with our need for a satisfactory theory of catalytic agents. We know experimentally the catalytic action of many substances on many reactions, but we have not even the first suggestion of an adequate theory. This is a subject of more vital importance than may appear at first sight. I wish to call your attention to two very important matters which depend directly upon catalytic agents. The first is the chemistry of plants. We can make in the laboratory many of the substances which the plant makes. Some of them, such as alizarine and indigo, we can make more cheaply than the plant can and of a higher degree of purity. As yet we cannot make any of them in the way the plant does, and this gap in our knowledge will have to be filled by the physical chemist, as the problem apparently does not appeal to the organic chemist. The plant does not use reverse coolers or sealed tubes; it does not boil with sulphuric acid or fuse with caustic potash; it has not metallic sodium and chlorine gas as reagents. The reagents on which the plant can draw are air, water and a few mineral salts. As catalytic agents it has heat, light, difference of electrical potential, enzymes—and itself, namely, living protoplasm. From the work of Bredig and others we know that colloidal metals, the so-called inorganic ferments, can be substituted for enzymes in some cases. As we do not yet know our limitations it is quite possible that we can substitute inorganic catalytic agents for the enzymes in all cases. If that proves to be true we can then duplicate everything except the plant itself, and we shall be ready to determine how closely we can duplicate the reactions of the plant. The experiments of Sabatier and Senderens in France are distinctly encouraging, even though they do not carry us very far. By means of nickel powder it is possible to reduce acetaldehyde to alcohol with hydrogen at 30°. This is the best result that has been obtained and it indicates the possibilities. When we get a satisfactory theory of catalytic agents we shall undoubtedly be able to duplicate many of the plant syntheses and our failures will be interesting as bringing us nearer to the most difficult problem of all—that of life. Pending the development of a satisfactory theory of catalytic agents, there is much to be done in the way of experimenting. In view of the fact that mixtures of two catalytic agents often act more intensely than would be expected from the behavior of each taken singly, it would appear advisable to determine the combined effects of inorganic ferments and ultra-violet light.

The second problem, which would be easier of attack if we had a satisfactory theory of catalytic agents, is that of the transmutation of the elements. This is now admitted to be distinctly a scientific problem though not one in which we have made much progress. It is usually assumed that it is a very difficult problem. While this may be true, we have not yet reached the point where we are justified in being certain of it. No one has ever attacked the problem systematically and all we can say is that the rate of change has been small under any conditions that we have yet realized. That is not surprising. We should naturally expect a low reaction velocity. The rate of change of radium is so slight that it could not be detected by any ordinary methods. The fact that we have never observed any transmutation of the elements does not prove that none has taken place. We had been making diamonds artificially for years, even for centuries, but nobody thought of looking for them in cast iron until after Moissan made his experiments a few years ago.

If we accept Lockyer's conclusions as to the state of things in the sun, we could undoubtedly break up many of the elements if we could hold them long enough at 6000° C. One difficulty is to get the temperature, and of course we must be cautious about conclusions based on simplified spectra. Many people have thought that radium was to be the catalytic agent which was to change all the elements, but the recent work of Rutherford seems to put an end to this idea. If radio-active lead, tellurium, and bismuth are merely these elements plus the radium emanation or one of its decomposition products, there is very little evidence to show that any of our well-established elements are undergoing any change from contact with radio-active substances.

Another possibility which has been suggested is that we could change our elements if we could pump energy into them and change their energy content. This would have to be done electrically if at all. I have been told that Stas was busy during the last years of his life trying to change sodium into something else by an electrical process. The difficulty is to pump energy into the element. Passing a heavy current through a metal produces no effect that we know of other than to raise the temperature. Taking the element in the state of gas enables us to employ a higher potential difference, but here the effectiveness of the method is limited by the appearance of the arc. The first stage in the problem would, therefore, be the attainment of the highest possible potential difference without causing arcing. In view of the remarkable insulating action of gases under high pressure, it seems as though the silent discharge through compressed gases were the thing to try. The difficulties people had in proving the dissociation of water at high temperatures makes us realize the possibility that we might decompose our elements and never know it, owing to the recombination taking place at once. If we are to simplify our elements by pumping energy into them, it appears that we should work with gases under high pressure, with the highest potential difference compatible with the absence of sparking, and with some application of the principle of the hot-cold tube.

While the methods of extremely high temperature and of high electrical stress have much to commend them on paper, they are liable to fail owing to the difficulty of attaining the proper temperature or the proper electrical stress. The ideal method would be to find a catalytic agent which would accelerate the rate of change and which would eliminate what we should then call the instable elements. Since there is no immediate prospect of our being able to predict the suitable catalytic agent and the conditions under which it is to be used, we must ask ourselves what is the scientific method of attacking the problem of the transmutation of the elements.

The answer is a simple one. We must start with the simplest case, study that thoroughly, and work up gradually to the more difficult tasks. We should begin with the cases in which we know a change is possible and should study the allotropic forms of the elements. At present our knowledge of these is disgracefully incomplete. We know a little about sulphur, phosphorus, carbon, selenium and tin, but even for these few elements our knowledge is incomplete and it is especially unsatisfactory in matters bearing on the rate of change. In most cases the change from one allotropic form to the more stable one is fairly slow. It is not even easy to get large amounts of gray tin. On the other hand, Saunders discovered, quite by accident, that there were a number of substances, notably quinoline, which convert amorphous selenium into the more stable, black, metallic modification. It is probable that similar results could be obtained with other elements. Kastle has shown that the rate of change of yellow mercuric iodide into the red form varies enormously with the nature of the solvent. The first thing that we need is a systematic study of the allotropic forms of the elements, considering reaction velocity as well as equilibrium. We next take up cases where the change from one form to another can be made increasingly difficult. The three di-substituted benzene compounds, as I have already said, are to be considered as different modifications, only one of which can be stable as solid phase at any given temperature and under atmospheric pressure. According to the text-books *o*-phenol sulphonic acid changes readily into *p*-phenol sulphonic acid on heating. When bromine acts on phenol in the cold, *p*-bromphenol is formed while *o*-bromphenol is formed when the reaction takes place at 180°. I have not been able to find any record of the *p*-brom compound changing into the *o*-brom compound on heating; but the experiment is worth trying. When we come to the three dibrombenzenes, we have a case where we know that the three forms are identical in composition and where there is certainly some sort of an equilibrium at the time of formation because the relative amounts of the modifications can be changed by varying the conditions of preparation. In spite of all this we know no way of converting two of these compounds directly into the third. We could undoubtedly do it if we could raise the temperature high enough, just as we could also convert the elements. It is as yet impossible to attain the temperature at which the elements change rapidly, while secondary reactions interfere in the case of the organic compounds. So long as we cannot change the two less stable forms of any di-substituted benzene compounds into the most stable form, there is no reason why we should expect to succeed in what may, perhaps, be the impossible task of simplifying the elements.

Summing up, the future developments in physical chemistry will comprise a theory of concentrated solutions, further applications of the phase rule and of the theorem of Le Chatelier, a systematic study of organic chemistry, and a theory of catalysis.

ELECTROLYTIC CHROMIUM, I

BY H. R. CARVETH AND W. R. MOTT

(1) Object of work. (2) Properties of the metal. (3) Results of previous workers. (4) Statement of the chemical problem. (5) Apparatus and method. (6) Electrolysis of chloride solutions. (7) Change in anode solution. (8) Electrolysis of sulphate solutions. (9) Conclusions.

1. Object of Work.— The electrodeposition of chromium is of very considerable practical as well as theoretical importance. The element is one of the large number which may be found in either the acid or the basic part of compounds, and which show different valencies in the various compounds. Consequently the results obtained from a study of its electrochemical behavior should be capable of application to many other cases. The present paper will consider only the cases where chromium acts as the base in trivalent compounds; subsequent work will deal with its electrolytic behavior in solutions of chromous salts and also when it forms part of the acid radical.

In many cases electrochemists have been successful in obtaining other metals either in a state of great purity or else in such forms as to open new fields for useful application. Although many processes have been proposed for the electrodeposition of chromium from aqueous solution, they are all, according to Goldschmidt,[1] to be discarded because of the complicated apparatus, high current density, high voltage, low current efficiency and consequent great expense. The statement[2] has been made however that the electrodeposition of the metal has been carried out successfully on a commercial scale by the Electrochemische Werke, in Bitterfeld, but the method employed is not given.

Even with the drawbacks mentioned above, it seems strange that chemists have not made use of an electrolytic method for the deposition of this metal in order to obtain a better knowledge of the properties of the element and its compounds. Cer-

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[1] Zeit. Elektrochemie, 7, 668 (1901).

[2] Chem. News, 81, 17 (1900); Jahrbuch der Electrochemie, 3, 233.

tainly the method for electrodeposition of the metal must be either unknown or else regarded as difficult, for otherwise the impure metal obtained by the Goldschmidt process would probably not have been used by Hittorf, Ostwald, Luther, Brauer and others in their work if by electrolysis the metal could have been obtained purer and in a form more convenient for working.

The advantages of a pure metal for electrometallurgical work are such that the metal produced by the Goldschmidt thermal process is said to compete quite successfully with the cheaper ferro-chromium, since the latter is less constant in composition.[1] But while from a commercial point of view, the utilization of chromium deposited from aqueous solutions may not be of great importance, some preliminary experiments performed with the object of obtaining the metal gave results so completely at variance with experiments previously recorded, that we have found it necessary to investigate more thoroughly some of the conditions which affect the current yield.

It is necessary to review some of the properties of the metal, physical, chemical and electrochemical.

2. *Properties of the Metal.*—Chromium is a hard white metal, the crystalline variety having a specific gravity according to Moissan of 6.92 at 20°. Its melting-point lies higher than that of platinum. It can be filed with difficulty but is polished quite readily, giving then a reflecting surface as good as that of silver, but more liable to tarnish (Cowper-Coles). Other observers (Hittorf, Moissan) have found however that it keeps its polish in air very well indeed. When deposited electrolytically, it has been found to be more readily scratched than nickel but less readily than silver; it must be remembered, however, that the hardness of a deposit may vary considerably with the conditions of its deposition. When alloyed with certain amounts of chromium, metals such as gold, tin, zinc, lead, copper and iron are made much harder and more resistant to

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[1] Le Blanc: "Die Darstellung des Chroms und seiner Verbindungen," p. 58.

strain and friction. These alloys present a very promising field for the metallurgist.

Like iron, nickel and cobalt, the metal occurs in both an active and a passive state. When active, the metal dissolves readily in hydrochloric or hot sulphuric acid to form the chromous salts. Periodicities in the rate of solution of the metal in acids were observed by Ostwald in 1900; the later work of Brauer (1901) showed that these were not observable when the chromium was pure. Hittorf[1] has shown that when the metal is brought into contact with the solution of free chlorine or bromine, with strong nitric acid, *chromic acid*, etc., in other words with the most vigorous oxidizing agents, the metal becomes passive, then acting as a noble metal. This passivity may at all times be destroyed by making the metal cathode in an acid solution. The metal may also become active by contact with highly concentrated solutions of strong acids even at ordinary temperatures; for this purpose may be used hydrochloric, hydrobromic, hydrofluoric, etc. Solutions of the chlorides of the alkalies and the alkaline earths act similarly near the boiling temperature. When made anode in hydrochloric or hydrobromic acid under such conditions that the halogen tends to be set free, the metal dissolves as the chromous salt.[2] If, however, it is anode under circumstances such that an evolution of oxygen may take place, it dissolves as chromic anhydride (hexavalent), the metal then becoming passive. In other cases as in alcoholic zinc chloride, the metal as anode seems to be trivalent. The effect of temperature on the anodic behavior is very marked; in most solutions where the metal dissolves as chromate, rise of temperature favors solution as the chromic or chromous salt.

In regard to the voltaic relations, it was found that, at ordinary temperatures, the metal was electronegative to zinc, cadmium, iron, nickel, copper, mercury and silver; solutions of mercury chloride and cupric chloride and bromide were reduced at the boiling temperature.

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[1] Zeit. phys. Chem. 30, 505 (1899).

[2] Hittorf: Zeit. phys. Chem. 25, 729 (1898). In these experiments the current density at the anode, and the concentration of the solutions used are not given.

From the results of his experiments, Hittorf concluded that the passivity is not due to a film, as is most probably the case with aluminum, but more probably to some peculiar allotropic (molecular) state of the metal.

3. Results of Previous Workers.—The successful electrodeposition of the metal was accomplished by Bunsen[1] when, recognizing the importance of current density and concentration as variable factors, he made use of a two-compartment electrolyzing vessel, the anode of which was a carbon cell which contained the acid, while the cathodic chamber held the chromium solution and the platinum electrode. The electrolyte was a solution of chromous chloride containing some chromic salt, and the electrolysis was carried on in the hot solution with a current density of about 67 amperes per square decimeter. When the current density was lowered, there separated "Wasserfreies Chromoxydoxydul" which dissolved in hydrochloric and sulphuric acids to form the chromous salts, hydrogen being evolved. He was successful in obtaining the metal from the chromic chloride, but this took place more readily when chromous salt was present. Bunsen considered that his "Chromoxydoxydul" had a formula between Cr_4O_5 and Cr_5O_6; it has recently been found by J. Férée[2] to be Cr_5O_8,H_2O.

In 1890, Placet and Bonnet took out patents in many countries dealing with the electrodeposition of the metal. In the American patent 526,114, September 18, 1894, may be found a summary of their claims, which cover a very wide range. They state that the most important compound from which chromium may be obtained commercially is chromic acid; that at concentrations of from one to two percent the metal may be precipitated but the deposition is more abundant the more concentrated the solution. They have also employed other compounds such as the chromates and bichromates, the sulphate or nitrate of chromium, chrome alum or other chromic salts; in all of these cases they add an alkaline sulphate or an alkaline earth metal to increase the deposition. They state that prior to their invention

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[1] Pogg. Ann. 91, 119 (1854).

[2] Bull. Soc. Chim. Paris (3), 25, 620 (1901).

"it is well known that no articles electroplated with chromium were ever produced."

At the suggestion of Le Blanc, Schick[1] attempted to repeat the experiments with some of the solutions specified by Placet and Bonnet, but obtained mere traces of chromium. Le Blanc states: "Diese Resultate stimmen auch mit gelegentlichen Arbeiten anderer Forscher überein, die ebenfalls beim Arbeiten nach den gegebenen Vorschriften keine Chromniederschläge bekommen konnten.[2] Danach kann es keinem Zweifel mehr unterliegen, dass das der französischen Akadémie von Placet vorgelegte Kilogramm Chrom[3] nicht auf dem angegebenen Wege erhalten worden sein kann oder dass wenigstens die zur Erzielung von guten Chromniederschlägen wesentlichen Bedingungen dort nicht angegeben worden sind." A more detailed discussion of this criticism will be given in a later paper.

The patents of Placet and Bonnet were followed by those of Möller and Street (1898) who used in their cathode chamber chrome alum, sodium sulphate, and water, in equal parts by weight. The current density employed was 40 amperes per square decimeter, the range being very limited; the temperature was 90° C. The yield per ampere hour, as given in the English patent, indicates a current efficiency of about thirty percent. The patent claims relate mainly to the byproducts at the anode and the maintenance of the composition of the solution.

In 1900, Cowper-Coles[4] found that a 25 percent chromic chloride solution at a temperature of 190° F (88° C) and with a current density of 40 to 50 amperes per square foot (approximately 4.3 to 5.3 per square decimeter) gave good deposits of chromium, especially when hydrochloric acid was added to redissolve the precipitated oxide. Other solutions were tried, but with unsatisfactory results.

J. Férée[4] electrolyzed solutions containing 10 percent hydro-

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[1] "Darstellung des Chroms und seiner Verbindungen," p. 16.

[2] Cowper-Coles: Chem. News, 81, 16 (1900); J. Férée: Bull. Soc. Chim. Paris (3), 25, 617 (1901).

[3] Comptes Rendus, 115, 945 (1892).

[4] l. c.

chloric acid and 16 percent crystalline chromic chloride with current densities of 15 amperes per dcm², obtaining excellent deposits. Using the same current density but a solution containing one-gram molecule of chromic chloride to three gram-molecules of potassium chloride per liter, he again obtained excellent deposits, with a current efficiency of 45 percent; the latter was determined by weighing the metal deposited.

In describing the method used by Bunsen, Borchers[1] states: "The author has frequently repeated this experiment and for the purpose of obtaining large amounts of the metal has altered the conditions of the experiment within certain limits but has always obtained satisfactory results by working within the limits of current density named and by using a high concentration in the cathode cell."

It was however the most recent work on this subject[2] which, by its unusual results, first attracted our attention to this subject. Neumann's student, Glaser, worked with solutions of chromic chloride, sulphate and acetate in the cathode chamber, while the anolyte consisted of mineral acids or salt solutions. The results for the chloride (100 grams metal per liter) are given in Tables I and II. The first table gives the effect of variation of the current density, the latter being expressed in amperes per square decimeter.

TABLE I

Current density	Products separated	Percent current efficiency
0.9	Chromous-chromic oxide	
1.8	First metal, then chromous-chromic oxide	
3.6	Metal mixed with chromous-chromic oxide	
4.5	Thin metal layer, later chromous-chromic oxide	5.4
7.2	Metal with less chromous-chromic oxide	23.4
9.1	Pure metal	38.4
13.7	Pure metal with crystal projections	38.0
18.2	Pure metal, mostly crystalline	38.6

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[1] "Electrometallurgy," p. 366 (1897).

[2] Neumann: Zeit. Elektrochemie, 7, 656 (1901).

As noted above, the work of Férée seems to indicate that the chromous-chromic oxide is not separated.

The manner in which the nature of the deposit is affected by variation in the concentration of the solution is indicated in Table II. The current density is not given but was presumably kept constant.

TABLE II

Grams metallic chromium per liter	Products separated	Percent current efficiency
210	Metallic powder mixed with chromous chloride	—
184	Metallic powder mixed with chromous chloride	—
158	Pure metal	56.6
135	Pure metal	49.0
105	Pure metal	38.4
79	Metal, then chromous-chromic oxide	—
53	Chromous-chromic oxide and hydrogen	—
26	Traces of chromous-chromic oxide, strong hydrogen evolution	—

These results were obtained at room temperature; in speaking of the effect of temperature, Neumann states that above 50° the chromium separated as a black powder, but that the efficiency changed but slightly.

With a different anode solution (not specified) he was able to obtain much higher efficiencies. In regard to this point Le Blanc states (p. 28): "There follows the incomprehensible remark that the current yield was increased from 57 percent to 89.5 percent by changing the anode solution. Or should this read by changing the cathode solution?"

The acetate solutions gave poor deposits and very low efficiencies.

According to Neumann, the electrolysis of chromium solutions would appear comparatively simple, and at first sight might seem to allow of easy duplication. This we have not found to be the case, for some factors which cause variation have not been considered at all. The temperature factor is by no means unimportant. He states nothing as to the length of the tests, the volume of the solution used, the area of solution exposed to the air, and other factors which in this particular case are of very considerable importance, especially the effect of the presence of the chromous salts formed during the progress of the electrolysis; nor is any statement made in regard to the very important experimental detail of the method of measuring efficiencies. Since many of these factors do not enter into the ordinary problems of deposition of metals, a formulation will now be attempted.

4. Statement of the Chemical Problem.—In the electrolysis of chromic chloride in aqueous solutions it is found that in the cathode chamber the current can produce results in the following way:

(1) Formation of chromous salt.
(2) Evolution of hydrogen.
(3) Precipitation of metallic chromium.
(4) Precipitation of an oxide or hydroxide.

The formation of oxy-salts is also a possibility. Moreover in the solution itself secondary reactions of a purely chemical nature may take place.

(*a*) Hydrolysis of the chromic salt with liberation of free hydrochloric acid or free base.

(*b*) Reaction of the chromous chloride with hydrochloric acid, forming chromic chloride and hydrogen.

(*c*) Absorption of oxygen from the air by the chromous chloride.

(*d*) Re-solution of the precipitated metallic chromium in the electrolyte, due to the metal being in its most active state.

(*e*) Diffusion of anode products to the cathode chamber and subsequent reaction.

These reactions change of course with the relative and absolute concentrations of the reacting substances; these are the chromic salts (at least two modifications), chromous salts (probably two modifications), basic salts, and free acid.

To determine then with absolute exactness the nature of the solution, there should be given, or in some way designated, the concentration of the following quantities: chromic chromium, chromous chromium, and acid radical. In the present work the products have not been analyzed at all stages, but it is hoped that sufficient data are given to allow reproduction of results.

Other variables that enter into the problem are the current density, temperature, solubility of the products of electrolysis, rate of diffusion of anolyte, velocity of the various reactions, and consequently the complete history of previous electrolysis and treatment of the solutions.

The factors that can be controlled more or less readily are the initial concentrations, the presence of air, the temperature and the current density. The control of these has guided us in the choice of the method employed.

5. Apparatus and Method—The usual arrangement of a two-compartment cell was used. In a large beaker was placed the porous cup which served as the diaphragm. In the experiments up to 51, the outer chamber was filled with dilute sulphuric acid ($d = 1.12$), the anode being a cylinder of lead. The porous cup which was filled with the chromium solution contained also a copper rod which served as the cathode, its cylindrical shape ensuring uniform current density. The temperature of the cathode solution could be controlled by passing through the glass spiral immersed therein water of any desired temperature. The porous cup had an internal diameter of 4 cm, and a working depth of 7 cm. The cathode wire had a diameter of 4 mm.

The general procedure was to electrolyze, using a well-cleaned copper cathode until 133 cc of hydrogen, corresponding to about 1000 coulombs, had been given off in the alkaline nickel voltameter. This electrode was then replaced by another and the amount of the deposit determined while a second electrode was being plated; in this way many entirely independent determinations were made in long runs on the same solution.

In the earlier stages of the work, the amount of metal deposited was determined by weighing, but a quicker method was soon required and devised. This consists in measuring the volume of the hydrogen evolved when the metal was dissolved in

15 percent hydrochloric acid. Our results confirmed those already recorded in the literature that the metal dissolves to form *chromous* and not chromic chloride, although the latter is formed slowly by the interaction of the acid on the chromous salt. No periodicity in the velocity of solution has been observed; this confirms the work of Brauer who ascribes this phenomena to impurities in the metal.

Previous workers have probably determined the current efficiency by weighing the metal deposited and then applying Faraday's Law, assuming that the metal was trivalent. In this work, we have deposited the metal from a solution in which the metal was trivalent and dissolved it to form a solution in which it is divalent. *To admit of comparisons with the efficiencies obtained by other observers*[1], the volume of hydrogen actually given off on dissolving the metal must therefore be increased by fifty percent. In all the tables given therefore the "efficiency" column indicates three halves of the observed number of cubic centimeters of hydrogen evolved by solution of the metal which was deposited when 100 cc of hydrogen was evolved in the voltameter.

Experimental work was done on solutions of the chloride, sulphate and oxalate of chromium. The experimental results have now to be considered.

6. *Electrolysis of the Chloride Solutions.*—To effect solution, the red insoluble chloride (Bender and Hobein C. P.) was moistened with water and put into the cathode chamber. With a platinum wire as cathode, a current was passed for a short time, causing the formation of a small amount of chromous chloride whose presence as is well known accelerates the velocity of solution of the chromic salt. Another method which we

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[1] It is not claimed that either the previous workers or ourselves have applied Faraday's Law to this case correctly when we assume that the trivalent ion is the one from which the metal is deposited; in fact there is every reason to believe that in this case where trivalent and divalent ions are involved in equilibrium relations, the theoretical 100 percent current efficiency must be calculated on the assumption of an intermediate but determinable valency. In view of our present ignorance of this subject, it has seemed advisable to adhere to the previously used methods of calculating efficiencies.

have devised consists in suspending the insoluble salt in water, adding a fragment of electrolytic chromium and a drop of hydrochloric acid and heating for a very short time. The concentrated solutions thus obtained held about one hundred grams of metallic chromium per liter and had a specific gravity of 1.185 at $t = 20°$; two others $d = 1.120$ and 1.260 were also employed when examining the effect of anolyte variation.

Maintaining the temperature constant at 20°, we now determined with the 100 gram solution the effect of current density upon the metallic deposit. The strongest and most adherent deposits were obtained with densities ranging between 10 and 40 amperes per square decimeter. When the range was extended from 40 to 90 amperes, the deposits became very much poorer while platings made between 90 and 200 amperes were so crystalline and had such little adherence that a paper edge could easily brush them away.

The quality of the deposit was greatly improved when the cathode was rotated quite rapidly; in fact the current density could then be doubled and still give a deposit as good as was obtained with the stationary electrode at the lower density.

A rise of temperature to 45° caused greater deterioration in the quality of the deposit than a change in the current density from 30 to 100 amperes.

The range of concentration of the solutions from which the metal may be deposited depends to a great extent upon the temperature. When the variables were properly controlled, it was found possible to obtain the metal from solutions containing one-half to one quarter of the minimum found by Neumann—53 grams per liter, $t = 15°$. Since in his paper he has stated nothing in regard to the control of his temperature, it seems probable that he disregarded the very considerable heating effect due to the high resistance of the more dilute solutions.

The questions at once arise—why has the temperature so marked an effect, and what influence upon the result has the chromous chloride which is formed by reduction?

The 100 gram chromic chloride solution was electrolyzed for several hours, the efficiency being determined at intervals of ten minutes. The results are given in Table III. The first column indicates the temperature, the second the cathode current density per square decimeter, the third the efficiency.

TABLE III.—CATHOLYTE, CHROMIC CHLORIDE CONTAINING 100 GRAMS METAL PER LITER

Experiment number	I Temperature	II Current density	III Percent efficiency
1	21°	50	4.5
2	24	51	6.7
3	23	50	9.0
4	23	53	11.2
5	23	51	12.5
6	22	51	16.7
7	22	50	19.5
8	21	50	22.5
9	20	51	25.9
10	20	51	28.0
11	19	50	29.2
12	19	49	28.0
13	21	47	28.0
14	20.5	47	28.0
15	21	49	29.2
16	22	50	29.2
17	22	51	29.2
18	22	51	28.0
19	22	22	23.4
20	22	22	23.4
21	22	70	27.0
22	22	70	30.4

Since the time required for each test was 10 minutes, Curve I plotted from the first eighteen results of Table III uses time in minutes as abscissa, hydrogen efficiency as ordinate. The curve indicates that, while at the outset the efficiency was very low, it steadily increased to the tenth measurement when it remained practically constant. Other and frequent experiments have shown a state of affairs exactly similar to the results obtained in the series ranging from (10) to (18)—that a fairly constant value of the efficiency (about 29 percent) may be maintained for long runs provided that the temperature, current density, and concentration are maintained constant. The nineteenth and twentieth tests showed that by lowering the current density the efficiency was lowered, while the last two tests showed that it was increased by raising the density. In these

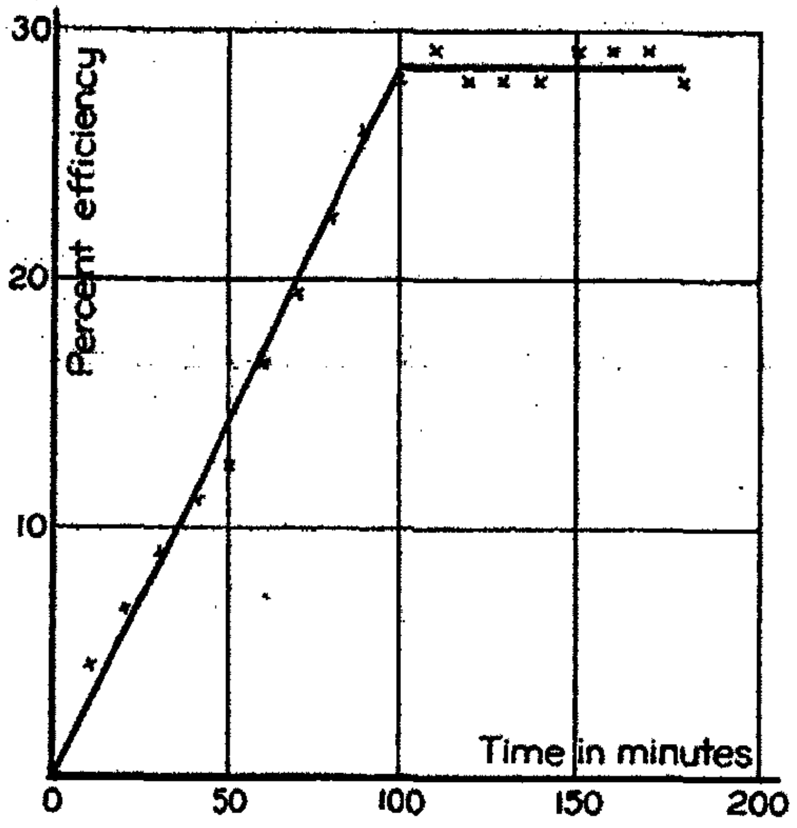

Fig. 1.

runs, the total chromium content had changed but very little by the removal of the small amounts of metallic chromium from the solution.

To explain the peculiar course of the curve, one may ask what chemical action takes place in the cathode chamber. Reduction of mercuric chloride proved that chromous chloride was formed. This compound, however, absorbs oxygen with very great rapidity. The rate at which this takes place will depend on the concentration of the chromous salt, the area of surface exposed to the air, the agitation and rate of change of the surface and the temperature.

The influence of the temperature was next examined; a chromic chloride solution of the same concentration was used. The current density was constant at 50. The results are detailed in Table IV.

TABLE IV.—CATHOLYTE, CHROMIC CHLORIDE CONTAINING 100 GRAMS METAL PER LITER

Experiment number	Temperature	Percent efficiency
23	52	Several runs, traces of metal
24	52	13.5
25	43	20.0
26	31	25.5
27	31–27	28.5
28	27–24	29.2
29	24–24	33.0
30	16	27.0
31	17	27.0
32	17–27	27.0
33	27–28	30.0
34	40	18.0

Long-continued runs at 50° showed very poor efficiencies under the same conditions which at 22° had given fair efficiency (Table III). Finally as much as 13.5 percent could be obtained at 52°, where at 22°, 28.5 percent had been found. On lowering the temperature the efficiency increased, having a maximum for this concentration at about 24°. At 16° the efficiency is lower than at 22°; other experiments show continuously decreasing efficiencies down to the lowest temperature at which we worked, zero degrees. Neumann has stated that the effect of temperature variation is slight; the results above given show that under some conditions at least this is not the case.

The time runs and the temperature tests offer evidence that the *chromous chloride is necessary to the deposition of the metal and that increase of temperature is not favorable to a high degree of concentration of the chromous salt in the solution.* But more direct evidence of the effect of oxidation was sought.

A solution of chromic chloride of the same concentration was electrolyzed until nearly constant results were obtained. Air and gas were then passed through this at intervals; the results are recorded in Table V and plotted in Curve II. Since the time required for each test was 10 minutes, the ordinate employed is time. Current density was constant at 70.

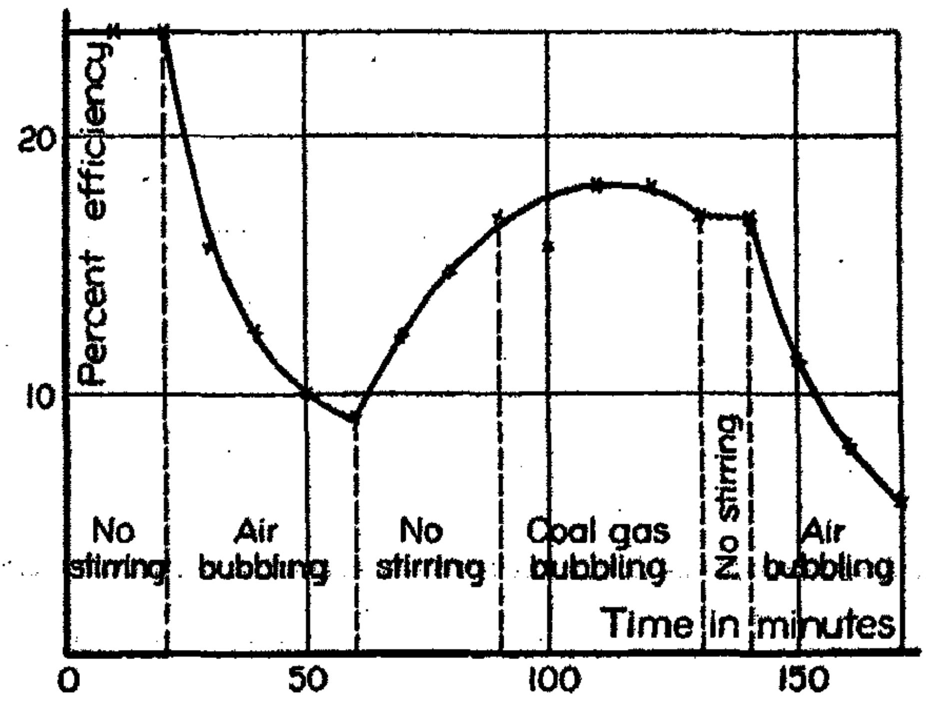

Fig. 2.

TABLE V.—CATHOLYTE, CHROMIC CHLORIDE, 100 GRAMS METAL PER LITER

Experiment number	Temperature	Percent efficiency
35	21°C	24.0
36	21	24.0
Air bubbled through the solution		
37	24–22	15.7
38	22	12.4
39	22	10.0
40	20	9.0
Stopped air blowing		
41	19	12.3
42	19	14.7
43	20	16.8
Gas passed		
44	19	15.7
45	19	18.0
46	19	18.0
47	18	16.8
Gas stopped		
48	18	16.8
Air passed		
49	22	11.2
50	20	7.9
51	13	5.7

It will be noticed that when air was passed into the cathode chamber, the efficiency fell continuously; that on stopping the blast it started to rise; that the stirring effect of an indifferent gas did not increase the efficiency materially but that on starting the current of air the yield again fell very decidedly.

Positive evidence as to the occurrence of a vigorous reaction between the air and some constituent of the solution is also given by the sudden rise in temperature of three to four degrees which took place when the air blast was started. The temperature of the air before passing was the same as that of the solution. Recoura[1] has determined the heat of oxidation of chromous chloride and found that very few substances absorb oxygen so vigorously.

There is every indication therefore that the current efficiency is closely connected with the presence in the solution of the chromous chloride. It is not maintained that the oxygen of the air is the only agent which tends to destroy this salt for there is every evidence[2] that it decomposes in the presence of hydrochloric acid, liberating hydrogen; increase of temperature would probably tend to accelerate this reaction, thus giving a reason for the decreased efficiency after a certain temperature has been reached. If now the efficiency depends upon the presence of the chromous chloride, not merely must the oxygen absorption be eliminated but the conditions for avoidance of the decomposition of the chromous chloride must be discovered. This presents the problem as one of general chemistry, involving the equilibrium and reaction velocities in the system chromium, hydrochloric acid, chromous and chromic chlorides, and hydrogen; the solution of this problem would help materially in advancing our knowledge of the electrochemical deposition of the metal from the chloride solutions.

From the theory of equilibrium the constancy of efficiency noted above is readily explained. It is probable that in the solution ratio of the relative masses of the chromous and chromic compounds has become practically constant. Whatever affects the

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[1] Ann. Chim. Phys. (6) 10, 18 (1881).

[2] Döring: Jour. prakt. Chem. 66, 65 (1902).

equilibrium, will influence the current yield; and as the equilibrium is affected by many chemical factors so also must be the electrochemical efficiency. This would easily explain the difference in the efficiencies obtained by different observers and indicate how difficult it is to obtain comparable conditions.

7. *Change in Anode Solutions.* In Neumann's paper, the statement was made that the anode chamber held mineral acids or salt solutions. Although nothing is stated as to the nature or the concentration of these anode solutions, the reader is told that by the alteration of the *anode* solution the yield was increased from 57 to 89.5 percent. If this statement be correct—and its accuracy was questioned by LeBlanc—the results produced by variation of the anolyte must indicate some of the factors which increase the efficiency.

To serve as anode solution, the following were made: normal potassium chloride and potassium hydroxide, sulphuric acid of specific gravity 1.13, ammonium ferrous sulphate three hundred grams per liter, ammonium oxalate saturated at room temperature, and ammonium hydroxide of the concentration ordinarily employed in the laboratory.

Since it is almost impossible to clean porous cups in any reasonable time (even by boiling for a week with distilled water changed twice a day), experiments were made at this stage to replace them by parchment fat extractors. These had to be discarded temporarily because of their small size, and the difficulties involved in making efficient cooling coils. Extra care was therefore taken to wash the cups as free as possible from soluble material. After this and before use, the cups were filled with the solution of the chromic chloride which diffused slowly outward.

In the experiments recorded in Table VI, the cathode solution was made from the red sublimed chloride which was dissolved by the methods already described. The density of the solution was 1.120, $t = 18°$; the cathode solution and current density (D = 57) were the same in each test, the anode solution along being varied. For the first ten runs an attempt was made to keep the temperature constant, after which it was allowed to rise. The runs as before were in a continuous series.

TABLE VI.—CATHOLYTE, CHROMIC CHLORIDE SOLUTION,
$d = 1.120$, D = 57

Anolyte, sulphuric acid		Anolyte, ammonium hydroxide		Anolyte, ferrous ammonium sulphate		Anolyte, ammonium oxalate	
Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency
23	10.6	23	8.2	23	8.5	25	6.1
25	10.8	24–27	12.1	24–27	12.3	27	16.5
25	11.2	27	14.7	27	13.9	27	18.0
25	9.0	27	15.7	27	15.7	27	19.1
25	9.0	27	16.9	27	16.9	27	22.5
25	9.0	27	18.0	27	18.0	28	19.6
25	9.0	27	18.6	27	18.3	28	19.1
25	7.5	27	18.0	27	16.9	28	19.6
25	4.5	27	14.7	27	15.7	28	19.2
25	3.4	27	11.2	27	14.7	28	21.4
25–30	9.0	27–45	4.5	27–39	10.8	28–35	20.2
30–35	9.0	—	—	39–44	5.7	35–40	19.6
35–36	9.0	—	—	44–53	3.3	40–43	19.2
36–38	7.9	—	—	53–59	1.1	43–45	19.2
						45–47	19.2
						47–49	16.8

Toward the end of every run, the deposits of metal became very poor. With sulphuric acid in the anode chamber, the deposits became very irregular; with ammonium hydroxide and ammonium ferrous sulphate the deposits were poor after the eighth test, hydroxide being apparently precipitated; with the oxalate the deposit became poor after the tenth test.

From these experiments one conclusion drawn by Neumann is confirmed— the efficiency may be increased very materially by change of the *anode* solution; but the results of Table VI show that in almost every case tried, *the efficiency rises, passes through a maximum and then falls again.* This effect had not been noticed in the electrolysis of the solution $d = 1.185$, with sulphuric acid as anolyte; if it is due to diffusion, it should be less marked the more concentrated the cathode solution.

Runs were now made with a more concentrated chromic chloride solution, $d = 1.260$, $D = 70$. Results are given in Table VII.

TABLE VII.—CATHOLYTE, CHROMIC CHLORIDE SOLUTION, $d = 1.260$, $D = 70$

Anolyte, sulphuric acid		Anolyte, ammonium hydroxide		Anolyte, potassium chloride		Anolyte, potassium hydrate	
Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency
24–27	13.5	27	39.4	27	23.7	26	31.5
27	20.3	27	38.3	26	25.9	26	30.3
29	19.1	27	37.0	26	26.4	26	30.3
30	24.1	27	37.0				
29	22.9	30–34	34.2				
29	22.9	34–38	38.3				
29	21.9	38–41	40.5				
28	20.3	41–43	42.7				
28–34	20.3	43–45	46.0				
34–38	13.5	45–46	50.5				
39	12.4	46–48	47.2				
		48–49	48.5				
		41–36	47.2				
		34–32	46.0				
		31	41.5				

With sulphuric acid, the efficiency after first increasing falls off with the time of the run; it is, however, very much greater than with the more dilute chloride solution. With ammonium hydroxide we wished to find the efficiencies when the temperature was not maintained constant; the results showed that there was a decided increase in efficiency as the temperature was raised up to 45°; in fact the highest efficiency obtained with chloride solutions was found here.

The results of Tables VI and VII indicate that diffusion from the anode solution is a very important factor. The oxygen dissolved therein does not seem to be so very important. This is evidenced by the slight difference between the last three anode solutions in Table VI, but the increase in acidity which we have previously found to lower the efficiency again appears important. Naturally, the presence of a base which may precipitate the hydroxide must be avoided; but the results seems to indicate that the diffusing base effects the equilibrium relations, perhaps displacing the relative masses of the compounds so as to favor higher efficiencies of metal deposition.

8. *Electrolysis of the Sulphate Solutions.*—Concurrently with the work on the chloride, experiments with the sulphate solutions were made to ascertain if higher efficiencies might be obtained with these.

The solutions used were analyzed, the chromium being determined as chromic oxide, the acid radical as barium sulphate. The salt was found to be strongly basic, having an excess of 14.1 percent of the chromic oxide; this excess is very frequent with the salts of chromium. With this salt, a solution of specific gravity 1.41 (hydrometer) was prepared; it contained 135 grams of chromium per liter. From this supersaturated solution a salt crystallized; the specific gravity of the solution became 1.398, the metallic content dropping to 127 grams per liter, corresponding to a 34 percent solution of the sulphate. A solution of specific gravity 1.250 was found to contain 83 grams per liter, one of specific gravity 1.172 held 59 grams, while for 28.5 grams per liter the specific gravity was 1.087.

In the tests, 100 cc of the solution were used in the cathode chamber, while the anode solution in all of the runs (except in Table XI) consisted of sulphuric acid $d = 1.12$. The current efficiencies were determined in the same manner as before.

In the first tests it was found that solutions holding 29.5 grams per liter (sp. gr. 1.087) yielded only traces of metal even after an hour's run; careful variations would undoubtedly have improved the yield very materially.

Table VIII gives an illustration of results obtained in a continued run when the current density and the temperature were allowed to vary simultaneously. In the next table current density and temperature were maintained constant and the effect of time of run and initial concentration examined. For the more dilute solution (59 grams) the efficiency rises rapidly

TABLE VIII.—CATHOLYTE, CHROMIC SULPHATE SOLUTION,
$d = 1.142$ at 23° C

	Current density	Temp.	Efficiency
1	55	25°C	21.0
2	55	31	28.5
3	47	27	24.0
4	33	27	21.0
5	33	24	24.0
6	17	20	15.0
7	19	18	19.5
8	35	21	25.5
9	50	24	39.0
10	67	29	51.0
11	67	29	64.5
12	130	31	70.5
13	67	26	51.0
14	67	26	57.0
15	67	25	51.0
16	36	25	46.5
17	36	25	48.0
18	36	20	43.5
19	36	20	48.0

to a maximum, then falls even more rapidly. This cannot be accounted for by a decrease in the amount of metal but is probably due to an increase in the acidity of the solution.

When the solution held 87 grams per liter, very good deposits were obtained from the start. After being electrolyzed for five hours, the solution was put into a stoppered bottle ; the next morning it was found to have liberated considerable hydrogen. The efficiency (28) was lower (although the temperature was slightly higher) and continued to fall during the subsequent two hours' electrolysis. But on the removal of the cooling coil (results not detailed in the table) the efficiency rose until at 36°, 40.5 percent efficiency was obtained, while cooling to 20° almost immediately decreased the hydrogen equivalent to 6 percent, then to 2.2 percent. Increase of temperature increased the yield to the figures previously obtained. With the most concentrated solution the current efficiency was at first much lower than with the other two solutions. After the

TABLE IX.—CATHOLYTE, CHROMIC SULPHATE

	59 grams Cr. per liter			87 grams Cr. per liter			135 grams Cr. per liter		
	Current density	Temp.	Percent efficiency	Current density	Temp.	Percent efficiency	Current density	Temp.	Percent efficiency
1	31	19°	6.7	29	17–19°	5.7	30	24–25°	1.1
2	32	19°	9.0	28	17–19°	8.4	30	25–24°	2.4
3	32	19°	12.7	28	17–19°	11.4	30	24–22°	6.1
4	34	19°	12.4	28	17–19°	12.9	30	22–23°	6.9
5	33	19°	15.0	31	17–19°	17.1	31	23–24°	7.9
6	31	19°	15.7	31	17–19°	18.0	31	24–24°	11.7
7	30	19°	17.2	31	17–19°	17.3	32	24–24°	12.9
8	30	19°	17.9	31	17–19°	20.4	32	24–23°	15.1
9	31	19°	19.8	32	17–19°	23.7	31	23–24°	18.1
10	31	19°	22.5	32	17–19°	26.2	32	24–24°	20.5
11	31	19°	28.1	32	17–19°	28.0	32	24–23°	22.1
12	32	19°	30.4	32	17–19°	26.4	31	23–23°	23.5
13	32	19°	22.5	32	17–19°	28.3	30	23–23°	25.3
14	33	19°	18.0	33	17–19°	28.6	30	23–22°	27.0
15	33	19°	14.5	33	17–19°	29.2	30	22–22°	31.5
16	33	19°	10.2	33	17–19°	31.4	34	22–23°	29.8
17				34	17–19°	31.5	32	23–23°	21.9
18				34	17–19°	30.4	32	23–23°	22.8
19				34	17–19°	29.3	31	23–24°	25.3
20				34	17–19°	31.5	31	24–25°	27.0
21				34	17–19°	32.5	32	25–24°	28.1
22				33	17–19°	32.5	33	24–25°	28.1
23				33	17–19°	31.9	34	25–25°	28.1
24				33	17–19°	31.9	33	25–25°	28.1
25				33	17–19°	32.5	34	25–26°	30.3
26				33	17–19°	31.9	—	—	—
27				34	17–19°	31.5	—	—	—
28				33	24	27.0	38	27–26°	33.7
29				33	22	28.6	38	26–26°	36.0
30				34	21	23.5	34	26–25°	36.0
31				32	20	25.9	34	25–25°	36.0
32				32	19	25.9	34	25–24°	36.6
33				30	19	24.7	33	24–22°	36.0
34				31	19	25.9	33	22–26°	37.1
35				31	19	24.9	33	26–29°	37.6
36				31	19	24.7	34	29–33°	38.3
37				30	19	24.7	34	33–35°	40.5
38				31	19	18.0			
39				31	19	18.0			
40				33	19	13.5			

sixteenth test, the solution was removed. Again hydrogen evolution was observed and also a much lower efficiency for the seventeenth test; the efficiency rose slowly as long as the temperature remained constant at 24–25°. Increase of temperature then raised the efficiency— a fact which is very noticeable in dealing with the sulphate solutions. This is also confirmed by the results given in Table X, obtained with a solution containing 87 grams per liter.

TABLE X.—CATHOLYTE, CHROMIC SULPHATE CONTAINING 87 GRAMS METAL PER LITER

Temp.	Current density	Percent efficiency
17–30	60	14.5
26–40	65	24.7
44–49	70	27.0
52–54	70	30.5
60–62	70	37.2
66–67	70	45.0
38–38	70	39.1
30–32	70	34.9

With the same solution it was possible to obtain at temperatures of 40–55° good deposits with a steady current efficiency of 30 percent extending over hours at a time.

In the electrolysis of the sulphate solutions we have not examined the effect of anolyte variation; there seems no doubt, however, that the cathode efficiency will be affected by diffusion, and that a continued high efficiency requires careful control of diffusion.

We have already noted that hydrogen is evolved whenever an electrolyzed solution is allowed to stand and that the current efficiency is invariably lower thereafter. The extent to which the chromic salt is reduced may be noted in the following table for the electrolysis of a solution containing 53 grams of the metal per liter, the gas evolved at the cathode and that evolved on the subsequent solution of the metal being noted. The hydrogen given off in the alkaline voltameter was 133.3 cc; the amount of hydrogen used in reduction is obtained by subtracting from 133.3 cc the sum of the values recorded in the two columns preceding.

TABLE XI.—ELECTROLYTE, CHROMIC SULPHATE CONTAINING 53 GRAMS METAL PER LITER

Temp.	Amps.	cc hydrogen evolved at cathode	(cc hydrogen evolved by chromium) × 1.5	cc hydrogen used in reduction
23–27	3.4	63.0	18.00	52.3
27–32	4.0	69.3	26.25	37.4
32–38	4.1–4.5	61.0	37.5	34.8
35–40	4.5	62.0	44.25	27.1
41–44	4.5	67.0	46.5	19.8
43	4.5	65.6	52.2	15.5

From these and similar experiments the reduction to the chromous salt seems to be favored by low temperatures; on the other hand, we note that the current efficiency for deposition of the metal is increased on raising the temperature.

The effect of air on the sulphate solution was examined in the same way as with the chloride, the solution used being the two-thirds concentrated. With temperature constant at 23°, current of 2.2 amperes, five consecutive runs showed efficiencies of 12.4, 13.5, 15.6, 16.8, and 19.1 percent; when air was blown in at rate of one liter per minute, the temperature remained practically constant, and the efficiencies fell slowly from 18.4 to 15.7, 14.6, 13.9 percent. The lowering of the efficiency was quite marked but by no means so rapid as in the case of the chloride.

A very interesting fact was observed when to avoid oxidation at the surface we added toluene or petroleum ether—the efficiency of metal deposition was reduced in a short time almost to zero.

Preliminary experiments made with both chloride and sulphate solutions showed that with rotating electrodes, better deposits might be obtained over a wide range of current density; since the efficiencies were somewhat lower than with stationary electrode, their use was abandoned. The effect, it will be noticed, is that of producing more rapid oxidation by the air, which must, of course, be avoided so far as possible.

9. *Conclusions.*—From our experiments the following conclusons are drawn:

(1) The presence of chromous salt appears to be essential to the successful deposition of the metal from its chloride or sulphate solutions. This has been proved by showing (*a*) that the current does work in reducing the chromous to the chromic salts; (*b*) that it is necessary to electrolyze the chromic salts for some time before the metal can be deposited with any considerable efficiency; and (*c*) that the efficiency is destroyed by oxidation of the chromous salt.

(2) Temperature has a very decided influence upon the efficiency of deposition; this result is in direct opposition to those recorded by Neumann. For each especial set of conditions there seems to be a temperature at which the loss in efficiency caused by the decomposition of the chromous salt is balanced by increased efficiency caused by other factors. For example, it was found that after the sulphate had been electrolyzed for some time, rise of temperature increased the efficiency; the same result was observed when the current density was lowered. For a chloride solution between 0° and 16°, the same effects were noticed. As might be predicted, the more concentrated the solution, the higher the temperature which may be advantageously employed.

(3) The nature of the anode solution affects the yield very considerably; that this is probably due to the diffusion of the anolyte into the cathode chamber is indicated by the peculiar results obtained in the continued efficiency runs.

(4) On continued electrolysis of the solutions of chromic salts, the efficiency rises from zero to a value which is practically constant. This may be accounted for by assuming that the absolute and relative masses of the chromous and chromic salts have, under the conditions employed, become practically constant in the solution. Any factor tending to change these relations will affect the current efficiency—for example, change of temperature, increase of acidity, change of concentration and the presence of catalytic agents such as toluene or petroleum ether.

(5) In the ordinary problems of electrochemistry, it is conceivable that in reducing from the higher stages of oxidation, that solution from which metal can be deposited may not be obtained. *For this reason solutions in which the metal shows its lowest valency should in this and in all analogous cases be used when it is desired to obtain good current efficiencies in the deposition of metal.*

We have also noted that the quality of the deposit is always bad when the current efficiency is less than five percent; an acid bath favors hard and strong deposits but causes lower efficiencies.

Any one who will study the electrodeposition of this metal will be impressed by the great number of factors which must be controlled; and it sometimes happens that the exact definition of conditions for the reproduction of the experiments are difficult. With the time at our disposal we have had to restrict the number of variations to be studied, but we believe that we have considered some of the factors which are usually overlooked in electrochemical work but which are of considerable importance.

Cornell University,
January, 1905.

ON THE LIBERATION OF HYDROGEN DURING THE ACTION OF SODIUM ON MERCURY

BY LOUIS KAHLENBERG AND HERMAN SCHLUNDT

It is a well known fact that when sodium amalgam is formed by the action of sodium on mercury the reaction proceeds with explosive violence and strong evolution of heat and light. Some time ago the former of us found that during the interaction of these two metals a considerable quantity of hydrogen gas is formed and that the sudden liberation and oxidation of this gas accounts for the explosion accompanying the reaction.

While the fact that hydrogen is thus liberated had been established, there remained the question as to how much hydrogen is evolved in the reaction by a given amount of sodium, and also a careful spectroscopic examination of the gas. Last summer we found time to investigate these points together.

Bright pieces of metallic sodium were quickly introduced into a eudiometer tube filled with pure, dry mercury inverted in a mercury bath. The gas, which was rapidly liberated, was measured and then the entire amalgam formed was treated with water, after which the alkaline solution formed was titrated with a standard solution of hydrochloric acid. Successive experiments performed with samples of sodium from different sources showed that the amounts of hydrogen liberated by a given weight of the metal varied but little. As an average of the tests made, it was found that each gram of sodium liberates 3.24 cc of hydrogen at 20° C and 750 mm barometric pressure; in other words, when treated with mercury, ordinary sodium evolves somewhat more than three times its volume of hydrogen at room temperature and atmospheric pressure.

The preliminary spectroscopic examination of the gas was made with the Universal Spectroscope made by A. Krüss in Hamburg, but the final inspection was made with a large direct vision spectroscope of particularly high dispersive power manufactured by A. Hilger in London. The latter instrument was kindly loaned to us by the department of physics of this university. The gas liberated as above described is dry and free from carbon dioxide, and otherwise quite ready to be introduced into a vacuum tube. The latter tube contained a platinum and an aluminum electrode in one case, and two platinum electrodes in another. A Boltwood's automatic pump was used in exhausting the tubes. It is quite unnecessary to describe the details of the experimental operations; suffice it to say, that all the precautions laid down by Travers in his admirable treatise on the manipulation of gases were carefully observed. We found the lubricant for stop-cocks which he recommends particularly helpful. The tubes were examined at different pressures, varying from about three millimeters to a small fraction of a millimeter. In all cases, however, the gas showed simply the spectrum of pure hydrogen.

As to the explanation of the liberation of the hydrogen during the reaction in question, it seems probable that ordinary sodium contains sodium hydride which is decomposed by the interaction with mercury.

In 1879, Sir Norman Lockyer[1] made some investigations on the supposed compound nature of the elements, in the course of which he found that carefully distilled sodium when condensed in a capillary tube and then placed in a retort and heated in a vacuum, gave off twenty times its volume of hydrogen. Assuming that in Lockyer's experiment the liberation of hydrogen was also due to the decomposition of sodium hydride contained in the sodium, and that his sodium contained at least no more sodium hydride than the samples we employed taken from the open market, it would follow that during the interaction of sodium on mercury not all the sodium hydride present is decomposed, for we obtained only about one-sixth as much hydrogen from a given volume of sodium as Lockyer did. It seems to us somewhat unlikely, however, that only a small fraction of the sodium hydride present should be decomposed by the mercury. The matter is quite worthy of further inquiry. It would be of special interest to determine whether pure sodium hydride is decomposed by

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[1] Chem News, 40, 101 (1879).

mercury, and if so, to what extent. Furthermore the behavior of other alkali metals toward mercury, and toward other metals as well, becomes an interesting subject for study.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, December, 1904.

NEW BOOKS

Chemical Statics and Dynamics, Including the Theories of Chemical Change, Catalysis, and Explosions. *By J. W. Mellor. 12 × 19 cm; pp. xiii + 528. New York: Longmans, Green and Co., 1904. Price: bound, $2.00.*—The headings of the chapters are: introduction; homogeneous chemical reactions; homogeneous side reactions; homogeneous opposing reactions; homogeneous consecutive reactions; the beginning of a chemical reaction; heterogeneous reactions; equilibrium and dissociation; electrolytic dissociation; catalysis and the theory of chemical change; fermentation; the influence of temperature on chemical reactions; the influence of pressure on chemical reactions; explosions.

Most of the smaller text-books on physical chemistry are merely condensed from Ostwald's *Lehrbuch*. This volume does not belong in this class. It stands on its own feet, so to speak. The book is a bit of work of which any one might be proud. The section on the measurement of instantaneous velocities will be of benefit to most chemists. The discussion of the "period of acceleration" is very clear. The reviewer was much interested in the treatment, p. 146, of the equilibrium between two solid allotropic forms. The chapters on catalysis, fermentation, temperature, and explosives are especially good. The periodic luminosity of phosphorus when oxidizing slowly, p. 311, is a point which is often overlooked, while "Liveing's switchback," p. 323, will probably be new to most readers of the book. The discussion of passive resistance is good and there is an admirable statement, p. 435, of the theorem of Le Chatelier. The effect of a cold copper ring, p. 446, in putting out the flame of a candle is an excellent instance of the way in which the temperature of ignition varies with the external conditions.

The sanity of the author in regard to mathematics is shown by the quotation, p. 19, from Huxley: "Mathematics may be compared to a mill of exquisite workmanship which grinds you stuff of any degree of fineness; but nevertheless what you get out depends on what you put in." On the same page is another interesting statement. "There is a prevailing notion that the agreement between the 'calculated' and 'observed' results is an infallible crucial test of any hypothesis. The agreement only shows that the hypothesis *may* be true. G. W. von Leibnitz long ago remarked that success in explaining facts is no *proof* of the validity of an hypothesis."

There are a few things which the reviewer would like to see changed in a subsequent edition. In view of the importance of diffusion for reaction velocity in heterogeneous systems, it would be well to treat diffusion as a case of reaction velocity. On p. 206, Ostwald's first value for the dissociation of water has been given instead of the value as corrected by Nernst. The color change of methyl orange, p. 215, is not due to its being a strong acid. On p. 235 some reference should have been made to the fact that the distribution law holds only in case the two liquids are not made any more miscible by the addition of the third component. It is distinctly unsatisfactory to treat fractional precipitation, p. 239, as a case of reaction velocity. It is a bit arbitrary, p. 342, to eliminate the solvent from the list of simple catalytic agents because it displaces the equilibrium. Even Ostwald has given up that position.

While the other books in this series have been good, this one is by far the best that has yet appeared. *Wilder D. Bancroft*

Flüssige Kristalle sowie Plastizität von Kristallen im allgemeinen, molekulare Umlagerungen und Aggregatzustandsänderungen. *By O. Lehmann. 24 × 31 cm; pp. vi + 264. Leipzig: Wilhelm Engelmann, 1904.*—The first and shortest portion of this stately volume is devoted to the plasticity of solids; the second part to a discussion of flowing crystals and of liquid crystals; while in the third part such matters are taken up as conceptions of liquid and of crystal, polymorphism, melting, amorphism and vaporization. A flowing crystal is one in which the surface tension is strong enough to round off the edges and ends of the crystals somewhat. When the surface tension is strong enough to give the crystal a spherical shape it becomes a liquid crystal. We have in this book a most complete and satisfactory account of the facts connected with flowing and liquid crystals. Curiously enough the author refuses to accept Tammann's distinction that all solids are crystalline and all liquids are not. In the definition of a liquid, p. 106, the author recognizes the existence of crystalline liquids. He is then of course very hard put to it to find any dividing line between an amorphous solid so-called and a liquid. A crystal is distinguished from an amorphous solid by being an anisotropic substance with a reversible solubility.

When one considers the vast amount of experimental data collected by the author and that he was fairly clear in 1877 as to the existence of inversion points, p. 187, it may seem a little surprising that the author has not had more influence on the development of physical chemistry. The reason for this appears to be that the author has not kept in touch with the developments. His remarks on the phase rule, p. 240, betray an almost pathetic misunderstanding of the situation. The discussion as to the solubility of amorphous sugar, p. 218, is not at all to the point. Though the author claims to have been the first to state that a solubility must be defined with respect to the solid phase, the quotations, p. 160, rather imply a lack of clearness even now.

In spite of these and other defects, the volume is a treasure-house of facts. The author has a real talent for discovering and collecting facts. One can open the book anywhere and be sure of finding something interesting: the action of alcoholic ferric chloride on marble, p. 214; the effect of one substance on the crystalline form of another, p. 118; the artificial production of layers, p. 21; etc., etc. The illustrations are something wonderful. The Prussian Academy of Sciences made a special grant to pay for the plates and it certainly was money well spent. *Wilder D. Bancroft*

The Study of Chemical Composition, an Account of its Method and Historical Development. *By Ida Freund. (Cambridge Physical Series). 14 × 22 cm; pp. xvi + 650. New York: The Macmillan Company, 1904. Price: bound, 18 shillings, net.*—After an introductory chapter we have chapters on: theories of combustion; Lavoisier and the law of conservation of mass; exact and approximate laws; Berthollet and the law of mass action: Proust and the law of fixed ratios; Dalton and the law of multiple ratios; Richter and the law of equivalent ratios; combining or equivalent weights; the ultimate constitution of matter; Dalton and the atomic hypothesis; Gay-Lussac and the law of the combining volumes of gases; Avogadro and the molecular hypothesis; Cannizzaro and the application of Avogadro's hypothesis to the determination of molecular and atomic weights; Petit and Dulong and the law of atomic heat; Mitscherlich and the connection between crystalline form and chemical composition; Mendeléeff and the periodic law; Kekulé and the doctrine of valency; Berzelius and isomerism; the ultimate constitution of matter and the genesis of the elements.

On p. 28 we find the distinction between hypothesis and theory stated so clearly that it is worth while to quote it in full: "When in a simple manner it [a hypothesis] correlates knowledge, when it is so elastic as to let the new at once fall into its proper place by the old, and when under its directions the quest for further knowledge becomes a direct advance along clearly indicated paths, then the hypothesis takes rank as a theory."

The general style of the book can perhaps best be shown by two quotations; the one on p. 544 is a paragraph of the author's. "Doubt has often been expressed as regards the importance and utility of the study of valency. The unnecessary and unsuccessful attempt made at one time by great masters of the science to class certain valency phenomena as exceptional, and the barrenness of the consequent dialectical discussion concerning constant and variable valency, afford some justification for such a view in the past. It must also be admitted that the study of inorganic chemistry has so far not been advanced to any degree by the doctrine of the different saturation capacity of the elements. But against this must be set the brilliant success achieved in the domain of organic study. Structural chemistry is based on the doctrine of valency; and it seems justified to describe as marvellous the results which have followed from the application of structural chemistry to the explanation of the phenomena of isomerism." On the last page of the book there is a quotation from Kekulé in 1867: "The question whether atoms exist or not has but little significance from a chemical point of view: its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena. More especially have we to consider the question whether a further development of the atomic hypothesis promises to advance our knowledge of the mechanism of chemical phenomena.

"I have no hesitation in saying that, from a philosophical point of view, I do not believe in the actual existence of atoms, taking the word in its literal signification of indivisible particles of matter—I rather expect that we shall some day find for what we now call atoms a mathematico-mechanical explanation, which will render an account of atomic weight, of atomicity, and of numerous other properties of the so-called atoms. As a chemist, however, I regard the assumption of atoms, not only as advisable, but as absolutely necessary in chemistry. I will even go further, and declare my belief that *chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses. Should the progress of science lead to a theory of the constitution of chemical atoms—important as such a knowledge might be for the general philosophy of matter—it would make but little alteration in chemistry itself. The chemical atoms will always remain the chemical unit; and for the specially chemical considerations we may always start from the constitution of atoms, and avail ourselves of the simplified expression thus obtained, that is to say, of the atomic hypothesis. We may, in fact, adopt the view of Dumas and of Faraday, that *whether matter be atomic or not, this much is certain, that granting it to be atomic, it would appear as it now does.*"

On page 283 it might have been well to have supplemented the statement in regard to Newton's acceptance of the atomic hypothesis and of the existence of a void by pointing out that the view generally held to-day is not that of Newton. The assumption of an all-pervading ether practically does away with the existence of a void. This is a very readable book and every one will look forward with pleasure to the succeeding volumes in this series.

Wilder D. Bancroft

Traité élémentaire de Physico-chimie ou Lois générales et Théories nouvelles des Actions chimiques. *By Emm. Pozzi-Escot. Préface de Eugene Jacquemin. 15 × 22 cm; pp. xvi + 627. Paris: Ch. Béranger, 1905. Price: bound, 20 francs.*—The author admits that the French technical chemists are not the equal of the Germans and he hopes to remedy this defect by teaching them physical chemistry. This is a laudable aim and it is to be hoped that the book will serve the purpose. The book is nothing like as good as the corresponding book by Walker for instance and it will not have much of a sale in this country. It is rather surprising to find Becquerel credited with being one of the discoverers of Faraday's law. As is the case in so many French books the spelling of proper names is very erratic.

Wilder D. Bancroft

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. *By Walter Nernst. Revised in accordance with the Fourth German Edition. 14 × 22 cm; pp. xxiv + 771. New York: The Macmillan Company, 1904. Price: $3.75.*—This new edition is the work of R. A. Lehfeldt who says in the preface: "The English publishers, in 1903, asked me to re-edit their translation. In doing this I have translated all the new matter contained in the fourth German edition, and revised certain parts of the old, in the endeavour to free the book from any mistakes and ambiguities that a first edition is so liable to contain. The bulk of the old text, however, remains as it was." We are very glad that an English translation of the last German edition is now available. It is a pity, however, that "the bulk of the old text, however, remains as it was." One would have thought that the experience of the publishers with the first English edition would have shown then the advisability, from a financial point of view, of having the whole text re-written.

Wilder D. Bancroft

Report of the Commission Appointed to Investigate the Different Electro-thermic Processes for the Smelting of Iron Ores and the Making of Steel in Operation in Europe. *By Eugene Haanel. 17 × 25 cm; pp. xiv + 223, 1904.*—This is the report of a Commission appointed by the Canadian government "for the purpose of investigating and reporting upon the different electro-thermic processes employed in the smelting of iron ores, and the making of different classes of steel, now in operation or in process of development, in Italy, France and Sweden. The special object of this investigation is the ascertainment of all facts in connection with these processes, which are necessary for determining the cost of one ton of product, the quality of the product, and cost of machinery employed, and such other facts as may be required for the formation of a judgment regarding the feasibility of introducing successfully in Canada electro-thermic processes for the production of iron and steel."

The Commission studied the Kjellin process at Gysinge, the Héroult process at La Praz, the Keller process at Livet, and the Stassano process at Turin. The metallurgist was Mr. F. W. Harbord and he comes to the following conclusions:

1. Steel, equal in all respects to the best Sheffield crucible steel, can be produced, either by the Kjellin or Héroult or Keller processes, at a cost considerably less than the cost of producing a high-class crucible steel.

2. At present, structural steel, to compete with Siemens or Bessemer steel, cannot be economically produced in the electric furnaces, and such furnaces can be used commercially for the production of only very high-class steel for special purposes.

3. Speaking generally, the reactions in the electric smelting furnace as regards the reduction and combination of iron with silicon, sulphur, phosphorus, and manganese, are similar to those taking place in the blast-furnace. By altering the burden and regulating the temperature by varying the electric current, any grade of iron, grey or white, can be obtained, and the change from one grade to another is effected more rapidly than in the blast-furnace.

4. Grey pig iron, suitable in all respects for acid steel manufacture, either by Bessemer or Siemens's process, can be produced in the electric furnace.

5. Grey pig iron, suitable for foundry purposes, can be readily produced.

6. Pig iron low in silicon and sulphur, suitable either for the basic Bessemer or the basic Siemens process, can be produced, provided that the ore mixture contains oxide of manganese, and that a basic slag is maintained by suitable additions of lime.

7. It has not been experimentally demonstrated, but from general considerations there is every season to believe, that pig iron low in silicon and sulphur can be produced even in the absence of manganese oxide in the iron mixture, provided a fluid and basic slag be maintained.

8. Pig iron can be produced on a commercial scale, at a price to compete with the blast-furnace only when electric energy is very cheap and fuel very dear. On the basis taken in this report, with electric energy at $10 per E. H. P. year, and coke at $7 per ton, the cost of production is approximately the same as the cost of producing pig iron in a modern blast-furnace.

9. Under ordinary conditions, where blast-furnaces are an established industry, electric smelting cannot compete; but in special cases, where ample water power is available, and blast-furnace coke is not readily obtainable, electric smelting may be commercially successful.

It is impossible to define the exact conditions under which electric smelting can be successfully carried on. Each case must be considered independently after a most careful investigation into local conditions, and it is only when these are fully known that a definite opinion as to the commercial possibilities of any project can be given.

Included in the volume is the report of a Commission on Ruthenberg's process for treating magnetic ores. The conclusion reached is that this process in its present form is absolutely worthless. *Wilder D. Bancroft*

Experimentelle Untersuchung von Gasen. *By Morris W. Travers. Mit einem Vorwort von William Ramsay. Deutsch von Tadeusz Estreicher. Nach der Englischen Auflage vom Verfasser unter Mitwirkung des Uebersetzers neu bearbeitet und erweitert. 14 × 23 cm ; pp. xii + 372. Braunschweig : Friederich Vieweg und Sohn, 1905. Price : paper, 9; bound, 10 marks.*—This is more than a mere translation; it is really a revised edition. The author has introduced much that has been worked out since the appearance of the English edition and the translator has added a chapter on the heat of vaporization of liquefied gases. The general appearance of the volume is admirable.

Wilder D. Bancroft

Grundbegriffe der allgemeinen physikalischen Chemie. *By Kurt Arndt. Zweite Auflage. 11 × 17 cm : pp. 48. Berlin : Mayer und Müller, 1905. Price : 80 marks.*—This little book contains a number of short sections which express in a very concise form the definitions used and the laws which are most frequently encountered in general chemistry. The subject-matter has been carefully selected and is expressed in a clear and dogmatic manner which will certainly appeal to every student of physical chemistry. *H. R. Carveth*

The Becquerel Rays and the Properties of Radium. *By R. J. Strutt. 15 × 23 cm ; pp. vi + 214. London : Edward Arnold, 1904. Price : 2.40 net.*—The scope of the present work is best set forth in the author's preface where he says "My object has been to give as clear and simple an account of the phenomena of radioactivity as the subject admits of, without sacrificing accuracy. The extraordinary properties of radium have excited general interest outside of the scientific world, and there are probably many who would be glad to learn something of the subject, if they could find it explained without the use of technicalities. However essential mathematical methods may be in developing the subject, they are seldom really necessary in presenting the results. Moreover, some idea of the train of reasoning can generally be given in ordinary language."

Some scientific knowledge is of course required to read the book intelligently from cover to cover, but a work of this kind is exceedingly valuable because a great deal of information is included in simple language. Moreover, the author is acknowledged an authority on the subject, and what he states may be relied on as accurate. This is most important in a book written with the express purpose of reaching the general reader. First impressions are as a rule the most lasting, and that such impressions of the subject of radioactivity may be gathered from this source is certainly gratifying.

The book is divided into eight chapters and three appendices. In the first chapter a good account is given of vacuum tube discharge, in which several simple drawings illustrate the text well. The work of J. J. Thomson in clearing up the nature of the cathode ray particles is treated admirably and the reader is made familiar with enough to enable him to understand the connection between this subject and radioactivity which begins in the next chapter.

The various active elements are treated historically, with accounts of the initial experimental work. When one reads of the Curie method of chemical separation of radium from pitchblende, on page 36, one finds the author unnecessarily popular. He offers no simple explanation of hydrochloric acid nor explains what is meant by a suitable flux but goes to the trouble of explaining sulphuretted hydrogen as "a compound of hydrogen and sulphur which possesses the smell characteristic of rotten eggs."

In the third chapter the properties and nature of the radiations are dealt with, including the chemical and physiological effects of the rays. The α, β and γ-rays are taken up in the order named, and the experimental work disclosing their nature is described. The chapter on ionization and absorption is clearly put, and includes almost all the familiar terms used by physicists, set to popular language,—a none too easy task. A simple example of absorption is taken from Mme. Curie's experiments on the α-rays from polonium. This is instructive and enables one better to understand the more general accounts of the experiments for the other types of rays.

The chapter on the changes occurring in radioactive bodies has to do more particularly with the emanation from radium and the evidence in favor of the disintegration theory. Changes in uranium, thorium, actinium and polonium are described, although for the two latter very little could be said at the time of writing. The extraordinary properties connected with the heating effect of radium and the emanation are discussed. The next chapter is full of the interesting subject of the radioactivity of the earth and the atmosphere.

The seventh chapter, on the ultimate products of radioactive change, runs of course a little into speculation; but there is ample room here for interesting prediction. It must be said that the author makes full use of his opportunity in this chapter, and in the succeeding one on the electrical theory of the nature of matter.

The three appendices are for students wishing to go more deeply into the subject, with instructions for carrying out the main experiments. As the subject of radioactivity advances by leaps and bounds, it easily happens that a book may miss important matter during the time of publication, and may become almost at once out of date. This is a fault, however, in common with all the other books on the subject and is easily rectified by a second edition.

On the whole, the book is well up-to-date and is much to be recommended to the general reader; and the author is to be congratulated on its timely production. *H. T. Barnes*

Propriétés et Essais des Matériaux de l'Electrotechnique. *By F. de Poncharra. pp. 152.*

Enroulements d'Induits à Courant continu. *By E. J. Brunswick and M. Aliamet. pp. 187.*

Abrégé de la Chimie des Parfums. *By. P. Jeancard and C. Satie. pp. 190. (Encyclopédie scientifique des Aide-mémoire). 11 × 19 cm. Paris: Gauthier-Villars; Masson et Cie. Price: paper, $2.50; bound, 3 francs.*

The subjects treated in these three volumes belong in the borderlands of physical chemistry. Insulating materials and conductors are already recognized as part of physical chemistry. The theory of the dynamo is not yet part of the working knowledge of most physical chemists though of course it should be. The chemistry of perfumes is not a matter with which the physical chemist concerns himself as yet. On the other hand the study of the effect of atmospheric variations on the composition of the essential oils, as referred to in the preface, should be physical chemistry. *Wilder D. Bancroft*

Physikalisches Praktikum. *By Eilhard Wiedemann and Hermann Ebert. Fünfte verbesserte und vermehrte Auflage. 15 × 24 cm; pp. xxx + 590. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: paper, 10; bound, 11 marks.*—The general plan of this work remains the same as that of two of the previous editions reviewed in this Journal (1, 714; 3, 606). Experiments have been revised, details in many cases have been improved, and mathematical formulas given. A chapter dealing with electrochemical measurements has been added.

In this work we have one of the best general laboratory guides for the student of chemistry who must have elementary measurements in physical and electrochemistry. In the following points it differs from books at present used for this purpose: its varied problems are those which the chemist meets at every turn; the experiments are specific; the methods of operation are described in detail; the results must be obtained within a certain error limit.

Some of the problems outlined require that the instructor be a well-trained chemist, since otherwise it would be difficult to reproduce the chemical variables of the problem in such a way as to obtain fairly accurate results. The work recognizes the field of the physical chemist, emphasizes its importance and at the same time is helpful in showing what methods may be adapted to work in the laboratory of physical chemistry. *H. R. Carveth*

Ricerche sperimentali. *Edited by R. Nasini. 15 × 22 cm; Padua: R. Stab. Prosperini, 1904.*—Some years ago (6, 140) we had the pleasure of calling attention to a volume of collected papers from the laboratory of Professor Nasini covering the years 1898-1900. The present volume is the second of the series and contains the twenty-four papers published in the three years 1901-1903. For quality and range this collection will compare favorably with the output from any except the largest laboratories. *Wilder D. Bancroft*

Kalendar für Elektrochemiker sowie technische Chemiker und Physiker, *fur das Jahr 1905. IX. Jahrgang. Mit einer Beilage. By A. Neuburger. 10 × 16 cm; pp. 504. Berlin: M. Krayn. Price: bound, 4 marks.*—The value of this volume is appreciated so thoroughly by all electrochemists that it is merely necessary to call attention to the appearance of the ninth edition. Seven pages are devoted to the Edison and the Jungner accumulators.

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.

Report of the international committee on atomic weights. *F. W. Clarke. Jour. Am. Chem. Soc.*, 27, *1* (*1905*).—The changes this year are indium to 115, iodine to 226.97, rubidium to 85.5, and samarium to 150.3. It is recognized that the value of 14.04 for nitrogen is wrong; but no change is made owing to the discrepancy between the volumetric and the gravimetric data. *W. D. B.*

On actinium. *A. Debierne. Comples rendus*, 139, *538* (*1904*).—Special experiments, carried out to a certain extent in conjunction with Giesel, have shown that Giesel's emanium is identical with Debierne's actinium.
W. D. B.

Density of nitrous oxide and atomic weight of nitrogen. *P. A. Guye and C. Pintza. Comptes rendus*, 139, *677* (*1904*).—Under standard conditions a liter of nitrous oxide is found to weigh 1.97788 grams. Since carbon dioxide and nitrous oxide are very nearly in corresponding states at equal temperature and pressure, the authors have compared the densities. From these data they deduce 14.013 for the atomic weight of nitrogen. In the same laboratory 14.004 has been found from the limiting density of nitrogen, 14.007 from weight determinations on N_2O, and 14.019 from volume determinations on N_2O. The mean of the four is 14.011. *W. D. B.*

The atomic weight of aluminum. *Koln-Abrest. Comptes rendus*, 139, *669* (*1904*).—The author started with an impure aluminum containing about 98.7 percent Al, dissolved this in hydrochloric acid, measured the hydrogen, and corrected for the impurities in the aluminum. He finds 27.09 for the atomic weight of aluminum ($O = 15.88$). It is not likely that this determination will be considered as adding much to our knowledge of atomic weights.
W. D. B.

The possibility of chemical reactions. *R. de Forcrand. Comptes rendus*, 139, *905*, *908* (*1904*).—While the author admits that a reaction can take place only in case it involves a decrease of free energy, he maintains that this criterion cannot be applied in general and that the law of maximum work is the only practical guide. In order to justify this the author excludes all so-called physical reactions, dissociation, etc. *W. D. B.*

A method of determining the thermal conductivity of copper. *G. F. C. Searle. Phil. Mag.* [*6*], 9, *125* (*1905*).—A method in use at the Cavendish laboratory by the students which has yielded excellent results. A copper rod is heated at one end by steam and the other end is cooled by a spiral of copper tube soldered to the rod, through which a constant stream of water flows. The amount of heat carried off by the water flow is measured as in the method of continuous-flow calorimetry by the temperature of inflow and outflow and the mass per second. In addition the temperature gradient down the bar is measured by two thermometers at known intervals. A sample set of readings is given. *H. T. B.*

On a recent series of calorimetric determinations. *P. Lemoult. Comptes rendus*, 139, *633* (*1904*).—It is shown that the recent calorimetric determinations of Fischer and Wrede can be represented satisfactorily by the author's formulas. *W. D. B.*

One-Component Systems.

On the boiling-points of homologous compounds. *S. Young. Phil. Mag.* [6], 9, *1* (*1905*). The rise of boiling-point for a number of series is considered mainly a function of the absolute temperature and the formula

$$\Delta = \frac{144.86}{T\,0.0148\,\sqrt{T}}$$

is proposed as a means of calculation. This formula was originally worked out for increments of CH_2, but it has been shown to hold for the halogen derivatives as well as for many other series.

A number of tables of boiling-points are compiled from the author's data as from many other observers and it is found that the differences between calculated and observed values of Δ are considerably greater for associating than for non-associating substances; also among the associating substances they are greatest for the alcohols and least for the acids. A very complete table of the esters is given.

Considering the data as a whole the values of Δ may be calculated from the formula with an error rarely exceeding 1.5°. *H. T. B.*

Preparation and properties of pure boron trifluoride and silicon tetrafluoride. *H. Moissan. Comptes rendus*, 139, *711* (*1904*).—Boron trifluoride was obtained by the action of calcium fluoride and sulphuric acid on boron anhydride; also by direct combination of boron and fluorine. It melts at —127° and boils at —101°. Silicon tetrafluoride was prepared in precisely analogous ways. It has a sublimation point at —97°. Under 2 atm pressure silicon tetrafluoride melts at —77°. Under a pressure of 181 cm Hg it boils at —65°. The critical temperature is —1.5° and the critical pressure 50 atm. *W. D. B.*

Two-Component Systems

Alloys of cobalt and nickel. *W. Guertler and G. Tammann. Zeit. anorg. Chem.*, 42, *353* (*1904*).—The freezing-point curve was determined relatively, and was found to be nearly a straight line between the freezing-point of nickel, and that of cobalt. The freezing-points of the pure metals were taken as about 1484° for nickel, and 1528° for cobalt. The nickel used contained about two percent of cobalt, and the cobalt about two percent of nickel. The form of the liquidus, and the time occupied in freezing lead the authors to believe that there is little difference between the composition of the melt and of the phase which is crystallizing. Like the gold silver series, these alloys are evidently perfectly isomorphous, forming a continuous series of solid solutions. The transformation from magnetic to non-magnetic nickel occurs at 323°. A similar change from magnetic to non-magnetic cobalt was discovered at 1150°. The curve for this transformation in the alloys was found to be practically a straight line between the inversion temperatures for the pure metals. This fact furnishes further evidence of the complete solubility of the metals in each other. The alloys were not examined microscopically, nor were the densities determined. *E. S. S.*

The tin amalgams. *W. J. van Heteren. Zeit. anorg. Chem.*, 42, *129*, (*1904*).—This is the completed research of which a preliminary report was made some time since by Roozeboom. The paper includes many interesting points. An equilibrium diagram is offered but is intended as a tentative one. As the result of many methods of investigation (analytical, electric, dilatometric, etc.) the author concludes that:

1. Molten tin and mercury are soluble in all proportions.

2. The eutectic concentration is practically that of pure mercury. The freezing-point curve consists of two branches. The first rises from the freezing-point of mercury to a temperature of —34.5° C and a concentration of 0.3 atomic percents. The second branch rises from this point to the freezing-point of tin.

3. The upper branch of the F. P. curve drops from 232° C in almost a straight line to 120°, then bends downward to 40°. From there it drops almost vertically.

4. From the melt either pure, or nearly pure tin crystallizes. Analytically, the solid phase was found to contain 94, and electrically 99, atomic percents of tin.

5. By electrometric methods the saturated alloy was found to contain 1.2 atomic percents of tin at 25°. The heat of amalgamation was found to be —3000 calories at 25°.

6. The transformation at —34.5° is observed in all concentrations between 0.3 and 85 atomic percents.

The author is led to suspect the existence of a solid solution in which tin occurs in a new modification. He is not able as yet to prove this. The change of grey into white tin and the reverse inversion could not be shown for amalgams. The evidence seems to indicate that this inversion temperature is lowered very much indeed. While the paper is not conclusive, it will prove interesting to all students of alloys. *E. S. S.*

The microscopic examination of metals. *J. H. B. Jenkins and D. G. Riddick. The Analyst*, 30, *2* (*1905*).—A paper intended to describe the methods of examination of alloys, but confined to the methods for steel. The description of methods is so brief as to be of little assistance to the beginner, and contains nothing new for those at all familiar with the subject. The authors state that copper and zinc form a series of compounds, which is not true. They state that above 100° carbon is present in steel as solid solution and that below 1000° the carbon combines with the iron to form Fe_3C which remains dissolved in the iron as solid solution. They advance no experiments in support of this hypothesis; and in the absence of any difference in physical properties to correspond with these supposed differences in the condition of the carbon, it is doubtful if there is any advantage in making the distinction. The paper is illustrated with a number of excellent photo-micrographs, those of oxide in copper being especially good. *E. S. S.*

Action of iodine on gold. *F. Meyer. Comptes rendus*, 138, *733* (*1904*).—Above 50° iodine vapor acts on gold at temperatures and there is formed an amorphous green aurous iodide, AuI. The reaction is reversible. When fused iodine acts on gold, there is formed a yellow crystalline aurous iodide.

W. D. B.

The absorption of hydrogen by rhodium. *L. Quennessen. Comptes rendus*, 139, *795* (*1904*).—It is not true that rhodium absorbs hydrogen more readily than palladium, nor is the metal from the ammonium chloride double salt more active than that from the corresponding sodium salt. *W. D. B.*

The solubility of gypsum as affected by size of particles and by different crystallographic surfaces. *G. A. Hulett. Jour. Am. Chem. Soc.*, 27, *49* (*1905*).—The author calculated that 418×10^7 ergs would be necessary to change a centimeter cube of gypsum (not a cubic centimeter as the author writes) to particles having a diameter of 0.1μ. Special experiments showed no measurable difference of solubility for different planes of a gypsum metal. Gypsum solutions reach the saturation point much more rapidly from unsaturated than from supersaturated solutions. *W. D. B.*

The formulas of tonometry and cryoscopy. *E. Ariès. Comptes rendus*, 139, *462* (*1904*).—The author deduces the formulas connecting change of concentration with change of boiling-point or freezing-point. *W. D. B.*

Boiling-point measurements on mixtures of volatile liquids. *C. Marie. Comptes rendus*, 139, *595* (*1904*).—When resorcine is dissolved in aqueous alcohol, the boiling constant is higher than that calculated from the constants of the pure liquids. When substances are added which dissolve in water only there is a lowering of the boiling-point. When substances are added which are soluble in alcohol only, the observed constant was practically that which these substances would have given if no water had been present. [This is probably a coincidence.] With the exception of the last result, there is nothing new about these experiments. *W. D. B.*

Molecular weight determinations by means of platinum thermometers. *H. T. Barnes, E. H. Archibald and D. McIntosh. Jour. Am. Chem. Soc.*, 27, *47* (*1905*).—The authors describe the use of a differential method for determining boiling-points, using two platinum resistance thermometers. The method is distinctly better than the data offered in illustration. *W. D. B.*

Multi-Component Systems

The complexity of dissolved sulphates. *A. Colson. Comptes rendus*, 139, *855* (*1904*).—When the copper in a concentrated copper sulphate solution is precipitated by hydrogen sulphide, the lowering of the freezing-point is doubled. From this the author concludes that the molecular weight of copper sulphate is double the formula weight. *W. D. B.*

Constitution and properties of tungsten steels. *L. Guillet. Comptes rendus,* 139, *519* (*1904*).—Steels containing 0.2 percent carbon show a pearlite structure until the tungsten content exceeds 10 percent. When they contain 0.8 percent carbon the pearlite structure holds only up to 5 percent tungsten. The pearlite steels are stronger the more tungsten they contain. *W. D. B.*

Properties and constitution of molybdenum steels. *L. Guillet. Comptes rendus,* 139, *540* (*1904*).—Steels containing 0.2 percent carbon show the pearlite structure until the molybdenum content exceeds two percent. With 0.8 percent carbon the molybdenum maximum drops to one percent. The molybdenum steels appear to be better technically than the tungsten steels having small percentages of tungsten. *W. D. B.*

The transformation temperatures of steels. *G. Charpy and L. Grenet. Comptes rendus,* 139, *567* (*1904*).—Comparative experiments show that the transformation temperatures in steel can be determined more exactly by measurements of electrical resistance or of volume change than from cooling curves. *W. D. B.*

A study of the mercury sulphocyanate complexes. *M. S. Sherrill and S. Skowronski. Jour. Am. Chem. Soc.,* 27, *30* (*1905*).—Solubility, freezing-point and electromotive force measurements were made. The authors claim to have shown the existence in solution of $K_2Hg(SCN)_4$ and of a complex of the general form $K_{2m}Hg_m(SCN)_{4m}$. *W. D. B.*

Study of the melting-point of minerals. *A. Brun. Arch. Sci. Phys. Nat.* (4) 18, *537* (*1904*).—The author had previously determined the melting-points of a number of minerals, using Seger cones to determine the temperatures. His results had been criticized by Vogt and Doelter. In the present paper the author repeats his determinations, using the calorimetric method. Apparently, the author considers the completely fused mineral as colloidal, and seems to use this term as synonymous with glassy. He considers the following temperatures as having a real significance: 1. The point at which the last traces of crystalline structure disappear. This, he says, may or may not coincide with the point of liquefaction; 2. The minimum temperature at which the colloid (glass) is deformed (liquefied): 3. The temperature at which crystallization begins in the colloid (glass): 4. The temperature at which sintering occurs. The author discovered some time ago that there is a difference in the properties of the crystalline and colloidal (glassy) silicate of the same composition. It is most important that authors should specify which of the above-mentioned temperatures is intended, when they speak of the melting-point of minerals. Vogt's work is criticized on the ground that the freezing mass was not stirred. That his own method of determining the freezing-points is even more subject to the same criticism, has not occurred to the author. It is difficult to see how any importance can be attached to the temperatures given. For example, point 2, of anorthite, was determined as the temperature at which a straight thread of the glass bent down under its own weight. Or, it was the point at which a large grain of the glass was flattened out by the weight of the mass of platinum used in the calorimeter. How the experimenter knew when the crystalline structure had *just* disappeared, is not explained. From what has been given it is evident that the author is not at all clear as to what he is trying to determine, and it comes therefore, as a surprise to find his results nearer the truth than those of Vogt and Doelter. *E. S. S.*

On the behavior of silicates on melting. *Michaela Vucnik. Centr. Min. Geol. Pal.* 1904, *295, 340, 364*.—Determining the freezing-points by the method of Doelter, the author studies the solubility of certain minerals in each other. Two general methods were used : 1. The partly frozen mass is chilled quickly so as to retain the minerals in the state in which they were present at the moment of quenching. 2. By allowing the mass to freeze very slowly and adding nuclei. Magnetite and anorthite after fusion gave a product which was chiefly spinel. This decomposition was partly the fault of the method of working. Anorthite and nedenbergite yielded augite with a little anorthite. The author expected that the anorthite would be the first product to freeze out of the melt. He assumes that he is dealing with a two-component system. As a matter of fact he has at least three and probably four components. Albite-nedenbergite give augite and some feldspar of about the composition of anorthite. A certain amount of magnetite formed, due probably to oxidation. Leucite-akmite gave chiefly magnetite. Olivine-albite gave magnetite and some hematite. From the author's description it would seem that olivine and augite gave two liquid layers. These are the facts as set forth by the author. When it comes to the theoretical discussion there is some room for doubt. The method of determining the freezing-points was to form little tetrahedrons of the minerals and place them in the furnace. The temperature at which melting began was determined by noting the rounding of the edges of these tetrahedrons. The temperature at which the mass seemed completely fused was taken as the freezing-point. The melting-points of the pure minerals were taken to be those determined by Doelter. The author then calculates the molecular weights of the minerals in question. He finds that the formulas of some of them must be doubled, and some sextupled in order to account for the observed lowering of the freezing-points. One may be permitted to doubt the author's conclusion, that the van't Hoff-Raoult relation can be applied "ohne weiteres" to silicate fusions. It should, at least, not be applied to such extremely crude determinations. *E. S. S.*

New studies on the meteorite from Canon Diablo. *H. Moissan. Comptes rendus*, 139, *773* (*1904*).—The carbon in the meteoric iron from Canon Diablo is present in all three forms, as amorphous carbon, graphite and diamond. Round the diamonds are shells of amorphous carbon and round these nodules are larger ones containing silicon, phosphorus and sulphur. *W. D. B.*

The composition of colloidal granules. *V. Henri and A. Mayer. Comptes rendus*, 139, *974* (*1904*).—The authors consider that the salts carried down by colloids are the result of absorption. *W. D. B.*

The state of colloidal matter. *G. E. Malfitano. Comptes rendus*, 139, *920* (*1904*).—The author looks upon "colloidal matter as consisting of a system formed of an electrolyte dissociated into ions and of insoluble molecules grouped round the ions." *W. D. B.*

Osmotic Pressure and Diffusion.

The molecular weights of radium and thorium emanations. *W. Makower. Phil. Mag.* [*6*] 9, *56* (*1905*).—The experiments described in the present paper were made in order to determine the molecular weights of the radium and thorium emanations more accurately than was attempted by Rutherford and Miss Brooks or by Curie and Danne.

The general method adopted was to cause the emanation to diffuse through porous plugs and to compare its rate with that of other gases of known molecular weight. Values obtained for the cadmium emanation are 85.5, 97 and 99 being near the upper limit of Rutherford.

Only comparative measurements could be made with the thorium emanation on account of its rapid decay. A constant current of air mixed with emanation was passed through porous walls and the concentration measured before and after passing through. As a result of the comparison the author confirms Rutherford's conclusions that the two emanations do not differ from one another in molecular weight. *H. T. B.*

Diffusion of helium through silica. *A. Jaquerod and F. L. Perrot. Comptes rendus*, 139, *789* (*1904*).—Helium cannot be used as a standard gas in quartz thermometers because it diffuses fairly rapidly through quartz at 1100° C.

W. D. B.

Retrograde diffusion in electrolyte. *E. Bose. Comptes rendus*, 139, *727* (*1904*).—It is pointed out that Abegg and Bose had worked out in 1899 the mathematical equations for cases similar to those recently studied by Thovert (7, 403). *W. D. B.*

Velocities

Chemical dynamics and statics under the influence of light. *M. Wildermann. Zeit. phys. Chem.*, 42, *257* (*1902*).—The author believes that the theorem of Le Chatelier can be applied to light phenomena. As he applies it, the equilibrium is displaced by light towards the system giving the greater absorption of light. In this form the statement is certainly wrong because it is in contradiction with Draper's law that a substance can be acted on only by rays which it absorbs.

W. D. B.

Catalytic action of certain substances on the formation of iron rust. *L. Lindet. Comptes rendus*, 139, *859* (*1904*).—Copper accelerates the rusting of iron while presence of zinc, lead, tin, aluminum, manganese or magnesium retards the reaction somewhat. Salts of arsenic protect the iron as do alcohol and methyl salicylate. Sugar, phenol and resorcine increase the rate of rusting and the same is also true of the chlorides and sulphates of potassium, sodium and ammonium. *W. D. B.*

Electromotive Forces

The measurement of the potential of the electrodes in stationary liquids. The determination of changes of concentration at the cathode during electrolysis. *H. J. S. Sand. Phil. Mag.* [6], 9, *20* (*1905*).—The author studies the change of concentration at the electrode in order to throw some light on electrode potential in electrochemical reactions. When the electrode-potential has been exceeded by a finite amount, the current strength becomes independent of it, being only limited by the velocity of convection and diffusion. The apparatus and method described was designed to obtain accurate data for the electrode-potential as influenced by the rate of diffusion and the depletion of the electrolyte around the electrode.

In particular, Haber's results are studied and the conclusion arrived at that the variations of electrode-potential with current density observed by him can therefore not be explained as the result of concentration changes at the cathode

H. T. B.

Thermoelectric inversion and the neutral point. *G. de Metz. Comptes. rendus,* 139, *417* (*1904*).—The author misunderstands the thermoelectric formulas and does not give his actual data, all of which tends to confusion. The author seems, however, to have shown that the formula of Avenarius does not hold at very low temperatures for thermocouples made of Pt-Au, Pt-Au, Pt-brass, Pt-Pb, Pt-Al, Pt-Ag and Ag-Zn while it does hold for Pt-Zn.

W. D. B.

A new form of registering pyrometer. *N. S. Kurnakow. Zeit. anorg. Chem.*, 42, *184* (*1904*).—A modification of the Roberts-Austen pyrometer for the construction of which it is necessary to consult the original paper.

E. S. S.

Electrolysis and Electrolytic Dissociation.

Influence of the anode on the electrolytic oxidation of potassium ferrocyanide. *A. Brochet and J. Petit. Comptes rendus,* 139, *855* (*1904*).—A potassium ferrocyanide solution was electrolyzed with a nickel cathode and a rotating anode. The anode current density was 5amp/qdm. The highest yield of ferricyanide was obtained with a copper anode, polished platinum coming next. A platinized electrode gave 45 percent efficiency as against 64 percent for the bright electrode. Nineteen different anodes were tried but there seems to be nothing that one can put in a general form except that magnesium, aluminum and silver form no ferricyanide. *W. D. B.*

The conductivity of saturated aqueous solutions of black and red mercury sulphide. *R. G. Van Name. Zeit anorg. Chem.*, 39, *108* (*1904*).—The conductivity for saturated solutions of red and of black mercury sulphide keeps on increasing the longer the solutions are shaken. The increase with the time is said to be greater than can be accounted for by any dissolving of the glass. For reasons which are not obvious the author therefore takes the specific conductivities at the end of the first hour as the true values. For the red sulphide at 25° the specific conductivity is about 0.012×10^{-6} and for the black sulphide about 0.024×10^{-6}. *W. D. B.*

Thermochemistry and acidimetry of methyl arsenic acid. *A. Astruc and E. Baud. Comptes rendus,* 139, *212* (*1904*)—When one equivalent of sodium hydroxide is added to methyl arsenic acid there is an evolution of 15430 cal; the second equivalent causes an evolution of 11930 cal. The acid is monobasic with turmeric and dibasic with Poirrier blue. *W. D. B.*

Dielectricity and Optics

Dielectric cohesion of saturated mercury vapor and mixtures containing it. *E. Bouty. Comptes rendus*, 138, *169* (*1904*).—The measurements were made in a quartz vessel. The dielectric cohesion of mercury at 17° is 354. Mixtures of mercury vapor with argon have a much higher dielectric cohesion than one would expect on the basis of proportionality. With carbon dioxide or hydrogen the discrepancies were smaller. *W. D. B.*

Radio-active lead, radio-tellurium and polonium. *A. Debierne. Comptes rendus*, 139, *281* (*1904*).—Varying the method of treatment will apparently enable one to obtain radio-active lead, tellurium or bismuth, from the same material. The author therefore concludes that the three are the same and that the name polonium is the one to keep. This is in accord with Rutherford's results though Rutherford rejects polonium also, considering radio-active lead, tellurium and bismuth merely as these metals plus one or more of the decomposition products of radium. *W. D. B.*

On radioactivity of mineral springs. *G. A. Blanc. Phil. Mag.* [*6*] 9, *148* (*1905*).—The author gives results of a study of the radioactive properties of the materials deposited by a certain number of mineral and thermal springs belonging to the Alpine region. In addition to traces of radium some thorium was also present. *H. T. B.*

Refractive index of solutions. *E. van Aubel. Comples rendus*, 139, *126* (*1904*).—Chéneveau (8, 527) believed that the effect of the solute on the refractive index of the solution was directly proportional to the concentration of the dissolved substance. The author shows that this supposed relation does not hold for a number of non-aqueous solutions. *W. D. B.*

The refractive indices of solutions. *C. Chéneveau. Comptes rendus*, 139, *361* (*1904*).—It is claimed that van Aubel (preceding review) forgot to take account of the density of the solvent. When van Aubel's data are calculated properly they confirm the formula of the author. *W. D. B.*

Change in the refractive index of an electrolyte under the influence of the current. *H. Bordier. Comptes rendus*, 139, *191* (*1904*).—The author finds that the decomposition of a solution by an electric current changes the index of refraction, an observation which is scarcely new or important. It is suggested that this change of refractive index be used as a measure of the current. From this suggestion one may guess at the extent of the author's knowledge of electrochemistry. *W. D. B.*

Color photographs obtained without a mercury mirror. *E. Rothé. Comptes rendus*, 139, *565* (*1904*).—The photographs were taken by the Lippmann method but without the mercury mirror, the glass side of the plate being turned toward the source of light. The spectrum is reproduced very accurately from orange to violet. The red is apt to have an orange tinge. *W. D. B.*

THE CHEMISTRY OF ELECTROPLATING[1]

BY WILDER D. BANCROFT

Although some results have been obtained by Mylius, Foerster, Glaser, Burgess and others, a glance at the recent text-books on electrochemistry will show how far we still are from any consistent theory of electroplating. The reason for this is to be found in our neglect of the chemistry involved. The electric current is merely one agent for bringing about certain chemical reactions; but this is often overlooked and many of us consider a decomposition by means of electricity as much more mysterious than a decomposition by heat, for instance. I hope to show that a study of chemical reactions and chemical analogies will at least give us the outlines of a theory of electroplating.

When we speak of a good metallic deposit we may mean good from the point of view of the analyst, the refiner, or the plater. The analyst must have a deposit of pure metal in a weighable form but that is all. The refiner must have a coherent deposit of pure metal, except in the case of silver. Neither the analyst nor the refiner cares about the smoothness of the deposit in the sense that the plater uses the word though the refiner is happier the smoother the deposit is. The plater must have an adherent smooth deposit which will burnish to an apparently amorphous surface. In the preliminary discussion we will rule out the plater and will call a deposit good when it is pure, coherent and free from trees. Afterwards we can consider the further problem of the production of a very fine-grained deposit. Since there are very few data for anything except aqueous solutions, we will consider these only, though the general principles are equally applicable to all solvents.

When working with moderate current densities a bad deposit is practically always due to the precipitation of a compound of the metal with the metal. When one of the single

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[1] A preliminary abstract of this paper was presented at the International Electrical Congress of St. Louis, 1904.

salts in the bath is sparingly soluble, as with the cyanides, this salt may precipitate. In most cases, however, the trouble is due to the presence in the deposit of oxygen either as oxide, hydroxide or basic salt. Whatever will dissolve the compound readily under the conditions of the experiment will prevent its deposition, by definition, and should therefore improve the quality of the deposit. This has been recognized for zinc by Mylius and Fromm[1] and by Foerster and Gunther[2]. It has been put in a more general form by Glaser[3]. I have made a list of the more important additions recommended in the refining, analysis or plating of zinc, nickel, lead, tin, copper and silver. These are given in Table I.

TABLE I.

ZINC

Sulphuric acid
Potash
Ammonium chloride
Ammonium sulphate
Aluminum sulphate
Potassium cyanide
Acid potassium oxalate

NICKEL

Sulphuric acid
Ammonia
Ammonium salts
Potassium cyanide
Sodium bicarbonate
Sodium bisulphite

LEAD

Acetic acid
Potash
Fluosilicic acid
Sodium nitrate

TIN

Sulphuric acid
Potash
Sodium pyrophosphate
Potassium carbonate
Acid potassium tartrate
Potassium cyanide

COPPER

Sulphuric acid
Ammonia
Alkaline tartrate
Ammonium oxalate
Potassium cyanide
Sodium bisulphite

SILVER

Nitric acid
Ammonia
Potassium cyanide
Potassium iodide

All the substances under zinc dissolve zinc hydroxide. The first four under nickel dissolve nickel hydroxide; the sodium bicarbonate probably serves to keep the acidity constant, while

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[1] Zeit. anorg. Chem., 9, 144 (1895).

[2] Zeit. Elektrochemie, 5, 16 (1898); 6, 301 (1899).

[3] Ibid., 7, 365, 381 (1900).

the sodium bisulphite occurs only in solutions containing free ammonia. The addition of boric acid, as recommended by Weston, helps to regulate the acidity when cast anodes are used. All the substances under lead dissolve lead hydroxide[1]. Stannous and stannic acids are soluble in sulphuric acid, in potash, and in a so-called sodium pyrophosphate solution; potassium carbonate is added only to neutralize an excess of free acid in stannous chloride solutions, while the cyanide and tartrate seem to be of very little value in the absence of free alkali, unless perhaps at the anode. Under copper everything dissolves the hydroxide except sodium bisulphite and this is added to cyanide solutions to prevent loss of cyanogen when the copper changes from the cupric to the cuprous form. Jordis[2] states that it makes the copper anode dissolve more readily. All four substances under silver dissolve freshly-precipitated oxide; in addition ammonia dissolves silver chloride while silver cyanide and silver iodide are soluble in potassium cyanide and potassium iodide respectively.

It is thus clear that there is a simple rational basis for many of the solutions in actual use. It must be kept in mind, however, that the rate of solution is more important than the actual solubility. Thus it is not easy to get a good deposit from an alkaline zincate solution at 20° whereas it is a comparatively simple thing to do this at 40° because the caustic soda reacts with zinc oxide or hydroxide much more rapidly at this temperature[3]. It does not follow from this that a higher temperature would necessarily be even better. At 90° the action of caustic soda on metallic zinc becomes an important factor. With copper sulphate solutions rise of temperature means increased formation of cuprous sulphate and this must be taken into ac-

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[1] Betts disputes the accuracy of Glaser's work on lead, but has not published a description of his experiments.

[2] Die Elektrolyse wässriger Metallsalzlösungen, 44.

[3] Foerster and Gunther, Zeit. Elektrochemie, 6, 302 (1899), obtained a good zinc deposit for a short while only. Such a state of things can occur only when the conditions have changed during the run, although they seem not to have recognized this.

count. In each of these cases a study of the chemical reactions shows the cause of the difficulty.

While there is much evidence in favor of Glaser's first generalization, that a metallic deposit is improved by adding to the solution substances which will dissolve the oxide, hydroxide or basic salt, there are only a few scattered experiments which can be cited in favor of Glaser's second generalization[1] that reducing agents improve the quality of the deposit. Glaser[2] observed that addition of pyrogallol or hydroquinone to a lead bath improved the deposit of electrolytic lead. Engels[3] states that the addition of hydroxylamine makes it possible to use higher current densities in the analysis of copper. It is believed that tin salts in solution improve the quality of a copper deposit[4] and it is known that ferrous salts are not disadvantageous. Good deposits of many metals are obtained from cyanide solutions and part of the effect, though certainly not the whole of it, may be due to the fact that potassium cyanide is a reducing agent. It is also possible that the merits of a tartrate solution may be due in part to the formation of reducing agents by oxidation at the anode[5]. In some experiments made at Cornell we have found that hydrazine improves the electrodeposition of cobalt and that resorcine has a slight favorable effect with zinc but apparently not with tin. The negative result in this last case may be due to the reducing power of the tin solutions. These instances will suffice to show that we do not yet know definitely how much influence a reducing agent has or how it varies with varying conditions. Since none of the reducing agents in question will reduce the oxide to metal, it seems very probable that the effect of the reducing agent as such is merely to prevent oxidation by dissolved oxygen. If so, the effect should disappear in a vacuum or in an atmosphere of nitrogen. It has not yet been possible to try this experiment.

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[1] Zeit. Elektrochemie, 7, 386 (1900).

[2] Ibid. 7, 381 (1900). Cf. Elbs and Rixon. Ibid. 9, 267 (1903).

[3] Smith. Electrochemical Analysis, 62.

[4] Borchers. Elektrometallurgie, 193.

[5] Luther. Zeit. Elektrochemie, 8, 647 (1902); Schilow. Zeit. phys. Chem. 42, 646 (1903).

We have next to consider the effect of higher current densities. When solutions are not stirred we soon reach a point at which an ever-increasing current density causes a bad deposit. This change in the quality of the deposit is always accompanied by an increased evolution of hydrogen and it is usually believed that the evolution of the hydrogen is the cause of the deposit going bad. This cannot be the whole truth because hydrogen is evolved freely during electrolytic analyses and yet the deposit remains good. Further, the so-called critical current density varies enormously with the size, shape, and distance apart of the electrodes, and also with the size and shape of the containing vessel, so that the data obtained by any one man usually cannot be duplicated by others. The most important factor is the rate of stirring[1]. If we rotate a smooth copper, zinc, or nickel cathode with sufficient speed it is by no means certain that there is any current density at which the deposit goes bad. With tin there does seem to be a limiting density but this is very possibly due to the formation of stannic salts in solution. It is intended to study this question in detail. The evidence favors the view that if a solution gives a good deposit at any current density, the deposit will be good at any higher current density, provided we prevent a change in the concentration and temperature of the film at the cathode.[2]

When a deposit becomes sandy or changes to a black powder, the polarization shows that there has always been the formation of a dilute solution at the cathode. In most cases this leads to the precipitation of an oxide or basic salt with the usual disastrous results. It is still an open question whether this is always the case. Foerster and Seidel[3] say that sandy deposits of copper are not due to the presence of oxide. If this statement is correct, we shall be forced to some such assumption as that the badness of the deposit is due to the pulsating or intermittent precipitation of hydrogen as a result of the inter-

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[1] Cf. Zimmermann: Trans. Am. Electrochem. Soc. 3, 243 (1903).

[2] This will probably have to be modified if an instable modification can precipitate at high current densities.

[3] Zeit. anorg. Chem. 14, 125 (1897).

mittent formation of a surface film impoverished as to metal. This explanation does not appeal to me personally and I prefer to believe for the present in the oxide formation even if I have to account for the apparent absence of hydrogen by assuming a reduction to metal after the harm has been done. It may also be due to the decomposition of cuprous sulphate according to the equation $Cu_2SO_4 = CuSO_4 + Cu$. This reaction takes place at the anode and may occur at the cathode under some conditions. Of course it is quite possible that the special case of black copper may be due to the disintegrating effect of the precipitation of occluded hydrogen or a hydride of copper, somewhat analogous to the disintegration of lead cathodes in caustic soda solution. Whatever view we may take of the matter it is certain that we are dealing with precipitation from a dilute solution and that a proper understanding of the situation can be obtained only by working with very dilute solutions, and with low current densities, stirring vigorously all the while. Only under these conditions can we feel certain that the concentration and temperature of the solution in contact with the cathode do not differ materially from the mean concentration and temperature of the whole solution.

Hydrogen may easily be indirectly the cause of a bad deposit. If hydrogen adheres as bubbles to the cathode, the deposition of the metal will become uneven and we shall have conditions favorable for treeing. A trouble of this sort can be cured chemically by adding an oxidizing agent to remove the hydrogen. It is known that copper solutions containing nitric acid will stand much higher current densities than will those acidified with sulphuric acid. It is clear that the prevention of hydrogen by means of an oxidizing agent may lead to the oxidation of the metal, in which case we are out of the frying-pan into the fire. Foerster and Gunther[1] had difficulties with hydrogen bubbles during the precipitation of zinc. They show that such oxidizing agents as chlorine and ammonium persulphate prevent the appearance of hydrogen without causing the

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[1] Zeit. Elektrochemie, 5, 22 (1898).

formation of zinc oxide. Such oxidizing agents as hydrogen peroxide and ammonium nitrate prevent hydrogen evolution but are worthless because they oxidize the zinc.

An oxidizing agent could probably be used to prevent occlusion of hydrogen by nickel, for instance. It is quite likely that the disadvantages would outweigh the advantage. In that case it would be better to approximate the same result by varying other conditions. The favorable conditions would be: a concentrated solution to insure a good deposit; a high temperature to lower the absorption coefficient; a nearly neutral solution to increase the decomposition voltage of hydrogen; and a high current density to give a fine-grained metal. For any given rate of stirring we should expect a limiting current density beyond which deterioration would occur. With increasing current density we get a finer deposit but there is also an increasing tendency to precipitate hydrogen and it is necessary to strike a balance between these two. All these conditions have been found experimentally by D. H. Browne[1], who puts in the further condition that the solution should contain a good deal of sodium chloride. An explanation for the effect of sodium chloride is offered by Pfanhauser.[2]

"People have hitherto used exclusively nickel baths containing ammonium salts to increase the conductivity or the complex nickel ammonium sulphate together with a little boric acid. The primary discharge of $NH_4^\cdot$ appears to be the cause of the nickel curling. Quite inconceivable forces are developed and in one experiment that went wrong I noticed that a film, which had already been precipitated in a heated solution to a thickness of about 0.3 mm, broke into two pieces with a loud noise and peeled off from the metal below.

"Just as $NH_4^\cdot$ combines with a mercury cathode, causes it to swell and then passes off, so $NH_4^\cdot$ appears to precipitate with the nickel at a nickel cathode, forming an alloy temporarily and going into solution again when this alloy breaks down at once. By this process the structure of the electrolytic nickel appears

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[1] Electrochemical Industry, 1, 348 (1903).

[2] Die Galvanoplastik, 43.

to be changed in such a way that tensions occur between the groups of molecules with the strain perpendicular to the lines of force in the solution.

"It is curious that this tendency to curl and tear does not appear when sodium salts are used to increase the conductivity. The bath recommended by Wilh. Pfanhauser, Sr. in 1880,

1 liter water
46 grams nickel sulphate
35 grams sodium citrate,

is admirably adapted for deposits of any desired thickness. The deposit is soft and ductile and quite smooth on the back, showing no crystalline structure."

The precipitation of magnesium with nickel has been studied by Coehn[1] and by Siemens[2]. In this case the magnesium does not dissolve. The sodium-nickel alloy has not been isolated. Siemens believes that the bad effect of ammonium salts is due to ammonium sulphate, mechanically enclosed.

We now come to what is the more interesting side of the question to the plater, to the factors affecting the size of the crystals in electrolytically deposited metals. It will be well first to see what can be found in the books on this subject. In one place Pfanhauser[3] is very definite as to the effect of current density. He says: "It is not to be denied that there is a certain analogy between the electrolytic precipitation of metals and the crystallization of salts. The change from liquid to solid always occurs with formation of crystals, and larger and more handsome crystals are obtained from solutions the slower the crystallization takes place. The comparison between the formation of crystals and electrolytic deposits is therefore justified in this point because one can detect a perceptibly crystalline structure when the metal has been precipitated with a very low current density. Under the microscope the fracture is seen to have a finer grain the higher the current density used,

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[1] Zeit. Elektrochemie, 8, 591 (1902).
[2] Zeit. anorg. Chem. 41, 249 (1904).
[3] Die Galvanoplastik, 73. Cf. also Wiedemann, Elektrizität, 2, 481.

in other words, the more sudden the change from the state of ions to that of metals."

When speaking about the deposition of copper Pfanhauser[1] is not so definite, though the conclusion reached is much the same. After stating that the crystalline structure must depend on two factors, the composition of the solution and the current [density] he goes on:

"Two opinions have been put forward with respect to the influence of these two factors. One is due to Smee and is to the effect that the current [density] and concentration of the bath both determine the quality of the metal. The second point is that of F. Kick to the effect that the structure of the galvanic deposit depends on the composition of the solution and is independent of the current [density].

"As a result of many experiments Smee reached the following conclusions:

"1. The metal is precipitated in an inhomogeneous form (powder, sponge or sand) when the current [density] is so high that hydrogen and metal are precipitated simultaneously.

"2. The metal is precipitated in a coarsely crystalline form when the current [density] is much below the value necessary to set free hydrogen.

"3. The metal will appear as a tough, fine-grained deposit when the current [density] is as high as it can be without precipitating hydrogen.

"Smee concludes therefore that by using a suitable current density deposits of any required character can be obtained from a bath of any concentration.

"H. Meidinger formulated the results of Smee's more definitely. For a deposit of given character the ratio of current density to concentration of solution is a constant value though the limits are not very sharp. If one obtains a certain quality of deposit from a concentrated solution, one will get the same deposit from a solution of half the concentration with half the current density, from a solution of one-third the concentration with one-third the current density, etc."

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[1] Die Herstellung von Metallgegenständen, 13.

Pfanhauser then quotes Hübl's experiment with copper. Hübl found that the precipitate became more finely crystalline as the current density increased or on addition of acid. He reports no change with concentration. Speaking also of copper, Zimmermann[1] says: "The fineness of the grain is dependent upon the current density, other things being equal, and the fineness increases with the current density until at a critical value, a powdery deposit will occur."

McMillan[2] says: "Like most other metals, silver, which is deposited by a current strong enough to evolve hydrogen simultaneously, is dark in colour, powdery, and non-adherent; it is in the spongy condition, and is useless as a coating. A weak current, on the contrary, gives a strong, malleable metal, adherent and coherent, and minutely crystalline. Some operators consider the commonly-employed current strength of 0.032 ampere per square inch (0.5 ampere per square decimetre) too high and prefer to reduce it to 0.013 ampere (0.2 ampere per square decimetre); but for all ordinary work the larger current volume will be found satisfactory, and will, of course, deposit a given weight of metal in a shorter period of time."

This last quotation may be taken to mean that the silver deposit becomes more finely crystalline with decreasing current density; but I think the author intended to draw a distinction only between a low and a too high current density. That is certainly the way in which we are to interpret the somewhat similar statements of Wiedemann.[3]

I have found nothing definite in regard to temperature. It is believed generally that better plating deposits are obtained from complex than from simple salts.[4] The views in regard to colloids will be referred to later.

It will now be well to run over briefly what our chemical analogies would lead us to expect as to the factors affecting the structure of electrolytically-deposited metals and then we can consider how closely the predictions are fulfilled.

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[1] Trans. Am. Electrochem. Soc. 3, 246 (1903).

[2] A Treatise on Electro-Metallurgy, 2nd Ed., 205.

[3] Elektrizität, 2, 481.

[4] Wiedemann, Elektrizität, 2, 525.

Rapid crystallization of a salt from solution gives us small crystals while slow crystallization leads to larger crystals. We should therefore expect the crystalline structure of electrolytically deposited metals to be finer the more rapid the precipitation, in other words the higher the current density. At high temperatures chemical precipitates are more crystalline than at lower temperatures. Two striking instances of this are barium sulphate and alumina. When precipitated cold, barium sulphate runs through the filter with distressing readiness. While the alumina obtained by hot precipitation in the Bayer process is not visibly crystalline, it is sandy and can be filtered and washed with ease. If we increase the difficulty of precipitation we should expect that the crystals would have more difficulty in reaching a large size. We therefore conclude that we shall get a more nearly amorphous deposit from a dilute solution than from a concentrated one, provided all other conditions remain the same. We can generalize this and say that the greater the potential difference between metal and solution the finer will be the electrolytic deposit. At one time I thought that this could be carried still farther and that we could say that neutral solutions would give coarser deposits than acid ones, that oxidizing agents would cause fine deposits and reducing agents coarser ones. Further experiments have shown that this is not generally true and that the effect varies from metal to metal and sometimes from concentration to concentration. Of course the specific nature of the metal will have a very important effect in determining the limiting size of the crystals just as in the case of cast metals or in the case of salt crystals. We should not expect the same variations with nickel as with zinc or antimony.

We know that the addition of a colloid to a solution increases the probability of a precipitate coming down colloidal, and that chemically-precipitated colloidal metals are rarely pure. From this we conclude that addition of colloid to a solution will make the electrolytic deposit more finely crystalline and that the carrying down of substance with the metal will tend to make an amorphous deposit, always provided that the substances carried down do not spoil the deposit entirely. Some of the solutions studied are given in Table II.

TABLE II.

	Zinc
A	$m/2\ ZnSO_4 + m/50\ H_2SO_4$
D	$m/10\ ZnSO_4 + m/50\ H_2SO_4$
G	$3m\ NaOH$ excess ZnO_2H_2
K	G diluted to 1/4 with $3m.NaOH$
	Copper
A	$20\ \%\ CuSO_4$
B	$A + m/20\ H_2SO_4$
C	$A + m.HNO_3$
	Silver
A	$m.AgNO_3$
B	$A + m_1AgNO_3$
C	B diluted to 1/10.

The letters will be used in referring to these solutions. When formaldehyde was added, 40 cc. of a 40 percent solution, this is shown by writing *Af*, etc. Experiments were also made with stannous chloride, sodium stannate, potassium silver cyanide, nickel sulphate, nickel chloride, lead fluosilicate and other solutions, but it is not necessary to give the concentrations for all these solutions. In referring to an experiment, A.20.2 will mean that solution A was electrolyzed at 20° with a current density of 2 amp/qdm. All solutions were stirred vigorously; all deposits were examined under the microscope, and photomicrographs were taken of most of them. Each metal was precipitated on a cathode of the same metal so as to avoid possible disturbances due to a second metal. It is believed that the results obtained are comparable and that they can be reproduced by any one who wishes so to do.

The results with zinc are given in Table III, the solution giving the smaller crystals being mentioned first. The headings show the factor that is being varied. The solutions tabulated are those only for which we have photomicrographs.

TABLE III.—ZINC

Current density		Concentration		Temperature		Formaldehyde	
finer	coarser	finer	coarser	finer	coarser	finer	coarser
A.40.10	A.40.1	D.40.1	A.40.1	A.40.1	A.70.1	Af.40.10	A.40.10
A.70.10	A.70.1	D.40.10	A.40.10	A.20.10	A.40.10	Gf.40.3	G.40.3
D.40.10	D.40.1	G.40.3	K.40.3	A.40.10	A.70.10	K.40.3	Kf.40.3

In Table IV are some of the data for copper.

TABLE IV.—COPPER

Current density		Temperature		Acidity		Formaldehyde	
finer	coarser	finer	coarser	finer	coarser	finer	coarser
A.20.2	A.20.0.2	B.20.2	B.40.2	B.20.2	A.20.2	Af.20.2	A.20.2
B.20.2	B.20.0.2	B.40.2	B.70.2	C.20.2	A.20.2		
B.20.2	B.20.0.2	B.40.2	B.70.2	B.20.2	C.20.2		

In Table V are some of the data for silver.

TABLE V.—SILVER

Current density		Current density		Concentration		Acidity	
finer	coarser	finer	coarser	finer	coarser	finer	coarser
A.20.2	A.20.$^1/_2$	B.20.20	B.20.2	C.20.$^1/_2$	B.20.$^1/_2$	A.20.$^1/_2$	B.20.$^1/_2$.
A.20.20	A.20.2	C.20.2	C.20.$^1/_2$	C.20.2	B.20.2	A.20.2	B.20.2
B.20.2	B.20.$^1/_2$	C.20.20	C.20.2	C.20.20	B.20.20	A.20.20	B.20.20

With zinc sulphate, sodium zincate, copper sulphate, silver nitrate and stannous chloride solutions, the crystals become smaller as the current density increases. The silver nitrate solutions are especially interesting. At St. Louis last summer the point was raised that it was impossible to obtain a fine-grained deposit of silver from silver nitrate solutions no matter how high the current density was raised. In our first experiments with silver nitrate, it was not possible to detect any effect due to current density. This was a bit discouraging. Since a silver salt is formed at the anode which increases the weight of the cathode deposit, it was thought that this same salt might affect the crystalline structure of the metal. The experiment was repeated using a porous cup to separate the anode and cathode solutions. We then obtained smaller crystals the higher the current density. The effect of very low current densities on the size of crystals appears strikingly in the experiments of Bucholz[1] and of Golding-Bird[2].

With an acidified copper sulphate or zinc sulphate solution the deposit becomes coarser as the temperature is raised from 20° to 40° and to 70°. With a zinc sulphate solution which is only faintly acid, the deposit is coarser at 70° than at 40° but is coarser at 20° than at the other two temperatures. I suspect that at 20° the slight acidity had no appreciable effect on the deposit while it becomes an important factor at 40°.

The effect of concentration is that required by the theory. With zinc sulphate, sodium zincate, copper sulphate and silver nitrate solutions, smaller crystals are obtained from the more dilute solutions than from the more concentrated ones. The deposit from the zinc sulphate solutions is coarser than from the sodium zincate solutions, this last being very smooth. From sodium stannate solution much smaller crystals are obtained than from a stannous chloride solution. It is well-known that silver and copper precipitate more nearly amorphous from potassium cyanide solutions than from nitrate solutions. It is not a case of a secondary precipitation giving a good deposit, as has sometimes been assumed, because the decomposition voltages of the copper and silver cyanide solutions used in plating are lower than the decomposition voltage of the corresponding pure potassium cyanide solutions. As we can get a plating deposit of silver from a silver nitrate solution under suitable conditions, it is obvious that there is no fundamental difference introduced by the formation of a complex salt. So far as the facts are known they can be formulated in the statement that the deposit is more finely crystalline the greater the potential difference between the metal and the solution. The same

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[1] Ostwald. Geschichte der Elektrochemie, 187.

[2] Phil. Trans. 1837, 37.

general principle should apply when we change the solvent and as a matter of fact a much coarser deposit is obtained from silver nitrate in aqueous solutions than from silver nitrate in pyridine solutions. It is probable that this will be found to be general, subject of course to revision if possible decomposition products of the solvent precipitate with the metal, as might easily happen with organic solvents.

While the effects of current density, concentration, and temperature can be classified without difficulty, the same cannot be said of the effect due to acidity, oxidizing agents and reducing agents. The addition of sulphuric acid in small amounts to a neutral copper sulphate solution causes a marked decrease in the size of the crystals, as was noted years ago by Hübl, who also states that increasing the acid concentration from 2 to 8 percent has no effect. While we have no definite proof, it is probable that the effect of the acid is connected with the elimination of cuprous sulphate. Addition of a large amount of nitric acid makes the deposit finer than that from the neutral solution but coarser than that from the sulphuric acid solution. Addition of nitric acid to a silver nitrate solution makes the deposit coarser for high current densities while it is hard to decide what the effect is at the lower densities. Formaldehyde makes the deposit from concentrated zinc sulphate (A) and concentrated zincate solutions (G) somewhat finer while it makes the deposit from dilute zincate solution (K) much coarser. It made the copper deposit from neutral copper sulphate solution a little finer. This whole matter will have to be taken up more thoroughly than I have yet been able to do, varying the relative amounts of the metallic salt and the reducing agent within wider limits.

Coming next to the question of colloids we know that the addition of glue to lead fluosilicate solutions improves the quality of the deposit enormously. In the laboratory we have tried the effect of ten grams of glue per liter. With zinc[1], copper and tin, the crystalline structure was much smaller than without the glue. With a silver nitrate solution we obtained a

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[1] Cf. Langbein. Handbuch der elektrolytischen Metallniederschläge, 412.

violet deposit which is apparently amorphous silver. Though we have not yet had time to test this thoroughly, it seems probable that we have here an explanation of "bright" deposits. A bright deposit is one in which the crystals are so small that the deposit is practically amorphous. By using less glue in our silver nitrate solution we have obtained a fairly bright deposit though it is yellowish in color. We have not yet analyzed the silver deposit from a solution containing glue but it is probably not pure. Carbon bisulphide is the substance most often added to a potassium silver cyanide solution to cause a bright deposit. This bright silver is said to contain sulphur.[1] When too much carbon bisulphide is present, the deposit is said to become black. I think that people have usually assumed that this black color was due to silver sulphide; but it now seems possible that a violet colloidal silver was precipitated. Jordis[2] states that bright deposits of many of the metals can be obtained from lactic acid solutions. Since the metal deposited from a solution of an organic acid may easily contain carbon, it becomes quite possible that there is an intimate connection between the two facts[3]. The bright silver deposits, obtained when zinc cyanide is added to the solution, are apparently due to the formation of an alloy[4].

It has been noticed by many people that a bright or burnished deposit can be obtained when one rotates the cathode and uses high current densities. The people who made these experiments were interested primarily in increasing the current density and they varied the speed of rotation and the current density simultaneously. Consequently one did not know whether the burnished effect was solely the result of the current density or not. To test this question, Mr. Snowdon made some experiments with a silver cyanide solution and a rotating cathode. The current density and speed of rotation were so adjusted that a bright deposit was obtained. Then the speed of rotation was kept con-

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[1] McMillan. A Treatise on Electro-Metallurgy, 2nd Ed. 204.
[2] Die Elektrolyse wässriger Metallsalzlösungen, 79.
[3] Cf. Foerster. Zeit. Elektrochemie, 5, 512 (1899).
[4] Langbein. Handbuch der elektrolytischen Metallniederschläge, 349.

stant while the current density was increased. Since an increase of current density would decrease the size of the crystals, the deposit should have become even brighter if the current density were the only factor. As a matter of fact the deposit was distinctly frosted. The only explanation that I have been able to find is that at the moment of precipitation there is a polishing effect due to surface friction. If more metal is deposited in the unit of time than can be polished, the metal is frosted. While this explanation may not seem satisfactory to everybody, it does account for the facts and this is certainly a point in its favor. It should be noticed that the frosted appearance caused by increasing the current density while holding the speed of rotation constant cannot be explained as due to impoverishment of the solution near the cathode because of the effect of an impoverishment would be to decrease the size of the crystals and therefore to make the deposit brighter and more amorphous.

It has been noticed that the presence of salts of cadmium, iron, lead and copper interferes with the satisfactory precipitation of zinc. The reason for this is very simple. These metals precipitate before zinc and set up a local circuit which oxidizes the zinc and causes the deposit to go bad. This local circuit may make trouble in other cases. When we have to plate a noble metal on a less noble one, we usually make use of a striking-bath in which the difference of potential between the two metals is not very great. This keeps down any non-electrolytic precipitation to a minimum. When we are depositing a less noble metal on a more noble one, we usually do not bother ourselves about the formation of a couple and we may thereby be led into serious error. Zinc will precipitate nicely on a zinc cathode when it will not deposit well on a copper cathode owing to the evolution of hydrogen.[1] The difficulty about precipitating zinc with a low current density is due chiefly to local action at the cathode.[2] It seems possible that this also accounts for its being so much more difficult to precipitate lithium on a platinum electrode than on

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[1] Cf. Cohen, Collins and Strengers: Zeit. phys. Chem., 50, 296 (1904).

[2] Cf. Gore: Proc. Roy. Soc. 37, 24 (1884) and the explanation by G. Wiedemann, Beibl. 9, 53 (1885).

an iron one. Another explanation for this particular phenomenon may be that lithium alloys with the iron cathode.

Another point of importance to the plater is the adhesion of the deposit. While it has been suggested that an adherent deposit can be obtained only when the two can combine to form compounds or solid solutions,[1] this contention does not seem to be in accord with the facts.[2] The surface between two metals is a thin weld and it must show the same strength no matter how it has been made. In other words the adhesion of an ideally-made electrolytic deposit will approach that of a casting having the same size of crystals. Presence of grease, of air-bubbles, or of occluded mother-liquor will impair the contact and weaken the joint. If the metal be deposited in a state of strain, the break will come at the weakest point. These are matters of general knowledge in making welds or castings and they are just as much first principles in electrolytic work. No one seems to have been struck by the absurdity of the statement, to be found in most books on plating, that nickel cannot be plated on nickel because it will not adhere.[3] If this were true it would not be possible to deposit more than an infinitesimally thin film of nickel electrolytically. While it requires a higher voltage to deposit nickel than copper, nickel does not precipitate copper to any appreciable extent when immersed in a copper sulphate solution. The nickel becomes passive and is probably covered with a thin film of oxide. What people mean is that an "active" nickel containing hydrogen will not adhere to a "passive" nickel. There is nothing surprising or mysterious about this. By making a strip of nickel the cathode in an acid solution for a few minutes before putting it in the nickel bath, Mr. Snowdon has been able to plate nickel on nickel getting a beautifully adherent deposit.

The one remaining point to be considered is the formation

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[1] Kahlenberg: Electrochemical Industry, 1, 201 (1903).

[2] Burgess: Ibid., 209.

[3] Watt and Philip: "Electroplating and Electrorefining," 2nd ed., p. 411. McMillan: "A Treatise on Electrometallurgy," 2nd ed., p. 243. Langbein: "Handbuch der elektrolytischen Metallniederschläge," p. 254.

of trees. As no experiments on this have yet been made in my laboratory, all that can be done is to point out some of the more obvious factors, leaving a fuller discussion of the matter until later. If we have a projection anywhere on the surface to be plated, the current lines will concentrate there and that portion will tend to grow faster than the rest. Any roughness of the original surface or of the deposited metal will tend to be increased by the current. This is a well-recognized fact. The decrease in potential difference caused by the growth of a tree will be greater, the greater the fall of potential per unit length of electrolyte. Other factors remaining the same this will depend on the current density and the conductivity of the solution. It is known to everybody that a high current density usually produces a rough deposit. The effect of dilute solutions or of those which conduct badly has also been recognized.[1] The addition of salts of the alkalies to plating solutions to decrease the necessary voltage is done partly from economical reasons and partly to make the deposit smoother. It must be remembered, however, that other factors have to be taken into account. Anything which produces large crystals causes a roughness of surface and is, therefore, favorable to the growth of trees. This accounts for the growth of trees in concentration cells even though the actual current densities are very small. That the growth is like a tree rather than like a bean-pole is due largely to concentration differences owing to insufficient stirring.[2]

Still another factor affecting treeing is that of surface tension. When we deposit silver from a solution by non-electrolytic methods, we get the silver precipitating on the inner surface of the glass vessel, forming a mirror. In cases of this sort we know that a crystal surface sets itself against the glass surface. If the glass is greasy the silver does not precipitate on it satisfactorily and does not adhere. It seems to me quite possible that there might be some solutions in which the surface tension between the metal and the solution was such

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[1] Wiedemann: Elektrizität, 2, 621. Cf. Foerster and Günther: Zeit. Elektrochemie, 6, 303 (1899).

[2] Cf. Zimmerman: Trans. Am. Electrochem. Soc., 3, 246 (1903).

that the electrolytically-deposited crystals did not adhere, quite apart from any question of cleanliness. This certainly seems to be the case with lead from lead acetate solutions, though the difficulty may be merely the result of the large size of the crystals.

The general results of this paper are:

1. A bad deposit is always due to the precipitation, direct or indirect, of some compound of the metal.

2. Addition to the solution of anything that will dissolve this compound will tend to prevent its precipitation and to improve the quality of the deposit.

3. Any beneficial action of a reducing agent as such is probably due to the removal of dissolved oxygen from the solution.

4. A fine-grained deposit is favored by high current density and potential difference, by low temperature, and by presence of colloids.

5. The adherence of deposits rests on the adhesion of the two metals.

6. "Treeing" is favored by anything which increases the fall of potential per unit length of the electrolyte or which increases the coarseness of crystallization.. Surface tension phenomena may also be a factor though this has not been proved.

7. The theory presented has been able to account for the phenomena due to composition and concentration of the electrolyte, to current density, temperature, solvent, colloids, other metals and cathodes. It has not accounted for the effect of acids and alkalies, nor for the effect of oxidizing and reducing agents; but this seems to be due to our ignorance of the chemistry of these solutions rather than to a defect in the theory.

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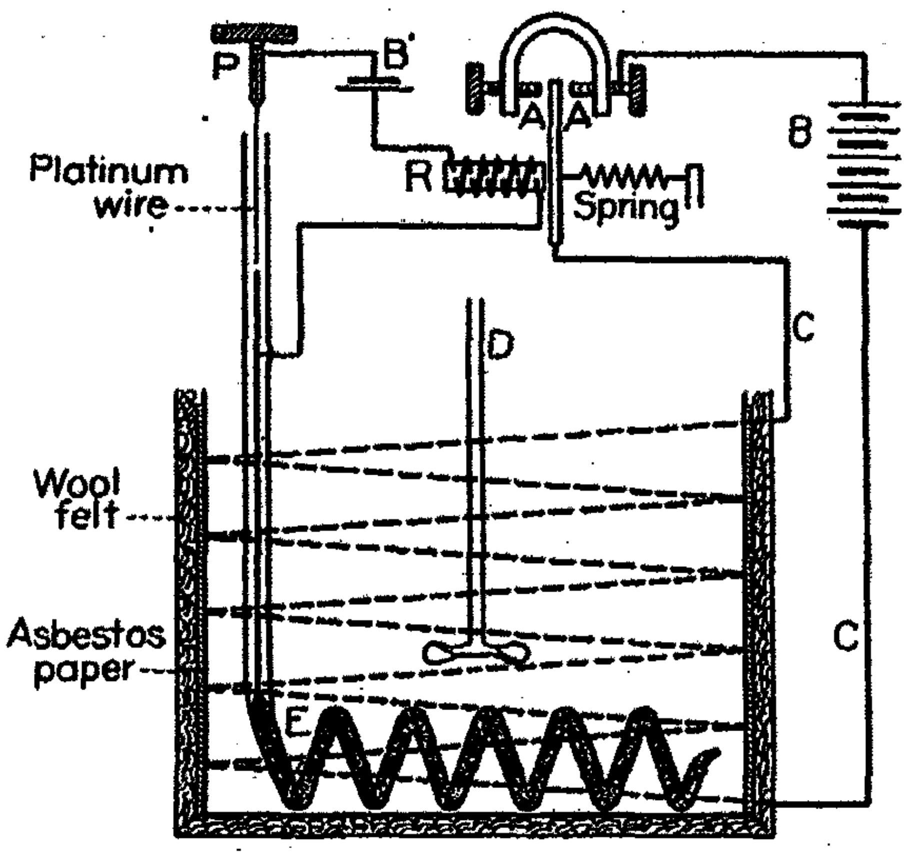
A SIMPLE ELECTRICAL THERMOSTAT

BY FREDERICK A. OSBORN

The thermostat described here may, perhaps, be considered as a simpler and modified form of the electrically heated and controlled thermostat of Geer.[1] It was devised to offer a simple, quick, and yet accurate means of controlling the temperature in laboratory work in conductivity.

The general details and the electrical connections are shown in the diagram. The heating of the 50-liter bath was accomplished by means of one layer of iron wire of five turns, carrying a 3-ampere current produced from eight storage cells.



AA = Platinum points.
B = Storage battery (8 cells).
B' = Storage battery (1 cell).
CC = Iron wire.
D = Stirrer.
E = Glass coil containing mercury.
R = Relay.

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[1] Jour. Phys. Chem., 6, 85 (1902).

The glass worm used as the regulating thermometer was 9.5 cm. in diameter and 16 cm. long. It holds 110 cm. of mercury. One U. S. storage cell No. 3 was used to operate the relay circuit and no harmful sparking has been noticed on the make and break of the circuit. The relay was one of 20-ohm resistance.

The bath was brought to within one-tenth degree of the required temperature and then a very little adjustment of the screw P put the bath into automatic regulation. The bath has many times been made self-regulating within fifteen minutes.

The large volume of mercury and the very large surface of the worm combine to make the regulator very sensitive, the relay very often throwing the current off and on while the Beckmann thermometer showed no change. On continuous runs of six to eight hours no change of 1/100 of a degree has been observed.

The advantages of the thermostat are:

1. The simplicity of construction and operation.

2. The ease and quickness with which the given temperature may be obtained.

3. Its constancy in automatically holding the temperature at the desired value.

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THE DEPENDENCE OF FREE ENERGY UPON TEMPERATURE

BY J. E. TREVOR

Two relatively recent articles, one by Richards[1], the other in connection therewith by van't Hoff[2], deal with the thermodynamic theory of free energy. The interest aroused by these articles seems to render desirable a critical examination of the theoretical results that they record.

An Integration by van't Hoff

When the thermodynamic state of a system is determined by 'normal variables', the difference of the specific heats of the system at two end-states having the same temperature is easily expressed by means of the free energy of the system. Van't Hoff's paper is primarily concerned with the integration of this relation with regard to the temperature, under the assumption that the difference of the specific heats is independent of the temperature.

Let us examine this operation from the beginning. When the state-variables of the system are the absolute temperature θ and the 'parameters'

$$x_1, x_2 \ldots x_n,$$

the specific heat c_x at constant parameters is defined by the equation

$$c_x = + \theta \frac{\partial \eta}{\partial \theta}$$

$$= - \theta \frac{\partial^2 f}{\partial \theta^2}, \qquad (1)$$

where η denotes the specific entropy, and f the specific free energy of the system. Considering two states characterized by different values of the parameters, and writing

$$\Delta c_x = c_x(x_{12}, x_{22} \ldots x_{n2}, \theta) - c_x(x_{11}, x_{21} \ldots x_{n1}, \theta)$$

$$\Delta f = f(x_{12}, x_{22} \ldots x_{n2}, \theta) - f(x_{11}, x_{21} \ldots x_{n1}, \theta),$$

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[1] Proc. Am. Acad. 38, 293; Zeit. phys. Chem. 42, 129 (1902).

[2] Boltzmann. Festschrift, 233 (1904).

we obtain from (1) the relation in question

$$(2) \qquad \frac{\partial^2 \Delta f}{\partial \theta^2} = -\frac{\Delta c_x}{\theta}.$$

The quantity Δc_x in this familiar equation is a function of the specified end-values of the variables. Integration over a temperature interval $\theta - \theta_0$ such that within it Δc_x is sensibly independent of the temperature yields

$$(3) \qquad \frac{\partial \Delta f}{\partial \theta} - \left(\frac{\partial \Delta f}{\partial \theta}\right)_0 = -\Delta c_x . \log \theta + \Delta c_x . \log \theta_0 .$$

Integrating again, writing $-\Delta\eta_0$ for the negative change, $\partial \Delta f / \partial \theta$, of the specific entropy at θ_0, we find

$$(4) \qquad \Delta f - \Delta f_0 = (\Delta c_x - \Delta\eta_0)(\theta - \theta_0) - \Delta c_x \theta . \log \frac{\theta}{\theta_0}.$$

This integration was executed by Helmholtz, in 1882, in his famous exposition of the free energy theory. In our notation, Helmholtz's equation (1*l*), found by integrating (1) with regard to the temperature, is

$$f - f_0 = (c_x - \eta_0)(\theta - \theta_0) - c_x \theta . \log \frac{\theta}{\theta_0}.$$

Writing this equation for two states at the same temperature, and subtracting, we obtain (4), the equation sought by van't Hoff.

If the equation (4) be written

$$(4a) \qquad \begin{aligned} \Delta f = & -\Delta c_x \theta . \log \theta \\ & + (\Delta c_x - \theta\eta_0 + \Delta c_x \log \theta_0) . \theta \\ & - \Delta c_x \theta_0 + \Delta\eta_0 \theta_0 + \Delta f_0 , \end{aligned}$$

and A be written for the coefficient of θ, and E_0 for the sum of the terms that do not contain θ, the equations (4*a*) and (3) become

$$\Delta f = E_0 + A\theta - \Delta c_x \theta . \log \theta$$

$$\frac{\partial \Delta f}{\partial \theta} = A - \Delta c_x (1 + \log \theta).$$

These equations appear to be identical with the equations (4*b*) and (4*c*) obtained by van't Hoff,

$$E = E_0 + AT - ST \log T$$

$$\frac{dE}{dT} = A - S(1 + \log T).$$

(It will be noted that van't Hoff writes E for Δf, and Q for the corresponding isothermal difference of energy Δe.) Yet van't Hoff's equations, with the meanings that he attaches to their terms, are incorrect. The reason for this is that van't Hoff integrates from $\theta = 0$, thereby assuming Δc_x to be entirely independent of θ. This assumption is inadmissible. The correct formulation is that of equation (4), and is due to Helmholtz.

The hypothesis of Richards

In the paper by Richards, cited by van't Hoff, it is inquired whether isothermal change of the heat capacity of a thermodynamic system "has any causal relationship to the relative magnitudes of the free energy change and the heat of the reaction." In a brief abstract[1] of this paper, I observed that the relation between the change of the heat capacity (for constant 'normal' parameters) and the simultaneous change of the free energy is that expressed by (2) above,

$$\Delta c_x = -\theta \frac{\partial^2 \Delta f}{\partial \theta^2}.$$

Again, from certain experimental data, Richards draws the conclusion 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

$$(5) \qquad \frac{\partial \Delta f}{\partial \theta} = -M \frac{\partial \Delta e}{\partial \theta},$$

where M is independent of θ. I commented on this by pointing out that such a relation does exist, and that it has the familiar form

$$\frac{\partial \Delta e}{\partial \theta} = -\theta \frac{\partial^2 \Delta f}{\partial \theta^2}.$$

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[1] This Journal, 7, 223 (1903).

It appears, however, if I correctly understand a letter from Prof. Richards on the matter, that the aim of the investigation in question was to establish, through appeal to experiment, an algebraic relation between the derivatives

$$\frac{\partial\Delta e}{\partial\theta} \text{ and } \frac{\partial\Delta f}{\partial\theta}.$$

From the principles of thermodynamics, such a relation cannot be obtained; it may be that none exists. Differentiation of

$$\Delta e = \Delta f + \theta\Delta\eta$$

yields a relation involving these two derivatives,

$$\frac{\partial\Delta e}{\partial\theta} = \frac{\partial\Delta f}{\partial\theta} + \frac{\partial(\theta\Delta\eta)}{\partial\theta};$$

and by combining this with (5), whereby we obtain

$$\frac{\partial\Delta f}{\partial\theta} = -\frac{\mathrm{M}}{1+\mathrm{M}}\frac{\partial(\theta\Delta\eta)}{\partial\theta},$$

and integrating from a temperature of reference θ_0, we find (5) to require

$$\Delta f - \Delta f_0 = -\frac{\mathrm{M}}{1+\mathrm{M}}\theta\Delta\eta + \frac{\mathrm{M}}{1+\mathrm{M}}\theta_0 \cdot \Delta\eta_0.$$

Now, in general we have

$$\Delta f - \Delta f_0 = \Delta e - \Delta e_0 - \theta\Delta\eta + \theta_0\Delta\eta_0;$$

whereupon elimination of

$$\Delta f - \Delta f_0 + \theta\Delta\eta$$

between these two equation yields

$$\Delta e - \Delta e_0 = \frac{1}{1+\mathrm{M}}\theta\Delta\eta - \frac{1}{1+\mathrm{M}}\theta_0\Delta\eta_0. \tag{6}$$

For $\Delta e - \Delta e_0$, we have

$$\Delta c_x = \theta\frac{\partial\Delta\eta}{\partial\theta} = \frac{\partial\Delta e}{\partial\theta}$$

$$\Delta e - \Delta e_0 = \int_{\theta_0}^{\theta}\Delta c_x d\theta;$$

and, for $\Delta\eta$,

$$\frac{\partial \Delta\eta}{\partial\theta} = \frac{\Delta c_x}{\theta}$$

$$\Delta\eta = \int_{\theta_0}^{\theta} \frac{\Delta c_x}{\theta}\, d\theta + \Delta\eta_0;$$

so, by substitution of these values, (6) becomes

$$\int_{\theta_0}^{\theta} \Delta c_x \left(\frac{1}{\theta_1} - \frac{1}{1+\mathrm{M}}\frac{1}{\theta}\right) d\theta = -\theta_0 \frac{\Delta\eta_0}{1+\mathrm{M}}\frac{1}{\theta} + \frac{\Delta\eta_0}{1+\mathrm{M}},$$

where θ_1 signifies the (constant) upper limit of the integral.

The assumption of (5) is, thus, equivalent to the hypothesis that the relation between Δc_x and θ is of the form

$$\int_{\theta_0}^{\theta} \Delta c_x \left(\frac{1}{\theta_1} - \frac{1}{1+\mathrm{M}}\frac{1}{\theta}\right) d\theta = a\left(1 - \frac{\theta_0}{\theta}\right),$$

where a is independent[1] of θ.

The meaning of the hypothesis of Richards

But the assumption proposed can be more simply expressed, it is equivalent to the hypothesis that isothermal changes of specific heat are proportional to the 1/M-th power of the temperature. This may be shown by combining the assumed relation (5),

$$\frac{\partial \Delta f}{\partial\theta} = -\mathrm{M}\frac{\partial \Delta e}{\partial\theta},$$

with the general thermodynamic equation

$$-\theta\frac{\partial^2 \Delta f}{\partial\theta^2} = \frac{\partial \Delta e}{\partial\theta}.$$

Eliminating $\partial\Delta e/\partial\theta$ between these equations, we replace (5) by the formulation

$$\frac{\partial \Delta f}{\partial\theta} = \mathrm{M}\theta\frac{\partial^2 \Delta f}{\partial\theta^2}.$$

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[1] It is a function of the end values of the parameters.

This equation, in the form

$$\frac{\partial}{\partial\theta}\log\frac{\partial\Delta f}{\partial\theta} = \frac{\partial}{\partial\theta}\log\theta^{1/M},$$

can be integrated with regard to θ, whence

$$(7) \qquad \frac{\partial\Delta f}{\partial\theta} = -\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta^{1/M};$$

whence integrating again,

$$(8) \qquad \Delta f = -\frac{M}{1+M}\,\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta^{1/M+1} + \frac{M}{1+M}\,\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta_0^{1/M+1} + \Delta f_0.$$

The isothermal change of specific heat satisfying the relation

$$\Delta c_x = \theta\,\frac{\partial\Delta\eta}{\partial\theta},$$

we have, by (7), since $-\Delta\eta = \partial\Delta f/\partial\theta$,

$$(9) \qquad \Delta c_x = \frac{1}{M}\,\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta^{1/M};$$

i. e., as asserted, Richards's assumption (5) is equivalent to the hypothesis that Δc_x is proportional to the 1/M-th power of the temperature.

Incidentally, it is not without interest to seek the form, as determined by (5), of the dependence of Δe on θ. By means of (7), the equation

$$\frac{\partial\Delta e}{\partial\theta} = \theta\,\frac{\partial\Delta\eta}{\partial\theta}$$
$$= \Delta c_x$$

becomes

$$\frac{\partial\Delta e}{\partial\theta} = \frac{1}{M}\,\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta^{1/M};$$

whence, integrating[1],

$$(10)\qquad \Delta e = \frac{1}{1+M}\,\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta^{1+1/M}$$

$$+\,\Delta e_0 - \frac{1}{1+M}\,\frac{\Delta\eta_0}{\theta_0^{1/M}}\,\theta_0^{1+1/M}.$$

Richards's assumption, then, as expressed by the equations (7), (9), (8), (10), may be stated in any one of the forms:

$$(7a)\qquad \Delta\eta = a_1\theta^{1/M}$$

$$(9a)\qquad \Delta c_x = \frac{a_1}{M}\,\theta^{1/M}$$

$$(8a)\qquad \Delta f = -\frac{Ma_1}{1+M}\,\theta^{1+1/M} + a_2$$

$$(10a)\qquad \Delta e = +\frac{a_1}{1+M}\,\theta^{1+1/M} + a_2;$$

where

$$a_1 = \frac{\Delta\eta_0}{\theta_0^{1/M}},\qquad a_2 = \Delta f_0 + \frac{Ma_1}{1+M}\,\theta_0^{1+1/M},$$

and M, a_1, a_2, are independent[2] of θ.

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[1] The sum of the additive terms in the equation (10) for Δe is equal to the sum of the additive terms in the equation (8) for Δf. For, when $\theta = 0$, we have $\Delta f = \Delta e$, and the equations (10) and (8) give

$$\Delta e_0 - \frac{a_1}{1+M}\,\theta_0^{1+1/M} = \Delta f_0 + \frac{Ma_1}{1+M}\,\theta_0^{1+1/M},$$

which reduces to

$$\Delta e_0 = \Delta f_0 + a_1\theta_0^{1+1/M},$$

which converts the sum of the additive terms in (10) to

$$\Delta f_0 + \frac{Ma_1}{1+M}\,\theta_0^{1+1/M},$$

identical with the corresponding sum in (8).

[2] Here M is a constant, and a_1, a_2 are functions of the end values of the parameters. As a check on these formulations, it may be noted that substitution for Δe and Δf from (10a) and (8a) in the general equation

$$\Delta e - \Delta f = \theta\Delta\eta$$

yields

$$a_1\theta^{1+1/M} = \theta\Delta\eta,$$

which is identical with (7a).

The hypothesis (9*a*) may be stated in a more elementary way when it is converted into a statement concerning the form of the specific heat $c_x(x;\theta)$. Writing (9*a*)

$$c_{x2} - c_{x1} = \frac{\alpha_2 - \alpha_1}{M} \theta^{1/M},$$

it appears that Richards's hypothesis is tantamount to the assumption that the dependence of c_x on the temperature must satisfy the relation

$$c_x = \frac{\alpha(x)}{M} \theta^{1/M} + \phi(\theta). \tag{9b}$$

So Richards's proposal sifts down to a hypothesis concerning the forms of the specific heats of thermodynamic systems. He assumes that isothermal changes of specific heat are proportional to a constant (the 1/M-th) power of the temperature. Most thermodynamic questions of fundamental importance sift down to questions about the forms of specific heats. And here is where *measurements* are needed. A comprehensive experimental study of the heat capacity of some one system throughout the region of its accessible states would be of great interest and value.[1]

Direct test of Richards's hypothesis

If, for any system, it should prove possible to make experimental determinations of Δc_x at different temperatures, these determinations could be employed to test the assumption of Richards as expressed[2] by the equation (9*a*),

$$\begin{aligned}\Delta c_x &= \frac{a_1}{M} \theta^{1/M}\\ &= A\theta^{1/M}.\end{aligned}$$

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[1] I learn from Professor Richards that such a study of more than one special case is now in progress at the Chemical Laboratory of Harvard College, under his direction.

[2] Professor Richards requests me to state that he "made no definite assertion concerning the constancy of M, but intended merely to suggest that the two coefficients were perhaps mutually functions of one another, with opposite signs." The statement in his paper is: "The free energy of a given reaction changes on the average about twice as fast as the total energy with change of temperature, but in the opposite direction. When the total energy increases, the free energy diminishes. Expressed algebraically, $(\partial A/\partial T) = -M(\partial U/\partial T)$, in which the value of M averages about 2." It is this formulation that is here discussed.

At two temperatures, θ_1 and θ_2, we should have two equations between the two unknowns A, M,

$$\begin{cases} (\Delta c_x)_1 = A\theta_1^{1/M} \\ (\Delta c_x)_2 = A\theta_2^{1/M}. \end{cases}$$

Eliminating A between these equations, we find

$$M = \frac{\log\theta_2 - \log\theta_1}{\log\Delta_2 - \log\Delta_1},$$

writing Δ_i for $(\Delta c_x)_i$. This is the equation for the determination of M from experiment. Eliminating M, we find

$$\log A = \frac{\log\theta_1 . \log\Delta_2 - \log\theta_2 . \log\Delta_1}{\log\theta_1 - \log\theta_2},$$

which is the equation for determining A from experiment.

It may be added that, if A,M be really constant throughout a region including the temperatures θ_1, θ_2, θ_3, we should find identically verified the relation obtained by eliminating A,M between *three* equations[1],

$$\begin{vmatrix} \log\frac{\theta_1}{\theta_2} & \log\frac{\theta_1}{\theta_3} \\ \log\frac{\Delta_1}{\Delta_2} & \log\frac{\Delta_1}{\Delta_3} \end{vmatrix} = 0.$$

Condition for the existence of a relation F = 0

In this matter it would be of the greatest interest to prove or to disprove the existence of a relation

$$F\left(\frac{\partial\Delta e}{\partial\theta}, \frac{\partial\Delta f}{\partial\theta}\right) = 0.$$

When the state of the thermodynamic system is determined by two normal variables x,θ, the necessary and sufficient condition for the existence of this relation is

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[1] The curiously symmetrical form of this relation is very apparent when it is written

$$\left(\frac{\Delta_1}{\Delta_3}\right)^{\log\frac{\theta_1}{\theta_2}} = \left(\frac{\Delta_1}{\Delta_2}\right)^{\log\frac{\theta_1}{\theta_3}}.$$

$$\begin{vmatrix} \frac{\partial^2 \Delta e}{\partial x \partial \theta} & \frac{\partial^2 \Delta e}{\partial \theta^2} \\ \frac{\partial^2 \Delta f}{\partial x \partial \theta} & \frac{\partial^2 \Delta f}{\partial \theta^2} \end{vmatrix} = 0.$$

Let us express the derivatives in this jacobian by means of derivatives of $\Delta\eta$. From

$$\begin{aligned} de &= \mathrm{X}dx + \theta d\eta \\ &= \left(\mathrm{X} + \theta \frac{\partial \eta}{\partial x}\right) dx + \theta \frac{\partial \eta}{\partial \theta} d\theta, \end{aligned}$$

we find

$$\frac{\partial \Delta e}{\partial \theta} = \theta \frac{\partial \Delta \eta}{\partial \theta}$$

$$\left\{ \begin{aligned} \frac{\partial^2 \Delta e}{\partial x \partial \theta} &= \theta \frac{\partial^2 \Delta \eta}{\partial x \partial \theta} \\ \frac{\partial^2 \Delta e}{\partial \theta^2} &= \frac{\partial \Delta \eta}{\partial \theta} + \theta \frac{\partial^2 \Delta \eta}{\partial \theta^2}; \end{aligned} \right.$$

and we have

$$\frac{\partial^2 \Delta f}{\partial x \partial \theta} = - \frac{\partial \Delta \eta}{\partial x}$$

$$\frac{\partial^2 \Delta f}{\partial \theta^2} = - \frac{\partial \Delta \eta}{\partial \theta}.$$

These values convert our jacobian to

$$- \theta \frac{\partial^2 \Delta \eta}{\partial x \partial \theta} \frac{\partial \Delta \eta}{\partial \theta} + \frac{\partial \Delta \eta}{\partial x} \frac{\partial \Delta \eta}{\partial \theta} + \theta \frac{\partial \Delta \eta}{\partial x} \frac{\partial^2 \Delta \eta}{\partial \theta^2} = 0,$$

which may be written

$$\frac{\partial}{\partial \theta} \log \frac{\frac{\partial \Delta \eta}{\partial x}}{\frac{\partial \Delta \eta}{\partial \theta}} = \frac{1}{\theta};$$

whence, integrating with regard to θ,

$$\frac{\frac{\partial \Delta \eta}{\partial x}}{\frac{\partial \Delta \eta}{\partial \theta}} = \frac{1}{\theta_0} \frac{\left(\frac{\partial \Delta \eta}{\partial x}\right)_0}{\left(\frac{\partial \Delta \eta}{\partial \theta}\right)_0} \cdot \theta$$

$$(11) \qquad = b\theta,$$

where b is a function of the end values of x. Making $x_2 - x_1 = dx$, and setting

$$\beta(x) = b(x, x + dx),$$

the equation (11) becomes

$$(12) \qquad \frac{\partial^2 \eta}{\partial x^2} = \beta\theta \frac{\partial^2 \eta}{\partial x \partial \theta}.$$

This is, then, the necessary and sufficient condition for the existence of a relation F = 0. It requires that the specific heat of the system shall satisfy the equation

$$(12a) \qquad \frac{\partial c_x}{\partial x} = \frac{1}{\beta} \frac{\partial^2 \eta}{\partial x^2}.$$

This condition, since

$$df = X dx - \eta d\theta,$$

may be written in the equivalent form,

$$(12b) \qquad \frac{\partial c_x}{\partial x} = -\frac{1}{\beta} \frac{\partial^2 X}{\partial x \partial \theta}.$$

It is not apparent that the principles of thermodynamics bear upon the possibility of the existence of this relation.

It is easily seen that the necessary and sufficient condition (11) is satisfied by Richards's formulation. This formulation has been shown to be equivalent to equations (7*a*) and (9*a*),

$$\Delta\eta = \Delta\alpha . \theta^{1/M}$$

$$\Delta c_x = \frac{\Delta\alpha}{M} \theta^{1/M},$$

from the first of which follows

$$\frac{\partial \Delta\eta}{\partial x} = \frac{d\Delta\alpha}{dx} \theta^{1/M};$$

wherefore these equations yield

$$\frac{\partial \Delta\eta}{\partial x} = \mathrm{M}\,\frac{d \log \Delta\alpha}{dx} \,.\, \Delta c_x,$$

in accordance with the condition (11)[1].

Cornell University. December, 1904.

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[1] Richards's conclusions, on p. 307 of his paper: "When the heat capacity of a system does not change during a reaction, and concentration influences are balanced, the free-energy and the total-energy changes of the reaction are equal and unchangeable with the temperature," are consequences of his fundamental assumption,

$$\frac{\partial \Delta f}{\partial \theta} = -\mathrm{M}\,\frac{\partial \Delta e}{\partial \theta}$$
$$= -\mathrm{M}.\Delta c_x.$$

For, when $\Delta c_x = 0$, it follows that

$$\frac{\partial \Delta f}{\partial \theta} = \frac{\partial \Delta e}{\partial \theta} = 0,$$

which is the second of the above statements; and, because of

$$\Delta f = \Delta e + \theta\,\frac{\partial \Delta f}{\partial \theta},$$

it follows that

$$\Delta f = \Delta e,$$

which is the first statement. Both, with the exception of the statement that $\partial \Delta e/\partial \theta = 0$, stand or fall with the fundamental assumption made.

REACTION-VELOCITIES IN HETEROGENEOUS SYSTEMS: WITH PARTICULAR REFERENCE TO ENZYME ACTIONS

BY GEORGE SENTER

In a recent paper by Nernst,[1] it is suggested that reaction-velocities in heterogeneous systems are not to be regarded as a measure of the rate at which chemical changes take place, but are, in most cases, conditioned by diffusion-velocities. According to this view, there is always equilibrium at the boundary between two phases; the changes which take time are (1) diffusion of substances to and from the boundary, (2) chemical reactions in the two phases. If changes of the first kind are rapid compared with the second, the velocity measured is really the velocity of a chemical reaction. If, on the other hand, the rate at which substances enter into reaction at the boundary or in one of the phases is rapid compared with the rate of diffusion to or from the boundary, the velocity measured is a diffusion-velocity. In such a heterogeneous reaction as the dissolving of marble at a plane surface in acids, the simple diffusion-changes might be supposed to be complicated by convection-currents, but definite conditions may be obtained by stirring the solution since the concentration in the main bulk of liquid is thus kept uniform and the diffusion may be regarded as confined to a thin film adherent to the surface of the marble. The thickness of the film, and consequently the rate of diffusion, will depend upon the speed of the stirring, and the dependence of the reaction-velocity upon the rate at which the solution is being stirred will evidently be a most important criterion as to whether the rate of a chemical change or a diffusion-velocity is being measured.

Brunner,[2] under Nernst's direction, has investigated several heterogeneous actions such as the rate of solution of marble and various metals in acids, and the electrolytic reduction of iodine;

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[1] Zeit. phys. Chem. 47, 52 (1903).

[2] Ibid. 47, 56 (1903).

the results obtained are in complete agreement with Nernst's theory.

It seems doubtful, however, whether the diffusion theory is capable of general application, and, in particular, whether the assumption of practically infinite reaction-velocities at the boundary of the two phases is always justifiable. The reactions selected for examination by Brunner are such that the chemical changes may be expected to be very rapid, so that it is scarcely surprising to find the diffusion theory borne out in these cases. On the other hand, Haber,[1] in an investigation of the electrolytic reduction of nitrobenzene, has come to the conclusion that the rate of reduction of this body at the surface of the electrode is slow compared with the rate of diffusion to the electrode, in contradiction to Nernst's theory. Similar views have been expressed by Sand.[2]

For the reasons just given it seems probable that no general theory of reaction velocities in heterogeneous systems can be given but that the relative part played by diffusion and by the actual chemical change is a matter for investigation in each case.

The question now arises as to what criteria can be employed to distinguish between a chemical velocity and a diffusion-velocity. The three following seem to be the best adapted for this purpose; a few words will be devoted to the consideration necessary to their proper application.

(1) Relation between diffusive power and reaction-velocity.

(2) Effect of substances which alter the viscosity of the solution on the reaction velocity.

(3) The temperature-coefficient of the reaction.

If the magnitude of the surface, the thickness of the diffusion layer and the diffusion coefficient of a substance are known, the rate of reaction to be expected on the diffusion theory can easily be calculated[3] and a comparison of this value with the ve-

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[1] Zeit. phys. Chem., 47, 257 (1904).

[2] Proc. Faraday Society, November, 1904.

[3] See Brunner. l. c.

locity actually found would at once show if the theory in question applies. This method would be applicable to diffusion toward a stationary surface, but would be very difficult to apply to colloidal solutions, since the extent of surface and the thickness of the diffusion layer could scarcely be even approximately estimated. Better results might be obtained by comparing the reaction-velocity between the same colloid and substances of known diffusive power. If the diffusion-path is of the same length in all cases and if the colloid is not decreased in activity through partial combination with the diffusing substance or with the products of action, then the rate of reaction ought to vary with the diffusive power. The possibility of partial combination between the reacting substances must not be lost sight of; the part played by this could be deduced with a fair amount of certainty from the dependence of the reaction-velocity on the concentration of the reacting substances and would, in any case, be small in dilute solution.

As regards the application of the second criterion, since the rate of diffusion is in all probability some simple function of the viscosity of the solution, it would seem as if the velocity of a heterogeneous action conditioned by a diffusion-velocity ought to be equally affected by the addition of two substances causing the same change of viscosity. The matter is, however, not quite so simple, since in this case also some of the added substances might diminish the activity of the substance to which diffusion is taking place either by entering into chemical combination with it or by decreasing its active surface in a mechanical manner. Although the reaction-velocity would still be a diffusion-velocity, it is clear that it might be very greatly modified by such additions and that the effect might be very much greater than any change due to alteration of the viscosity.

We now come to the third method of distinguishing chemical velocities from diffusion-velocities: the magnitude of the temperature-coefficient of the action. With scarcely any exceptions, chemical actions in homogeneous systems are enormously accelerated by increase of temperature; for a rise of temperature of 10° the reaction-velocity is doubled or trebled. Change of temperature has much less influence on the rate of diffusion of dissolved substances in water; for almost all substances the increase is about 2.5 percent per degree between 10° and 50° or the ratio of the velocities at t + 10° and t° (which we may call the velocity-quotient for 10°) is about 1.26.

Brunner found that the velocity-quotient for 10° for the actions investigated by him amounted to about 1.5; much less than the average for a chemical reaction but considerably greater than the average increase of diffusion-velocity with temperature. Since there can scarcely be any doubt that the velocities in question are diffusion-velocities, it seems probable that, as Brunner suggests, the thickness of the diffusion-layer decreases with rise of temperature, thus shortening the diffusion-path and giving an increased reaction-velocity.

Since we know so little of the mechanism of chemical actions in heterogeneous systems we are not entitled to say without further investigation that the high value of the temperature-quotient characteristic of reactions in homogeneous systems will also be found in heterogeneous actions. If, however, a large temperature-quotient is found for a heterogeneous action, it seems quite justifiable to conclude that we are dealing with a chemical velocity, since no case of a large temperature-quotient for a diffusion-velocity has yet been met with.

The above general considerations will now be employed in discussing the question as to the applicability of Nernst's theory to reactions in colloidal solution and more particularly to enzyme actions.

Velocity of enzyme action

Up to the present, very little has been published with reference to the possible importance of Nernst's theory for reactions in colloidal solution.

Nernst,[1] without entering into details, has pointed out that the results obtained by Bredig and his pupils, in the investigation of the catalytic decomposition of hydrogen peroxide by colloidal platinum, can be explained simply on his theory. Herzog[2] has

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[1] l. c. p. 55.

[2] Zeit. phys. Chem. 41, 416 (1904).

expressed the opinion that Nernst's theory can be applied to enzyme actions in general, and, on the assumption that the diffusion-velocity is a simple function of the viscosity of the solution, has proposed a formula with two constants which represents with considerable accuracy the results obtained by Henri[1] for the rate of inversion of cane sugar by invertase.

The author[2] has discussed the probable mechanism of the decomposition of hydrogen peroxide by platinum and by haemase and has come to the conclusion that the velocities measured are diffusion-velocities, the true chemical change being very rapid in comparison. The small values of the temperature-quotient (1.7 for the platinum catalysis, 1.5 for the haemase catalysis) lend some support to this conclusion. Stress has been laid upon the importance of the Brownian movements of colloidal particles in keeping the concentration in the main bulk of liquid constant, this constituting the chief difference between such actions and those investigated by Brunner.

I will now attempt to elucidate the nature of the reactions in question by applying the general methods referred to in the first part of this paper. As regards the connection between reaction-velocity and the diffusive power of the substances undergoing decomposition, few accurate investigations seem to have been carried out. Gayon and Dubourg[3] find that some specimens of yeast ferment dextrose much faster than laevulose while others show just the contrary behaviour. This behaviour is due in all probability to stereochemical differences between the different yeasts and could not easily be reconciled with the diffusion theory of reaction-velocity. This matter would well repay further accurate investigation.

The effect of other substances on the reaction-velocity between enzyme and substratum throws considerable light on the question under discussion. Adrian Brown[4] found that while invert sugar retarded considerably the hydrolysis of cane sugar by

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[1] Lois générales de l'Action des Diastases, Paris, 1903.

[2] Proc. Roy. Soc. 74, 201 (1904).

[3] Comptes rendus, 110, 369 (1890).

[4] Jour. Chem. Soc. 81, 373 (1902).

invertase, a much stronger solution of lactose had practically no retarding effect. Henri[1] found that while glucose only slightly retarded the hydrolysis of cane sugar by invertase, laevulose slowed down the action very considerably. Similar results with other sugars were afterwards obtained by Armstrong.[2]

These results seem quite sufficient to disprove Herzog's theory. No formula which fails to take into account the specific retarding effect exerted by various substances can be used to represent the course of an enzyme action.

As has been already pointed out, however, this does not suffice to prove that diffusion plays no part in the reaction-velocity. The retarding effect of laevulose on the activity of invertase may be due to combination between the sugar and the enzyme, part of the latter thus rendered inactive. We might then imagine that only the free particles hydrolyze the sugar which reaches them by diffusion, whereas diffusion to the combined particles is interrupted.

The temperature-coefficient of enzyme actions has been investigated in a good many cases; the more important results are given here in tabular form.[3] In the second column are given the temperatures at which the velocity-constants have been determined; the third column contains the velocity-quotient for 10°.

Dr. Bayliss has kindly allowed me to make use of the last-quoted, as yet unpublished results obtained by him for the action of trypsin on caseinogen, for which I here express to him my best thanks.

It will be seen from the table that the velocity-quotient is in most cases much higher than would be expected for a diffusion-velocity and corresponds to the usual quotient for a chemical action; this confirms the conclusion arrived at above that the velocity of at least some enzyme actions is a chemical velocity.

Lipase and urease show a very small temperature-coefficient. As regards lipase this may be partly due to the way in which

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[1] l. c.

[2] Proc. Roy. Soc. 73, 516 (1904).

[3] The greater part of the results here quoted are taken from a table given by Herzog. Zeit. für allg. Physiologie, 4, 193 (1904).

Reaction	Temps. of observation	Vel. quotient for 10°
Emulsin and salicin (Tammann)	$K_{0} - K_{30}$	2.4
Maltase and maltose (Lindner and Krober)	$K_{10} - K_{20}$	1.9
Lipase and ethyl butyrate (Kastle and Loevenhart)	$K_{10} - K_{20}$	1.3
Lipase and monobutyrin (Hanriot)	$K_{20} - K_{26}$	1.6
Pepsin (Herzog)	$K_{19{\cdot}4} - K_{29{\cdot}6}$	2.28
Trypsin (Herzog)	$K_{10{\cdot}4} - K_{29{\cdot}5}$	2.87
Urease and urea (Miquel)	$K_{20} - K_{30}$	1.4
Trymase and dextrose (Herzog)	$K_{14{\cdot}5} - K_{24{\cdot}5}$	2.8
Rennet (Fuld)	$K_{30} - K_{40}$	3.2
Invertase on sugar (O'Sullivan and Tompson)	$K_{0} - K_{15{\cdot}5}$ $K_{15{\cdot}5} - K_{25{\cdot}5}$ $K_{25{\cdot}5} - K_{45}$	2.3 1.9 1.6
Diastase on starch (Muller and Thurgau)[1]	$K_{0} - K_{10}$ $K_{10} - K_{20}$ $K_{20} - K_{30}$	2.5 2.0 2.0
Trypsin on caseinogen (Bayliss)	$K_{20{\cdot}7^\circ} - K_{30{\cdot}7^\circ}$ $K_{30{\cdot}7^\circ} - K_{38{\cdot}7^\circ}$	5.3 3.25

the coefficient has been determined. If the products of reaction exert a great retarding effect as they do in the case of lipase the ratio of the amounts decomposed in equal times at different temperatures is no true indication of the dependence of the rate of reaction on temperature, nor can the ratio be calculated from the velocity-constants obtained by means of the simple logarithmic formula since the latter is not then applicable. The best method of finding the relation between reaction-velocity and temperature is to determine the times necessary to reach the same stage of the action at different temperatures. For these reasons the value 1.3 given in the table for lipase cannot be depended upon nor can the true value be calculated with any certainty from Kastle and Loevenhart's results.

It is not at all improbable that in some enzyme actions the velocity of the chemical action may be comparable to the diffusion-

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[1] The velocities given by Muller and Thurgau and quoted by Oppenheimer (Ferments, Eng. Edition, p. 159) are inaccurate since no allowance has been made for the change of concentration of the starch during the action which is considerable at the higher temperatures. I have recalculated his results on the assumption that 80 percent. of the starch is transformed into maltose (Brown and Heron: J. Chem Soc., 35, 596 (1879)).

velocity, so that the observed rate of reaction depends on both changes. In such a case, since the chemical action is more affected by temperature than the diffusion-velocity, the latter alone would determine the rate of reaction at higher temperatures and, in the absence of other complications, we might expect to find the velocity-quotient decreased rapidly with rise of temperature. This effect would, however, be difficult to distinguish from the normal decrease of the velocity-quotient with rise of temperature, as observed in homogeneous actions.

The diffusion-theory would, under any circumstances, scarcely apply to reactions between two colloids, such as diastase and starch, unless, indeed, the action which requires time takes place between the diastase and much simpler substances than the starch itself.

From what has been said above, it will be clear that, though the available data are insufficient to allow quite definite conclusions to be drawn, they tend to show that Nernst's hypothesis does not apply to the particular actions discussed.

The formula which best represents the velocity of enzyme action is that proposed by Henri and applied more particularly to the hydrolysis of cane-sugar by invertase. This investigator starts from the very plausible assumption that part of the enzyme is rendered inactive by forming loose compounds with the cane-sugar and invert sugar present and obtains the formula

$$\frac{dx}{dt} = \frac{\phi(A-x)}{1 + m(A-x) + nx}$$

where ϕ represents the amount of enzyme present, A the original concentration of cane-sugar and x the amount of invert sugar formed at the time t. Although this formula represents satisfactorily the course of the action over a fairly wide range of concentration, it cannot be maintained that the assumptions on which it is founded are therefore true. The deviation of most enzyme actions from the simple logarithmic formula for a monomolecular action is a fairly regular one and it is only to be expected that the introduction of two additional constants should give a good agreement with the observation over a fairly wide range. The above consideration probably explain how Herzog found a quite different theory borne out by Henri's observations although, as we have seen, there are objections to be made to Herzog's views. Herzog himself quite recognizes the uncertainty of conclusions arrived at in this way.

Nernst has pointed out that it is not justifiable to apply the law of mass action to heterogeneous actions, since the law in question is deduced from kinetic considerations regarding the probability of meeting of molecules, and doubtless this objection holds good with regard to such changes as the dissolving of marble by acids. It is not at first evident that there is any objection to applying the law to reactions in colloidal solution, in which the Brownian motion of the particles corresponds to molecular motion in homogeneous systems and the reaction velocity is probably some function of the number of collisions. There is, however, the difficulty that we have no exact measure of the active mass in the case of colloids; the activity cannot, in general, be put equal to the amount of colloid present but varies with the method of preparation and age of the solution, etc.

Summary

1. Reasons have been given for supposing that Nernst's theory of reaction-velocities in heterogeneous systems is not of general application.

2. The general methods which might be employed to distinguish between chemical reaction-velocities and diffusion-velocities in heterogeneous systems have been discussed.

3. From a discussion of some of the most accurately investigated enzyme actions it has been concluded that the velocities measured are chemical reaction-velocities.

4. It has been shown that the formula recently proposed by Herzog to represent the course of enzyme actions does not accord with the observed facts.

5. It has been suggested that the relative parts played by diffusion and by the velocity of chemical change in enzyme actions depends upon the particular reaction investigated and upon the conditions of experiment.

Chemical Department
St. Mary's Hospital Medical School
London, W. January, 1905.

RADIO-ACTIVITY OF SOME DEEP WELL AND MINERAL WATERS

BY HERMAN SCHLUNDT AND RICHARD B. MOORE

During the past six months we have tested several of the deep well waters of Columbia, Missouri, for radio-activity, preliminary to a survey of the principal mineral and deep well waters of the state for radio-active properties, which we have jointly undertaken. The water from the University deep well was tested first, by the electroscopic method. The gas obtained by boiling the water was found to be radio-active, due to the presence of radium emanation. In these early experiments an aluminum leaf electroscope of the C. T. R. Wilson type was employed. It was of light construction and had a capacity of about one-half liter, consequently the quantity of gas which could be conveniently introduced after partial exhaustion was limited to about 200 cc. In our preliminary tests a boiler having a capacity of ten liters was used and no measures were taken to fix the carbon dioxide. As the deep well waters here contain bicarbonates in considerable quantity the total volume of the gas obtained upon continued boiling was greatly in excess of the capacity of our electroscope. Instead of working with smaller quantities of water or fixing the carbon dioxide, the gas was collected in three nearly equal portions of about 150 cc., each fraction being tested separately. When the last fraction was in the electroscope the fall of the leaf was but slightly faster than the normal air leak of the instrument. The first fraction was unmistakably radio-active while the activity of the intermediate portion was found to have fully double the combined effect of the other two fractions. Similarly when the carbon dioxide was fixed, and the smaller volume of gas then obtained was collected in two fractions, a marked difference was found in the quantity of emanation present in the two fractions. A further study of the concentration of the emanation in different fractions of the gas, obtained by boiling radio-active water, was then made, the results of which are given below.

In the course of our early experiments, the work of Boltwood[1] on the ratio of radium to uranium in certain minerals, came to our notice. In his investigations Boltwood employed an electroscope which answered our needs in every respect. Hence in the continuation of our tests two electroscopes of the Boltwood design were employed. In addition, the quadrant electrometer method of measuring radio-activity was used in conjunction with the electroscopic method in all our subsequent work. The details of our experiments follow.

Apparatus and Method of Work

The Electroscopes.—Two air-tight electroscopes of the C. T. R. Wilson type were constructed according to the specifications given by Boltwood[1]. The Boltwood form consists of a rectangular brass frame 15 × 10 × 5 cm, fitted on the front and back with pieces of plate glass. On the top the frame carries a short piece of wide glass tubing surmounted by a threaded brass ring, into which a removable brass cap screws. A short piece of glass tubing passes through a hole in the cap and a brass rod is cemented in the glass tube by means of wax. The lower end of the brass rod extends into a rod of sulphur which serves as the insulator. The plate to which the leaf is fastened is embedded to a short distance in the other end of the sulphur rod. A special feature of the Boltwood electroscope is the device for charging it.[2] A piece of soft iron wire is suspended from a hook on the brass rod which projects out through the screw cap. The wire extends just below the sulphur insulator and terminates in a loop. In its normal position the wire does not touch the plate carrying the leaf, but by bringing a magnet near the wire, it can be deflected so as to make metallic contact between the brass rod extending out through the cap and the plate to which the leaf is fastened. All of the brass joints are soldered and the others are made air-tight by means of hot wax, except the joint between the brass ring and cap, where a rubber

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[1] Am. Jour. Sci. (4) 18, 97 (1904).

[2] The same device was used by Strutt: Phil. Mag. (6), 5, 680 (1903).

washer excludes the air. The electroscope is provided with two good brass stop-cocks.

One of the instruments used by us was provided with a leaf of thin aluminum foil, fastened to an aluminum plate by means of collodion. The other instrument had a gold leaf which was fastened to a nickel-plated brass plate by moistening the upper portion of the plate and then pressing it gently against the gold leaf. The volume of the aluminum leaf electroscope was 489 cc. and that of the gold leaf instrument was 590 cc. A small stick of sealing-wax was used for charging the instruments. Metallic connection between the leaf system and the rod projecting out of the electroscope was made by deflecting the iron wire with a magnet. The charged sealing-wax was then touched to the brass rod and by gentle rubbing the desired deflection of the leaf was produced. After withdrawing the magnet and sealing-wax, the rod and cap were earthed for an instant.

For ascertaining the rate of fall of the aluminum leaf a short, flat piece of thermometer scale, graduated to twentieths, was fastened on the outside to the back glass plate of the instrument, the scale facing the glass. By means of a mark on the plate supporting the leaf, and another on a wall beyond, a line of sight was established. By noting the time for the leaf to fall 25 small divisions, which lie between the same two points on the scale, very concordant results were obtained without the aid of a microscope or a stop-watch. Twenty small divisions of the scale measured 9.1 mm. A potential of 280 volts produced a deflection of the 25 scale divisions between the two chosen limits of observation.

The gold leaf electroscope was securely fastened to a wooden base. The fall of the gold leaf was observed by means of a microscope firmly supported by a wooden clamp which was bolted to the base of the electroscope. The glass scale in the eye-piece was divided into ten divisions and each of these divisions was again divided into tenths. The diameter of the field corresponding to the hundred small divisions of the scale was 5.2 mm. Hence each tenth division equaled 0.052 mm. The time required for the leaf to fall 60 small divisions between the same two points of the scale was measured with a stop-watch recording fifths of a second.

The normal air leak of the electroscopes was higher during the daytime than at night. In either case the rate of leak was low. For the aluminum leaf electroscope containing air at atmospheric pressure, the average leak during the daytime was about 0.4 small division of the scale, *i. e.*, 0.18 mm per hour. In the case of the gold leaf electroscope the normal air leak was 4.2 small divisions, or 0.21 mm per hour.

The Quadrant Electrometer and Accessories.—A Dolezalek instrument was employed in the tests for radio-activity by the use of the quadrant electrometer. The directions given by Rutherford[1] in his book on radio-activity for the measurements of ionization currents by means of the quadrant electrometer, were carefully followed. A set of water batteries served for charging the needle whose deflection was observed by means of a reading telescope. With a potential of 135 volts on the needle a deflection of 360 divisions was obtained on a millimeter scale one meter from the mirror, for a difference of potential of one volt between the quadrants of the electrometer.

The testing vessel[2] was an air-tight cylindrical vessel, 15 cm in diameter and 30 cm high. It was made of heavy galvanized sheet iron and was provided with two brass stop-cocks. The insulated central brass rod was furnished with a guard ring which was kept earthed during the tests. The vulcanite insulator carrying the central rod and guard ring was cemented into the top of the testing vessel by means of sulphur and sealing-wax. A potential of 150 volts applied to the testing vessel was found ample for obtaining saturation values for the ionization currents measured. The electrometer and testing vessel were placed in a cage made of wire netting which was well earthed.

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[1] Rutherford, "Radio-activity" (1904).

[2] Rutherford, "Radio-activity," pp. 81-83. Bumstead and Wheeler. Am. Jour. Sci. (4) 17, 97 (1904).

The connections were made in the usual way, the testing vessel being placed on a base supported by vulcanite legs. One pole of the water battery—156 cells—was earthed, the other was connected to the outside of the testing vessel. The central rod of the latter was connected to one pair of quadrants, the other pair being earthed. The wire connecting the central rod of the testing vessel with one pair of quadrants of the electrometer also had an earth connection. The switching device employed for breaking the earth circuit was the one used by Professor Stewart of the physics department. Two good-sized pieces of sealing-wax about 10 cm. high and 10 cm. apart, were fastened to the metallic floor of the cage and the connecting wire, which was heavy, was embedded in their tops. A stout wire ring, 3 cm in diameter, encircled the wire and was held in contact with it by means of a spring fastened to the earthed floor of the cage. By pulling a string attached to the wire ring and running over a pulley above, the observer at the telescope could break the earth circuit when he wished to make a reading.

The air leak of the testing vessel was found to be about 30 mm divisions per minute.

Separation of the Emanation.—The emanation dissolved in the water was obtained by boiling the water and collecting the dissolved gases. A section of the apparatus employed in this operation is shown in the accompanying figure. The boiler *A* was of the Mixter type.[1] It was made of tinned iron and had a capacity of about 10 liters. It was fitted with a one-hole rubber stopper and a glass tube *a*, about 15 cm long which extended 10 cm up into the inner tube of a good-sized Liebig condenser, *C*. To the inner tube of the condenser a side tube was fused to which the leveling reservoir *B* was connected by a rubber tube about 1 meter long. A piece of rubber tubing was slipped over the tapering end of the condenser tube on which a separating funnel of about 150 cc capacity was placed. *E* represents the form of gas burette employed for measuring the gas. The operation of collecting the gas was carried out as follows: The boiler

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[1] Bumstead and Wheeler: Am. Jour. Sci. (4) 17, 97 (1904).

was completely filled with the sample of water to be tested, to which a few cubic centimeters of strong caustic soda solution were generally added, and the condenser and accessories put in place as shown in Fig. 1. About half a liter of water was then poured into the overflow reservoir *R* of the boiler. This water served as a seal, and by it any leakage of the gas during the process of boiling was readily detected. The leveling reservoir *B* was then filled with freshly boiled distilled water, the stop-cock of the separating funnel opened, and the reservoir raised in order to fill the condenser tube and funnel with water. The gas burette, also filled with boiled distilled water, was then connected as figured. On heating, the gas which collected in the funnel was transferred in such fractions as desired to the gas burette by raising the reservoir *B*, and opening the cocks *c* and *d*. The different fractions of gas were collected in different burettes of suitable size. For the determination of the total quantity of emanation, the gas burette may be dispensed with. By substituting a somewhat larger separating funnel the entire volume of gas was collected in it without any mishaps. The boiling was continued about twenty minutes. In transferring the gas to the

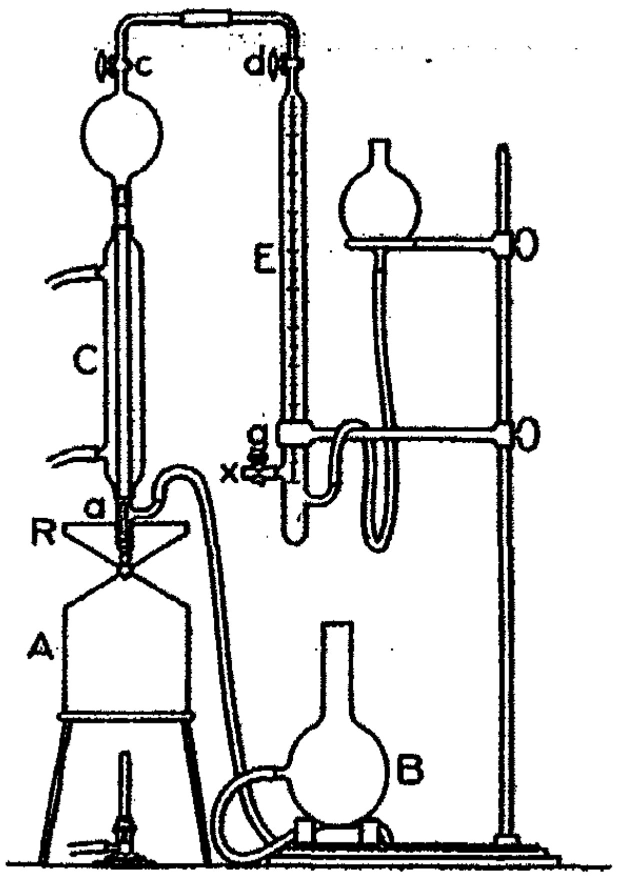

Fig. 1

electroscopes or testing vessel, it was passed through a small drying train which consisted of a small wash vessel containing strong sulphuric acid, connected to a phosphorus pentoxide tube with a bulb for glass-wool and a plug of cotton.

The Standard.—For expressing the radio-activity of the different water samples, the standard[1] proposed by Boltwood was adopted. In his investigations[2] on the ratio of radium to uranium in certain minerals, Boltwood has shown that the quantity of radium present, in the uranium minerals examined, is directly proportional to the amount of uranium the minerals contain. The standard based on this relation is the quantity of emanation associated with a natural mineral containing a known weight of uranium. Our results on the radio-activity of waters are expressed in terms of the unit representing the amount of radium emanation associated with 1×10^{-4} grams of uranium in a natural mineral.

The electroscopes and the testing vessel used with the quadrant electrometer were standardized by means of a sample of uraninite. Dr. Boltwood kindly offered to compare our sample of uraninite with his standard in his carefully standardized electroscope. As a result of this comparison he found that the total quantity of emanation associated with a given weight of our mineral represents the presence of 68.91 percent of uranium. Our own chemical analysis gave 69.18 percent of uranium. The total emanation, Dr. Boltwood points out, consists of two portions, the larger of which is present in the mineral and is liberated when the latter is dissolved in acids and the solution boiled. A much smaller proportion of the emanation, however, is given off by the mineral in the cold, the amount varying with the mineral and different samples of the same mineral. Dr. Boltwood found that a portion of the finely pulverized uraninite, subsequently used by us in standardizing our instruments, loses 6.2 percent of the emanation in the cold. Hence the emanation separated upon dissolving the mineral represents 93.8 percent of its total emanating power.

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[1] Am. Jour. Sci. (4), 18, 381 (1904).

[2] Ibid., (4), 18, 97 (1904).

The operation of standardizing was carried out as follows: A sample of the finely powdered mineral, 0.0157 gram, was weighed out into a flask of about 50 cc capacity. The emanation separated from this weight of mineral upon solution represents the total emanation associated with 0.01 gram uranium in it. A rubber stopper fitted with a small dropping funnel and a short delivery tube was then connected to the side tube x, of the gas burette which had previously been filled with freshly boiled distilled water to which a few cubic centimeters of sodium hydroxide had been added. A few cubic centimeters of nitric acid, sp. gr. 1.2, were then poured into the drop-funnel, the leveling reservoir of the gas burette lowered below the level of the acid in the drop-funnel, and then by opening the pinch-cock g and the stop-cock of the drop-funnel most of the acid was allowed to flow into the flask. The stop-cock was then closed, and the flask gently heated until the uraninite had dissolved. If any gas collected in the stem of the funnel during this operation it was displaced by water introduced through the funnel. By withdrawing the flame for a moment sufficient water was allowed to flow from the burette into the flask to continue the boiling for 15 minutes. The gas collected in the burette after standing for 15 minutes was then introduced into the instrument to be standardized in the same manner as the water gases were transferred. After three hours, when the imparted activity had reached its maximum, the rate of leak was determined. For the aluminum leaf electroscope this leak was equal to 6.90 divisions per minute (= 3.13 mm), which corresponds to a fall of potential of 79.4 volts per minute. Hence a fall of one small division per minute represents the total emanation associated with $\frac{1}{6.9} \times 0.01 = 14.5 \times 10^{-4}$ grams of uranium in our mineral. For the gold-leaf electroscope the fall of the leaf was equal to 48.5 small divisions per minute (= 2.522 mm), which represents a drop of 98 volts per minute. Then a fall of one small division per minute represents 2.06×10^{-4} grams of uranium. In standardizing the testing vessel only one-half of the gas collected was introduced. The values here given, however, refer to the entire sample of mineral, 0.0157 gram. The ionization current after three hours produced a movement of 22.4[1] mm divisions per second; and a movement of 1 mm division per second represents 4.46 × 10^{-4} grams uranium.

Experimental results

The waters that were tested for radio-active properties include samples from three of the deep wells in the city of Columbia, Mo., a cistern on the University campus containing rain water, and a spring about a mile south of the campus, known as Rollins Spring. The radio-activity of the gases obtained from the samples of these waters is given in the table below in terms of the uranium standard. The gases were introduced into the instruments for the tests within half an hour after the completion of the boiling, and the reading obtained after the gases had been in the instrument for three hours was used as the basis of the calculations. The normal air-leak of the instrument was deducted in each case. 9.8 liters of water were used for each test.

Source of the sample	Radio-activity per liter of water
University deep well	1.48 × 10^{-4} g uranium
Christian College deep well	1.68 × 10^{-4} " "
City Water Works " "	0.25 × 10^{-4} " "
Cistern, University campus	0.17 × 10^{-4} " "
Rollins Spring	4.45 × 10^{-4} " "

That the radio-active properties of the gases from the different samples of water were due to the presence of radium emanation was determined (1), by noting the rate of decay of the activity with the time, and (2) by comparing the curve of decay thus obtained directly with the curve obtained when air known to contain radium emanation was present in the instruments. A solution of "radium" was prepared by dissolving 10 mg of a radium preparation of activity 240 in a liter of water contained in a 2 liter flask. About 20 cc of the air standing over the solution was introduced into the instruments and the rate of decay

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[1] The air leak has been deducted from this value.

determined for two weeks. A very close parallelism was found between these curves and the curves which represented the decay of the activity of the water gases—the activity falling to half value in about three and one-half days. The values for the radio-activity in the table were not corrected for the slight decay of activity during the time which elapsed between the collection of the water and the introduction of the gases into the instruments. In most of the tests the operation of collecting the water samples and separating the gases was completed in about two hours. The value given for University deep well water is the average of five determinations, in two of which the quadrant electrometer method was employed. The other values each represent the average of two determinations, one obtained by each method. With the same water, but working with samples collected on different days, the greatest difference in the values obtained by the two methods was 11 per cent.

The three deep wells enumerated are not more than a mile apart, and are believed to be in the same limestone formation. They differ somewhat in depth—the Christian College well being 666 feet deep—while the University and City Water Works wells are of about the same depth—937 feet. The water of Rollins Spring also issues from a limestone formation. The low value for the emanation in the water of the city deep well is therefore somewhat anomalous. In each case the samples of water were taken directly from the discharge pipes. The method of pumping the waters, however, was found to be different. The University and Christian College waters are pumped by means of a lift pump, while the water from the city well is lifted by means of compressed air, forced into the water, about 2 cubic feet of air being required for every gallon of water discharged. It therefore did not seem improbable that some of the emanation was separated from the water in case of the city well, by the large volume of air forced into it. This supposition was tested by comparing two samples of air, one of which was collected directly over the water where it issues from the discharge pipe, while the other air sample was taken about 50 feet distant. No difference could be detected, both samples giving the normal air leak.

None of the water examined contained radium salts in solution. In case of two of the waters a sample of 6 liters was evaporated and the residue tested for radio-active properties in a testing vessel having a detachable base provided with a mercury seal. The other samples of water were tested for radium salts, by storing the water from which the emanation had been separated for two weeks and then boiling off the gas a second time, and testing it. The addition of 20 cc of a saturated solution of barium chloride to six liters of water and precipitation of the barium as sulphate also gave a precipitate which proved inactive.

The results obtained on the concentration of the emanation in the different fractions of gas liberated by boiling samples of water are given in the following selected examples. In an experiment with 9.8 liters of water from the University deep well the gas was collected in four fractions. No sodium hydroxide was added to fix the carbon dioxide. The fractions were introduced into the partially exhausted testing vessel in the order given in the table, and the rate of leak was taken for each fraction. From 5 to 10 minutes were required for introducing each fraction, and about 5 minutes were consumed for determining the rate of leak each time.

Number of fraction	Volume	Percent of total activity
3	81 cc	10.5
4	126 cc	0.8
1	181 cc	48.7
2	87 cc	40.0

As the first fraction represents the gas set free up to the time when boiling had just begun, the results show that fully one-half of the emanation is separated after boiling has actually commenced.

In another experiment with a sample of the University deep well water, in which the carbon dioxide was fixed by adding a little concentrated sodium hydroxide solution, the volume of the gas separated up to the time when boiling had just begun was 153 cc. By boiling for twenty minutes another fraction of 19 cc was obtained. The radio-activity of the two fractions was then measured by means of the quadrant electrometer. The second fraction contained 55 percent of the emanation.

Another sample of the University deep well water, treated with sodium hydroxide, when heated to 95°, yielded 129 cc of gas. A second fraction of 75 cc was obtained by boiling. The first fraction was introduced into the aluminum leaf electroscope, the second into the gold leaf electroscope, and after three hours the fall of the leaves was noted. The second fraction contained 74 percent of the emanation.

A small quantity of emanation was dissolved in about three liters of distilled water, which had previously been boiled and cooled, by bubbling some of the air through it which was contained in a two liter flask, partly filled with "radium" solution, employed in a previous experiment. The water was then boiled and the gas collected in two fractions. The first fraction of 48 cc, which represents the gas separated by heating the water to 95°, contained 13 percent of the emanation. The second fraction of 22 cc, obtained by boiling, contained 87 percent. The measurements were made with the gold leaf electroscope, the first fraction being introduced first. The emanation present per liter of water in this experiment was equivalent to 44.5×10^{-4} grams of uranium.

In one experiment the water remaining in the inner tube of the condenser and in the leveling reservoir *C* after the first fraction of gas had been separated, was boiled and the gas obtained from it was tested for activity in one of the electroscopes. As the rate of leak was only slightly greater than the normal air leak, the relatively small proportion of emanation found in the fraction of gas liberated before boiling begins, is not due to its absorption by the comparatively cool water in the condenser tube through which it bubbles.

Summary of Results

The radio-activity of some deep well waters and a mineral water at Columbia, Mo., was determined quantitatively by both the electroscopic and quadrant electrometer methods.

The radio-activity was due to the presence in the waters of radium emanation.

The relative activity of different fractions of gas separated by heating natural waters containing relatively small amounts of radium emanation, was determined. Moreover, it was found that the different fractions of gas obtained by boiling distilled water which was made radio-active by dissolving radium emanation in it, shows the same characteristic difference in content of emanation, as gases separated from natural waters.

Less than one-half of the emanation is separated with the gas set free up to the time when boiling begins.

Chemical Laboratory,
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February, 1905.

NEW BOOKS

The Recent Development of Physical Science. *By William Cecil Dampier Whetham. 14 × 20 cm; pp. xii + 344. Philadelphia: P. Blakiston's Son and Co., 1904.*—In this popular exposition of "some of the more important developments of the experimental investigations for which the last few years have been remarkable," the topics chosen by the author for discussion are the liquefaction of gases and the absolute zero of temperature, fusion and solidification, the problems of solution, the conduction of electricity through gases, radioactivity, atoms and ether, and astrophysics.

The chapter on the liquefaction of gases brings out the recent striking increase of the range of temperatures available for experimental work in physics and chemistry, and indicates how these extreme temperatures are measured. The chapter on fusion is in the main an account of recent work on the structure of metals and alloys. In the chapter on the problems of solution we find a discussion of the osmotic pressure theory of solutions and the theory of electrolytic dissociation, with an account of the behavior of solutions of colloids. The treatment of the conduction of electricity by gases, of radioactivity, and of atoms and ether is an account of the experimental and speculative work recently assembled by J. J. Thomson and Rutherford. The chapter on astrophysics discusses the more recent spectroscopic studies of the sun and stars, and the pressure due to radiation especially as applied to elucidate the curious phenomena exhibited by the tails of comets.

In an introductory chapter on the philosophical basis of physical science, the ideas presented by the author are about as follows. The object of natural science is to construct a consistent and harmonious model that shall represent to our minds the phenomena presented by our senses. The different sciences are not individual parts of a whole, they are different aspects of a whole. No one of these aspects is essentially more fundamental than any other; in particular, the conviction that a complete mechanical explanation of every phenomenon is possible and fundamental is fallacious. Of two related phenomena, either may be regarded as cause and the other as effect [here the author fails to grasp the important distinction between spontaneous and effected changes of state]. The 'uniformity of nature' is a necessary postulate of physical science. A physical law is a statement of the results of experience. The important thing is to investigate how phenomena are related, not why they appear.

The author's treatment of his topics is sufficiently careful and interesting to make it undesirable to quarrel with features with which one may disagree. It will give to the general reader a very fair idea of the methods of the physicist and physical chemist, and of the nature of some of the problems of experimental science that stands in the foreground of interest at the present time. Such a work, too, is especially to be greeted because of the relative scarcity at all times of good popular essays on topics of the exact sciences. The mechanical execution of the book is commendable. *J. E. Trevor*

Avogadro and Dalton: The Standing in Chemistry of their Hypotheses. *By Andrew N. Meldrum. With a Preface by Francis R. Japp. 14 × 22 cm; pp. 113. Edinburgh: William F. Clay, 1904. Price: 3 shillings, net.*—The essay, whose publication has been made possible by a grant from the Carnegie Trustees, is divided into two parts. The first deals with the relations of Avogadro's Hypothesis to Gay-Lussac's law and to the kinetic theory of gases, and with the methods of molecular and atomic weight determinations; the second, with "the essentials of Dalton's theory," the atomic weight systems of Berzelius, Gmelin, Gerhardt and Laurent, and Cannizzaro, and the relative standing of Dalton's atomic theory and Avogadro's hypothesis.

The author's conclusions may best be stated in his own words: "Not content with the fact that Dalton discovered the law of combination in multiple proportions, that he gave a great impulse to the chemical theory of the nineteenth century, and that his conception of the atom dominated nearly fifty years of chemical work, Dalton's eulogists must needs insist that his ideas are still adhered to, in a system of chemistry dominated by a hypothesis to which Dalton was opposed" . . . "the modern theory draws a distinction between the molecule and the atom of an element which is absolutely foreign to the Daltonian theory" . . . "The truth is, that eulogy of Dalton is uttered at random, and has been carried to lengths far beyond the requisites of science."

"Just as all politicians profess patriotism, the chemists of all schools profess 'chemical methods' . . . but Avogadro's hypothesis, or nothing, is the special basis of Laurent and Gerhardt's system" and of the modern system of chemical formulas.

W. Lash Miller

Die Silikatschmelzlosungen mit besonderer Rücksicht auf die Mineralbildung und die Schmelzpunkt-Erniedrigung. *By J. H. L. Vogt. 18 × 27 cm. I. Ueber die Mineralbildung in Silikatschmelzlösungen. pp. v + 161, 1903; II. Ueber die Schmelzpunkt-Erniedrigung der Silikatschmelzlösungen. pp. 235, 1904. Christiania: Jacob Dybwad.*—The first part deals chiefly with the effect of the composition of the solution on the nature of the solid phase first separating as the melt cools. It was necessary to convince petrographists that the most infusible phase was not necessarily the one to crystallize first. The work of Vogt's shows that we are dealing in most cases with a multi-component system following all the laws for such systems and differing from many systems that have been studied only in the greater readiness with which the melt hardens to a glass instead of to a crystalline mass.

The second part is concerned especially with the lowering of the freezing-point, with the heats of fusion, and with the specific heats. The mixtures of silicates are classified so far as may be according to Roozeboom's general types for systems in which solid solutions may occur.

The two parts bring out very clearly the importance of physical chemistry to petrographists and it is with special pleasure that we recall the fact that this very problem of the scientific study of the behavior of fused rock masses is now being taken up systematically by the Geophysical Laboratory at Washington. This book of Vogt's should be studied by every physical chemist who is interested in the future developments of his subject. The only criticism to be passed upon it is that the author in his enthusiasm has not always distinguished

sharply between what is exact in physical chemistry and what is only approximation theory.
Wilder D. Bancroft

Jahrbuch der Elektrochemie. *Berichte über die Fortschritte des Jahres. 1903. Herausgegeben von Heinrich Danneel. X. Jahrgang. 16 × 24 cm; pp. xii +930. Halle: Wilhelm Knapp, 1905. Price: paper, 26 marks.* — Some years ago the German electrochemical society developed into the Bunsen society. With this volume the *Jahrbuch der Elektrochemie* becomes a *Jahrbuch der physikalischen Chemie* in everything except title. Take it all in all, the change is a good one though the reviewer must confess to a slight feeling of regret. Dr. Julius Meyer writes the chapter on the phase rule and Dr. Sackur those on catalysis and contact chemistry. The chapters on the theory of electrons, dielectric conductivity, and electrical phenomena in gases are written by Dr. F. Harms. Dr. M. Mugdan contributes the chapters on the theory and practice of accumulators and on the aluminum rectifier while Dr. P. Askenasy writes those on inorganic products and the processes involved. Organic preparations fall as before to Prof. Elbs, while Dr. J. Hess discusses metals and electromagnetic separation. The chapters on the mass law and on hydrolysis are written by Dr. H. Ley while the remaining portions of the volume are the work of the editor.

Among the many interesting subjects treated in this volume may be cited the work on the Wehnelt interrupter, p. 40; on the capillary electrometer, p. 43; on the solidification of silicates and aluminates, p. 82; on antitoxines, p. 178; on platinum, iridium and nickel anodes, pp. 392, 403; on ozone and hydrogen peroxide, p. 395; on electrolysis with alternating currents, p. 413; on rotating electrodes, p. 477; on the mercury cathode, p. 479; on Birkeland's nitric acid process, p. 577; and on electric steel, p. 718.
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.

The significance of changing atomic volume IV. *T. W. Richards. Zeit. phys. Chem.*, 49, *5* (*1904*).—The more compressible an element, the greater is the contraction when a compound is formed. Other things being equal the more volatile compound has the larger molecular volume. Since polymerization and crystallization may alter the internal pressure, it is not difficult to account for apparent exceptions. *W. D. B.*

On regularities in homologous series. *O. Biach. Zeit. phys. Chem.*, 50, *43* (*1904*).—It was already known that a greater regularity in the melting-points of a homologous series was obtained if the series was divided into two, an odd and an even one. The author shows that this is true for the melting-points, the boiling-points, the molecular volumes, the viscosity, the optical rotation, the solubility, the heats of combustion, the electrolytic dissociation constants, the reaction velocities, the specific heats, the heats of formation, the dielectric constants, the rates of diffusion, and the migration velocities of the anions. *W. D. B.*

Components and the phase rule. *R. Wegscheider. Zeit. phys. Chem.*, 49, *229*; *W. Nernst. Ibid.*, *232*; *A. Byk. Ibid. 233* (*1904*); *R Wegscheider. Ibid.* 50, *357* (*1905*).—A continuation of the polemic (8, 512). *W. D. B.*

One-Component Systems

Heats of vaporization of oxygen and sulphur dioxide. *T. Estreicher. Zeit. phys. Chem.*, 49, *597* (*1904*).—The heat of vaporization of 1 gram of sulphur dioxide at atmospheric pressure was found to be 95.9 cal while Mathias deduced values of 95.7–96.2 cal. For 1 gram of oxygen the author finds 57.8 cal. Other people have obtained values varying from 50.8 (Behn) to 80 (Dewar). Shearer found 61 cal. *W. D. B.*

Physical-chemical studies on tin. VI. *E. Cohen and E. Goldschmidt. Zeit. phys. Chem.*, 50, *225* (*1904*).—The specific gravity of electrolytically precipitated tin is apparently a function of the current density, the value rising from 6.80 to 7.20 at 15° when the current density was increased from 0.75 to 12.50 amp/qdm. This variation is due to the crystals carrying down some stannous chloride. When a correction is made for this, the specific gravity of tetragonal or white tin at 15° is 7.25. Tetragonal tin changes into rhombic tin at about 170°; the exact temperature will be determined later. There are therefore three known, stable modifications of tin: gray tin, stable below 20; tetragonal or white tin, stable from 20° to about 170°; rhombic tin, stable from about 170° to the melting-point, 232°. *W. D. B.*

The question of accurate molecular weight determinations from the vapor density. *M. Reinganum. Zeit. phys. Chem.*, 48, *697* (*1904*).—"From the observations of Young on isopentane a very good value for the molecular weight was obtained, using an equation for a slightly compressed gas.

"By the same method good determinations of molecular weights were obtained from the observations of Ramsay and Steele [*7*, 597].

"From the law of corresponding states it is shown that the results of these experimenters on the variations of vapors from the gas laws are consistent.

"The variations were measured by a simple method." *W. D. B.*

The more accurate gas equation. II. *J. B. Goebel. Zeit. phys. Chem.*, 49, *129* (*1904*).—An attempt to deduce the formulas used in the previous paper (8, 512). It is doubtless a praiseworthy thing to construct interpolation formulas; but it does seem a pity not to be willing to call these formulas empirical.

W. D. B.

The more accurate gas equation. III. *J. B. Goebel. Zeit. phys. Chem.*, 50, *238* (*1904*).—A calculation for a number of substances of the specific attraction constant ϵ from the formula.

$$\epsilon = 10^8 \times 1.45 \frac{a}{M^2}.$$

W. D. B.

Two-Component Systems

Zinc-antimony alloys. *K. Moenkemeyer Zeit. anorg. Chem.*, 43, *182* (*1905*).—Freezing-point curve was determined, and found to have two maxima corresponding to Zn_3Sb_2 and ZnSb. Eutectics at 97.5, 37.5 and 21 percent zinc. A transformation point is found in zinc at 321°. The rise of this temperature with increasing amounts of antimony is taken as an indication that the compound Zn_3Sb_2 forms solid solutions with zinc. However, the eutectic was detected in compositions within 1 per cent of the composition of the compound. Zinc seems to separate pure from the compositions between 97.5 and 100 per cent Zn. The change from the α- to the β-form seems to occur at a definite temperature, from which it is inferred that $Zn_3Sb_2 + Zn$ as solid solution does not break down with the separation of Zn. Microstructure shows eutectic 5 percent either side of Zn_3Sb_2, and 2.5 percent either side of ZnSb. No examination was made to see if eutectic could be detected in alloys nearer the composition of the compounds. The temperature determinations were made on 25 gram samples and no mention was made as to whether or not the alloys were stirred to prevent supercooling. Since the work was under Tammann's supervision it is safe to assume that such important details were not overlooked. The heat of transformation from α-into β-zinc was calculated to be about 1 gram calorie. No annealing experiments were made to determine what were the limits of the solid solutions. The density of Zn_3Sb_2 is 6.30, and for ZnSb 6.41. It is not justifiable to quote Cooke's determinations of the composition of the solid and melt, in view of Joule's experiments showing how impossible it was to separate the crystals from the mother-liquor even with pressures of over 100,000 pounds per square inch. Four good photomicrographs accompany the paper.

E. S. S.

Freezing-point curves for nitrophenols and naphthalene. *A. Saposchnikow. Zeit. phys. Chem.*, 49, *688* (*1904*).—From mixtures of *o*-nitrophenol and naphthalene the two components crystallize pure. With dinitrophenol (2,4) and naphthalene a compound occurs which is stable at its melting-point; but the compound melts lower than the phenol. With trinitrophenol and naphthalene there is a compound, stable at its melting-point and melting higher than either of the components. The same case occurs with trinitrocresol and naphthalene. *W. D. B.*

The specific volumes as a characteristic of metallic compound. II. *E. Maey. Zeit. phys. Chem.*, 50, *200* (*1904*). — Data are given for zinc-antimony, cadmium-antimony, copper-antimony, silver-zinc, silver-cadmium, copper-cadmium, silver-mercury, zinc-mercury, cadmium-mercury, cadmium-zinc, bismuth-zinc, lead-zinc, bismuth-lead. No real care was taken to insure that the alloys had reached equilibrium; but the result is unsatisfactory even if we make full allowance for this. In the zinc-antimony curve the author finds only one compound instead of two. In the silver-zinc curve he gets nothing corresponding to the numerous breaks found by Heycock and Neville in the freezing-point curve. Density determinations, even if properly made, afford a very crude method of determining solid phases. *W. D. B.*

The phenomena occurring when the plait-curve meets the solubility curve. *A. Smits. Zeit. phys. Chem.*, 51, *193* (*1905*).—A general discussion of the relations when the solubility curve ends owing to solution and vapor becoming identical. This case is realized with ether and anthraquinone, mercuric iodide, silver nitrate, potassium nitrate, cadmium iodide, potassium iodide, or alizarine; also with ammonia and anthraquinone. The two curves do not meet with ether and anthracene, ether and *p*-oxybenzoic acid, ether and borneol, ethyl acetate and anthraquinone, acetone and anthraquinone. *W. D. B.*

The solubility of some sparingly soluble salts in water at 18°. *F. Kohlrausch. Zeit. phys. Chem.*, 50, *355* (*1904*).—The solubilities at 18° of thirty-three sparingly soluble salts have been calculated from the author's conductivity determinations. The results are presented in tabular form.

W. D. B.

The lowering of the freezing-point in very dilute solutions of strong electrolytes. *H. Jahn. Zeit. phys. Chem.*, 50, *129* (*1904*).—Very careful measurements were made on the freezing-points of dilute solutions of the chlorides of lithium, sodium, potassium and caesium; also of sodium and potassium bromides. The results cannot be made to fit the dilution law. For dilute solutions the author's more elaborate formula describes the facts. For concentrated solutions we are forced to assume increased migration velocities.

W. D. B.

The lowering of the vapor-pressure in aqueous solutions. *A. Smits. Zeit. phys. Chem.*, 51, *33* (*1905*).—The molecular lowering of the vapor-pressure of aqueous solutions of sodium chloride passes through a minimum at about *n*/2. No such phenomenon occurs with sodium nitrate solutions. Sodium nitrate solutions do not follow the dilution law but potassium nitrate solutions do, up to normal solutions, when the dissociation is calculated from the vapor-pressures. *W. D. B.*

Molecular weight determinations in solid solutions, III. *F. W. Küster. Zeit. phys. Chem.*, 50, *65* (*1904*).—The author has determined the freezing-point curve and boiling-point curve for mixtures of *p*-dichlor- and *p*-dibrombenzene. The two substances form a continuous series of solid solutions. Solubility determinations were also made in a 90 percent aqueous alcohol. No satisfactory distribution ratio could be calculated though the total molecular solubility increases practically linearly from one pure component to the others.

The freezing-point curve for trichlorphenol and tribromphenol showed the existence of two series of solid solutions with a eutectic temperature. Solubility determinations were also made with dilute methyl alcohol as solvent. These results present nothing unexpected.

One interesting point brought out in this work is that accurate melting-point determinations can be made in capillary tubes. Landolt had thought that this was not possible but the author shows that Landolt raised the temperature too rapidly. By not working under equilibrium conditions, Landolt, of course, obtained discordant results. *W. D. B.*

Molecular weight determinations in solid solutions. IV. *F. W. Küster. Zeit. phys. Chem.*, 51, *222* (*1905*).—The vapor-pressures of *p*-dibrombenzene and *p*-dichlorbenzene were determined and then the partial pressures of mixtures. From 0.43 molecular percent *p*-dichlorbenzene, the partial pressure curve for *p*-dibrombenzene appears to lie above the vapor-pressure for the pure bromide. The author seems to think that this difference is real; but it is much more probable that it is merely a matter of experimental error. *W. D. B.*

Vapor-pressures of solid solutions, II. *A. Speranski. Zeit. phys. Chem.*, 51, *45* (*1905*).—Experiments were made on isomorphous mixtures of *p*-$C_6H_4Br_2$ with *p*-C_6H_4ClBr and of *p*-$C_6H_4Br_2$ with *p*-$C_6H_4Cl_2$ at 0°–15°. The discussion of the results is not clear; but the conclusion reached is that the laws for liquid solutions hold for solid solutions, a conclusion which may mean anything.

W. D. B.

Properties of nitric acid and sulphuric acid mixtures. *A. Saposchnikow. Zeit. phys. Chem.*, 49, *697* (*1904*).—The vapor-pressure curve for mixtures of nitric and sulphuric acids at 25° shows a peculiar flat between 80 and 95 per cent nitric acid, for which no explanation is offered. The density curve shows a maximum at about 12.5 percent nitric acid. The specific conductivity curve shows a minimum at about 97.5 percent nitric acid and a maximum at about 7.5 percent. *W. D. B.*

The dissociation of hydrobromic and hydrochloric acids. *M. Bodenstein and A. Geiger. Zeit. phys. Chem.*, 49, *70* (*1904*).—At 1000° abs HCl is found to be 0.002 percent dissociated and 0.8 percent at 2000° abs. Hydrobromic acid is 0.18 percent and 6.0 percent dissociated at the same temperatures respectively.

W. D. B.

Multi-component Systems

Decomposition of hydrated mix-crystals, II. *R. Hollmann. Zeit. phys. Chem.*, 50, *567* (*1905*).—The author distinguishes four groups. The two components form the same hydrates; the two components form two sets of isomorphous hydrates but one component forms an intermediate hydrate which the other does not; the two components form one set of isomorphous solutions, while the other hydrates do not match; no stable hydrate of the one component is isomorphous with any hydrate of the other component. *W. D. B.*

The composition and solubilities of the double chlorides of iron and the alkalies. *F. W. Hinrichsen and E. Sachsel. Zeit. phys. Chem.*, 50, *81* (*1904*).—At 21° sodium chloride and hydrated ferric chloride apparently form a continuous series of solid solutions. With potassium chloride one double salt was found, $FeCl_3.2KCl.2H_2O$. At the potassium chloride end there is said to be a series of solid solution while it is left doubtful what happens at the ferric chloride end. With caesium chloride two double salts were obtained, $FeCl_3.3CsCl.H_2O$ and $FeCl_3.2CsCl.H_2O$. It is a little difficult to know what the authors actually found because they did not determine the water of crystallization in the solid solutions. They also speak of pure $FeCl_3$ crystallizing at 21° when it is obvious that they mean $FeCl_36H_2O$. One cannot help wondering whether they were equally careless in other details. *W. D. B.*

On decrease of solubility. I. *H. Euler. Zeit. phys. Chem.*, 49, *303* (*1904*).—Some experiments were made on the precipitating action of salts on ether, ethyl acetate and aniline. There is also a tabulation of the data for solutions saturated with respect to two salts having an ion in common. *W. D. B.*

On changes of solubility. *G. Geffcken. Zeit. phys. Chem.*, 49, *257* (*1904*).—Solubility determinations for hydrogen, oxygen, nitrous oxide and carbon dioxide in aqueous solutions. The percentage decrease of solubility is greater the lower the temperature. The percentage decrease in solubility is a function of the nature of the gas. Colloids have practically no precipitating effect. *W. D. B.*

On the existence of hydrates in concentrated aqueous solutions of electrolytes. *H. C. Jones and F. H. Getman. Zeit. phys. Chem.*, 49, *385* (*1904*).—Sixty-eight electrolytes have been studied and all gave too large molecular lowerings in concentrated solutions. In general the results are more abnormal the larger the amount of water of crystallization which the solid salts can take up. The authors conclude that practically all salts form hydrates in solution. *W. D. B.*

Chromate, bichromate and chromic acid. *R. Abegg and A. J. Cox. Zeit. phys. Chem.*, 48, *725* (*1904*).—Mercuric chromate was treated with varying concentrations of aqueous potassium bichromate and the amounts of basic mercuric chromate formed were determined. On the assumption that the equilibrium between mercuric chromate and basic mercuric chromate depends only on the amount of free chromic acid, the authors calculate the equilibrium between potassium chromate, potassium bichromate and chromic acid. The accuracy of the assumption was not tested. It appears that chromic acid is a weak acid and that a molecular solution of potassium bichromate is about 60 percent hydrolyzed into potassium chromate and free chromic acid. *W. D. B.*

Systems composed of silicic and hydrofluoric acids. *E. Baur. Zeit. phys. Chem.*, 48, (*1904*).—Fluosilicic acid vapor dissociates with decreasing pressure and rising temperature but it was not found possible to express this change mathematically. An aqueous fluosilicic acid with a concentration of 13.3 per cent H_2SiF_6 gives a vapor in which the ratio of hydrofluoric acid to silicon fluoride is the same as in the solution, namely $2HF.SiF_4$ (Cf. 8, 444). Experiments were also made on the equilibrium between silica and hydrofluoric acid. The "equilibrium constant" varied from 1.4×10^{-7} to 247×10^{-7}, and 163×10^{-7} is taken as the true value. From this constant the author calculates the heat of reaction. It may be worth noting that the agreement between the 'calculated' and the observed value was not close. *W. D. B.*

Addition to the "study of the equilibrium $CO + H_2O = CO_2 + H_2$." *O. Hahn. Zeit. phys. Chem.*, 48, *735* (*1904*).—A better though not a satisfactory agreement between theory and experiment (7, 402) can be obtained by using the earlier observations of Le Chatelier on the heats of reaction at different temperatures. *W. D. B.*

The effect of liquid air temperatures on the physical and other properties of iron and its alloys. *J. Dewar and R. A. Hadfield. Proc. Roy. Soc.*, 74, *326* (*1905*).—Small test pieces of iron alloys were tested as to tensile strength and ductility at the temperature of liquid air. It was found that this low temperature produced a marked increase in the strength and a decreased ductility. The increase in hardness is a continuous function of the temperature, and not due to the presence of a critical point at some lower temperature. For low carbon steels the increase in strength is about threefold, while the ductility falls to zero.

A specimen containing over 1 percent of carbon still remains soft after quenching in liquid air, a fact which the authors regard as remarkable. As is well-known, liquid air may be held in the mouth without freezing the tongue, which would seem to indicate that the rate at which it cools things is not so very great. The fact that it does not wet iron at ordinary temperatures would seem to assure a reasonably slow rate of cooling for the specimens which were quenched in liquid air. This view is supported by the authors' results, for the specimens so quenched all showed the properties of annealed iron. Consequently there does not seem to be much that is remarkable in the results of quenching steel in liquid air.

Iron alloyed with Si, Al, Tu, Cr and Cu, gave the same results as to the increase in strength, and diminished ductility at this low temperature.

Nickel acts energetically in the direction of reducing the brittleness induced in iron by these low temperatures. Thus while increased strength results, there is but little if any decrease in ductility.

Manganese steel, very low in carbon, behaves very much the same as the very low carbon steels. With 12.64 percent Mn and 1.23 percent carbon, the steel was very brittle at the liquid air temperature. It showed an elongation of 30 percent when it had returned to room temperatures. Quenching these steels in liquid air is without any more effect than would result from quenching them in water. These steels do not alter their properties due to exposure to low temperatures. Steels containing high carbon, and with chromium and nickel as the other elements, were more brittle, while with less carbon and more nickel the steel is practically unaffected by liquid air.

Ternary alloys with Ni-Si, Mn-Cr, Mn-Si, Cr-Al, Cr-Si, Cr-Cu, Cr-Tu, do not differ from the ordinary alloys, *i.e.*, they show increased tenacity, and decreased ductility, at 182°. While Fe-Cu-Mn shows an increased tenacity at low temperatures, it shows no decrease in ductility. In this alloy the 1.5 percent Cu present completely neutralized the effect of the manganese. Iron mixed with Co-Mn-Si, Cr-Mn-Si, or Ni-Mn-Al showed nothing unusual.

Iron with 0.6 percent C, 0.04 percent Mn, 14.55 percent Ni, is the most ductile form of iron known, although alloyed with two metals either of which would alone produce extreme brittleness. This alloy has an elongation of 75 percent and retains an elongation of 25 percent at the temperature of liquid air. With C 1.18, Mn 6.05, Ni 24.30, the metal is more ductile at −182° than at room temperatures. All of these test pieces were checked magnetically to make certain that there was no change in the magnetic properties of the iron, *i. e.*, presumably no change in the nature of the iron.

Pure nickel showed an increase in tenacity from 29-46 tons, and in ductility from 43-51 percent when immersed in liquid air. The manganese tested was comparatively brittle. Aluminum increases in tenacity from 8 to 15 tons, and in elongation from 7 to 27 percent. The following statement is rather remarkable. "Iron is a crystalline metal, whereas nickel appears to be much more amorphous; it is possible, therefore, that nickel tends to prevent iron crystallizing." The complete monograph is promised. *E. S. S.*

Vaporization of solids at ordinary temperature. *C. Zenghelis. Zeit. phys. Chem.*, 50, *219* (*1904*).—The author has suspended strips of silver foil over moistened CuO, ZnO, Fe_2O_3, Cr_2O_3, CrO_3, MnO_2, PbO, Pb_3O_4, PbO_2, CoO, Ur_3O_8, MoO_3, As_2O_3, Sb_2O_3. In the course of time the silver was attacked by the vapor of the oxide and an alloy of silver with the metal was formed. These alloys were usually gold-colored. In many cases the presence of the second metal could be shown analytically. *W. D. B.*

Theory of colloids. II. *J. Billitzer. Zeit. phys. Chem.*, 51, *129* (*1905*).—The essential features of the author's theory are that a precipitated colloid is practically neutral; that precipitating ions have the opposite electrical charge from the colloids which they precipitate;. that the precipitating ions act as condensation nuclei; and that a colloid is more stable the finer the particles. The author distinguishes between real and pseudo-colloids, the real or typical colloids being precipitated by very small concentrations of electrolytes while a much higher concentration is necessary to precipitate the pseudo-colloids. Colloidal metals, FeO_3H_3, As_2S_3, Sb_2S_3, etc. are typical colloids while albumen, gelatine, etc. are pseudo-colloids.

The author applies these principles to "the protective action which colloids exert upon each other; the mutual precipitation of colloids; the peculiarities of reversible and irreversible coagulation; the solvent action of certain ions; and some peculiarities of pseudo-colloids." The value of the paper is decreased by the author's inability to present his ideas in a clear-cut fashion. There seems also to be no good reason why the terms hydrosol and hydrogel should be barred. *W. D. B.*

On the gases dissolved in minerals. *K. Huettner. Zeit. anorg. Chem.*, 43, *8 (1905)*.—Gautier has already shown that Tilden's hypothesis as to the gases dissolved in minerals is incorrect. In this investigation the minerals were heated to 800°–850° in an atmosphere of CO_2. In thirty different minerals examined the gases resulting varied between 4–70 percent CO, 14–88 percent H, and 5–96 percent N. Small amounts of rare gases were found in some cases. The hydrogen comes from the action of water on ferrous compounds, while the CO results from the reduction of the CO_2 by hydrogen. A good deal of the hydrogen comes from the action of water on metallic iron from the iron mortar. The author found that by igniting the minerals in a stream of CO_2, allowing them to cool in a stream of hydrogen and after washing out the excess of hydrogen, igniting the mineral again in CO_2, quite appreciable amounts of hydrogen were absorbed, and could be driven off again by re-igniting. He showed that upon dissolving the mineral in acids, no CO resulted, thus proving that the CO detected results from the action of the hydrogen on the CO_2.

E. S. S.

Osmotic Pressure and Diffusion

Hydrodiffusion of electrolytes. *L. W. Öholm. Zeit. phys. Chem.*, 50, *309 (1904)*.—A series of very careful measurements on the rate of diffusion of electrolytes in aqueous solutions shows that the diffusion coefficient passes through a minimum as the solution is diluted. Nernst's formula appears to hold for infinite dilution. The results are in accordance with the prediction of Arrhenius that with increasing concentration the diffusion coefficient should first decrease owing to decreased dissociation and should then increase owing to molecular attraction, etc. *W. D. B.*

The diffusion of salts in solution. *J. C. Graham. Zeit. phys. Chem.*, 50, *257 (1904)*.—This paper gives the additional experimental details which were not included in the first and shorter publication (8, 376). *W. D. B.*

Velocities

The effect of metals on the hydrolysis of cane sugar. *R. Vondracek. Zeit. phys. Chem.*, 50, *560 (1905)*.—From these experiments it appears that pure metals as such exert no catalytic effect on the inversion of sugar. The action is due either to the hydroxides of the metals or to the oxygen dissolved in them. *W. D. B.*

The kinetics of nitration. *H. Martinsen. Zeit. phys. Chem.*, 50, *385 (1904)*.—The nitration of nitrobenzene in concentrated sulphuric acid is a reaction of the second order. Nitrous acid has no effect. The reaction velocity is a maximum for a solution containing 0.7 mol. water to one of sulphuric acid. The nitration of dinitrotoluene (2,4) and of the three nitrobenzoic acids is also a reaction of the second order. In aqueous solution the nitration of phenol is a complicated reaction. The velocity increases with increasing concentration of nitric, nitrous and sulphuric acids, of potassium, sodium and strontium nitrates; it decreases with increasing concentration of phenol. *W. D. B.*

Chemical kinetics of the benzoin synthesis. *E. Stern. Zeit. phys. Chem.*, 50, *513* (*1905*).—The rate of formation of benzoin is proportional to the concentration of potassium cyanide and to the square of the concentration of the benzaldehyde. The reaction appears to be due to the catalytic action of cyanide as anion, the complex anion of potassium silver cyanide having no effect. At 0° addition of benzaldehyde to a solution of potassium cyanide in aqueous alcohol causes a decrease in the conductivity; but this effect has practically disappeared at 70°. *W. D. B.*

Hypochlorous acid, III. *J. Sand. Zeit. phys. Chem.*, 50, *465* (*1904*).—At 70° the rate of decomposition of chloric acid by hydrochloric acid is apparently a reaction of the fifth order, according to the equation,

$$ClO'_3 + 2H^{\cdot} + 2Cl' = ClO' + 2HClO.$$

This reaction runs practically to an end in the other direction at ordinary temperatures. From measurements of the two reaction velocity constants and the heat of reaction the author calculates the equilibrium constants at 70° and at 20°. *W. D. B.*

The oxidation of the iodide ion to hypoiodite as an intermediate stage in some reactions. *J. Brode. Zeit. anorg. Chem.*, 49, *208* (*1904*).—"It is shown that the rate of the three reactions:

I. $2H_2O_2 = 2H_2O + O_2$ (with iodide ion catalysis in neutral solution),

II. $H_2O_2 + 2HI = 2H_2O + I_2$ (in acid solution),

III. $H_2O_2 + 2Na_2S_2O_3 + 2H^{\cdot} = 2H_2O + Na_2S_4O_6 + 2Na^{\cdot}$ (with iodide ion catalysis in dilute acid solution),

follow the same formula $dx/dt = kC_{H_2O_2}C_I$ and that the constants are the same for reactions II and III while that for reaction I is twice as large. This is due to the fact that the reaction velocities in all three cases depend on the same intermediate reaction (probably $H_2O_2 + I' = H_2O + OI'$)." In reaction I two intermediate stages are assumed. *W. D. B.*

The rate of substitution of a nitro group in ***o-*** **and** ***p*-dinitrobenzene by an alcoholate.** *A. Steger. Zeit. phys. Chem.*, 49, *329* (*1904*).—Reviewed (3, 515) from Recueil Trav. Pays-Bas., 18, 13 (1899). *W. D. B.*

Effect of water on the rate of substitution of a nitro group in ***o*-dinitrobenzene by oxymethyl or oxyethyl.** *C. A. Lobry de Bruyn and A. Steger. Zeit. phys. Chem.*, 49, *333* (*1904*).—In aqueous alcoholic solution the reaction velocity decreases with increasing water content while the reverse is true over the concentrations in question when methyl alcohol is used instead of ethyl alcohol. *W. D. B.*

Effect of water on the rate of formation of ether. *C. A. Lobry de Bruyn and A. Steger. Zeit. phys. Chem.*, 49, *336* (*1904*).—The rate of reaction for ethyl iodide and sodium ethylate in aqueous alcohol solution decreases with increasing water content. With sodium methylate dissolved in methyl alcohol, addition of water first increases and then decreases the rate of reaction. *W. D. B.*

The rate of substitution of a halogen by an oxyalkyl group in some nitrohalogen derivatives of benzene. *P. K. Lulofs. Zeit. phys. Chem.*, 49, *341* (*1904*).—The rate of reaction for sodium ethylate in alcoholic solution on a nitrohalogen benzene compound is decreased by addition of water. With methyl alcohol and sodium methylate addition of water first increases and then decreases the reaction velocity. *W. D. B.*

The mechanism of the ether formation from alkyl halides and alcoholates. *C. A. Lobry de Bruyn and S. Tijmstra. Zeit. phys. Chem.*, 50, *436* (*1904*).—It is believed that the reaction between ethyl iodide for instance and sodium ethylate depends to a certain extent on an infinitesimal dissociation of the ethyl iodide. While the sodium iodide formed during the reaction appears to have no effect on the rate, a direct addition of sodium iodide does decrease the rate. It was thought that the ether formed during the reaction might neutralize the effect of the sodium iodide formed simultaneously; but addition of equivalent quantities of sodium iodide and ether causes the same decrease in rate that was obtained by adding sodium iodide alone. No explanation for this phenomenon has yet been found. *W. D. B.*

The hydration of milk-sugar in solution. *C. S. Hudson. Zeit. phys. Chem.*, 50, *273* (*1904*).—Reviewed (9, 71) from Jour. Am. Chem. Soc., 26, 1065 (1904).

Heterogeneous catalytic reactions, II. *M. Bodenstein. Zeit. phys. Chem.*, 49, *41* (*1904*); 50, *610* (*1905*).—The first paper is merely an expansion of one which has already been reviewed (8, 448). The second is a rather unsatisfactory reply to a criticism by Stock (next review). *W. D. B.*

Note on the decomposition of arsine. *A. Stock. Zeit. phys Chem.*, 50, *111* (*1904*).—A criticism of a paper by Bodenstein (8, 448 and preceding review). *W. D. B.*

Reaction velocity in catalytic reactions. *C. Kullgren. Zeit. phys. Chem.*, 51, *108* (*1905*).—A reply to Euler (8, 521). *W. D. B.*

The decomposition of ammonium nitrite. *A. A. Blanchard. Zeit. phys. Chem.*, 51, *117* (*1905*).—A reply to Arndt (8, 523). *W. D. B.*

The action of enzymes, I. *H. P. Barendrecht. Zeit. phys. Chem.*, 49, *456* (*1904*).—The author develops the hypothesis that the action of enzymes is one of radiation. In consequence he deduces quite different formulas from those obtained by Henri. *W. D. B.*

Theoretical and experimental investigations on the action of enzymes, toxines, antitoxines and agglutinines. *V. Henri. Zeit. phys. Chem.*, 51, *19* (*1905*).—The author outlines his programme for studying the enzymes. He believes that the action of enzymes is to be divided into at least three parts: the distribution between the colloid and the solution; the rate at which this distribution takes place; and the reaction velocity itself. The author criticizes the hypotheses of Barendrecht, Visser and Herzog, explaining why he thinks each is radically wrong. *W. D. B.*

The rate of solution of zinc. *E. Brunner. Zeit. phys. Chem.*, 51, *95* (*1905*).—Zinc containing lead dissolved in hydrochloric acid at a much slower rate than could be accounted for. The rate of dissolving of pure zinc in an iodine solution appears to be a function solely of the rate of diffusion of the zinc. Zinc containing lead dissolves less rapidly. When zinc dissolves as anode, the current density for a given polarization is practically independent of the concentration of the zinc salt in the solution provided this concentration is not excessively small. *W. D. B.*

Theoretical discussion of reactions taking place in two or more successive stages. *C. L. Jungius. Zeit. phys. Chem.*, 49, *368* (*1904*).—The author shows that the apparent reaction velocity may be abnormal even in cases where equilibrium is reached. There is nothing new about this (Cf. 4, 705). *W. D. B.*

Comment on the paper by C. L. Jungius. *A. Mittasch. Zeit. phys. Chem.*, 50, *613* (*1905*).—It is claimed that the substance of Jungius's paper (preceding review) is to be found in an article by the author (6, 277). As a similar treatment is to be found in a paper by the reviewer (4, 705) it seems as though the author were unnecessarily sensitive. *W. D. B.*

Reaction velocity and free energy. *M. Bodenstein. Zeit. phys. Chem.*, 49, *61* (*1904*).—It is pointed out that the rates with which hydrogen combines with the halogens seem to stand in some relation to the free energies of the systems. These should, therefore, be good systems with which to begin the study of the factors governing reaction velocities. *W. D. B.*

On reaction velocity and free energy. *E. Brunner. Zeit. phys. Chem.*, 51, *106* (*1905*).—It is pointed out that the chemical potential depends on the logarithm of the concentrations while the reaction velocity is proportional to the concentrations. The author does not see how this can be reconciled with the formula.

$$\text{Reaction velocity} = \frac{\text{Driving force}}{\text{Chemical resistance}}.$$

The author has overlooked the fact that the electrical potential depends on the logarithm of the concentrations and yet we have the relation $C = E/R$ where the current is approximately proportional to the concentration in the Daniell cell for instance if we keep the electromotive force constant by diluting both solutions equally. *W. D. B.*

Electromotive Forces

Mercuric sulphate and normal cells. *G. A. Hulett. Zeit. phys. Chem.*, 49, *483* (*1904*).—In order to obtain mercurous sulphate entirely free from basic salt, it should be formed by electrolyzing a sulphuric acid solution (1:6) using a mercury anode and keeping the solution well stirred. The current density is about 0.5 amp/qdm. The mercurous sulphate should be washed finally with cadmium sulphate solution if intended for the Weston cell and with zinc sulphate if intended for the Clark cell. *W. D. B.*

Reduction of mercurous chloride by silver chloride. *J. N. Brönsted. Zeit. phys. Chem.*, 50, *481* (*1904*).—In the cell Ag | *AgCl* KCl *HgCl* | Hg the current flows through the solution from the silver to the mercury although the reduction of mercurous chloride by silver is an endothermal reaction. The author determined the temperature coefficient in this cell and showed that the Helmholtz formula applies. *W. D. B.*

The electromotive forces at the surface of animal membranes in contact with salt solutions. *G. Galeotti. Zeit. phys. Chem.*, 49, *542* (*1904*).—The living skin of the frog shows a potential difference against salt solutions while the dead skin does not. The sign and magnitude of the potential difference varies with the nature of the salt solution. There is no potential difference with solutions of potassium chloride, bromide or iodide. The results can best be explained by the theory of concentration cells assuming different permeabilities of the inner and outer layer of the skin for different ions. *W. D. B.*

Polarization with cathodic evolution of hydrogen. *J. Tafel. Zeit. phys. Chem.*, 50, *641* (*1905*).—The experiments were made with such current densities that a copious evolution of hydrogen took place. The cathode potential increases with increasing current density; and, with most metals, varies also with the time. The metals, lead, cadmium, silver, and copper, appear to have two different states as shown by two different potentials. If some of the anode solution is added to the cathode solution, a fall of potential takes place. The substance in the anode solution which produces this effect is apparently not an oxidizing agent. A more plausible hypothesis seems to be that it is platinum. With mercury and with platinized platinum a very constant cathode potential is obtained. With mercury and to a lesser extent with cadmium and lead the relation of the cathode potential E to the current density is given by the equation

$$E = a + b \log J$$

where a and b are constants. The cathode potential decreases with rising temperature although the value of b increases with rising temperature in the case of mercury. *W. D. B.*

Relations between cathode potential and electrolytic reduction. *J. Tafel and K. Naumann. Zeit. phys. Chem.*, 50, *713* (*1905*).—The electrolytic reduction of caffeine and succinimide in sulphuric acid solution takes place only with cathodes of mercury, lead and cadmium.

The reduction does not take place at lead cathodes when the potentials of these in pure acid fall below 1.6-1.7 volts.

Although the potentials of lead and mercury are the same in pure acid, caffeine is reduced more rapidly at a mercury cathode and succinimide at a lead cathode.

The state of the lead surface is of minor importance. Previous results to the contrary were due to impurities in the electrolyte which were more disturbing with polished lead cathodes than with 'prepared' ones.

In dilute sulphuric acid solution addition of caffeine depolarizes a mercury cathode. Small additions of caffeine increase the potential of a lead cathode slightly while larger additions decrease it. Small additions of succinimide increase the potentials of mercury and lead. Addition of caffeine depolarizes a tin cathode to a certain extent although no reduction can be detected.

In the reduction of caffeine the relation between cathode potential and reduction efficiency can be expressed by logarithmic formulas similar to that obtained by Haber in his work on nitrobenzene. The authors assume that the evolution of hydrogen and the reduction are co-ordinate irreversible processes and that the cathode potential is due "to the compulsory accumulation of hydrogen in some form at the surface of the cathode." *W. D. B.*

The behavior of iridium, platinum, and rhodium anodes in dilute sulphuric acid. *J. B. Westhaver. Zeit. phys. Chem.*, 51, *65* (*1905*).—In *n*/10 H_2SO_4 iridium anodes are the least polarizable, rhodium anodes come next, while platinum anodes polarize the most readily when high current densities are used. With low current densities platinum is less readily polarizable than iridium. With iridium electrodes a value of 1.06 volts is obtained for the hydrogen-oxygen gas cell. It is pointed out that one must be careful about interpreting the breaks in the current-voltage curve. *W. D. B.*

Comment on the paper by Messrs. Luther and Brislee. *E. Bose. Zeit. phys. Chem.*, 49, *227* (*1904*).—Attention is called to the fact that Luther and Brislee (8, 146) have apparently overlooked an earlier paper by the author (3, 58). The author believes that Luther and Brislee would have modified their conclusions somewhat if they had been familiar with the literature.

W. D. B.

Anodic decomposition curve for hydrochloric acid between platinum electrodes. *R. Luther and F. J. Brislee. Zeit. phys. Chem.*, 50, *595* (*1905*).—A reply to Bose (preceding review.) *W. D. B.*

Addition to the paper on electro-capillary phenomena. *J. Billitzer. Zeit. phys. Chem.*, 49, *709* (*1904*).—Some additional data are cited to prove that the previous experiments (8, 590) were not vitiated by the action of dissolved oxygen on mercury. *W. D. B.*

Theory of electrocapillary phenomena, III. *J. Billitzer. Zeit. phys. Chem.*, 51, *167* (*1905*).—It is pointed out that we can get an agreement between theory and experiment for the relation between potential difference and the maximum surface tension of mercury if we assume that the surface tension of mercury depends on the potential difference as well as on the thickness of the electrical double layer. The paper deals chiefly with the varying polarization capacity of mercury. *W. D. B.*

Electrolysis and Electrolytic Dissociation.

Physical-chemical studies on so-called explosive antimony. II. *E. Cohen, E. Collins and T. Strengers. Zeit. phys. Chem.*, 50, *291* (*1904*).—Experiments were made with aqueous solutions of antimony trichloride, tribromide, triiodide, and trifluoride; also with antimony trichloride in methyl alcohol solution. In each case the apparent equivalent weight was a function of the current density. Since no explosive antimony was formed during the electrolysis of the fluoride solution, it is probable that the apparent variation is not necessarily connected with this phenomenon. Merely as a precaution it seems to the reviewer that it would be desirable to make one series of runs with antimony fluoride, using an antimony cathode instead of a platinum one.

W. D. B.

A new process for preparing electrolytic iron. *S. Maximowitsch. Zeit. Elektrochemie*, 11, *52* (*1905*).—It has been shown by others that electrolytic iron contains an excess of hydrogen which renders it very brittle. The author seeks to avoid the presence of the hydrogen ion in the electrolyte by using the carbonate solution. The bath consisted of 20 percent $FeSO_4 + 7aq$, 5 percent

$MgSO_4 + 7aq$, in six liters. To this 25 grams of $NaHCO_3$ is added. The skin of ferric salt which forms on the surface serves to protect the bath from further oxidation. From time to time, more carbonate is added. The concentration of the $Fe(HCO_3)_2$ in the bath was 0.23 percent. The current density was between 0.2 and 0.3 ampere. The first precipitate was slightly brittle, but as the bath aged, the metal deposited reached a tensile strength of 5180 kg/cm², and could be bent sharply without breaking. The current efficiency reached 99 percent. The bath can be renewed by running in a stream of CO_2. In view of the fact, that the beneficial effect of magnesium salts on nickel deposits, is due to the formation of a solid solution of the magnesium in nickel, it would be interesting to learn if it exercises a similar influence in this case. *E. S. S.*

Conductivity determinations on solutions of sodium in absolute and aqueous alcohols and in mixtures of two alcohols. *S. Tijmstra. Zeit. phys. Chem.*, 49, *345* (*1904*).—Solutions of sodium in absolute methyl alcohol conduct better than those in absolute ethyl alcohol, and these last conduct better than solutions in absolute propyl alcohol. No limiting values can be determined for these solutions. Owing to the decrease in viscosity the molecular conductivity of solutions in propyl alcohol increases faster than the dilution. The behavior of solutions in mixed alcohols can be calculated from the behavior of the solutions in the pure solvents. Addition of water increases the conductivity of all ethyl alcohol solutions and of concentrated methyl alcohol solutions. In more dilute methyl alcohol solutions addition of water causes the conductivity to pass through a minimum. It is suggested that this may be due to a change of migration velocity. *W. D. B.*

Electrical conductivity of sodium and potassium chlorides in aqueous alcohol. *B. Schapire. Zeit. phys. Chem.*, 49, *513* (*1904*).—The molecular conductivity of sodium and potassium chlorides in aqueous alcohol decreases with increasing alcohol content, the percentage decrease becoming less as the total amount of alcohol increases. For any given alcohol concentration the results can be expressed by the Kohlrausch formula, so-called,

$$\frac{\Lambda_\infty - \Lambda}{\Lambda^p} = cn^{\frac{1}{2}}$$

where p and c are constants deduced for that series from the observations. Wakeman's formula holds for all the solutions of sodium chloride in which the concentration of the salt is held constant while that of the alcohol varies. From the results the author concludes that alcohol changes the degree of dissociation and the migration velocities. *W. D. B.*

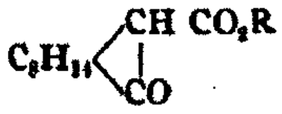
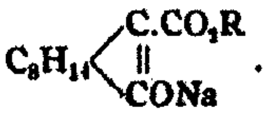
Measurement and calculation of equilibria for highly dissociated acids. *K. Drucker. Zeit. phys. Chem.*, 49, *563* (*1904*).—By assuming arbitrary values for the migration velocity of hydrogen it is possible to make some but not all of the stronger acids follow the dilution law. Calculations were made of the distribution constant for benzene and water, the electrolytic dissociation constant in water, and the polymerization constant in benzene. [It seems to the reviewer very doubtful whether such calculations show anything more than skill in juggling data.] Only one variation from the dilution law for mixtures of two acids could be detected in solutions more dilute than 0.02*n*. With more concentrated solutions variations could be detected. *W. D. B.*

Determinations of complex acids by means of isohydric solutions. *R. Hofmann. Zeit. phys. Chem.*, 51, *59* (*1905*).—Sulphuric and iodic acids follow the laws for isohydric solutions and therefore form no complexes. Chromic and iodic acids do not follow these laws and therefore form complexes. Isohydric solutions of sulphuric and phosphoric acids or of hydrobromic and phosphoric acids could not be prepared. The conclusions are valid only so long as one admits that isohydric solutions should show no change on mixing (4, 274). *W. D. B.*

Dielectricity and Optics

Fluorescence and the solvent. *H. Kauffmann and A. Beisswenger. Zeit. phys. Chem.*, 50, *350* (*1904*).—The authors have found a number of substances which fluoresce with different colors depending on the nature of the solvent. Raising the temperature causes a marked displacement towards the violet end of the spectrum. The authors believe that there is a connection between the displacement of the fluorescence and the dielectric constant of the solvent. *W. D. B.*

The effect of inactive substances on the optical rotation of the glucoses. *I. A. Milroy. Zeit. phys Chem.*, 50, 443 (*1904*).—The optical rotation of β-glucose is increased by phosphoric acid, arsenic acid, boric acid, sodium chloride, sodium sulphate, potassium nitrate, calcium chloride, barium chloride, magnesium chloride, aluminum chloride, aluminum acetate, cerium sulphate, lead acetate, sodium tungstate, ammonium molybdate, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetone, acetaldehyde, and glycerol. The optical rotation is decreased by bases and by borax, mercuric chloride, aniline hydrochloride, dimethylaniline hydrochloride, phenol and pyrogallol. Magnesium sulphate, ammonia alum, thorium nitrate, uranyl nitrate, copper nitrate and ferric chloride have no effect. *W. D. B.*

Salt formation in solutions. I. *J. W. Brühl and H. Schröder. Zeit. phys. Chem.*, 50, *1* (*1904*).—By spectrochemical methods it is shown that in methyl, ethyl, and amyl alcohol solutions the ketone ester  $C_8H_{14}<\begin{matrix}CH\ CO_2R\\ |\\ CO\end{matrix}$ changes into the enol salt  $C_8H_{14}<\begin{matrix}C.CO_2R\\ \|\\ CONa\end{matrix}$. This salt is somewhat dissociated in dilute methyl and ethyl alcohol solutions but not in amyl alcohol solutions. The different chemical behavior of this salt in different salts is referred to dissociation and polymerization. *W. D. B.*

Formation of salts in solution. II. *J. W. Brühl and H. Schröder. Zeit. phys. Chem.*, 51, *1* (*1905*).—When acetacetic ester is added to an alcoholic solution of sodium ethylate, there is an instantaneous change to the enol form. The general reaction is the same as that studied in the first paper (preceding review). *W. D. B*

The possible decomposition of racemic compounds by circularly-polarized light. *A. Byk. Zeit. phys. Chem.*, 49, *641* (*1904*).—After a discussion of the methods proposed for making optically asymmetric substances it is shown that alkaline copper dextro- and laevo-tartrates have slightly different absorption coefficients for circularly-polarized light. From this it is deduced that an alkaline copper racemate solution would gradually become optically active if exposed to circularly-polarized light. The action of the earth's magnetism on the circularly-polarized light reflected from water surfaces is such that we are said to have conditions which account for the development of an asymmetric flora. *W. D. B.*

Action of low temperatures on dye-stuffs. *J. Schmidlin. Comptes rendus,* 139, *731* (*1904*).—At the temperature of liquid air an alcoholic solution of rosaniline hydrochloride is much less red than normally but shows a beautiful yellow green fluorescence. Alcoholic fuchsine and eosine solutions show fluorescence at low temperatures. Methylene blue and malachite green show no change and no change could be detected in any solid dye-stuff or in any dyed silk or cotton. *W. D. B.*

The spectra of compounds. *E. Wiedemann. Boltzmann's Festschrift, 826* (*1904*).—When studying the electroluminescence of inorganic compounds, a special type of spectra was obtained. These spectra consist of a continuous light band upon which are superimposed narrow darker or lighter bands. A description is given of the spectra of a number of inorganic compounds. *W. D. B.*

Disappearance in the oscillating spark of lines present in the spectra from certain stars. *A. de Gramont. Comptes rendus,* 139, *188* (*1904*).—The author has determined what lines in the spectrum of silicon do not disappear under a self-induction of 0.03 henry and what lines do. The lines that disappear are to be found only in the hottest or helium and hydrogen stars. Stars like the sun show the lines appearing in the arc spectrum while still cooler stars show no lines of silicon. What Lockyer has considered to be the most persistent lines of silicon are believed by the author to have nothing to do with silicon and to be air lines. *W. D. B.*

Spectrum regularities and the atomic weight of radium. *G. Rudorf. Zeit. phys. Chem.,* 50, *100* (*1904*).—The author shows that the formulas d/A = const and $\log A = a + b \log d$ are not exact, where A is the atomic weight and d the difference in oscillation frequency for a pair of lines in the arc spectrum. The calculation of 258 for the atomic weight of radium is, therefore, unsound. No pairs have yet been found in the lithium spectrum. *W. D. B.*

Crystallography, Capillarity and Viscosity

The permanence of crystallitic forms in crystals. *F. Osmond and G. Cartaud. Comptes rendus,* 139, *404* (*1904*).—Attention is called to some of the peculiarities that may result from creating a surface film when polishing an alloy. The remedy is of course to remove the surface film. *W. D. B.*

The evolution of structure in metals. *G. Cartaud. Comptes rendus,* 139, *428* (*1904*).—The author has succeeded in polishing zinc, tin and lead alloys. When the surface film is removed the outlines of the crystals are seen. It is a little difficult to make out exactly what the author thinks about the cellular structure which is obtained on etching the surface film. *W. D. B.*

Contribution to the crystallography of the salts of NH_4, K, Rb, and Cs. *B. Gossner. Zeit. Kryst. Min.* 40, *69* (*1904*).—By means of density determinations on the crystals which separate from the solutions of the mixed salts, the author tries to show the relations existing between the salts of the alkalies.

NH_4Cl–NH_4I. From the density determinations it seems that these salts form only a very limited series of mixed crystals. It is not possible to state the limiting concentrations because the author made no analyses.

KI–NH_4I. From the density determinations it would seem that these salts are completely isomorphous.

Double salts of ferric chloride with NH_4Cl, KCl, $RbCl$, and $CsCl$.

Formula	Density	*a* : *b* : *c*	
$2KCl.FeCl_3H_2O$.	2.000	0.6847 : 1 : 0.7023.	Rhombic.
$2KCl.FeCl_3H_2O$.	2.372	0.6959 : 1 : 0.7171.	"
$2RbCl.FeCl_3H_2O$.	2.897	0.6676 : 1 : 0.7186.	"
$2CsCl.FeCl_3H_2O$.	3.317	1.0724 : 1 : 0.4595.	"

The caesium salt differs widely from the other alkalies not only in its axial ratio, but also in having no cleavage, whereas the other alkalies have a distinct octahedral cleavage. By changing the conditions of crystallization, the author was able to get a complete series of densities for mixed crystals of the caesium and ammonium salts. The series consisted of two kinds, the ammonia type and the caesium type. The compositions of the two are not given. From this and other experiments the author concludes that the salts of NH_4, K, Rb, and Cs, form an isomorphous group which show also isodimorphism. In the pure condition, only the one form is known for the salt, the second modification occurring in the isomorphous mixtures. *E. S. S.*

The thickness of the capillary film between homogeneous phases of liquid and vapor, and the critical phenomena. *G. Bakker. Zeit. phys. Chem.*, 49, *609* (*1904*).—The surface layer between liquid and vapor is very thin, possibly infinitely thin, near the freezing-point. Near the critical temperature the film may be very thick and may show a continuously varying density. In this way the author accounts for the so-called abnormal results obtained by de Heen, Mathias, Traube, Teichner and others. It is not necessary to assume a difference between liquid and gas particles. *W. D. B.*

Surface-tension influences on beer and beer brewing. *F. Emslander and H. Freundlich. Zeit. phys. Chem.*, 49, *317* (*1904*). — The authors sum up their results in the following words. "Many of the phenomena noted in connection with beer and its preparation may be explained as due to surface-tension effects (absorption of colloids, heat of gelatinization, effect of surface on supersaturation of gases, etc.)." *W. D. B.*

Internal friction of solutions. *A. E. Dunstan. Zeit. phys. Chem.*, 49, *590* (*1904*).—Mixtures of alcohol with benzene and benzaldehyde show a minimum viscosity. Mixtures of water with methyl alcohol, ethyl alcohol and acetic acid show a maximum viscosity. There is neither maximum nor minimum for mixtures of alcohol with acetone, carbon bisulphide and mercaptan.

W. D. B.

ELECTROLYTIC CHROMIUM, II

BY H. R. CARVETH AND B. E. CURRY

(*a*) *Unusual cathodic deposits.* (*b*) *Previous work on electrolysis of chromic acid.* (*c*) *Chemical reactions of chromic acid.* (*d*) *Electrochemical relations.* (*e*) *Preliminary electrolyses.* (*f*) *Experiments with pure acid.* (*g*) *Effect of probable impurities.* (*h*) *Comparison of efficiencies.* (*i*) *Effect of products of reaction.* (*j*) *Conclusions.*

(*a*) *Unusual Cathodic Deposits.*—In the first paper on "Electrolytic Chromium"[1] it was remarked that a great diversity of opinion existed as to the possibility of depositing chromium from solutions of chromic acid or chromates. The selection of such a problem for investigation would by many chemists be regarded as an absolute waste of time; but a brief review of the cases where unexpected precipitations at the cathode had been observed confirmed us in the belief that the subject deserved study. The results which are presented in this paper will show that the work of a chemist which for half a century has been considered absolutely false can now, in part at least, be repeated and that a number of hopelessly contradictory statements made by different observers may be reconciled.

In dealing with the cases where the anion or a part of it is deposited at the cathode, two distinct classes of phenomena are met; in the first, the element deposited is a conductor, in the second it is a non-conductor of electricity. In the case of the latter, there is very little doubt that the deposition is not a primary electrolytic effect but that it is due to chemical replacement or reaction. As illustrations may be cited the cathodic deposition of iodine, sulphur and selenium from aqueous solutions of their "ic" acids.

The fused or aqueous alkaline salts of the following elements have served as electrolytes from which have been obtained the conducting metals—lead, tin, zinc, tellurium, arsenic, silicon,

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[1] Carveth and Mott: Jour. Phys. Chem., 9, 231 (1905).

molybdenum, tungsten, uranium, ruthenium and osmium. In these cases the metal is supposed to exist in the solution mainly as part of the anion; nevertheless, to explain conductivity and other results, the assumption has to be made that metallic cations are also present in the solution. The electrodeposition of the metal from such solutions is effected only when a definite electromotive force has been reached. Two explanations of this fact are given: The first is that the deposition from the solution is not necessarily electrolytic but is more probably chemical, being caused by the reaction between the hydrogen or alkali metal and the electrolyte; the second regards the deposition as primarily electrolytic; since the relative number of cations of the element may be very small, the efficiency may be very low.

Does chromium in the chromates exist as part of the anion or part of the cation? Hittorf and Lenz[1] have measured the relative velocity n of the cation in potassium chromate and have found for dilution $v = 1.85$, $n = 0.488$(H); for $v = 2$, $n = 0.49$(L); for $v = 4$, $n = 0.53$(L); for potassium bichromate $v = 4.3$, $n = 0.498$(H). Walden[2] has found the following values for the molecular conductivity (μ) of the various chromates at the dilutions named (v).

	$0.5K_2CrO_4$	$0.5K_2Cr_2O_7$	$0.5K_2Cr_3O_{10}$	H_2CrO_4
v	μ	μ	μ	μ
32	121.2	114.4	275.4	354.5
64	127.5	116.6	283.0	358.2
128	132.1	117.5	285.9	360.6
256	136.0	118.0	286.0	360.1
512	138.4	118.6	283.4	358.1
1024	140.5	120.8	278.2	354.2

Ostwald[3] pointed out that chromic acid is weaker than carbonic, that it gives very small depressions of the freezing-point and that its salts are of the type $M_2Cr_2O_7$; these reasons combined with the results of Walden have caused him to ascribe to chromic acid in solution the formula $H_2Cr_2O_7$. In direct oppo-

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[1] Ostwald: "Lehrbuch," 2, 1, 607.

[2] Zeit. phys. Chem., 2, 71 (1888).

[3] Ibid., 2, 78 (1888).

sition to Ostwald, Abegg and Cox,[1] consider that in a bichromate solution there are present few Cr_2O_7 ions, and that the ions are formed from the monochromate which being a weak acid hydrolyzes; also that CrO_3 exists free in the solution. The greater conductivity of the monochromates as compared with the bichromates which hold the same amount of alkali, they explained by assuming that the chromate ion moves more rapidly than the bichromate ion, and that in the case of the monochromate the hydroxyl ion produced in the hydrolysis increases the conductivity. The first assumption is not in accord with the results of Hittorf and Lenz as recorded above.

Connected with the study of constitution is the heat of neutralization. Thomsen found that when chromic acid was neutralized by one, two or four molecules of sodium hydrate, there was a heat evolution of 13100, 24700, 25200 calories, whereas for sulphuric acid similar experiments gave 14600, 31000 and 31000 calories. On the other hand, chromic acid when treated with a stronger acid such as hydrochloric forms a chromic salt; in solution, therefore, it should be ionized the same way as other weak bases.

Is the evidence as thus summed up absolutely conclusive that the constitution of chromic acid in solution is well known, that the chromium always exists as part of the anion, and that at no time the CrO_3 dissociates to form hexavalent chromium cations?

(*b*) *Previous Work on the Electrolysis of Chromic Acid.*—Since the anodic oxidation of chromic salts to chromates is a work of commercial importance, considerable work has been done upon it; in regard to the reactions at the cathode, the statements made are very unsatisfactory. The first one to undertake the electrolysis of the acid seems to have been Geuther.[2] His electrolyzing vessel was provided with sealed-in platinum electrodes; working with a current from four Bunsen elements, he examined the gas evolution at the electrodes and the amount of the metal deposited, while the concentration of the solutions

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[1] Zeit. phys. Chem., 48, 725 (1904).

[2] Liebig's Ann., 99, 314 (1856).

was varied. He was able to weigh the chromium which he obtained. One set of his results is given in Table I. The I which he thought he was using is practically the tenth part of an ampere, since calculation (Table I) indicates that 0.7801 I for 1177 seconds produces 7.650 mgms of oxygen, or that 8 grams would require 96017 coulombs. Working on the assumption that 96540 coulombs will deposit 8 grams of oxygen, we have, in order to determine the efficiencies, added the last column. The nomenclature is that used by Geuther. In the table, the numbers refer to his experiment; the solution used is then given; I refers to the current intensity (approximately tenths of amperes); D to the time in seconds; Cr to the weight in milligrams of the chromium found; O_{Vol} to the volume in cc of oxygen in the electrolyzing vessel reduced to 0° and 760 mm, and O to the weight in milligrams of this gas; O_I to the calculated weight of oxygen which should have been evolved by the current; H_{Vol} to the volume in cc of hydrogen in the electrolyzing vessel reduced to 0° and 760 mm, and H to the weight of this gas; H_I to the weight of the hydrogen corresponding to the current passed. The percentage of hydrogen deficiency computed from the hydrogen columns (the deposition of the metal being ignored) is given in the H_D column. The last column gives the number of grams of chromium which would be deposited by 96540 coulombs.

The current densities employed must have been very great since platinum wires were used; but for solutions of practically the same concentration, this may have been maintained sufficiently constant. Other results obtained by Geuther indicated that at the anode, *more* oxygen was evolved than corresponded to the Faraday law. This is indicated in the following table, the numbering of the original article being retained; the numbers in the first column refer to the solutions of Table I. The last column is our own addition to Geuther's table.

Some other results obtained by Geuther are to be noted. He states that the amount of metal deposited seems to reach a maximum when the solution contains one part of chromic acid to ten parts of water; also that the amount of metal deposited

TABLE I

		I	D	Cr	O_{vol}	O	O_I	H_{vol}	H	H_I	H_D	Cr
	Strength of solution	Current tenths amperes	Seconds	Mgms.	Volume cell oxygen	Weight cell oxygen	Weight voltameter oxygen	Volume cell hydrogen	Weight cell hydrogen	Weight voltameter hydrogen	Hydrogen deficiency	Grams per 96540 coul
1	4.76 percent, new	0.780	1177	3.00	8.614	12.320	7.650	8.214	0.7343	0.9566	23.24	3.13
2	4.76 percent, used in 1	0.780	881	2.20	6.621	9.470	5.728	6.128	0.5478	0.7161	23.50	3.07
3	9.09 percent, new	1.822	1136	9.00	17.583	25.150	17.250	10.246	0.9159	2.1566	57.53	4.17
4	9.09 percent, partly renewed	1.909	891	7.00	13.620	19.480	14.180	9.149	0.8178	1.7722	53.85	3.94
5	Residue from 4	1.909	776	6.00	12.216	17.473	12.345	8.520	0.7616	1.5435	50.65	3.88
6	14.28 percent, new	3.526	696	10.50	17.586	25.153	20.455	9.922	0.8869	2.5568	65.48	4.10
7	Used in 6	3.307	660	9.20	17.586	25.153	18.189	9.940	0.8885	2.2736	60.53	4.04

TABLE II.

	I	D	O_{vol}	O_l	O	O÷ID	Excess	Excess
Solution	Current tenths of amperes	Sec-onds	Volume cell oxygen	Weight cell oxygen	Weight volta-meter oxygen	Mgms oxygen per coulomb	Oxygen in mgms	Percent of oxygen
3	1.822	282	3.796	5.418	4.283	0.01056	1.135	29.9
	—	579	8.329	11.913	8.793	0.01129	3.210	38.53
	—	1017	15.250	21.810	15.440	0.01177	6.370	41.78
	—	1136	17.583	25.150	17.250	0.01215	7.900	44.92
4	1.909	271	3.797	5.431	4.312	0.01050	1.119	29.47
	—	570	8.330	11.914	9.070	0.01095	2.844	34.15
	—	891	13.620	19.480	14.180	0.01145	5.300	38.91
5	1.909	264	3.813	5.453	4.201	0.01097	1.252	32.60
	—	567	8.365	11.965	9.022	0.01105	2.942	35.18
	—	776	12.216	17.473	12.345	0.01179	5.128	42.00
6	3.526	172	3.799	5.435	5.055	0.00896	0.380	10.00
	—	355	8.338	11.925	10.433	0.00953	1.492	17.89
	—	477	11.780	16.848	14.020	0.01002	2.828	24.01
	—	696	17.586	25.153	20.455	0.01025	4.698	27.98
7	3.307	163	3.799	5.435	4.492	0.01008	0.943	24.26
	—	337	8.338	11.925	9.287	0.01070	2.638	31.63
	—	454	17.780	16.848	12.512	0.01122	4.336	24.38
	—	660	17.586	25.153	18.189	0.01152	6.964	39.61

diminishes as the current is passed. The more concentrated the solutions the greater is the reduction; the further the electrolysis has been carried, the less is the reduction. The amount of chromium deposited stands in direct relation to the hydrogen deficiency.

The theoretical views expressed by Geuther (combined with the novelty of his results) caused Buff[1] to undertake the electrolysis of chromic acid. The electrolysis was performed in a small vessel into which platinum wires were sealed; the gases were collected in U-tubes. Four Bunsen elements supplied the current. With a 5.13 percent acid solution, he performed experiments which are recorded in Table III. In the last two experiments, sulphuric acid was added.

Buff was successful neither in obtaining a deposit of metallic chromium nor in noting an excess of oxygen at the anode. He

[1] Liebig's Ann., 101, 1 (1857).

TABLE III

	Time minutes	Degrees tan. galv.	cc oxygen evolved	cc hydrogen evolved	Hydrogen in voltameter	Percentage evolution hydrogen	Electrodes
1	20	1.5	25.4	19.0	51.5	36.9	Platinum wires
2	6	7.9	35.3	32.5	73.6	44.1	Platinum wires
3	6	7.55	35.1	7.4	70.0	10.5	1.5 × 1 inch
4	5	6.8	—	2.2	50.8	4.3	1.5 × 1 inch
5	4	9.65	—	7.2	62.0	16.1	1.5 × 1 inch
6	4	9.4	—	0.6	57.2	1.0	1.5 × 1 inch
7	5	12.8	—	1.6	61.2	2.6	1.5 × 1 inch

therefore claimed that the results of Geuther were unreliable, basing this on the criticism that the galvanometer used by the latter had not been calibrated against the hydrogen voltameter, whereas Buff's results were obtained by use of a gas voltameter. The reply of Geuther[1] does not insist upon the reliability of his experimental work. He states: "Was die Electrolyse der Chromsäure betrifft, so hat Buff gezeigt dass sich bei meinem Messungen der Stromintensität, welche mit einer Tangentenboussole ausgeführt werden, deren Magnetnadel wohl nicht die zu diesen Messungen erforderliche Empfindlichkeit besessen haben mag, ein Irrthum eingeschlossen haben müsse. Dadurch wurden allerdings *die* Gründe beweislos, welche aus den Messungen abgeleitet worden waren, nicht aber die anderen dort angeführten.' The subject seemed closed to discussion by a second paper from Buff[2] and the complete experimental work of Geuther utterly discredited.[3]

In 1878 Morges[4] stated that chromic acid in dilute solution was reduced to chromium chromate by the current. Bartoli and Papasogli[5] electrolyzed the acid making use of graphite electrodes; again the statement was made that metallic chromium was obtained.

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[1] Liebig's Ann., 109, 129 (1858).

[2] Ibid., 110, 278 (1858).

[3] Le Blanc: "Darstellung des Chroms," p. 91.

[4] Comptes rendus, 87, 15 (1878); compare also Favre, Ibid., 73, 890, 936 (1871).

[5] Gazz. chim. Ital., 13, 47 (1883).

In 1894, Placet and Bonnet were granted an American patent,[1] the specifications of which are, in all probability, more complete than those of the earlier European patents. They state that of the electrolytes which they use, "the most important of these compounds is chromic acid, either the *commercial*[2] acid, or chromic acid obtained from chromate or bichromate of an alkali metal." They also patented the use of most of the soluble chromic salts. To vary the shade of the metal, they added small amounts of other acids. The concentrations of the electrolytes used are given, but the only clue to the other experimental conditions which they may have used is indicated in another of their patents[3] where high current densities are suggested. Their statement is: "By increasing the pressure an electric current may be passed, having an illimitable power. Under these conditions a composite body does not exist which may not be decomposed." As to the yields, the American patent states: "By our processes, as hereinafter set forth, we obtain electrodeposited chromium of great purity in coherent masses of sufficient size for various industrial uses, and of various colors as may be desired. In these processes, we use salts and compounds of chromium which heretofore have never been used or proposed for use for the purpose in view, and from which in the manner hereinafter pointed out metallic chromium is produced in sufficient quantity and with sufficient economy to constitute an industrial process, very different from the result of laboratory experiments by which the production of minute specimens of metallic chromium has been hitherto attempted."

In his monograph on chromium, Le Blanc[4] devotes many pages to a review of the patents of Placet and Bonnet, and finally in conclusion states that either the metal cannot be obtained in the way indicated in the patents or that at least all of the necessary conditions are not there given in detail.[5] He cites the fact that Cowper-Coles, Ferée, and Shick had been unsuccessful in

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[1] U. S. Patent, 526114, September 18 (1894).

[2] Italics inserted by the authors of this paper.

[3] English patent, 19344 (1890).

[4] "Darstellung des Chroms," pp. 3-17.

[5] Compare Jour. Phys. Chem., 9, 235 (1905).

their attempts to reproduce the conditions indicated in the patents. In the "Jahrbuch der Electrochemie," I, 174, the criticism of the Placet-Bonnet patent is: "Nach der erwähnten Vorschriften ist aber eine Fabrication nie möglich." Ahrens[1] states: "Die Patentschrift ist indessen so abgefasst dass, auf dem darin angegebenen Wege, Chrom unmöglich fabriziert werden kann."

In 1899, Reese[2] electrolyzed chromic acid examining the effect produced on the electrolyte by the gases evolved. As an electrolyzing vessel he used a burette; the cathode was put at the bottom so that the rising hydrogen passed through a long column of the acid. With pure acid of normal concentration, he found no reduction even after an electrolysis of twenty-four hours; when, however, traces of sulphate or sulphuric acid were present, reduction was quickly effected "but there was always a limit reached when no further reduction took place." Potassium bichromate behaved in exactly the same way as the acid. Neither the current density employed nor other important experimental details are given. The results, however, might at first sight seem to be in direct opposition to those obtained by Geuther and Buff, both of whom found considerable reduction.

This historical review raises several questions: (1) May metallic chromium be deposited in the electrolysis of chromic acid solutions? (2) If so, under what conditions and what is the current yield? (3) Why is there such a great diversity of experimental results, and conclusions? (4) Is there reduction at the cathode or oxidation at the anode? (5) Is the statement of Geuther in regard to the excess of oxygen at the anode correct?

(*c*) *Chemical Reactions of Chromic Acid.*—In every electrochemical study, an accurate knowledge of the oxidation and reduction possibilities of the compounds involved is necessary. This is especially needed in the case of the compounds which are considered in this paper.

Chromic acid is a very powerful oxidizer, or in other words

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[1] "Handbuch der Electrochemie," p. 442.

[2] Am. Chem. Jour., 22, 162 (1899).

it is very easily reduced; in fact, even hydrogen[1] will effect the reduction of saturated solutions. Catalytic agents such as platinum would probably accelerate this reduction. The more pure the acid, the less readily it is reduced; this is shown by the work of Gawalovski[2] who found that pure acid reacts with alcohol very slowly, but that the addition of an acid accelerated the reaction very decidedly. This is another confirmation of the results of Bancroft who showed that the addition of an acid raised the potential of an oxidizer. Another illustration of this principle where chromic acid is again involved is the Grove cell where zinc and graphite electrodes are used in a mixture of sulphuric and chromic acid. With the low current density at which the cell is used, the acidified chromic acid acts as an almost ideal depolarizer since by the addition of the sulphuric acid, its oxidation potential has been very much increased; the result is the formation of chromic sulphate as the cell is discharged.

The reverse operation—the oxidation of chromic salts to chromates—may be effected by the use of oxidizers such as manganese or lead peroxide, potassium permanganate or chlorine in acid solutions.

(*d*) *Electrochemical Relations.*—Chromium is an element which shows at least three different valencies; the electrochemical relations have been worked out by Luther[3] who, assuming the potential —0.56 for the Ostwald normal electrode, gives the following values:

Potential of metallic chromium against its divalent salts = 0.3 volt.
Potential of metallic chromium against its trivalent salts = 0.2 volt.
Potential of metallic chromium against its hexavalent salts = —0.9 volt.

The question of the potential of the metal in solutions of chromium chromate was not considered. The theoretical method employed by Luther was criticized by Hittorf[4] on the ground

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[1] Ludwig: Liebig's Ann., 162, 47 (1872).
[2] Zeit. analyt. Chem., 17, 179 (1878).
[3] Zeit. phys. Chem., 36, 389 (1900).
[4] Zeit. Elektrochemie, 7, 257 (1900).

that chromium in chromic acid was not a reversible electrode since from the chromate solutions it was impossible to obtain the metal; while Luther admitted this last fact, he claimed that it did not affect the conclusions which he had drawn.

Hittorf has shown that chromium, when used as anode, goes into solution with different valencies according to the conditions used. The electromotive forces involved are illustrated by the combination chromium, potassium chloride, sodium nitrate, silver nitrate, silver. When active chromium was used, Hittorf found an electromotive force of 1.006 volts, silver being cathode. This value increased as the temperature rose, finally forming a constant element. At the lower temperature, the rate of solution showed the metal hexavalent while at the higher it tended to become divalent.[1] It seems very probable both from the work of Hittorf, and from some experiments that we ourselves have made that the changes of valency are not discontinuous but that systematic study would show all stages of valence (anodic efficiency) lying between hexavalent and divalent.

The fact that the metal goes into solution at the anode as a hexavalent ion may be explained by the modern theory of the voltaic cell thus—the metal has a solution tension which is determined by the presence in the solution of hexavalent chromium ions. As shown above, Luther has calculated this value as —0.9 volt; nevertheless in the inconclusive work on the constitution of chromic acid which at the beginning of this paper we have quoted, there was no mention whatever of the possibility of the presence of hexavalent chromium ions in the solution. The nearest approach to such a suggestion was made by Abegg and Cox who claimed that free CrO_3 exists in the solution.

To explain the results of Hittorf and Luther, the assumption must therefore be made that some hexavalent chromium ions—cations—exist in the solution of chromic acid. This assumption would be given some support if proof could be adduced that

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[1] This is probably an illustration of a general principle that rise of temperature favors the formation in the solution of compounds in which the dissolving anode shows its lower valency. We may later examine the limitations of this suggestion in relation to the heat and electrical energies involved in the changes of valence.

chromium can be deposited from chromic acid; and while it rarely happens that a cathode reaction is the exact converse of the anode reaction, nevertheless some information as to the action of reversible electrodes should be obtained from the cathode reactions.

We pass at once therefore to the results obtained in the actual electrolyses of chromic acid.

(*e*) *Preliminary Electrolyses.*—As electrolyte there was selected a chromic acid which contained considerable sulphate as impurity. This was washed repeatedly with concentrated nitric acid and dried in an air-bath at 160°. The electrodes which were used throughout the investigation were platinum wires 0.4 mm in diameter, 30 mm long; the area of these was approximately 0.004 square decimeter. With various concentrations of the chromic acid, we now made a series of electromotive force-current measurements. For two reasons these results are not given: a very careful analysis of the acid had not been made and hence it is impossible to reproduce the measurements, and secondly, the runs were not carried far enough to determine with exactness the exact decomposition voltages. Nevertheless chromium deposits were obtained; the measurements gave, therefore, very rough indications as to the current densities which were necessary. For solutions ranging in concentration from one to fifty percent acid, the current density at which an instantaneous deposition of metal was observed was about 80 amperes per sq. dcm. at 18° while twice this density was necessary at a temperature of 90°.

At the lower current densities hydrogen was liberated. The question was at once raised as to the absorption of this gas by the metal. Of a quantity of chromium deposited from chromic acid solution, 0.6979 gram when heated gave 24.6 cc of hydrogen at $t = 20°$, $p = 750$ mm; as a rough approximation then, one volume of electrolytic chromium had absorbed 250 times its volume of hydrogen. This metal shows then, perhaps, even greater power for absorbing hydrogen than palladium, platinum, iron and nickel.

Chromic acid labeled "C. P., free from sulphate" was now obtained from a reputable firm. Again sulphate was found in considerable amounts. Reduction to chloride and precipitations as barium sulphate showed 0.23 percent of free acid; the precipitate was white and lost but little weight on repeated washings with hydrochloric acid. When barium chloride was added to the chromic acid solution strongly acidified with hydrochloric acid, the percentage of sulphate found was only 0.14 percent. However more of the sulphate precipitated from this solution after the filtrate had stood for several days, the total percentage increasing to 0.20 percent of sulphuric acid impurity. Nitric acid was also present in minute amounts.

The solutions were electrolyzed in a well-stoppered cylinder which was kept in a bath of constant temperature. The ammeter readings served only for a rough adjustment, since an alkaline nickel voltameter was always kept in circuit. The gases from the voltameter were analyzed repeatedly to check the accuracy of the results obtained. The cathode deposit was weighed after careful washing and drying in the air-bath. The gases evolved from the cells were collected in a Hempel burette and then analyzed for oxygen, using the alkaline pyrogallol and phosphorus absorption methods.

With temperature constant, but varying current, a run was now made using 50 cc of a 14.28 percent acid solution. This concentration was chosen in order to allow comparisons with the work of Geuther; most of the tables refer therefore to this strength. The results are given in Table IV, which, as in all subsequent tables, is arranged as follows: The first column gives the number of the experiment, the second the time in seconds, the third the number of cc of gas found in the voltameter, the fourth the cc of gas in the cell. The number of cc of oxygen found in this cell gas is shown in the next column, while the difference between the figures in the fourth and fifth columns gives the number of cc of hydrogen recorded in the sixth column. The percentage deficiency of hydrogen given in the seventh column is calculated on the assumption that no other decomposition had taken place. The eighth row gives the number of milligrams of the metal deposited. The last row which is to be found only in Table IV indicates the ammeter reading.

For all other series, the temperature and current were kept quite constant.

TABLE IV

14.28 percent acid; cylinder electrolyzer; $t = 21°$

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr	Amperes
1	3300	80.2	76.4	26.7	49.7	6.9	0.0	0.11
2	363	84.0	71.2	28.0	43.2	22.7	7.8	1.20
3	360	83.8	—	—	—	—	8.0	1.20
4	364	87.0	72.8	29.0	43.8	26.2	9.7	1.20
5	960	84.4	67.0	28.1	38.9	30.9	10.8	0.45
6	1020	89.0	70.0	29.6	40.4	31.9	10.8	0.45
7	271	92.2	78.0	30.7	47.3	23.1	9.9	1.70
8	259	94.5	81.4	31.5	49.9	20.8	9.1	1.95

It will be noted that for a current of 0.11 ampere (area of anode and cathode in every case equals 0.004 sq. dcm.) there was a slight reduction but no deposition of metal. Increase of current density caused greater reduction and some metal deposition. Thereafter in most of the runs, efficiency in reduction is practically synonymous with efficiency in metal deposition.

A run was now made to ascertain how the efficiency varied with the time of electrolysis when the temperature and current were constant. Between experiments (5) and (6), (7) and (8) electrolysis was continued for some time during which no analyses were made. Results are given in Table V.

The metal deposited in (1) Table V weighed 8 milligrams; the cathode deposit was not again determined until (10) and (11) when in each case 2 mgms was found. This series shows that the percentage reduction as well as the metal deposition fall off as the run was continued.

(*f*) *Results with Pure Acid.*—Reese had stated that with pure chromic acid he was unable to get any reduction whatever. We therefore obtained a chromic acid from Merck which by the Krauch test showed no impurities. Analysis showed that there was present 0.01 percent of free sulphuric acid, and very slight traces of nitric acid and alkali metal. While recrystallization would undoubtedly have given us an acid still more pure, it

TABLE V

14.28 percent acid; cylinder electrolyzer; current = 1.2 amperes; $t = 22° \pm 2°$

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
1	354	84.6	71.1	28.2	41.9	25.7	8.0
2	351	84.0	67.4	28.0	39.4	29.6	—
3	360	83.0	66.5	27.6	38.9	29.6	—
4	380	87.0	70.3	29.0	41.3	28.8	—
5	340	85.5	68.9	28.5	40.4	29.1	—
	1800	—	—	—	—	—	—
6	362	85.8	69.4	28.6	40.8	28.6	—
	3600	—	—	—	—	—	—
7	345	84.4	77.5	28.1	49.4	12.2	—
	4200	—	—	—	—	—	—
8	360	87.3	82.1	29.1	53.0	8.9	—
9	382	87.2	82.8	29.0	53.8	7.2	—
10	365	83.6	79.4	27.9	51.5	7.5	2.2
11	343	82.6	79.2	27.5	51.7	6.1	2.2

would have required the greatest care and a long time to obtain by the necessarily slow crystallization an acid much purer. The probabilities are that the acid is at least as pure as any that has been used in conductivity or electrolytic work. In all our subsequent electrolyses we have therefore used this acid.

When a 14 percent solution of this acid was electrolyzed for two days with a very low current derived from a two-volt circuit, no reduction was observed and no metal was deposited. A current-electromotive force curve showed the decomposition voltage at which metal was observed as 2.31 volts; hydrogen was evolved from 1.6 volts or even lower. The electrolyzing cell was connected to a four-volt circuit; metal deposition and darkening of the solution were noticed almost immediately when the circuit was closed. It seems very probable, therefore, that Reese used low currents for his electrolyses and that he was below the point at which metal deposition was to be expected.

For the experiments cited in the last paragraph and in all subsequent work, we have made use of a glass-stoppered glass cell in order that the possible reduction of the chromic acid by organic matter which might come from a rubber stopper should be completely eliminated. The cathode was fastened into a ground glass stopper which could be readily cleaned and weighed. The anode was sealed in at the bottom. The gases evolved were led through a side arm into a gas burette. The small content of the cell (3 cc) enables one to control the temperature very readily, while another advantage is that a run may be carried to a final stage in a very short time. The small gas space over the solution also allows one to reproduce conditions with great exactness.

With this purer acid, and the glass electrolyzer, runs were made to find the effect of temperature; the current used, 0.5 ampere, corresponds to a density at anode and cathode of 125 amperes per square decimeter. The results obtained at 20° are given in Table VI, at 90° in Table VII.

TABLE VI

14.28 percent acid; glass electrolyzer; current = 0.5 amp; D anode = D cathode = 125; $t = 20°$

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
1	960	96.2	89.8	31.9	57.9	9.8	3.6
2	960	94.5	92.8	31.0	61.8	1.9	0.9
3	780	79.5	79.5	26.7	52.9	0.2	0.4
4	960	92.4	91.0	30.8	60.2	2.2	0.7
	4800	—	—	—	—	—	—
5	1020	93.9	93.0	31.0	62.0	1.0	0.4

TABLE VII

14.28 percent acid; current = 0.5 amp; D anode = D cathode = 125; $t = 90°$

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
1	900	90.6	90.5	30.2	60.3	0.2	0.2
2	840	90.1	89.0	29.8	59.2	1.2	0.3
	3600	—	—	—	—	—	—
3	1080	98.4	97.1	31.7	65.4	0.3	0.2
	1080	—	—	—	—	—	—
4	840	97.9	96.2	32.0	64.2	1.5	0.2

It was necessary to stop the series after the fifth run (Table VI) because of the presence of a large amount of an insoluble precipitate.

It will be noticed that in the electrolysis at 20°, metal is deposited from the first and that the reduction and metal deposition decrease as the run continues. Small errors in analysis are of course greatly magnified when dealing with cases showing such little reduction as is here found. At the higher temperature reduction and metal deposition are insignificant.

(*g*) *Effect of Impurities.*—Comparison of Tables IV and V with VI indicate that, as was noted in a discussion of the reactions of chromic acid, a slight amount of impurity may have a very noticeable effect on the reduction. Geuther had made his acid from potassium bichromate and sulphuric acid, while Buff and Reese made use of C. P. acid. None of the chemists who have written about the electrolysis of chromic acid have described the methods by which the pure acid may be obtained and tested. It is a long and difficult operation to free it from the sulphuric acid used in its manufacture and the sodium sulphate which occurs as the bye-product, or the nitric acid which is used in freeing from the sulphuric. It seemed possible then that the deliberate addition of impurities might enable one to duplicate the results obtained especially in the cases where the object of the work had been purely commercial, and where under no circumstance would a chemically pure chromic acid have been used.

To the 14.28 percent chromic acid solution was added sulphuric acid in amounts sufficient to make its concentration one percent. The other conditions were the same as had been employed in Table VI, namely $t = 20°$, current 0.5 ampere. The results are given in Table VIII.

In all cases the metal deposit scaled very badly, and in some cases fell into the solution so that the results are approximations only. A duplicate set of determinations for metal only gave the following numbers in milligrams—19.1, 20.8, 16.2, 17.3, 0.9, 7.8, 1.9, while in the solution was 20 milligrams of scale deposit. It is at once apparent that the effect of the sulphuric

TABLE VIII

14.28 percent chromic + 1 percent sulphuric; current = 0.5 amp; D anode = D cathode = 125; $t = 20°$

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
1	930	98.5	52.3	31.1	21.2	66.2	15.2
2	935	98.2	55.2	30.8	24.4	62.7	19.8
3	510	57.3	33.1	16.1	17.0	55.5	11.4
	3600	—	—	—	—	—	—
4	570	71.4	43.8	21.3	22.5	52.8	6.4
	7200	—	—	—	—	—	—
5	535	60.3	58.7	19.0	39.7	1.2	3.0

acid has been to increase the reduction and the metal deposition to a very great extent. In fact, in the runs recorded in Table VIII and its duplicate, *one-half of the total chromium content of the solution was removed as metal*, and even then the limit had not been reached. As before noted, the reduction fell off as the run was continued; neither oxygen excess nor ozone formation has been observed.

The platinum anode was now replaced by a lead anode of the same area and a run made under conditions identical with (2) of Table VIII. As was to be expected there was a greater deficiency of oxygen while the reduction was only 55.4 percent in place of 62.7 percent.

A solution was now made up which contained 14.28 percent of chromic + 1 percent sulphuric acid + 1 percent potassium sulphate. It was electrolyzed under conditions identical with those used in VI and VIII. The results are given in Table IX.

In runs 1 and 2 the metal scaled very badly; from 3 to 6 the metal was black. The first run shows great reduction, high metal deposition (at the rate of 4.6 grams metal per 96540 coulombs) and considerable oxidation; as the run continues, the reduction and metal deposition drop off very considerably while oxidation efficiency decreases more slowly.

To the 14.28 percent chromic acid was now added potassium chromate to make a 1 percent solution in respect to the chro-

TABLE IX

14.28 percent chromic + 1 per cent sulphuric + 1 percent potassium sulphate ; current = 0.5 amp ; D anode = D cathode = 125 : *t* = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
1	900	93.5	44.2	25.4	18.8	69.8	22.6
2	780	87.7	45.8	27.6	18.2	68.8	16.8
	4500	—	—	—	—	—	—
3	900	90.3	85.7	27.7	58.0	3.6	0.5
	4500	—	—	—	—	—	—
4	870	93.2	91.0	29.5	61.5	0.9	0.9
5	960	98.0	95.8	28.4	64.6	0.9	0.7

mate. The conditions of electrolysis remained constant. The results are given in Table X. The extent of the reduction and the amount of metal deposition is less than was observed in the cases where other substances were added.

TABLE X

14.28 percent acid + 1 percent potassium chromate ; current = 0.5 amp ; D anode = D cathode = 125 ; *t* = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
1	840	91.8	81.4	30.0	51.4	16.0	5.2
2	900	97.4	90.0	31.3	58.7	9.4	2.6
	5400	—	—	—	—	—	—
3	1000	99.8	96.3	32.7	63.6	4.3	2.0
	7200	—	—	—	—	—	—
4	960	97.5	95.7	31.7	64.0	0.4	0.6

Nitric acid has also been added to the 14.28 percent chromic acid to form a solution holding 0.5 percent nitric. The results are given in Table XI. The metal was dark colored, but nevertheless fair yields were obtained.

One run was made with hydrochloric acid as an impurity to the extent of 1 percent. The oxygen and chlorine in this as also in Table XIII were not determined separately. There is again to be noted high reduction, high oxidation, and fairly good metal deposition.

TABLE XI

14.28 percent chromic + 0.5 percent nitric; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Per-cent reduction	Mgms Cr
1	990	94.0	76.0	31.2	44.8	28 4	6.8
2	960	92.4	80.4	30.6	49.8	19.1	5.1
	3600	—	—	—	—	—	—
3	990	95.1	93.6	30.9	62.7	1.1	0.8
	5400	—	—	—	—	—	—
4	960	94.2	93.8	31.1	62.7	0.16	0.4

TABLE XII

14.28 percent chromic + 1 percent hydrochloric; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen and chlorine	Cell hydrogen	Per cent reduction	Mgms Cr
1	960	93.6	58.7	21.6	37.2	40.3	15.2

With potassium chloride the results of the first run resemble in a very marked degree those obtained with hydrochloric acid. As in Table X, however, when the run is continued, oxidation, reduction and metal deposition soon cease.

TABLE XIII

14.28 percent chromic + 1 percent potassium chloride; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen and chlorine	Cell hydrogen	Percent reduction	Mgms Cr
1	1020	96.2	62.4	23.8	39.6	38.2	14.8
	14400	—	—	—	—	—	—
2	1020	95.0	95.0	31.5	63.5	—	0.2

(*h*) *Comparison of Efficiencies.*—From the work of Geuther, we may not tell exactly what current densities were used; but with an acid of the same concentration (14.28 percent) we have by adding impurities been able to obtain results which practically agree with his so far as the rate of metal deposition and hydrogen deficiency are concerned. This is readily seen by comparing 6 and 7 of Table I with 1 and 2 of Tables VIII and IX. Under no circumstances have we by working within a temperature range of 20° to 90°, current density of 10 to 250 amperes, concentration from 1 percent to 50 percent, been able with a *pure* acid to get results at all comparable with those of Geuther.

An attempt was made to duplicate Buff's experiment 4, Table III. With the 5.13 percent solution, he had used electrodes 1.5 square inches in area; the current at its maximum had evolved in the voltameter 14.5 cc of hydrogen per minute. This corresponds to a density of about 10 amperes per square decimeter if both sides of the cathode are considered. With a voltage of 2.45 and current of 0.025 ampere, we made a run of 4200 seconds; there was no metal deposition and no measurable reduction. The current was now increased to 0.08; the corresponding voltage was 2.66. Results are given in Table XIV.

TABLE XIV

5.13 percent chromic acid; current = 0.08 amp; voltage = 2.66
D anode = D cathode = 20; t = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction
1	4020	64.5	63.2	20.1	42.3	1.6
2	3720	60.4	60.0	19.9	40.1	0.5

For this run also, no metal was found. The results correspond with those already given (p. 367) and indicate that at the current density employed the decomposition voltage for metal deposition had not been reached.

It will be seen that the reduction instead of being 95 percent as with Buff is more nearly 1% or 2%. While it must be admitted that the use of the same concentration, temperature and current density does not mean that experimental conditions have been accurately reproduced, it would appear that the most reasonable explanation which we can offer for the reduction observed by Buff and Geuther is that the acid they used was impure. Buff's results are not comparable with those of Geuther since the latter was working above the decomposition voltage while the latter was using densities corresponding to points below this.

Our results prove conclusively that Placet and Bonnet were right in stating that metallic chromium can be obtained by the electrolysis of commercial chromic acid. We have also found that other statements made by them in their patent, are true.

The failure of so many chemists is probably due to the use of too low current densities, combined possibly with the belief that it could not be done.

The results of Reese were readily reproduced by using a current density which corresponded to a voltage lower than the decomposition voltage; with greater current densities, however, the purest acid is quickly reduced.

Greater efficiency of reduction and metal deposition has been obtained by the addition of sulphuric than with hydrochloric or nitric acid. The pure acid shows very low efficiency of deposition; it is our belief that while a purer acid might show still less, the actual deposition is not always caused by the presence of impurity.

Why does the sulphuric acid increase the efficiency? It is well recognized by electrochemists that the efficiency of a metal deposition varies very considerably with the number of ions of the metal present in the solution. With a small number, low efficiencies are expected; as this number increases, the efficiency will increase. We suggest, therefore, that the sulphuric acid has increased the number of chromium cations in the solution. It is probable that in its presence, the dissociation of the chromic acid is forced back to the CrO_3 stage and that the secondary dissociation of this into hexavalent chromium cations is thereby increased.

Another method of expressing the same result is this—when sulphuric acid reacts with CrO_3, the latter behaves as a base, and hexavalent chromium tends to be formed, although normally the trivalent salt is the more stable form. It does not seem at all improbable therefore that the various acids and also various salts tend to increase the ionization of chromium acid to hexavalent ions, and that this effect is shown in the increase of efficiency of deposition of the metal.

(*i*) *Products of Reduction.*—In every case examined, where the chromic acid was reduced, the solution was colored brown and the reactions showed the presence of chromic salts. When alkali was also formed at the cathode, there was formed a brown precipitate which on treatment with hydrochloric acid evolved chlorine. This is probably the compound already found by Geuther, Buff and Morges who regard it as CrO_2 or chromium chromate, $CrCrO_4$.

A compound corresponding to the same formula has been made by other methods: for example, Maus[1] found that chromic sulphate or chloride treated with potassium chromate, or chromic hydroxide in the presence of chromic acid reacted to form it. In other words an oxidizing acid or the salt of the acid might be reduced by a compound in which the element occurred in a lower valency, to a product in which the element had an intermediate valency.

Now these chemical conditions are the ones which have been reproduced in the electrolytic cell. In the solutions to which were added sulphuric, nitric or hydrochloric acid, if a partial reduction could have taken place with formation of the chromic sulphate, nitrate or chloride, there would have been a reaction between these compounds and the chromic acid, with formation of the chromium chromate, heat also being evolved. In other words, the reduction to the CrO_2 stage would be more readily effected than the reduction to the trivalent stage.

So also when an alkali salt was added, there might be assumed a tendency for the chromic acid to reduce at the cathode to the chromic salt, which either as chromic hydroxide or the alkaline chromite would, according to the Maus reaction,

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[1] Pogg. Ann., 9, 127 (1827).

tend to form CrO_2. In place of the reaction proceeding in two distinct stages, however, the one observed in the electrolysis was the precipitation of the solid. This was noticed with the solutions used in Tables X and XIII.

We have already noted that in every case examined, the yield of chromium and the extent of reduction decrease as the reaction proceeds, that is, as the chromic acid changes to its lower stage of oxidation. The conclusion might at once be drawn that the presence of the reaction products decreased the efficiency, were it not that not merely is metallic chromium removed but that the chromium chromate precipitates.

A solution was therefore selected in which this precipitation might to a certain extent be avoided—that used in Table VIII. With 2 cc of this solution corresponding to 148 mgms of the metal, five runs were made under the following conditions: time 960 seconds, current 0.5 amp., D anode = D cathode = 125, t = 20°. The weights of the deposit were 20, 18, 16, 15 and 4 mgms respectively, while a slight amount scaled off. The total amount of chromium left in the solution was then about one-half the amount originally present. The sixth run was then made—this is number (6) in Table XV. The original solution was then diluted to one-half and a run made—(1) in Table XV.

TABLE XV

Chromic + sulphuric; Cr content = 74 mgms; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Volt. gas	Cell gas	Cell oxygen	Cell hydrogen	Percent reduction	Mgms Cr
6	700	75.0	65.7	23.7	42.0	3.8	1.0
1	660	70.5	40.0	21.9	18.1	61.0	15.6

While the conditions are not absolutely comparable, the different results obtained in (6) and (1) indicate that the presence of the chromium chromate causes a very decided decrease in the yield.

As stated above, the oxidation power of chromic acid is increased by the presence of an acid—in other words, the chromic acid is more readily reduced in the presence of an acid. Is it then possible to reduce the chromic acid quantitatively to a chromic salt by the agency of the current? Le Blanc[1] says it cannot be done unless a diaphragm is used. "Nur solange man, wie Street, in alkalischer Lösung arbeitet und das Chromoxyd sich unlöslich ausscheidet, wird die Regeneration zu Chromat an der Anode praktisch zu vernachlässigen sein, falls man nicht etwa Diaphragmen zu Hilfe nimmt." Buff[2] found that at low current density chromic acid acidified with sulphuric is readily reduced to chromic sulphate and potassium chromate to chrome alum. To check his statement we took 2 cc of a 14.28 percent chromic acid, 2 cc of concentrated sulphuric acid, and 2 cc of water. No diaphragm was used. With anode density of 750 amperes, cathode density of 50 amperes, a current of 3 amperes in ten minutes effected complete reduction. Ozone formation was also noted. In fact, this is a very easy method of reducing chromic acid when it is desired to avoid the introduction of organic impurities. The Grove cell offers an illustration of the case where the reduction effect is found when current is being withdrawn from the cell.

A cell which would offer considerable interest is composed of chromium and graphite electrodes in sulphuric and chromic acid. If a diaphragm were used, this would form a storage cell, but its efficiency would probably be very low.

The experiments recorded in Tables IV to XIII have shown therefore some of the conditions by which it is possible to pass from hexavalent chromium to what is probably the tetravalent chromium chromate stage, the metal being deposited while the electrolytic reduction proceeded, but not however until a definite voltage (current density) was reached. The experiment cited in the last paragraph has shown some of the conditions by which the hexavalent may be carried to the trivalent stage. Carveth and Mott examined a few of the conditions involved in the reduction from the chromic to the chromous salts, being concerned more with the efficiencies of metal deposition.

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[1] "Darstellung des Chroms," p. 72.

[2] Liebig's Ann., 101, 8 (1857).

Commercial Methods.—It is now easy to see some of the difficulties which are involved in the continuous deposition of chromium from its solutions. If an anode were employed which was practically a pure chromium in an electrolyte of chromic chloride or sulphate, it might seem difficult to select the conditions of concentration, temperature, and current densities at which the rate of solution (apparent anode valency) was exactly counterbalanced by the rate of deposition of the metal. The solution must not become acid because of the ease of decomposition of the chromous salt; in fact a slightly alkaline reaction seems to favor an increased cathode efficiency. It is very probable that the exact conditions for this deposition will be worked out and that as in other cases the sulphate (or chloride) will be the salt employed.

The use of chromic acid or chromates in acid solution will probably be restricted to the cases where fine platings are required, since the current efficiency is very low. Electrodeposition from a fused bath offers very distinct possibilities.

There is no doubt that as soon as the commercial demands warrant, methods for the electrodeposition of chromium in any form will be devised.

(*j*) *Conclusions.*—In the study of the cathode reactions, at least three but more probably four or more different stages of oxidation are met; this means that in the various solutions there are chromium ions with four different valencies. When the equilibrium relations between metallic chromium and its ions have been determined, the question will be decided as to whether or not the anode reaction is the converse of the latter.

In regard to the constitution of chromic acid solutions, the following facts must be noted: (A) The study of the equilibrium relations point to the existence of free CrO_3—a radical composed of a conductor and a non-conductor of electricity. So far as we are aware, no known compound of such a combination is known which conducting the current in aqueous solution is not by the supporters of the theory of electrolytic dissociation supposed to be dissociated into ions; (B) Chromium as anode may dissolve to form CrO_3. If dissolving to form an ion, this will be hexavalent. There is a continuous passage from the conditions where it dissolves divalent (and every one concedes its ionization because a salt is formed) to the conditions where it dissolves hexavalent (where ionization has not been conceded, because an acid was formed); (C) Chromium may be deposited from chromic acid after a definite decomposition voltage has been reached.

1. This evidence therefore makes it seem very probable that in chromic acid there exists a number of hexavalent chromium cations in equilibrium with many other ions, and that chromium in chromic acid may be considered a reversible electrode.

2. The main part of the work of Geuther is correct. Metallic chromium is deposited in the electrolysis of solutions of chromic acid, but this requires a high current density, which in this case is synonymous with a high decomposition voltage. For example, using platinum wires as electrodes Geuther used currents of from 0.07 to 0.35 ampere—very great densities, probably higher than we have used. On comparing with our own results the very great percentage reductions and the high metal depositions which he obtained we conclude that his acid must have been impure. The oxygen excess which he found at the anode, we have never been able to find; his admission that his tangent galvanometer was wrong probably explains this. After the decomposition point is reached, the efficiency of metal deposition and the reduction of the acid go hand in hand; a chromium chromate is probably formed.

The results of Buff are readily understood when the current density he employed is calculated. Under no conditions have we been able to get deposition of the metal at a current density as low as he used; nor have we with any but very impure acids been able to duplicate his results.

Like Buff, the other workers, Schick, Cowper-Coles and Ferée have probably used too low current densities; it seems very improbable that their materials were purer than those used in the investigation.

Some of the claims of Placet and Bonnet are sound. It is very probable that solution of *commercial* chromic acid and of chromates to which have been added various substances which aid in the reduction may not be used in a continuous and economical process for the extraction of chromium, since the efficiency is so rapidly decreased by the formation of the reduction products. By oxidizing these, however, it would be possible to continue the extraction of metal, making the process continuous. There is nothing to prevent the use of this method in the laboratory for the purpose of making pure chromium.

By selection of the proper impurity (*e. g.*, sulphuric acid) we have been able in a continued electrolysis to recover in the metallic form more than half the total chromium present in the solution. Had the reduced products been oxidized, this yield could have been carried to any limits desired.

The criticisms of Le Blanc on the work of Geuther, Placet and Bonnet, and Street need radical change. The only justification for such criticism was due to the experimental conditions not having been described in sufficient detail by the various workers.

3. Electrolytic chromium may occlude as much as two hundred and fifty times its volume of hydrogen.

4. It is possible to reduce chromic acid to the trivalent chromic salts in the presence of an excess of a mineral acid.

As previously stated, we regard chromium merely as the type of a large number of elements which, according to the degree of oxidation, are either acid or basic in their properties. The methods which we have used should, we think, be capable of application to numerous other cases, such as the rare earth elements.

Of the work planned, but a small part is completed. It is our hope that the interest attached to the work will induce other electro-chemists to enter the field.

Cornell University, April, 1905.

FREE ENERGY AND HEAT CAPACITY

BY J. M. BELL

Introduction

The question of the existence of a fundamental connection between changing heat capacity, change of free energy, and heat of reaction was raised by Richards[1] in 1902. In his paper are given experimental data, from which the inference is drawn that the change of total energy with the temperature stands in a simple ratio to the change of free energy with the temperature. Equivalent to this conclusion of Richards is that of van't Hoff,[2] namely, that the change of heat capacity stands in a simple ratio to the temperature coefficient of electromotive force. Quite recently, Haber and Tolloczko[3] have declared that the conclusions arrived at by Richards and van't Hoff are of the utmost importance, an importance which will perhaps direct physico-chemical research along somewhat new channels.

The objects of this paper are, first, to make a critical examination of the data from which the above conclusions are drawn, with special reference to the extent of the probable error in the observations, and to the degree in which errors of such magnitude would affect the calculations; second, to examine critically the assumptions which are made in the calculations; and, third, to discover whether the conclusions are in accord with the assumptions and in accord with the available experimental data.

Notation

The notation used in this paper is that employed by Trevor,[4] viz.,

E is the total energy of the system before the isothermal change, and ΔE is the change of energy during the reaction.

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[1] Proc. Am. Acad., 38, 293 (1902); Zeit. phys. Chem., 42, 129 (1902).

[2] Boltzmann Festschrift, p. 233 (1904).

[3] Zeit. anorg. Chem., 41, 436 (1904).

[4] Jour. Phys. Chem., 9, 299 (1905).

This latter corresponds to U used by Richards, and to Q used by van't Hoff.

F is the free energy of the system before the isothermal change, and ΔF is the change of free energy during the reaction. ΔF corresponds to A used by Richards, and to E used by van't Hoff.

θ is the absolute temperature; Richards and van't Hoff use T.

c is the heat capacity of the system at constant 'normal' parameters, the state variables of the system being the 'normal' variables $x_1, \ldots x_n, \theta$; and Δc is the change of the heat capacity in the isothermal reaction.

Discussion of the data

The possible experimental errors in the data, upon which Richards bases his conclusions, will be ascertained, in order to determine how errors of such magnitude would affect the results. The calculation of the change of heat capacities, upon which the conclusions are based, have been made mainly from the data of Marignac[1]. Regarding the degree of accuracy of his results, Marignac says: "J'ai porté les chaleurs spécifiques avec quatre décimales, telles qu'elles m'étaient données par la moyenne des cinq ou six déterminations, faites sur chaque solution. On peut sans inconvénient supprimer la quatrième décimale, puisque la troisième peut être déjà affectée d'une erreur de 1 ou 2, rarement de 3 unités." Taking account of the errors, we shall repeat Richards's calculation[2] for the case of the Daniell cell in which the initial solution is of the composition $CuSO_4.200H_2O$. The equation is, of course,

$$Zn + CuSO_4.200H_2O = Cu + ZnSO_4.200H_2O.$$

For the specific heat of a solution of the composition $CuSO_4.200H_2O$, Richards takes the mean of two figures given by Marignac, (*a*) 0.9504, the specific heat between 18° and 25°, and (*b*) 0.9527, the specific heat between 22° and 53°, thereby assuming that for this temperature range, the specific heat does not perceptibly change. This assumption will be discussed

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[1] Ann. Chim. Phys., (5) 8, 418 (1876).

[2] Loc. cit., p. 296.

more at length later. Supposing for the moment that this assumption is justifiable, it is evident that there is an error of at least 2 in the third place of decimals. However, as the calculation has been made taking the mean as the true value, let us suppose that there is an error of 1 in the third place. The calculation, taking account of the errors is:

Factors:	**Mayers**
$CuSO_4.200H_2O$, (0.9516 ± 0.0010) × (3762.7) × (4.181) =	14970 ± 15
Zn	26
Total factors,	14996 ± 15
Products:	
$ZnSO_4.200H_2O$, (0.9523 ± 0.0010) × (3764.5) × (4.181) =	14989 ± 15
Cu	24
Total products,	15013 ± 15
Difference,	17 ± 30

It will be seen that the error is out of all proportion to the small difference which the figures seem to show. Further, in case the possible error is 2 or 3, which it may be, the error in the data indicating the change of heat capacities will be approximately 60 or 90 mayers respectively. In the ten cases cited by Richards, the greatest change of heat capacity is calculated as 124 mayers, while in most of the cases this change of heat capacity is given as numerically less than 70 mayers. Hence it follows that not only is the actual change of heat capacity uncertain within rather wide limits, but also that the sign of this difference in a great majority of the cases actually cited is just as uncertain. Thus it can be asserted that Richards's conclusions, both of which involve statements regarding the sign and magnitude of the change of heat capacity, are based on insufficient experimental evidence.

Richards's conclusion is at variance with an assumption

One of the inferences which Richards has sought to establish is that $\frac{\partial \Delta E}{\partial \theta}$ and $\frac{\partial \Delta F}{\partial \theta}$ stand in a simple ratio, and it is claimed that this inference is supported by experimental data. $\frac{\partial \Delta F}{\partial \theta}$ is the temperature coefficient of the free energy change, or in this case the temperature coefficient of the electromotive force, and

$$\frac{\partial \Delta E}{\partial \theta} = \Delta c,$$

where Δc is directly calculated from the data, the accuracy of which has been discussed above. However, even if the data were approximately correct, the figures do not warrant the inference of a linear relation between $\frac{\partial \Delta E}{\partial \theta}$ and $\frac{\partial \Delta F}{\partial \theta}$. The ratio $\frac{\partial \Delta F}{\partial \theta} : \frac{\partial \Delta E}{\partial \theta}$ is given as varying from 1:0.13 to 1:1.70 giving an average of 1:0.53, an "average" which can scarcely have any significance. From this "average" it is deduced that

$$\frac{\partial \Delta F}{\partial \theta} = -M \frac{\partial \Delta E}{\partial \theta},$$

in which the value of M "averages" about 2. We shall assume temporarily that this equation holds, and examine whether it is at variance with the assumption, tacitly made by Richards, that Δc is independent of the temperature. It has been shown by Trevor[1] that this hypothesis of Richards, of the proportionality of $\frac{\partial \Delta F}{\partial \theta}$ and $\frac{\partial \Delta E}{\partial \theta}$, is tantamount to the hypothesis that Δc is proportional to the 1M-/th power of the temperature. Assuming the "average" of Richards to be correct, it follows that

$$\Delta c = a\theta^{1/M},$$

where a is independent of θ; in other words, the isothermal change of heat capacity is dependent upon the temperature. However, in calculating the specific heat of $CuSO_4.200H_2O$, Richards takes the mean of two measurements, the one having the end temperatures 18° and 25°, and the other the end temperatures 22° and 53°. In taking such an average the tacit assumption is made that the specific heat of $CuSO_4.200H_2O$ is independent of the temperature. Further, Richards has taken the only figure given for $ZnSO_4.200H_2O$, the end temperatures being 20° and 52°. These specific heats are assumed to be

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[1] Loc. cit., p. 299.

equivalent to the specific heats at 18° C, an assumption which is not in accord with the result which the data are adduced to prove.

A linear relation between $\partial\Delta E/\partial\theta$ and $\partial\Delta F/\partial\theta$ does not exist

It has been shown that the data used by Richards involve errors of observation which vitiate the conclusions drawn from them, and that, even though the data were correct, an assumption has been made in the calculation which is out of harmony with the inferences drawn from the data. Further, the existence of such a relation as

$$\frac{\partial\Delta F}{\partial\theta} = -M\frac{\partial\Delta E}{\partial\theta}$$

cannot be proved or disproved from purely theoretical considerations alone, wherefore we must appeal to experiment.

By differentiation of the free energy equation

$$\Delta F = \Delta E + \theta\frac{\partial\Delta F}{\partial\theta}$$

we obtain

$$-\theta\frac{\partial^2\Delta F}{\partial\theta^2} = \frac{\partial\Delta E}{\partial\theta}$$
$$= \Delta c.$$

From this equation it follows that the sign of Δc is different from that of the change of the temperature coefficient of ΔF with the temperature. Further, it follows that if $\frac{\partial\Delta F}{\partial\theta}$ is constant over any range of temperature, then $\Delta c = 0$ over that range. Several cases will be considered.

It has been shown by Streintz[1] that for the lead storage cell in which the sulphuric acid concentration is 0.0005 gram-mol. per liter, the electromotive force is a linear function of the temperature, between 20° and 65°. This cell has even been suggested by Dolezalek[2] as a thermo-element. Streintz found that $\frac{\partial\Delta F}{\partial\theta}$

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[1] Wied. Ann. 46, 499 (1892).

[2] Die Theorie des Bleiaccumulators, p. 54 (1901).

is negative and constant over the temperature range considered.

It follows that in this case $\Delta c = 0$, and hence that there exists no linear relation between $\frac{\partial \Delta F}{\partial \theta}$ and $\frac{\partial \Delta E}{\partial \theta}$.

Another case of reversible cell where $\frac{\partial \Delta F}{\partial \theta}$ is constant is that of the amalgam cells. Richards and Lewis[1] have shown that for the cadmium amalgam cell, the temperature coefficient is constant and positive over the range 0 to 24°, and for the zinc amalgam cell, the temperature coefficient is constant and positive over the range 0° to 30°.

In the above cases $\frac{\partial \Delta F}{\partial \theta}$ was found to be constant over a comparatively small temperature range. Weber,[2] however, has stated that within temperature ranges of over 400°, there is no appreciable change in the heat capacity of many systems of the type

$$Pb \mid PbCl_2 \mid Cl_2$$

and of the type

$$Pb \mid PbCl_2 \mid PbBr_2 \mid Pb,$$

and consequently

$$\frac{\partial \Delta E}{\partial \theta} = 0.$$

Yet in all such cases he found that the value of $\frac{\partial \Delta F}{\partial \theta}$, the temperature coefficient of the electromotive force, is of considerable magnitude. From these results also it follows that Richards's conclusion of a fundamental linear relation between $\frac{\partial \Delta F}{\partial \theta}$ and $\frac{\partial \Delta E}{\partial \theta}$ is at variance with the experimental data.

In all the above cases $\frac{\partial \Delta F}{\partial \theta}$ has been found to vary linearly with the temperature, hence $\frac{\partial^2 \Delta F}{\partial \theta^2}$ vanishes, and hence $-\theta \frac{\partial^2 \Delta F}{\partial \theta}$ vanishes. Consequently $\frac{\partial \Delta E}{\partial \theta}$, at least over consider-

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[1] Zeit. phys. Chem., 28, 1 (1899).

[2] Zeit. anorg Chem., 21, 305 (1899).

able ranges of temperature, is zero, and, as $\frac{\partial\Delta F}{\partial\theta}$ in the cases considered is of considerable magnitude, it follows that there is no algebraic relation between $\frac{\partial\Delta F}{\partial\theta}$ and $\frac{\partial\Delta E}{\partial\theta}$.

Richards[1] has more recently said: "Recent study has made it appear highly probable that a change in heat capacity during a reaction is the chief, if not the only, reason why the total energy change (or the heat of the reaction) is not equal to the electrical work which the reaction performs in a galvanic cell." This is equivalent to the statement that the term $\theta\frac{\partial\Delta F}{\partial\theta}$ of the Helmholtz equation probably vanishes when $\Delta c = 0$. That this is more probably incorrect has been indicated by the experiments of Streintz, Richards and Lewis, and Weber. In these cases Δc was found to vanish over considerable temperature ranges and $\frac{\partial\Delta F}{\partial\theta}$ had a definite value.

There are certain cases where $\frac{\partial\Delta F}{\partial\theta}$ does not vary linearly with the temperature, *i. e.*, in a temperature-electromotive force diagram the curve is not a straight line. Such cases are given by Ochs[2] for oxidation and reduction cells. Of the large number of such cells studied by Ochs, the three cited below most probably conform to the necessary condition of reversibility, and only in so far as they are completely reversible do the conclusions drawn from the data hold good. At all points on the curve for $HMnO_4 + H_2SO_4$, $\frac{\partial\Delta F}{\partial\theta}$ is positive. The curve shows a point of inflexion, and therefore $\frac{\partial^2\Delta F}{\partial\theta}$ has both positive and negative values, depending on the temperature. The same is true of the curve for $CrO_3 + H_2SO_4$.

Hence for these cases there can be no linear relation between $\frac{\partial\Delta F}{\partial\theta}$ and $\frac{\partial^2\Delta F}{\partial\theta}$, *i. e.*, between $\frac{\partial\Delta F}{\partial\theta}$ and $\frac{\partial\Delta E}{\partial\theta}$. In the case of

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[1] Trans. Am. Electrochem. Soc., 6, II, 12 (1904).

[2] Inaugural Dissertation. Über Oxydations und Reduktionsketten. Basel, 1895.

$Mn_2(SO_4)_3 + H_2SO_4$, $\frac{\partial \Delta F}{\partial \theta}$ is positive and $\frac{\partial^2 \Delta F}{\partial \theta^2}$ is negative, and hence $-\theta \frac{\partial^2 \Delta F}{\partial \theta^2} = \frac{\partial \Delta E}{\partial \theta}$ is positive. Consequently $\frac{\partial \Delta F}{\partial \theta}$ and $\frac{\partial \Delta E}{\partial \theta}$ have the same sign, whereas Richards's equation

$$\frac{\partial \Delta F}{\partial \theta} = -M \frac{\partial \Delta E}{\partial \theta},$$

where M is positive, would necessarily make $\frac{\partial \Delta F}{\partial \theta}$ and $\frac{\partial \Delta E}{\partial \theta}$ carry opposite signs.

Van't Hoff's calculation

The subject of a possible relationship between the change of heat capacity and the temperature coefficient of electromotive force has been taken up quite recently by van't Hoff.[1] In the Helmholtz equation

$$\Delta F = \Delta E + \theta \frac{\partial \Delta F}{\partial \theta}$$

van t Hoff replaces ΔE by $\Delta E_0 + \Delta c.\theta$ where ΔE_0 is the heat of reaction at the absolute zero of temperature. It is assumed in this substitution that Δc is independent of the temperature, an assumption which in general is inadmissible. Assuming, however, that Δc is constant over a temperature range θ_0 to θ, we obtain, on replacing ΔE by $\Delta E_0 + (\theta - \theta_0)\Delta c$,

$$\theta \frac{\partial \Delta F}{\partial \theta} = \Delta F - \Delta E_0 - (\theta - \theta_0)\Delta c,$$

or, rearranging,

$$\frac{1}{\theta} \frac{\partial \Delta F}{\partial \theta} - \frac{\Delta F}{\theta^2} = - \frac{\Delta E_0}{\theta^2} - \frac{\Delta c}{\theta} + \frac{\Delta c}{\theta^2} \theta_0,$$

and integrating between temperature limits θ_0 and θ

$$(\alpha) \qquad \Delta F = (\Delta E_0 - \Delta c \theta_0) + \left\{ \frac{\Delta F_0 - \Delta E_0}{\theta_0} + \Delta c (1 + \log \theta_0) \right\} \theta - \Delta c\, \theta \log \theta,$$

which is the same in form as van't Hoff's equation (4*b*). Differentiation yields

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[1] Boltzmann Festschrift, p. 233 (1904).

$$\frac{\partial\Delta F}{\partial\theta} = \frac{\Delta F_0 - \Delta E_0}{\theta_0} + \Delta c\,(1 + \log\theta_0) - \Delta c\,(1 + \log\theta)$$

or

$$\frac{\partial\Delta F}{\partial\theta} + \Delta c\,(1 + \log\theta) = \left(\frac{\partial\Delta F}{\partial\theta}\right)_0 + \Delta c\,(1 + \log\theta_0),$$

which is identical in form with van't Hoff's equation (4*c*) if we make

$$A = \left(\frac{\partial\Delta F}{\partial\theta}\right)_0 + \Delta c\,(1 + \log\theta_0).$$

The above equation (α) as has been pointed out by Trevor[1] was deduced by Helmholtz in his famous free-energy paper.

The physical interpretation given by van't Hoff to this constant A is that

$$A = 2\log\frac{C_B}{C_A}$$

where C_A and C_B are the end concentrations of the solution in the cell, and the term AT of his equation (4*b*) corresponds in some way to the energy derivable from concentration changes. Haber and Tolloczko[2] have put the same interpretation on this term, although no proof is given. The constant A is made to vanish on the ground that $C_B = C_A$. By the vanishing of A

$$\frac{\partial\Delta F}{\partial\theta} = -\Delta c(1 + \log\theta)$$

and the condition for the vanishing of A is

$$\left(\frac{\partial\Delta F}{\partial\theta}\right)_0 = -\Delta c(1 + \log\theta_0),$$

which it is desired to prove. The above equation really indicates that if, at any temperature θ_0 of a temperature range over which Δc is constant, equation (4*d*) holds, then equation (4*d*) holds at every temperature of that temperature range.

It is possible, however, to show that such an equation as (4*d*) cannot hold under the conditions which van't Hoff has imposed. For it has been demonstrated by Trevor[1] that the ex-

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[1] l. c. p. 299.

[2] l. c. p. 438.

istence at any definite temperature of a proportionality between $\frac{\partial \Delta F}{\partial \theta}$ and Δc is the necessary and sufficient condition that

$$\Delta c = \alpha \theta^{\beta}$$

where α and β are independent of θ. This is at variance with the original assumption that Δc is independent of the temperature. It may be definitely stated, therefore, that under the conditions postulated, A does *not* vanish, and consequently any deductions made on the assumption that $A = 0$ are incorrect. Wherefore, the correct form of the relation between $\frac{\partial \Delta F}{\partial \theta}$ and Δc is

$$\frac{\partial \Delta F}{\partial \theta} = A - \Delta c(1 + \log \theta),$$

and as A depends on the initial temperature and does not vanish, it follows that $\frac{\partial \Delta F}{\partial \theta}$ and Δc, cannot stand in a simple ratio to each other.

In conclusion it should be stated explicitly that the most general formulation of the relation between the heat of reaction and the free energy is the Helmholtz equation. In his book recently published Traube[1] says: "Die Gleichung von Helmholtz bedarf nach diesen fundamentalen Festellungen von Richards eines Korrektionsgliedes, dessen Grösse von dem Unterschiede der spezifischen Wärmen abhängt." This statement is incorrect, for the assumption of Richards of a linear relation between $\frac{\partial \Delta E}{\partial \theta}$ and $\frac{\partial \Delta F}{\partial \theta}$ merely imposes one arbitrary specific limitation, namely that the change of the heat capacity is a particular function, in this case a power, of the temperature. The assumption of van't Hoff, that the change of heat capacity is independent of the temperature, merely imposes another arbitrary specific limitation. Each of these formulations is therefore less general than that of Helmholtz. Both assumptions involve attempts to formulate some integral expression for $\int_{\theta_0}^{\theta} \Delta c d\theta$ and thus to divide the term ΔE of the Helmholtz

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[1] Grundriss der physikalischen Chemie, p. 321 (1904).

equation into the sum of two terms, ΔE_0 the heat of reaction at the temperature θ_0, and the integral expression for $\int_{\theta_0}^{\theta}\Delta c d\theta$.

In this paper it has been shown that

1. The inferences of Richards and van't Hoff regarding the sign and magnitude of the change of heat capacity are based on insufficient experimental data.

2. Richards's conclusion of a proportionality between $\frac{\partial\Delta E}{\partial\theta}$ and $\frac{\partial\Delta F}{\partial\theta}$ is at variance with the assumption tacitly made in the calculation that Δc is independent of the temperature.

3. The existence of a general linear relation between $\frac{\partial\Delta E}{\partial\theta}$ and $\frac{\partial\Delta F}{\partial\theta}$ does not accord with the experimental data available.

4. The dependence of the constant A upon concentration changes was not proved by van't Hoff or by Haber and Tolloczko, and in the case of no change of concentration of the cell-solution, the assumption that A vanishes leads to a result which is out of harmony with the assumption that Δc is independent of the temperature.

Cornell University, January, 1905.

THE ELECTROLYTIC PRECIPITATION OF SILVER

BY RALPH C. SNOWDON

The precipitation of metals by electricity has, until very recent years, been regarded as something more or less in the hands of an invisible and uncontrollable power, and if good or bad results were obtained in specific cases, the greater portion of the conditions governing them were attributed to luck. It has been the object of about a year's work in this laboratory to show that the precipitation of metals from aqueous solutions particularly for plating purposes is as easily controlled and as purely chemical as any of our processes, the electric current being simply a means to an end and having the nature of any of our power factors.

Considerable work has been done on the precipitation of the metals, zinc, copper and tin, to furnish a part of the experimental data in a report by Professor Bancroft before the International Electrical Congress at St. Louis[1], on "Chemistry of Electroplating," and we have followed out the same lines in the subsequent work on silver.

It is a well known and accepted fact in general chemical practice that substances which are precipitated from solutions separate out larger crystals if they are precipitated slowly, and that an approximate relation exists between the size of the crystals and the speed of precipitation. The ordinary formation of barium sulphate from soluble barium salt solutions and of crystals of copper sulphate of extraordinary size from copper sulphate solutions may be cited as examples of this fact. Now the current controls the speed of the reaction in the case of electrolytic precipitation, so we are justified in saying that the size of the crystals of the metal decrease with the increase in current density at the cathode unless secondary or extraordinary reactions take place. Also the decrease in the size of the crystals due to the addition of various organic and inorganic compounds to the electrolyte is to be expected from our present con-

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

ception; zinc, copper and tin all fall in line with the theory and they also show a marked increase in size of crystal between 20° and 70°, those at 70°, all other conditions the same, being the largest. Rotating the cathode or stirring vigorously by other means tends to flatten out the crystals probably by simple skin friction, and it is possible to obtain a bright polished deposit in many cases by running up the speed of the cathode and using a correspondingly high current density. This apparent limiting speed and current density in the case of decreasing crystal size is of some interest in the precipitation of silver from solutions which usually do not give a satisfactory plating deposit. It is true that even our voltameter deposits are sometimes unsatisfactory because of their tendency to form large crystals and fall off.

Therefore the object in this investigation was to proceed with the study of the effect of current density and speed of rotation of the cathode upon the electrodeposition of silver, and to ascertain the possibility of obtaining a plating deposit of silver from the nitrate solution.

The first experiments were tried with a normal silver nitrate solution, silver anode and small rotating disc of copper plated with silver for cathode. This method of operation was of no use whatever because the reactions at the anode and cathode acted together in a manner detrimental to the purpose of the investigation, giving results seemingly independent of current density and speed of rotation. After several unsatisfactory runs this method of procedure was abandoned in the light of some recent work on the silver voltameter by Richards[1] and others where they use a porous diaphragm to separate the anode and cathode solutions. By means of the diaphragm the peroxynitrate of silver, $3Ag_2O.5O.AgNO_3$,[2] which is formed at the anode is kept from the cathode and its influence is thus eliminated. Our cell was then changed to suit the new conditions by the

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[1] Richards, Collins and Heimrod: Proc. Am. Acad., 35, 123 (1899); Richards and Heimrod: Ibid., 37, 415 (1902); Guthe: Phys. Rev., 19, 138 (1904).

[2] Mulder and Heringa: Recueil Trav. Pays-Bas., 15, 1 (1896).

addition of a 100 cc. porous cup which contained the silver nitrate solution under examination, and in which the cathode rotated. Outside the diaphragm and near its bottom was the platinum anode in its 20 percent nitric acid electrolyte. All was contained in a 500 cc. beaker. The cathodes were small copper discs 7 cm^2. in area soldered to a vertical shaft and speeded to about 2200 R. P. M. by a small electric motor. The lower face of the disc was plated with silver from a cyanide solution to be described later and then burnished. This operation was repeated two or three times in order to ensue a non-porous deposit. The remainder of the disc stem and the drop of solder were coated with paraffin and we had by this means an inexpensive and efficient cathode. These cathodes were then rotated within the porous cup, a fresh one being used for each change in conditions. After each of the longer runs and each two of the shorter ones, we changed the silver nitrate solution which by continued use became more or less dilute and affected by diffusion of nitric acid from the anode compartment.

Endosmose was also prevented by keeping the level of the cathode solution higher than that in the anode compartment and by previously saturating the porous cup with the silver nitrate solution. The diaphragm worked very successfully in keeping the anode formation from the cathode chamber and very excellent results were thereby obtained, which followed the line of prediction very closely.

The solutions of silver nitrate used were made up as follows:

1. Normal $AgNO_3$.
2. Normal $AgNO_3$, normal HNO_3.
3. 1/10 normal $AgNO_3$, 1/10 normal HNO_3.

Five runs on each of the solutions were made, using the current densities, actual currents, voltages and times of run as indicated in the following table:

We made photomicrographs (enlargement, 91 diameters) of each cathode as soon as it was dry, and then lacquered it to check tarnishing as much as possible. These photomicrographs show that the size of crystal decreases with the increase in current density, although the real difference between the size of the

Solution No. 1. T = 19°

	Current density Amp/dm²	Actual current amperes	Volts	Time Minutes
1	0.5	0.035	1.20	30
2	2.0	0.140	1.33	10
3	4.0	0.280	1.62	10
4	10.0	0.70	2.55	8
5	20.0	1.40	5.60	5
		Solution No. 2		
1	0.5	0.035	1.21	30
2	2.0	0.140	1.30	15
3	4.0	0.280	1.60	15
4	10.0	0.70	2.0	15
5	20.0	1.40	2.45	10
		Solution No. 3		
1	0.5	0.035	1.25	30
2	2.0	0.140	1.80	15
3	4.0	0.280	—	—
4	10.0	0.70	—	—
5	20.0	1.40	7.4	10

crystal faces in the first two runs of each set is very small and at times seemingly negative but the *crystal aggregations* change regularly in size. The decrease in size of crystals between the third and fifth runs is genuine, although the change is not great and it seems as though the maximum speed attainable with our motors is not suitable for the higher current densities. It is also noticed that the crystals in the cases of high current densities are laid on in mound-like masses following the direction of rotation, and are not separate individuals.

From these experiments we are justified in saying that in the case of silver nitrate solutions, the size of the crystals of electrolytically precipitated silver decreases with the increase in current density and that the "chemistry" idea is based on firm foundations. Some people have observed that rapid stirring of the electrolyte and a high current density at the cathode tend to make a metal deposit smoother and more homogeneous. The Elmore process for making seamless copper tubes is an instance of this. All other experimenters along this line have varied both conditions simultaneously and since this explained but little, the present work was carried out, varying only one condition at a time.

In the previous work on the silver nitrate solutions, we kept the speed of the cathode very nearly the same in all cases, so the actual effect of stirring could not be observed excepting in a general way. If this betterment of deposit in the case of rapidly rotated electrodes or unusually agitated solutions is due to simple friction of the electrode against the solution or the rapid renewal of discharging ions, then we should expect that a decrease in the rate of stirring would allow the deposit to become less homogeneous, more crystalline or "tree-like" and ultimately bad. In order to observe the effect of such a decrease in the rate of stirring, the silver cyanide solution again came into play because it gave the nearest to a bright deposit of any of the plating solutions. The solution is:

15 g $AgNO_3$.
Enough KCN to redissolve the precipitate formed.
1000 cc. water.

Under ordinary conditions in a simple electrolytic cell with silver anode, this solution precipitates the silver as a beautifully white coating having a matte appearance, but if the cathode be speeded to about 2200 R. P. M. the deposit comes out almost bright. The conditions and results of experiments follow:

Potassium Silver Cyanide Solution. T = 20°

1.	2.0 amp/dm²	Speed 2200 R. P. M.
	2½ minutes	Deposit *nearly* bright
2.	2.0 amp/dm²	Speed 500 R. P. M.
	2½ minutes	Deposit decidedly matte
3.	1.0 amp/dm²	Speed 2200 R. P. M.
	5 minutes	Deposit decidedly matte
4.	10.0 amp/dm²	Speed 2200 R. P. M.
	5 minutes	Deposit decidedly matte

The copper cathodes previously described were used but they were not plated with silver before the runs. A silver anode was used. Several trials were necessary before the conditions were obtained for a bright deposit, working from a low current density and a high current density toward a happy medium. The data for these have been omitted because they indicate but little. The reason why the current density of 10 amp/dm^2 did not give a bright deposit is because the speed and current density are factors depending upon each other, and in this case the silver was precipitated out of the solution too rapidly to be burnished by the swiftly moving cathode. However, the difference between Run 1 and Run 2 shows that the ideas advanced are correct as far as we have gone and that the speed is a very important factor. The difference between 1 and 3 confirms still further the conceptions in regard to increase in crystal-size with decrease in current density.

There is but little doubt that if means were at hand by which the cathode could be rotated at higher speeds a place would appear where a burnished deposit might be obtained from even a silver nitrate solution, one of the poorest solutions from which to precipitate a good deposit of silver.

During the investigation, the effect of glue on the deposition of silver was studied since it is usually conceded that the addition of organic "colloids" causes wonderful effects when precipitating metals chemically or by electricity. Three experiments, which were made on silver nitrate solution No. 1, gave rather interesting results. These were done in the diaphragm cell previously described. The lowest current density was used because it usually forms large crystals of the metal. Our conditions were as follows:

MOLECULAR SILVER NITRATE SOLUTION No. 1, T = 19°.
Speed rotation 2200 R. P. M.

1.	0.5 g glue per liter.	C. D. 0.5 amp/dm^2.	Smooth purple deposit.
2.	3.0 g glue per liter.	C. D. 0.5 amp/dm^2,	Smooth yellow deposit going purple.
3.	10.0 g glue per liter.	C. D. 0.5 amp/dm^2.	Smooth purple deposit.

A precipitate of colloidal silver was obtained in each of the cases, Nos. 1 and 3 being purple in color and almost perfectly amorphous while No. 2 had a yellowish color which darkened slowly on standing to nearly purple. The three colloidal deposits which we did obtain had no visible crystal structure and were nearly bright. They resembled those precipitated by M. Carey Lea from silver salts of organic acids by purely chemical means. The phenomenon is rather unusual and we have not tried to work out the conditions under which the various forms of collodial silver may be obtained, but leave this for a further research. The general results of this paper are:

A very finely crystalline deposit of silver can be obtained from a silver nitrate solution by rotating the cathode rapidly and keeping the anode and cathode solutions separated.

The size of the crystals decreases with the increase in current density and the increase in the rate of stirring at the cathode.

The addition of small amounts of organic "colloids" to the solution makes the deposit very amorphous and causes the precipitated metal to assume a colloidal state.

The presence of free nitric acid decreases the size of crystals but slightly.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University.

THE ELECTROLYTIC PRECIPITATION OF NICKEL ON NICKEL

BY RALPH C. SNOWDON

It has been noticed in many books on technical electroplating that nickeled work which is to be replated must be entirely freed from the previous deposit of nickel or the subsequent plating will be in vain. McMillan says in regard to this: "It is even more important in nickeling than in silvering or gilding that an existing film of nickel be entirely removed, or the new deposit will most certainly lack adhesive properties."[1] He[2] also mentions that suspending wires should be used but once because the subsequent deposits of nickel will peel off and give trouble in the bath. This peeling also causes thick deposits of nickel to be rather undesirable.[3]

Burgess and Hambuechen[4] have noticed this peeling and non-adherence in the case of other deposits, and they say: "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 electrodeposition 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. . . . The same phenomenon has previously been pointed out in the electrolytic separation of nickel."

The real reason why the deposit curls up any more than the same metal would, if it were not electrolytically prepared seems to be due to the metal being deposited in a state of strain which is undoubtedly caused by absorbed hydrogen[5] or uneven

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[1] McMillan: "A Treatise on Electrometallurgy," 2nd ed., p. 243.

[2] Ibid., p. 245.

[3] Ibid., p. 246.

[4] Jour. Phys. Chem., 7, 409 (1903).

[5] W. McA. Johnson: Trans. Am. Electrochem. Soc., 3, 255 (1903).

deposition of the metal.[1] There is no evidence that a hydride of nickel is formed. This would hardly account for the fact that the original metal and the deposit do not adhere. Prof. Bancroft suggested that the first metal had become covered with a film of some oxide which could not be removed by ordinary methods of cleaning, or, in other words, the surface was made "passive."

The reaction undoubtedly takes place with great readiness in the case of nickel, iron and aluminum, according to Burgess and Hambuechen.[2] Therefore, if this surface be treated with some strong reducing agent, we should have a metal free from oxide which would take an adherent deposit if it were transferred immediately to a plating bath through which current is flowing. The most convenient way in which to do this is by making the passive metal cathode in an acid solution and passing a fairly large current for a short time. This will cause a heavy evolution of hydrogen, part of which will be taken up by the metal and the oxide will be reduced. Quick washing and transferring to the plating bath should give us a metallic surface upon which an adherent deposit could be plated.

For the preliminary treatment of the nickel cathodes, we prepared a 3-normal solution of hydrochloric acid and used a current density of 8 amperes per square decimeter. The electrodes were both of nickel and were placed about 4.25 cm. apart. The run lasted four minutes. Hydrogen was evolved copiously at the cathode. As soon as sufficient treatment had been given the cathode it was washed in clean water and plunged into the regular plating solution which was made up:

$(NH_4)_2SO_4.NiSO_4.6H_2O$	80 g
Water	1 liter

The other conditions:

Area cathode	1/4 dm^2
Current density	2.0 amp/dm^2
Voltage	3.8 volts
Temperature	18°
Time	1/2 hour.

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[1] D. H. Browne: Electrochemical Industry, 1, 348 (1903).

[2] Jour. Phys. Chem., 7, 409 (1903).

In case a rolled nickel anode is used, the solution must be kept neutral or only very slightly acid by means of ammonium hydroxide. Too great acidity causes the precipitation of a spongy deposit. In our case the deposit came out perfectly smooth and so adherent that it could be burnished and scratch-brushed with impunity.

In order to demonstrate the difference between a prepared or "active" cathode and one ordinarily cleaned we performed another experiment under precisely the same conditions as before, but simply scratch-brushed and cleaned the nickel plate before making it cathode. On removing from the plating solution about half the precipitated nickel had curled up, a slight rubbing causing it to fall off.

Therefore the conclusions to be drawn from this paper are:

1. Nickel can be precipitated upon the "active" nickel cathode and caused to adhere without difficulty.

2. Nickel cannot be successfully plated on other nickel because of the presence of a thin film of oxide which cannot be removed except by vigorous reduction.

3. The "active" state is very instable.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University.

MOLECULAR ATTRACTION, IV. ON BIOT'S FORMULA FOR VAPOR PRESSURE AND SOME RELATIONS AT THE CRITICAL TEMPERATURE

BY J. E. MILLS

The $\frac{\partial P}{\partial T}$ of a liquid

In a preceding paper[1] we examined the following equation, which had been proposed on theoretical grounds by Mr. H. Crompton:

$$(1)\qquad L = 2\int_v^V p\partial v = 2RT\log_e\frac{d}{D} = \frac{9.154}{m}T\log\frac{d}{D}\text{ cals.}$$

(L is heat of vaporization, v and V denote volume of liquid and vapor, d and D the density of liquid and vapor, p is pressure, T is temperature, m is molecular weight, R is the constant of the gas equation, PV = RT.)

It was there shown that this equation gives at low temperatures where the vapor pressure is small, results for the heat of vaporization that are invariably and usually very considerably too large. But at the higher temperatures examined, that is as the critical temperature is approached, the results given by the equation appeared to be correct. The evidence there given as to the correctness of this equation at high temperatures was very considerable and justified further use of the equation. Therefore in that paper we combined the usual thermodynamical equation for calculation of the heat of vaporization,

$$(2)\qquad L = \frac{T}{J}(V - v)\frac{\partial P}{\partial T} = 0.0_431833\,T(V - v)\frac{\partial P}{\partial T}\text{ cals.}$$

with the equation of Crompton given above, and obtained equation 15 of that paper, *viz.:*

$$(3)\qquad \frac{\partial P}{\partial T} = \frac{287500}{m}\,\frac{\log\frac{V}{v}}{V - v}$$

We there showed that the limit approached by this equation as

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[1] Jour. Phys. Chem., 8, 593 (1904).

the critical temperature was approached and V approached v in value, was,

$$\frac{\partial P}{\partial T} = \frac{124860}{m V}. \tag{4}$$

We at that time overlooked the fact that this equation 4 could be expressed in the very simple form,

$$\frac{\partial P}{\partial T} = \frac{2 R}{V}. \tag{5}$$

Here V is the critical volume and R is the usual gas constant, and we have the striking conclusion that *at the critical temperature the* $\frac{\partial P}{\partial T}$ *of the liquid (vapor) is exactly twice what it would be for that substance as a perfect gas occupying the same volume.* Expressed in this form the bearing of equation 3, or its limiting forms, on the kinetic relations of a liquid and its vapor, assumes more importance and justifies closer study.

Accordingly by means of equation 4, we calculated, and give in Table I, the values of the $\frac{\partial P}{\partial T}$ at the critical temperature for twenty substances. The critical data used is that given by Dr. Young.[1] This data is more correct than that given in earlier papers. (We would here note that in the third paper on Molecular Attraction[2] we overlooked this corrected data, but have since repeated the calculations there given using the corrected data and find no material change in the results or conclusions there expressed.)

For comparison with these values the $\frac{\partial P}{\partial T}$ can be calculated from any equation connecting vapor pressure and temperature. Of the numerous equations that have been proposed the one usually known as Biot's has proved by far the most serviceable. It takes the form,

$$\text{Log } P = A + b.\alpha^t + c.\beta^t. \tag{6}$$

By differentiating and changing to Naperian logarithms we get

$$\frac{\partial P}{\partial T} = 5.3019\ P(b.\log \alpha.\alpha^t + c.\log \beta.\beta^t). \tag{7}$$

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[1] Phil. Mag. [5], 50, 291 (1900).

[2] Jour. Phys. Chem., 8, 593 (1904).

Since we had previously used Biot's formula for calculating heats of vaporization more directly, we found it easier to throw equation 7 into the form,

$$\frac{\partial P}{\partial T} = 0.031414\ \mathrm{PA}, \tag{8}$$

where $A = 168.775\,(b.\log \alpha.\alpha' + c \log \beta.\beta')$.

The constants for this equation have already been given[1] for all of the substances examined, except those noted below.

Ethyl oxide. $A = \text{antilog}\,(\bar{1}.9882227 - 0.00172541\,t) + \text{antilog}\,(\bar{1}.7399799 - 0.00869664\,t)$, $t = t\ {}^\circ\mathrm{C}$.

Benzene. $A = \text{antilog}\,(\bar{1}.4256719 + 0.0001302029\,t) + \text{antilog}\,(0.1799122 - 0.00410411\,t)$, $t = t\ {}^\circ\mathrm{C}$.

Methyl alcohol. $A = \text{antilog}\,(\bar{1}.5561254 - 0.00011584\,t) + \text{antilog}\,(0.2151667 - 0.00400204\,t)$, $t = t\ {}^\circ\mathrm{C}$.

Ethyl alcohol. $A = \text{antilog}\,(\bar{2}.3965216 + 0.003377538\,t) + \text{antilog}\,(0.3342413 - 0.00317576\,t)$, $t = t\ {}^\circ\mathrm{C}$.

Propyl alcohol. $A = \text{antilog}\,(\bar{2}.8340346 + 0.001641423\,t) + \text{antilog}\,(0.3135244 - 0.00342975\,t)$, $t = t\ {}^\circ\mathrm{C} - 20$.

The constants for ethyl formate and methyl acetate were kindly sent me by Dr. Young (work yet unpublished) and the constants for methyl formate I have calculated and will publish later.

The values of the $\frac{\partial P}{\partial T}$ at the critical temperature as obtained from these Biot equations are shown in Table I.

Of the twenty substances compared in Table I it will be seen that the $\frac{\partial P}{\partial T}$ from equation 4 has a higher value than the $\frac{\partial P}{\partial T}$ calculated from Biot's formula in all cases except di-isobutyl, normal octane, and ethyl alcohol. The difference is usually very marked.

In work done upon an equation of the form, $P = bT - a$, Ramsay and Young[2] made a study of the $\frac{\partial P}{\partial T}$ of ether at constant

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[1] Jour. Phys. Chem., 8, 383 (1904).

[2] Phil. Mag. [5], 23, 435 (1887).

TABLE I

Substance	Critical temperature	$\frac{\partial P}{\partial T}$ from Equation 4	$\frac{\partial P}{\partial T}$ from Biot	Δ	A
Ethyl oxide	194.45°C	441.9	391.6	50.3	0.46068
Di-isopropyl	227.35	349.6	321.0	28.6	0.43795
Di-isobutyl	276.8	258.8	261.6	—2.8	0.44672
Isopentane	187.8	405.7	367.8	37.9	0.46822
Normal pentane	197.2	402.3	364.8	37.5	0.46331
Normal hexane	234.8	339.9	315.9	24.0	0.44826
Normal heptane	266.85	291.9	286.9	5.0	0.44782
Normal octane	296.2	254.5	256.8	—2.3	0.43647
Benzene	288.5	487.0	445.4	41.6	0.38961
Hexamethylene	279.95	406.0	376.0	30.0	0.39583
Fluo-benzene	286.55	460.1	430.7	29.4	0.40428
Carbon tetrachloride	283.15	452.7	416.7	36.0	0.38808
Stannic chloride	318.7	355.2	332.5	22.7	0.37689
Methyl formate	214.0	725.6	619.2	106.4	0.43872
Ethyl formate	235.3	545.0	479.7	65.3	0.43091
Methyl acetate	233.7	548.3	502.3	46.0	0.45454
Methyl alcohol	240.0	1061.1	971.1	90.0	0.51729
Ethyl alcohol	243.1	747.0	796.7	—49.7	0.52998
Propyl alcohol	263.7	568.3	562.4	5.9	0.47181
Acetic acid	321.65	729.2	574.6	154.6	0.42066

volume, Young,[1] later a similar study for iso-pentane, and Rose-Innes and Young[2] correspondingly for normal pentane. At the critical volume the value of the $\frac{\partial P}{\partial T}$ obtained at constant volume becomes identical with the value of the $\frac{\partial P}{\partial T}$ denoting the increase in vapor pressure of the liquid. Therefore it is possible in these three cases by comparison with the values of the $\frac{\partial P}{\partial T}$ obtained in the above papers to determine whether the values of the $\frac{\partial P}{\partial T}$ calculated from Biot's formula or those obtained from Equation 4 are correct. The result is shown below, the values of the $\frac{\partial P}{\partial T}$, at the exact critical volume having been obtained from the

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[1] Phil. Mag. [5], 38, 569 (1894).

[2] Ibid. [5], 47, 353 (1899).

above-mentioned papers by interpolation and entered in the column marked "Observed."

Substance	Volume	From Biot	Equation 4	Observed
Ether	3.814	391.6	441.9	436
Isopentane	4.268	367.8	405.7	401 to 411
Normal pentane	4.305	364.8	402.3	406.7

In every case the values accord to within the limit of experimental error with the values derived from Equation 4, and are uniformly higher than the values derived from Biot's equation. (It is not possible to extend the comparison to the alcohols and acetic acid studied by the observers above mentioned, for these liquids are associated and Equation 4 depending on the molecular weight, could not give correct results.)

On Biot's formula for vapor pressure

It seemed to us reasonable to conclude from the above comparison that the ratios of the $\frac{\partial P}{\partial T}$ calculated from Equation 4 at the critical temperature and shown in Table I were the correct values and that the values obtained from Biot's formula were in error. Fortunately we had a means of verifying this conclusion directly.

If the vapor pressure curve be plotted against the temperature, the $\frac{\partial P}{\partial T}$ is the tangent to the curve. Assuming that Biot's formula does correctly represent the vapor pressures until the critical temperature is approached (an assumption justified by a very careful examination of the curves over the entire range of temperature) it is evident that if the $\frac{\partial P}{\partial T}$ calculated from Biot's formula then becomes too low it must be because the vapor pressure curve as calculated from Biot's formula is below the true vapor pressure curve. We accordingly subtracted the observed vapor pressures from the calculated in the immediate neighborhood of the critical temperature and obtained the results shown in Table II. In every case except normal octane, stannic chloride, and the associated substances (methyl alcohol, ethyl alcohol, and acetic acid), the calculated minus the observed vapor pressures does give negative differences at the highest temperature compared (usually the critical temperature itself). With regard to these five exceptions, the associated substances cannot give exactly correct results by the use of Equation 4 and their evidence does not, therefore, bear upon that equation. Normal octane and stannic chloride are the only substances whose divergence can be considered as evidence against the conclusion above derived and it is sufficient to point out in explanation a remark made by Dr. Young[1] when the vapor pressures of normal octane were published. He there states that the observed values of the vapor pressure above 280° C for *normal octane, stannic chloride, and acetic acid*, are probably *too low* owing to an error in the temperature scale, *i. e.*, in the boiling-points of the liquids used as a heating jacket.

A close examination of the observed and calculated vapor pressure curves reveals the fact that no matter how the constants for Biot's formula be altered, they cannot exactly represent the true vapor pressures in the neighborhood of the critical temperature. The deviation is very slight, usually negligible when the vapor pressure is considered, because the proportional error is very small. But when the $\frac{\partial P}{\partial T}$ is considered the proportional error is very large.

Since Biot's formula was empirical and in the immediate neighborhood of the critical temperature was forced to fit a curve it could not exactly follow, it usually happens that the curve of observed vapor pressures cuts the curve of calculated vapor pressures in the neighborhood of the critical temperature, the observed vapor pressure curve having, of course, the steeper trend. This is at once evident on reference to Table II by the change from positive to negative values of the differences between the calculated and observed vapor pressures.

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[1] Jour. Chem. Soc., 77, 1147 (1900).

We would here point out the great accuracy of these measurements made by Drs. Ramsay and Young and by Dr. Young and his co-workers. The conclusion that the calculated minus the observed vapor pressure should be negative near the critical temperature was wholly theoretical on our part. That we should be able at once to verify this conclusion from the measurements when the differences were so small as to have been laid by the observers themselves on the errors of measurement (the regularity of the differences having escaped observation) speaks for itself as to their accuracy and skill. The observed and calculated vapor pressure lines are almost indistinguishable even at the critical temperature and when drawn to a large scale.

TABLE II

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Ethyl oxide	170°C	300.5	303.5	18622	18671	— 49
	180	336.3	345.2	21804	21775	29
	185	354.9	368.8	23532	23623	— 91
	190	374.1	399.5	25355	25513	—158
	192	382.2	415.8	26111	26331	—220
	193	385.8	429.7	26495	26800	—305
	194.45	391.6	441.9	27060		
Di-isopropyl	180	186.6	187.2	11536	11535	1
	200	236.5	236.0	15752	15693	59
	220	296.2	302.6	21062	21009	53
	225	312.9	327.1	22585	22588	— 3
	227.35	321.0	349.6	23330	23360	— 30
Di-isobutyl	220	128.6	123.0	7941	7937	4
	240	165.7	155.6	10883	10905	— 22
	260	212.5	196.9	14660	14651	9
	270	240.4	225.7	16929	16905	24
	274	253.9	240.1	18006		
	276.8	261.6	258.8	18640	18660	— 20

TABLE II—(*Continued*)

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Isopentane	140	204.4	208.3	11620	11634	— 14
	160	264.0	267.7	16285	16320	— 35
	180	335.9	348.1	22262	22270	— 8
	185	356.1	377.6	23992	24000	— 8
	187	364.4	393.2	24713	24730	— 17
	187.4	366.4	400.1	24854	24880	— 26
	187.8	367.8	405.7	25005	25018	— 13
Normal pentane	160	235.0	237.4	14032	14060	— 28
	180	299.7	303.5	19362	19345	17
	190	336.5	347.4	22540	22500	40
	195	355.9	378.1	24271	24255	16
	197	363.8	397.2	24991	25020	— 29
	197.2	364.8	402.3	25063	25100	— 47
Normal hexane	180	163.8	162.9	9659	9650	9
	200	210.2	207.3	13385	13348	37
	220	266.4	264.8	18133	18100	33
	230	299.0	303.8	20957	20955	2
	234	313.0	328.2	22181	22220	— 39
	234.8	315.9	339.9	22433	22510	— 37
Normal heptane	220	162.0	153.2	10130	10105	25
	240	207.6	194.8	13811	13790	21
	260	264.4	252.5	18511	18470	41
	264	277.4	269.5	19595	19610	— 15
	266.5	285.8	286.4	20300		
	266.85	286.9	291.9	20399	20430	— 31
Normal octane	240	130.9	122.8	8184.5	8219	—34.5
	260	167.5	154.8	11156	11185	— 29
	280	212.6	196.7	14942	15015	— 73
	290	239.0	224.8	17198	17126	72
	296.2	256.8	254.5	18734	18730	4
Benzene	240	269.5	273.7	19369	19352	17
	260	333.0	337.4	25376	25329	47
	280	408.9	420.0	32772	32782	10
	288.5	445.4	487.0	36409	36395	— 14

TABLE II—(*Continued*)

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Hexamethylene	240	246.7	249.8	17961	17973	— 12
	260	305.2	307.6	23461	23439	22
	270	338.9	344.4	26680	26667	13
	277	364.6	379.3	29140	29206	— 66
	279	372.3	394.0	29878		
	279.95	376.0	406.0	30234	30260	— 26
Fluo-benzene	240	258.5	260.4	18190	18161	29
	260	322.3	321.4	23977	23960	17
	280	400.9	405.3	31182	31217	— 35
	286.55	430.7	460.1	33905	33912	— 7
Carbon tetrachloride	240	266.8	271.7	19596	19633	— 37
	260	328.6	333.4	25532	25528	4
	280	402.9	415.6	32825	32825	0
	283.15	416.7	452.7	34114	34181	— 67
Stannic chloride	240	148.7	166.9	9915	9915	0
	260	184.9	212.9	13242	13290	— 48
	280	227.3	269.9	17351	17454	— 103
	310			25294	25079	215
	318.7	332.5	355.2			
	319.35			28283	28079	204
Methyl formate	180	431.8	443.5	27163	27040	123
	200	537.8	569.6	36839	36685	154
	210	595.4	661.1	42502	42510	— 8
	213.5	616.2	714.8	44622	44670	— 48
	214.0	619.2	725.6	44932	45030	— 98
Ethyl formate	160	199.8	200.6	10830	10847	— 17
	180	259.3	259.1	15405	15385	47
	200	329.0	330.8	21271	21148	123
	220	409.8	422.9	28640	28527	113
	230	454.7	483.1	32961	32968	— 7
	235.3	479.7	545.0	35436	35535	— 99

TABLE II—(*Continued*)

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Methyl acetate	180	262.8	258.0	15152	15118	34
	200	338.8	332.3	21146	21085	61
	220	429.8	429.3	28804	28705	99
	230	481.8	497.9	33360	33358	2
	233.7	502.3	548.3	35180	35212	— 32
Methyl alcohol	180	411.1	385.0	20016	20089	— 73
	200	560.8	520.4	29688	29787	— 99
	220	747.9	709.5	42676	42573	103
	230	851.9	830.4	50651	50414	237
	238.5	951.7	973.3	58310	58329	— 19
	240.0	971.1	1061.1	59759	59660	99
Ethyl alcohol	200	430.8	353.0	22182	22164	18
	220	576.6	491.5	32196	32097	99
	240	763.7	675.0	45519	45504	15
	242.5	790.0	731.2	47463		
	243.1	796.7	747.0	47939	47850	89
Propyl alcohol	220	334.0	293.9	18667	18679	— 12
	240	428.0	390.1	26263	26194	69
	260	540.0	505.1	35908	36103	— 195
	263.7	562.4	568.3	37947	38120	— 173
Acetic acid	280	367.5	426.8	24055	24123	— 68
	300	460.3	534.9	32312	32043	269
	310	511.4	600.7	37168	36943	225
	320	565.4	710.9	42550	42553	— 3
	321.65	574.6	729.2	43480	43404	76

In order to show that Equation 4 does give results in accord with Biot's formula at points considerably below the critical temperature we give in Table II the values of the $\frac{\partial P}{\partial T}$ calculated from both formulas at intervals for some 50° C below the critical temperature. We have already pointed out that Equation 4 itself becomes inaccurate at yet lower temperatures.

Correct values for μ' near the critical temperature

Since Equation 4 enables us to obtain in the neighborhood of the critical temperature more nearly correct values for the $\frac{\partial P}{\partial T}$ than we had been able to obtain in previous papers when working with Biot's formula we concluded to use these values and test more thoroughly the equation,

$$(9) \qquad \frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu'$$

discussed in previous papers[1]. If the value of the $\frac{\partial P}{\partial T}$ from Equation 3 be substituted in the thermodynamical equation, 2, the values of the heat of vaporization so calculated are the same as those obtained from Equation 1. Therefore using these values and substituting them in Equation 9 we obtain the corrected values for the constant. The results so obtained at those points nearest the critical temperature are given in Table III under the heading "New." For comparison we give under heading "Old" the values that we had previously obtained for μ' at this same temperature when using the $\frac{\partial P}{\partial T}$ obtained from Biot's formula in calculating the heats of vaporization thermodynamically. Also we give under the heading "Mean," the average value of the constant previously adopted. Agreement is not of course to be expected for the four associated substances last shown in the table. For the other substances there is little question but that the constants so obtained agree with the mean values to within the limit of experimental error except in the cases of di-isobutyl, normal heptane, normal octane, and methyl acetate. We are unable to explain the smaller values obtained from these four substances but the proof that Equation 9 does hold as near the critical temperature as it is possible for measurements to be made is now complete for ethyl oxide, di-isopropyl, isopentane, normal pentane, normal hexane, benzene, hexa-methylene, fluo-benzene, carbon tetrachloride, stannic chloride, methyl formate, and ethyl formate.

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[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904).

TABLE III

Substance	Temperature	Old μ'	New μ'	Mean μ'	Critical temperature	From Equation 12 μ'	$\frac{PVm}{T}$
Ethyl oxide	193	90.7	102.0	104.4	194.4	102.1	16360
Di-isopropyl	225	92.0	96.8	98.1	227.4	96.5	16660
Di-isobutyl	274	86.4	82.3	86.3	276.8	80.7	16370
Isopentane	187.4	99.3	107.0	105.4	187.8	107.0	16710
Normal pentane	197	98.8	109.9	109.9	197.2	109.4	16570
Normal hexane	234	94.2	99.5	102.85	234.8	99.2	16290
Normal heptane	266.5	90.8	91.0	98.75	266.9	90.8	16170
Normal octane	290	91.0	84.8	93.0	296.2	84.2	16140
Benzene	280	107.8	111.2	109.5	288.5	110.5	16610
Hexamethylene	279	98.1	104.7	103.6	280.0	104.5	16820
Fluobenzene	280	84.7	85.75	85.6	286.55	85.2	16440
Chlorbenzene	—	—	—	81.2	360.0	81.5	16490
Brombenzene	—	—	—	56.1	397.0	56.3	16380
Iodobenzene	—	—	—	44.4	448.0	43.8	16500
Carbon tetrachloride	280	43.9	45.5	44.1	283.15	45.3	16940
Stannic chloride	280	22.15	26.96	26.04	318.7	25.87	16680
Methyl formate	213.5	101.2	120.1	121.5	214.0	119.8	15910
Ethyl formate	234	94.0	104.4	107.2	235.3	103.9	16040
Methyl acetate	233	96.6	103.8	109.5	233.7	103.6	15800
Methyl alcohol	238.5	259.4	264.3	305.0	240.0	262.4	13705
Ethyl alcohol	242.5	197.2	178.9	241.2	243.1	179.9	15495
Propyl alcohol	260	157.0	144.6	199.2	263.7	143.7	15590
Acetic acid	320	116.4	150.6	—	321.6	150.7	12502

The value of μ' at the critical temperature

It is possible to extend this proof quite to the critical temperature itself. Substituting in Equation 9 the value of L given by the thermodynamical equation, 2, and the value of $E_1 = .0_4 31833 P(V - v)$, we have

$$\frac{.0_4 31833 \left(T \frac{\partial P}{\partial T} - P\right)\left(V - v\right)}{\sqrt[3]{d} - \sqrt[3]{D}} = \mu', \tag{10}$$

and obtaining the limit of this equation as V approaches v in value we have for the equation at the critical temperature, where $V = v$, the form

$$.0_4 955\, V^{\frac{4}{3}}\left(T \frac{\partial P}{\partial T} - P\right) = \mu'. \tag{11}$$

As we have shown, the most correct value for the $\frac{\partial P}{\partial T}$ available at this temperature is that given by Equation 4 and substituting this value in the equation we get,

$$(12) \qquad \mu' = V^{\frac{1}{3}}\left(\frac{11.924T}{m} - .0_4955PV\right).$$

This equation is the same as Equation 17 of the third paper[1]. Here V, T, and P, are the critical volume, temperature, and pressure, respectively, and *m* is the molecular weight of the substance under consideration. The equation is interesting because it gives a method for calculating the constant of molecular attraction μ' in terms of the critical constants and the molecular weight of the substance. Since the molecular weight enters into the equation it evidently cannot be applied to associated substances. Again using the critical data already referred to, given by Young, the values obtained from this equation are shown in Table III, above. Except for di-isobutyl, normal heptane, normal octane, methyl acetate, and to a less degree for ethyl formate, the agreement with the mean values of μ' is excellent and we may therefore regard the truth of Equation 9 as having been established at the critical temperature itself for fifteen of the nineteen substances under consideration. (Ethyl formate decomposes slightly at the higher temperatures which is sufficient to account for the divergence, three percent, there observed.) We have already shown that normal heptane and normal octane give constant values for μ' in Equation 9 over a range of more than 200° C in temperature. We have unpublished results showing the same to be true for methyl acetate. Di-isobutyl did give a variation of several percent at low temperatures, a divergence that we think was sufficiently explained.[2] It would seem probable therefore that the divergences shown by these four substances at the critical temperature must be due to some change or decomposition taking place in the substance at that temperature and that Equation 9 is applicable for all normal substances quite up to the critical temperature.

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[1] Jour. Phys. Chem., 8, 593 (1904).

[2] Ibid., 8, 595 (1904).

Ratio of the theoretical to the actual critical density

In a preceding paper[1] we showed that the molecular attraction at unit distance, μ, was equal to $c\mu'\sqrt[3]{m}$. Therefore we have from Equation 12,

$$(13) \qquad \mu = c\sqrt[3]{mV}\left(\frac{11.924T}{m} - .0_4955PV\right).$$

In the same paper on the assumption that the critical temperature was the point where the kinetic energy of the molecules was just balanced by the molecular attraction we derived Equation 24 of that paper, viz.:

$$(14) \qquad \mu = c'\frac{T}{m}\frac{\sqrt[3]{m}}{d},$$

where T is the critical temperature and *d* is the critical density. We can now combine this value of μ with the value of μ given in Equation 13 and obtain,

$$(15) \qquad c'\frac{T}{m}\frac{\sqrt[3]{m}}{d} = c\sqrt[3]{mV}\left(\frac{11.924T}{m} - .0_4955PV\right),$$

whence,

$$(16) \qquad \frac{PVm}{T} = \text{constant}.$$

We show the values of $\frac{PVm}{T}$ in Table III and it will be seen that hexamethylene and carbon tetrachloride alone (the associated substances being excepted) give a value more than three percent from the average value 16293.

$\frac{.0_416014Pm}{T}$ is the theoretical critical density and Equation 16 is really the ratio of the theoretical, D_c, to the actual critical density, d_c, and can take the form,

$$(17) \qquad \frac{Dc}{dc} = \text{constant}.$$

The relation in this form has been fully discussed by Dr. Young.[2] It here appears as a necessary consequence of the ideas that we

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[1] Jour. Phys. Chem, 8, 630 (1904).

[2] Phil. Mag., [5] 50, 291 (1900).

have advanced though we did not foresee that such would be the case, and hence are justified in considering the deduction of this relation as further evidence that those fundamental ideas upon which this series of papers is based are correct.

It may seem unusual that we should have been able to derive two different equations for μ (Equations 13 and 14) in terms of the critical constants. This is due to the fact that the critical temperature besides possessing the property that the molecular attraction just balances the kinetic energy of the molecules —the relation upon which Equation 14 is based—can also be viewed as a boiling-point and from this point of view permits the deduction of Equation 13. We hope shortly to complete a paper applying these ideas of molecular attraction more fully to the boiling-point.

We should also point out that by combining Equation 11 with Equation 14, we get

$$(18) \qquad \frac{T}{m} = cV\left(\frac{T\partial P}{\partial T} - P\right),$$

where c is a constant. This equation can be solved so as to give any one of the variables at the critical temperature in terms of the others and the molecular weight. It is not feasible now to further examine this equation, since the only correct values for the $\frac{\partial P}{\partial T}$ are obtained from Equation 4 and this at once reduces the equation to the form of Equation 16.

Dr. Young[1] has shown that the average constant of Equation 17 is $\frac{1}{3.827}$. Since the theoretical critical pressure is therefore 3.827 times the actual critical pressure it follows from the gas law and Equation 5 that at the critical temperature,

$$(19) \qquad \frac{\partial P}{\partial T} = \frac{7.654P}{T}.$$

This equation can be obtained directly from Equation 18 but the constant is then unknown.

SUMMARY.

1. It is shown that the $\frac{\partial P}{\partial T}$ for a liquid (vapor) at the critical temperature is exactly twice what it would be for the same substance as a perfect gas occupying the critical volume.

2. It is shown that Biot's formula for vapor pressure cannot be made exactly to fit the true vapor pressure curve in the immediate neighborhood of the critical temperature. When the pressure is considered, the proportional error is very small. When the $\frac{\partial P}{\partial T}$ is considered, the proportional error is large and the values obtained from Biot's formula are too small.

3. The equation, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \mu'$, where μ' is the constant of molecular attraction, is shown to be applicable with exactness in the immediate neighborhood of, and at, the critical temperature for fifteen out of nineteen substances considered. The equation has already been proved accurate at lower temperatures.

4. It is shown that the constant of molecular attraction, μ', can be calculated from the critical constants and the molecular weight.

5. The known fact that the ratio of the theoretical critical density to the actual critical density is a constant for all substances is shown to follow necessarily from the fundamental ideas and equations upon which this series of papers is based.

University of North Carolina,
April 3rd, 1905.

NEW BOOKS

Studies in General Physiology, I and II. *By Jacques Löeb. (The Decennial Publications of the University of Chicago.) 15 × 22 cm.; pp. xxiv + 782. Chicago: The University of Chicago Press, 1905. Price: bound, $7.50 net.*—" A single leading idea permeates all the papers of this collection, namely, that it is possible to get the life phenomena under our control, and that such a control and nothing else is the aim of biology. Thus the reader will notice that in a series of these publications I have tried to find the agencies which determine unequivocally the direction of the motion of animals, and he will also notice that I consider a complete knowledge and control of these agencies the biological solution of the metaphysical problem of animal instinct and will. In taking up the problem of regeneration I started out with the idea of controlling these phenomena, and considered it my first aim to find means by which one organ could, at desire, be caused to grow in the place of another organ. Thus the experiments on heteromorphosis originated. As far as the problem of fertilization is concerned, it seemed to me that the first step toward its solution should consist in the attempt to produce larvae artificially from unfertilized eggs in various classes of animals."

"We have seen that the heliotropic movements of animals possessing a nervous system are determined in all respects by the same external conditions, and depend in the same way on the external form of the body as do the heliotropic movements of plants, which have no nervous system. *These heliotropic phenomena cannot, therefore, depend upon specific characteristics of the central nervous system.*"

"In the biological literature one still finds authors who treat the 'instinct' or the 'will' of animals as a circumstance which determines motions, so that the scientist who enters the region of animated nature encounters an entirely new category of causes such as are said continually to produce before our eyes great effects, without it being possible for an engineer ever to make use of these causes in the physical world. 'Instinct' and 'will' in animals, as causes which determine movements, stand upon the same plane as the supernatural powers of the theologians, which are also said to determine motions, but upon which an engineer could not well rely.

"My investigations on the heliotropism of animals led me to analyze in a few cases the conditions which determine the apparently accidental direction of animal movements which, according to traditional notions are called voluntary or instinctive. Wherever I have thus far investigated the cause of such 'voluntary' or 'instinctive' movements in animals, I have, without exception, discovered such circumstances at work as are known in inanimate nature as determining movements. By the help of these causes it is possible to control the 'voluntary' movements of a living animal just as securely and unequivocally as the engineer has been able to control the movements in inanimate nature. *What has been taken for the effect of 'will' or 'instinct' is in reality the effect of light, of gravity, of friction, of chemical forces, etc.*"

"The fact that *Fundulus* can be thrown from sea-water into distilled water without any considerable swelling, or without any visible injurious effects may find its explanation through the influence that various ions have upon the absorption of liquids. The above-mentioned experiments on the absorption of liquids by the muscle have shown that the simple osmotic theory of absorption which has been accepted by botanists cannot possibly be correct."

"A pure solution of NaCl of the same concentration as sea-water is a strong poison for many (if not all) marine animals. The poisonous effects of this solution are due to the Na ions. The same is true for pure equimolecular solutions of $CaCl_2$ and KCl. The poisonous effects of the Na ions are antagonized by the addition of a small amount of Ca and K ions. Through the presence of these two ions the Na ions in the ocean lose their poisonous effect. The Na ions of the blood would not allow the tissues to live. The presence of Ca, K, and possibly other ions counteracts the poisonous effects of Na ions in the blood. This is the reason why tissues live longer in Ringer's solution than in a physiological salt solution. The reason for all these peculiar effects of the Na, Ca, and K ions is that these (and other) ions form combinations with the proteids of the protoplasm. The various metal proteids show various physical properties. Muscles are only contractile as long as they contain all three classes of ions in a certain proportion, which, however, may vary within certain limits. In a pure solution of NaCl, Na ions will gradually take the place of the Ca and K ions in the ion proteids of the tissues, and this leads to a loss of contractility or irritability. This is the reason why a pure NaCl solution is poisonous. For the same reason pure equimolecular solutions of the other chlorides are also poisonous.

"If we consider the fact that the eggs show at least a beginning of a segmentation under 'normal' conditions, the act of fertilization assumes a different aspect. The spermatozoon can no longer be considered *the cause* or *the stimulus* for the process of development, but merely an agency which *accelerates a process that is able to start without it*, only much more slowly. Substances that accelerate chemical or physical processes which would occur without them are called catalyzers (Ostwald). According to this definition we may assume that the *spermatozoon carries a catalytic substance* into the egg, *which accelerates the process that would start anyhow, but much more slowly.*

"The spermatozoon not only starts the development of non-parthogenetic eggs, but it is also the bearer of the hereditary qualities of the male. From our experiments it becomes evident that these two functions of the spermatozoon are not necessarily bound together, for nobody would assume for an instant that the hereditary qualities that are carried by the spermatozoon could be imparted to the egg by a change in the inorganic constituents of sea-water. We have learned to attribute the different activities of a cell to different enzymes. We must in future consider the possible or probable separation of the fertilizing qualities of the spermatozoon from the transmission of hereditary qualities through the same."

These extracts bring out the author's point of view and the scope covered by the papers. The first article was published in 1889 and the last in 1902. A few footnotes have been added in 1903. *Wilder D. Bancroft.*

Vorlesungen über die Prinzipe der Mechanik. *By Ludwig Boltzmann.* **Zweiter Teil, enthaltend : Die Wirkungsprinzipe, die Lagrangeschen Gleichungen und deren] Anwendungen.** *14 × 22 cm ; pp. x + 335. Leipzig : Johann Ambrosius Barth, 1904. Price : paper 9, bound, 10 marks.*—In discussing the first part of this important book, we remarked that it is a modernized return to the classic form of dynamics, with all the necessary assumptions systematically and most carefully registered. The present volume partakes of the same character, and is particularly rich in its discussion of the meaning and the limitation of the principles treated. Such discussions coming from Boltzmann, vitalized by the charm and clearness of his style, have unique value.

In the first part of the book there is a detailed account of generalized coördinates and the Lagrangian equations of motion, applied in the second part to rotational rigid dynamics. Naturally the work of Euler and of Poinsot makes up much of the chapter.

The time integrals of the mechanical variations are elaborately expounded, the principle of static action having already been given in the first chapter. Least action follows in the third chapter, varying action and the Hamiltonian transformations in the fifth.

The fourth chapter is an account of Helmholtz's cycle theory, and of its relation to thermodynamics. Although this subject has been systematically treated in the reprints of Helmholtz's lectures, Boltzmann's analysis of the same beautiful theory will none the less be welcomed.

In the preface the author expresses the hope that even the non-mathematical reader may not be daunted by his equations. If Boltzmann believes that such a man will follow these searching discussions, we fear that he is doomed to disappointment. On the other hand, the man who has a little mathematics would often have preferred more explicit mathematical statements. To most people, analysis without equations and geometry without figures are particularly trying. To get into one's own mind the equation or the figure in the mind of the author is always the most tedious thing in the reading of mathematics. We mention this only because the book before us is the work of a master who is aiming not only to be critical and accurate, but above all things to be intelligible.

The book will be found very valuable in connection with the work of advanced classes in physics. Apart from this, Boltzmann's conception of the limitations of dynamics is of permanent value, particularly at the present time where dynamics is being shorn of much of its academic dignity.

Carl Barus

An Introduction to the Theory of Optics. *By Arthur Schuster. 15 × 22 cm ; pp. xv + 340. London : Edward Arnold, 1904. Price : $4.00.*—Schuster's book gains compactness in comparison, for instance, with the well-known book of Preston, inasmuch as all geometric optics and physical optics of different grades of completeness are avoided. The demonstrations are throughout tersely to the point, and require in the first or descriptive part (201 pages) little beyond a sound knowledge of the calculus. One would have wished, perhaps, that for the convenience of the reader Schuster had put his variables and constants as far as possible into the diagrams ; but as these are well constructed and in abundance, there is not much room for complaint.

The first two chapters, on periodic and wave motion, naturally presuppose dynamics. The treatment throughout is remarkably straightforward and complete. Very little, as for instance the laws of propagation of compressional and transverse spherical waves, is merely asserted. In the announcement of Huyghens's principle, the reason why waves progress in one direction only is pointed out.

The critical use made of the optical path and of a ray defined as the shortest optical path is noteworthy, as Schuster treats it in the manner of a connecting link between geometric optics and the undulatory theory. The early introduction of Rayleigh's and Stokes's methods, and the absence of anything like shirking in the discussion of the intensities of reflected and of transmitted light is unusual. Total reflection is quite rigidly presented by the usual imaginary method.

In the chapter on interference we meet with an inquiry into the occurrence of diffraction at the edges, and of the laws for channeled spectra. The colors of thin plates are at once treated for an indefinite number of rays. Diffraction begins with a complete exhibition of the properties of successive annuli and of strips, in spite of the fact that the direct integrations are avoided. Throughout the chapter on diffraction a simplification of Fresnel's method is advantageously used to the exclusion of the more usual procedure due to Cornu. Schuster's theory of the grating as a grooved or periodic structure is quite modern; and the elegant method of Runge, the essentials of which may be traced back to Rowland, is adhered to. Detailed treatment is given of Michelson's echelon grating.

In the theory of optical instruments, simplifications of Airy's and of Lommel's methods are adopted, with advantage. Naturally an appreciative summary of Rayleigh's great investigations on kindred subjects is given. Chapters on propagation in crystalline media and on the interference of polarized light close the first part of the book.

The second part is more severe, containing a detailed discussion of optical theory both from the elastic and from the electromagnetic points of view. Dispersion and absorption follow in the way opened by the famous investigation of Sellmeyer. The chapter on rotatory effects gives a very full account of the investigations which have accumulated around the discovery of Zeeman. Rayleigh's dynamics of the blue sky and his treatment of group velocities and wave velocities are discussed in connection with general deductions on the transmission of energy. A chapter on the nature of light closes the volume.

Schuster's book is remarkable for the quantity of matter which he has compressed into a relatively small volume; and he has done this by avoiding everything of an antiquated nature and by simplifying complicated investigations in ways which are often original and highly ingenious. *Carl Barus*

Zur Bildung der ozeanischen Salzablagerungen. *By J. H. van't Hoff. Erstes Heft. 14 × 23 cm; pp. vi + 85. Braunschweig: F. Vieweg und Sohn, 1905. Price: paper, 4 marks.*—All physical chemists will rejoice that van't Hoff has decided to present in book form his work on the Stassfurt salt deposits. The papers which are now welded into a whole, range in date from 1887 to 1904 though thirty-six out of the thirty-nine have been published since van't Hoff went to Berlin in 1896. This first volume deals with the equilibrium between the chlorides and sulphates of sodium, potassium and magnesium. The subject-matter is presented in five chapters: crystallization; time; temperature; pressure; applications. *Wilder D. Bancroft*

Éléments de Chimie inorganique. *By W. Ostwald. Traduits de l'Allemand par L. Lazard. Seconde Partie: Métaux. 16 × 25 cm; pp. 446. Paris: Gauthier-Villars, 1905. Price: paper, 15 francs.*—The French translation of the first part of Ostwald's Inorganic Chemistry appeared last year (8, 579). The translation of the second part appears with commendable promptness. It is a pleasure to note the presence of a twenty-four-page index at the end of the volume. *Wilder D. Bancroft*

Percentage Tables for Elementary Analysis. *By Leo F. Guttmann. 15 × 23 cm; pp. vii + 43. New York: The Macmillan Company, 1904. Price: $1.10.*—These tables have been compiled for the purpose of aiding the analyst in the rapid calculations of the results of analysis of compounds containing carbon, hydrogen and nitrogen. Given the mass of the substance taken and the weight of the water or carbon dioxide or the volume of the nitrogen found, the calculation to percentage composition from these tables requires but a moment. The work is carefully compiled and is a useful laboratory book.

H. R. Carveth

Vier-und fünfstellige Logarithmentafeln nebst einigen physikalischen Konstanten. *16 × 24 cm; pp. 24. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: 0.80 mark.*—This book of tables contains the logarithms of numbers but not the trigonometric functions. Two pages of physical constants are also given. The selection of the tables shows a compromise between the very useful card table of logarithms and the larger works. *H. R. Carveth*

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.

Elements and compounds. *W. Ostwald. Jour. Chem. Soc.*, 85, *506* (*1904*).—The author defines "a substance or a chemical individual as a body, which can form hylotropic phases within a finite range of temperature and pressure." "Elements are substances which never form other than hylotropic phases." This part of the paper is admirable and should be studied by every chemist. It seems to the reviewer that the deduction of the law of combining weights is hopelessly bad. *W. D. B.*

Twelfth annual report of the committee on atomic weights. *F. W. Clarke. Jour. Am. Chem. Soc.*, 27, *177* (*1905*).—The more important new determinations are those on nitrogen, iodine, rubidium, beryllium, indium and tungsten. The author feels that "the atomic weights which need immediate attention are those of silver, sodium, potassium chlorine, bromine, iodine, nitrogen, carbon and sulphur." Hydrogen might well have been included in this list but was omitted owing to the explicit assumption that the hydrogen-oxygen ratio is fixed. There is no real reason, however, why we should assume that this is any more accurately known than the ratio of silver to chlorine for instance. *W. D. B.*

A revision of the atomic weight of iodine. *G. P. Baxter. Proc. Am. Acad.*, 40, *419*; *Jour. Am. Chem. Soc.*, 26, *1577* (*1904*); *Zeit. anorg. Chem.*, 43, *14* (*1905*).—The author draws the following conclusions:

1. The atomic weight of iodine is found to be 126.975 (O = 16.000).

2. Richards and Wells's value for the atomic weight of chlorine, 35.467, is confirmed.

3. The existence of an element of the halogen family of higher atomic weight than iodine is shown to be improbable.

4. The specific gravity of pure fused silver iodide is found to be 5.674 at 25° referred to water at 4°. *W. D. B.*

A revision of the atomic weight of cadmium. *G. P. Baxter and M. A. Hines. Jour. Am. Chem. Soc.*, 27, *222* (*1905*).—From a preliminary analysis of cadmium chloride a value of 112.47 is obtained for cadmium, assuming 107.93 for silver and 35.473 for chlorine. *W. D. B.*

A revision of the atomic weight of rubidium. *E. H. Archibald. Jour. Chem. Soc.*, 85, *776* (*1904*).—Rubidium chloride and bromide were analyzed. The atomic weight found for rubidium is 85.48. *W. D. B.*

The calculation of atomic weights. *J. Meyer. Zeit. anorg. Chem.*, 43, *242* (*1905*).—The author postulates that the accuracy of an atomic weight determination, other things being equal, is proportional to the amount of substance taken. He recalculates the values obtained by different experimenters for sulphur and shows that his calculations give more consistent results than do those of Clarke or of Ostwald. *W. D. B.*

The atomic weight of silicon. *W. Becker and J. Meyer. Zeit. anorg. Chem.*, 43, *251* (*1905*).—Weighed amounts of silicon tetrachloride were decomposed by cold water and the silica weighed. This gave a value of 28.21 for silicon. It seems a pity that the chlorine should not also have been determined. The melting-point of pure silicon tetrachloride was found to be —89°.

W. D. B.

Some remarks on the theory of valence. *R. Abegg. Zeit. anorg. Chem.*, 43, *116* (*1905*).—The author considers the problem why we have the mixture $Fe + FeCl_2$ instead of the compound $2FeCl$. He is rather inclined to think that the subchloride can exist in solution though only to an infinitesimal amount. He cites the existence of BaCl in fused $BaCl_2$. Attention is also drawn to the fact that J. J. Thomson and Drude postulate more valences than the normal. *W. D. B.*

The conception of valence. *R. Abegg and F. W. Hinrichsen. Zeit. anorg. Chem.*, 43, *122* (*1905*).—The authors claim that there is nothing known that prevents the assumption of a constant maximum valence. At temperatures and pressures at which phosphorus pentachloride cannot exist, phosphorus pentafluoride is stable. We cannot say, therefore, that phosphorus is trivalent under those conditions. It is also urged that people should not say valency when they mean affinity. This does not seem unreasonable. *W. D. B.*

The relation of the hypothesis of compressible atoms to electrochemistry. *T. W. Richards. Trans. Am. Electrochem. Soc.*, 6, *II*, *7* (*1904*).—"Let us imagine, then, that each collision of atomic combination starts or transfers a vortex or some other form of self-perpetuating shock. Then the deposition of a given number of chemical equivalents will result in the transfer of a given number of shocks, or a given quantity of electricity, and Faraday's law is explained. . . .

"For example, the electrical conductivity of solids is in many cases what it would be expected to be, if their atoms were compressible. Atomic distortion would be expected to interfere with the ready transference of the vortices. The simpler the crystalline form, the less distorted would be the individual atoms, and the more easily would the vortices be received and transmitted from one atom to another. On the other hand, with irregular atoms, permanently distorted by chemical affinity, the uneven structure would receive and transmit the vortices less easily, and the potential energy of the mutual repulsion would be converted into heat. As a matter of fact, the two best electrical conductors among metals, silver and copper, crystallize in the regular system, and the poorest solid conductors among pure metals, bismuth, antimony and arsenic, are of less symmetrical crystalline structure. The non-metals which are all poor conductors, are still more noticeably complex in symmetry; and such non-conducting substances as bromine and iodine must be very much distorted in atomic shape, if their atoms are compressible, because these atoms must be much compressed on one side, by their firm union to form the diatomic molecules, and only slightly compressed on the other sides, by their feeble cohesion, indicated by great volatility. The relatively slight conductivity of alloys and compounds points in the same direction; for heterogeneity of atomic structure would imply irregular internal pressures, great atomic distortion, and hence poor conductivity. The considerable effect on conductivity of even slight impurity in a metal and the extremely low conductivity of substances like glass and cellulose are well-known, and accord with this interpretation." *W. D. B.*

The composition of beryl. *J. H. Pollok. Jour. Chem. Soc.*, 85, *1630* (*1904*).—The author believes that beryllium chloride can be separated by distillation into two portions, the first distillate containing an unknown element having an atomic weight well above 35. These conclusions are valid only in case the author was really distilling and analyzing pure, anhydrous beryllium chloride. The author's experiments with beryllium sulphate indicate clearly that he has not mastered all the peculiarities of that charming substance. *W. D. B.*

On the complexity of beryllium. *C. L. Parsons. Jour. Am. Chem. Soc.*, 27, *233* (*1905*).—A discussion of Pollok's paper (preceding review). It is believed that the results are due to moisture. *W. D. B.*

The heat of formation of beryllium chloride. *J. H. Pollok. Jour. Chem. Soc.*, 85, *603* (*1904*).—The heat of formation of beryllium chloride is 155000 cal; the heat of solution in water is 44500 cal; the heat of solution in absolute alcohol is 37400 cal. *W. D. B.*

The free energy of formation. *H. v. Jüptner. Zeit. anorg. Chem.*, 42, *235* (*1904*).—The author has calculated and tabulated the change of the free energy and of the heat of formation with the temperature for a number of reactions. At 1500° abs the free energy of the reaction $C + O = CO$ is greater than the heat of reaction. *W. D. B.*

One-Component Systems

The melting-points and inversion-points of some salts. *K. Hüttner and G. Tammann. Zeit. anorg. Chem.*, 43, *215* (*1905*).—The authors have determined the melting-points of the salts, $LiCl$ 605°, $NaCl$ 810°, $NaBr$ 749°, NaI 664°, KCl 778°, KI 790°, $RbCl$ 713°, Li_2CO_3 735°, $CsSO_4$ 1019°; also melting-points and inversion points for Na_2CO_3 853° and 450°, K_2CO_3 894° and 410°, $LiSO_4$ 859° and 575°, Na_2SO_4 897° and 235°, K_2SO_4 1074° and 587°, $RbSO_4$ 1074° and 657°, $NaMoO_4$ 692° and 610° and 400°, K_2MoO_4 926° and 200°?, Na_2WO_4 698° and 570°, K_2WO_4 906° and 300°-200°. With lithium sulphate, sodium sulphate, sodium tungstate and the second inversion-point for sodium molybdate, the heat of inversion is greater than the heat of fusion, a phenomenon that had never been noted before. The heat of inversion is practically zero with potassium molybdate and potassium tungstate but the volume change is quite marked. *W. D. B.*

Preparation of absolute nitric acid. *F. W. Küster and S. Münch. Zeit. anorg. Chem.*, 43, *350* (*1905*).—" Absolute nitric acid exists only in the form of snow-white crystals below —41° C. The nitric acid crystals fuse to a yellowish liquid which is a solution of nitrogen pentoxide and water in nitric acid. In dry air this solution becomes colorless, losing anhydride until the acid contains 98.6 percent HNO_3. This acid is volatile without change."

W. D. B.

The use of carbon for the study of temperatures in the electric furnace. *F. A. J. Fitz-Gerald. Trans. Am. Electrochem. Soc.*, 6, I, *31* (*1904*).—The density of carbon varies with the temperature to which it has been heated. By placing samples of test carbon in different portions of an electric furnace, the densities of the carbons at the end of the run will give an approximate idea of the distribution of temperature in the furnace. At about 800° a fifteen-hour run is necessary to bring the carbon to its final equilibrium. The time at higher temperatures would undoubtedly be less. *W. D. B.*

The vapor density of hydrazine hydrate. *A. Scott. Jour. Chem. Soc.*, 85, *913* (*1904*).—"These experiments prove :—

1. That at 100° in a vacuum, hydrazine hydrate in vapor is dissociated into hydrazine and water to the extent of 58 percent, and that at 140° this dissociation is complete.

2. That at 183° under ordinary atmospheric pressure a further change takes place, namely, the decomposition of hydrazine into nitrogen and ammonia.

3. That at 460°-480°, not only is this further change completed, but the ammonia itself begins to decompose.

4. That at 183° the oxygen of the air attacks the hydrazine, especially when under somewhat increased pressure, although under similar pressures in an atmosphere of nitrogen, hydrazine seems to be stable in presence of water, but not at 300°.

The initial temperature and the rate of the decomposition seem to be considerably influenced by the nature of the surfaces to which the hydrazine vapor is exposed, as well as by its dilution with other gases." *W. D. B.*

Two-Component Systems

Freezing-point curves of dynamic isomerides: ammonium thiocyanate and thiocarbamide. *A. Findlay. Jour. Chem. Soc.*, 85, *403* (*1904*).—1. The freezing-point curve of ammonium thiocyanate (m. p. 149°) and thiocarbamide (m. p. above 177°) is of the simplest form, consisting of two branches meeting at a eutectic point (104.3°).

2. The natural freezing-point is 114°-115°, the stable solid form being ammonium thiocyanate.

3. Neither the freezing-point curve, nor the cooling curve, nor the analysis of the solid phase gives any indication of the formation of a compound of ammonium thiocyanate and thiocarbamide stable at temperatures in the neighborhood of the freezing-point curve.

4. The transformation of ammonium thiocyanate into thiocarbamide and vice-versa does not appear to be accompanied by any heat effect.

5. The "stability limits" of dynamic isomerides (including desmotropic forms) are defined as the natural freezing-point and the eutectic point for the stable and unstable forms respectively. *W. D. B.*

Studies on the dynamic isomerism of α- and β-crotonic acids. I. *R. S. Morrell and E. K. Hanson. Jour. Chem. Soc.*, 85, *1520* (*1904*).—The authors determined the freezing-point curves for mixtures of α- and β-crotonic acids and intend later to determine the natural freezing-point of the system. They give data also for the composition of the melt after six hours' heating at temperatures varying from 100° to 170°. As equilibrium was not reached in any one of these experiments, the figures given mean practically nothing. At the most they illustrate the well-known fact that reaction velocity increases with rise of temperature and they were not undertaken to prove that. *W. D. B.*

Studies on comparative cryoscopy. II. *R. W. Robertson. Jour. Chem. Soc.*, 85, 1617(*1904*).—The author has studied the apparent molecular weights of aromatic acids in phenol solutions as shown by the freezing-point method. He finds "that those acids which are the most difficult to esterify show the smallest 'rate' of association." *W. D. B.*

The vapor pressure of sulphuric acid solutions and the molecular condition of sulphuric acid in concentrated solution. *B. C. Burt. Jour. Chem. Soc.*, 85, *1339* (*1904*).—The author has determined the boiling-points of sulphuric acid solutions under diminished pressures and has constructed pressure-concentration isotherms from these data. For solutions containing more than 25 percent H_2SO_4 the apparent molecular weights are below 32° and decrease nearly linearly with increasing concentration of sulphuric acid. *W. D. B.*

The density and expansion of sulphuric acid in aqueous solution. *J. Domke and W. Bein. Zeit. anorg. Chem.*, 43, *125* (*1905*).—A very careful and exhaustive study of the change of the density of sulphuric acid solutions with concentration and temperature. The results show that Pickering's data were very accurate though of course the authors do not accept conclusions based on a second differential. *W. D. B.*

Density determinations with the pipette. *F. W. Küster and S. Münch. Zeit. anorg. Chem.*, 43, *373* (*1905*).—Using an automatic overflow 100 cc pipette of proper construction, the error of a single reading should not exceed one in a hundred thousand. Density determinations with a pipette are therefore quite accurate enough for preparing standard solutions. A table is given for preparing a normal hydrochloric acid solution from an acid having a density between 1.0500 and 1.1400. *W. D. B.*

A microscopical method of determining molecular weights. *G. Barger. Jour. Chem. Soc.*, 85, *286* (*1904*).—If two solutions are isotonic, there will be no tendency for the solvent to distil from one to the other. The author places drops of two solutions in a capillary tube and examines them under the microscope to see which way distillation takes place. On this he bases a method for molecular weight determinations which requires the use of very small quantities of material. The method presupposes a practically non-volatile solute. When worked with 90 percent alcohol or aqueous acetic acid, the results mean absolutely nothing. *W. D. B.*

The basic properties of oxygen. *E. H. Archibald and D. McIntosh. Jour. Chem. Soc.*, 85, *919* (*1904*).—The authors have isolated and analyzed a number of compounds of the halogen acids with alcohol, acetone, methyl ether and ethyl ether. If we write structural formulas for these substances we must assume that the valency of oxygen increases from 4 to 12 as the temperature falls. This of course may be so; but there is always the other alternative of confessing one's ignorance and not writing structural formulas. *W. D. B.*

The basic properties and quadrivalence of oxygen. *D. McIntosh. Jour. Am. Chem. Soc., 27, 26 (1905).*—Methyl ether and methyl alcohol crystallize at low temperatures with hydriodic acid and hydrobromic acid in the molecular ratio of one to one. From the author's point of view the oxygen in these compounds is quadrivalent. By increasing the valence of chlorine from one to three, he is able to reduce the valence of oxygen in some of the hydrochlorides (preceding review) from twelve to six. *W. D. B.*

The formation of ammonia from the elements. *F. Haber and G. van Oordt. Zeit. anorg. Chem., 43, 111 (1905).*—This is merely a preliminary notice. At 1000° an equilibrium between ammonia, nitrogen and hydrogen can be reached from both sides in presence of iron as catalytic agent. Nickel is less satisfactory. About two parts in ten thousand of ammonia remain undecomposed when equilibrium is reached. *W. D. B.*

Multi-component Systems

The affinity of the alkali oxides for different anhydrides. *D. G. Gerassimoff. Zeit. anorg. Chem., 42, 328 (1904).*—It is shown that the same equilibrium is reached at a given temperature and a constant partial pressure of SO_3, whether one starts from Li_2WO_4 or from $Li_2SO_4 + WO_3$. Experiments were made at 880° with the tungstates and vanadates of lithium, sodium, potassium, rubidium and caesium. Experiments were also made at 880° under a constant partial pressure of CO_2 with mixtures of the alkali carbonates with WO_3, VO_3, Nb_2O_5, Ta_2O_5, TiO_2 or Al_2O_3. *W. D. B.*

Studies of dynamic isomerism. II. *T. M. Lowry and W. Robertson. Jour. Chem. Soc., 85, 1541 (1904).*—If a substance changes slowly into an isomeric form, it may be possible to get a solution saturated with respect to the first form before practically any change into the other form has taken place. Under these circumstances the difference between the final and the initial solubilities represents the amount of the second form in the solution. The method has worked well with the nitro-derivatives of camphor. *W. D. B.*

Studies of dynamic isomerism, III. *T. M. Lowry. Jour. Chem. Soc., 85, 1751 (1904).*—"The main result of the experiments now described is to show that in the case of glucose and galactose the proportion of α-sugar in solution decreases as the amount of water in the solvent increases. This result is ascribed to the presence in the aqueous solutions of a third form of the sugar.

"In methyl alcoholic solutions, one-half of the sugar is in the α-form. The remainder probably consists almost entirely of the β-sugar, since the third form can be present only in very minute quantities. The α- and β-forms are therefore equally stable in the solution, although the α-form, being the less soluble, is the first to crystallize when the solution is evaporated.

"In the mixture ($EtOH + H_2O$), the proportion of α-sugar falls to 40 percent. This might be due to the presence of 60 percent of the β-sugar. A more probable explanation is that the solution contains equal proportions of the α- and β-forms, namely 40 percent of each, 20 percent of the sugar being present in a third hydrated form.

"On account of the excessive solubility of glucose and galactose in water, the measurements could not be extended to aqueous solutions, but it is clear that an even smaller ratio of initial to final solubility must be anticipated under these conditions. It is, therefore, evident that although in anhydrous solvents the mutarotation of glucose and galactose may be almost wholly due to isomeric change, the change of rotatory power in aqueous solutions may be to a large extent due to the formation of a third hydrated form of the sugar.

"It is considered probable that the third form of the sugar is the aldehydrol and that this forms an intermediate stage in the interconversion of the stereoisomeric α- and β-sugars." *W. D. B.*

The polysulphides. I. *F. W. Küster and E. Heberlein. Zeit. anorg. Chem.*, 43, *53* (*1905*).—The solubility of sulphur in sodium sulphide solution varies but little between 0° and 50°. The solubility is a maximum for a *n*/16 solution of sodium sulphide. Sodium tetrasulphide appears to exist in solution in equilibrium with a number of other compounds. The hydrolysis is less the more sulphur there is in solution. Polysulphides are salts of the acid $H_2S.S_x$, and are analogous to the polyiodides. *W. D. B.*

The solubility of lithium carbonate in alkali salt solutions. *C. Geffcken. Zeit. anorg. Chem.*, 43, *197* (*1905*).—Potassium nitrate, chloride and chlorate increase the solubility of lithium carbonate up to a certain point where the solubility passes through a maximum. Sodium chloride acts in the same way. The sulphate of sodium and potassium increase the solubility of lithium carbonate much more than do the chlorides. No maximum was observed. Ammonium salts increase the solubility of lithium carbonate enormously. *W. D. B.*

The formation of periodides in organic solvents. *H. M. Dawson. Jour. Chem. Soc.*, 85, *467* (*1904*).—A number of nitro compounds dissolve mixtures of potassium iodide and iodine more readily than either substance alone. When the solutions are saturated with respect to potassium iodide the ratio I_2 : KI in the solution is practically unity. When the solution is saturated with respect to iodine, the ratio I_2 : KI in the solution is practically 4 : 1. If the only solid phases possible are iodine and potassium iodide, this result is impossible because the two ratios must become identical when the solution is saturated with respect to both substances. If another solid phase is possible, an analysis of it should have been given. *W. D. B.*

The formation of periodides in nitrobenzene solution. II. *H. M. Dawson and E. E. Goodson. Jour. Chem. Soc.*, 85, *796* (*1904*).—This is more work similar to that in the first paper (preceding review) and subject to the same criticisms. The authors did make an admittedly inaccurate analysis of one solid phase, but no one knows whether it was a possible solid phase at the temperature at which the experiments were carried out. *W. D. B.*

Influence of moist alcohol and ethyl chloride on the boiling-point of chloroform. *J. Wade and H. Finnemore. Jour. Chem. Soc.*, 85, *938* (*1904*).—There is a minimum boiling-point at 55.5° for the ternary system, chloroform, alcohol and water. The presence of a trace of ethyl chloride in the chloroform made from alcohol is the reason it is better as an anaesthetic than chloroform made from acetone. *W. D. B.*

The hydrolysis of ammonium salts. *V. H. Veley. Jour. Chem. Soc.*, 87, *26* (*1905*).—The author finds that boiling solutions of ammonium salts lose more ammonia the weaker the acid. He looks upon this as proof positive that this is the result of hydrolysis and not of a direct dissociation into free base and free acid. It is not clear to the reviewer how one is to distinguish conclusively between the two sets of equations.

I. $NH_4Cl + H_2O = NH_4OH + H^{\cdot} + Cl'$ and $NH_4OH = NH_3 + H_2O$.

II. $NH_4Cl = H^{\cdot} + Cl' + NH_3$.

The two formulations become identical with vanishing concentration of NH_4OH and under the conditions of the experiments the concentration of the NH_4OH is apparently negligible. If the author were to make experiments with ammonium acetate in alcohol he would probably modify his conclusions.

W. D. B.

Note on the efficiency of centrifugal purification. *T. W. Richards. Jour. Am. Chem. Soc.*, 27, *104* (*1905*).—Quantitative measurements of the efficiency of centrifugal purification. With a sodium nitrate containing some free nitric acid, two centrifugal filtrations purified the substance as much as nine gravity filtrations would have done. The most satisfactory method of centrifugal washing is to stir the crystals with a small amount of water and then to filter this off centrifugally. *W. D. B.*

The silicates, IV. *E. Jordis and E. H. Kanter. Zeit. anorg. Chem.*, 42, *418* (*1904*).—A preliminary study of the action of the alkaline earths on colloidal silicic acid. Since no effort is made to determine whether the authors are analyzing one or more solid phases, it is practically impossible to tell what has been found. The authors do not even analyze their solutions.

W. D. B.

On silicates, V. *E. Jordis and E. H. Kanter. Zeit. anorg. Chem.*, 43, *48* (*1905*).—Time experiments on the reaction between silicic acid and lime in a one percent calcium chloride solution. *W. D. B.*

On silicates, VI. *E. Jordis and E. H. Kanter. Zeit. anorg. Chem.*, 43, *314* (*1905*).—Finely-powdered quartz was boiled for four hours with solutions of barium, strontium and calcium hydroxides. Analyses were then made but there is nothing to indicate what these analyses were expected to show. As in the previous papers it is quite impossible to find out what the authors think they are trying to do. This seems a pity when one remembers how easy the problem really is. *W. D. B.*

Historical facts as to the investigation of the silicates of the alkaline earths. *E. Jordis. Zeit. anorg. Chem.*, 43, *410* (*1905*).—A brief outline of what Le Chatelier did and did not prove in regard to the silicates of the alkaline earths.

The article is the result of the author having come across an early paper by Le Chatelier which had apparently been overlooked by everybody.

W. D. B.

The absorption of water by clay. *J. M. van Bemmelen. Zeit. anorg. Chem.*, 42, *314* (*1904*).—It is shown in the case of some Surinam clays that the absorption and loss of water at 15° is a reversible phenomenon but marked by hysteresis. *W. D. B.*

The affinity constants of aniline and its derivatives. *R. C. Farmer and F. J. Warth. Jour. Chem. Soc.*, 85, *1713* (*1904*).—The dissociation and hydrolysis constants of the salts of weak bases with strong acids were determined from the distribution coefficients observed when the solutions were shaken with benzene. The data are given in tabulated form at the end of the article.

W. D. B.

The solubility of barium sulphate. *F. W. Küster and G. Dahmer. Zeit. anorg. Chem.*, 43, *348* (*1905*).—Since barium chloride does not react with chromic sulphuric acid, chromic chloride ought to increase the solubility of barium sulphate. This was found to be the case, though equilibrium is reached very slowly. *W. D. B.*

Complex salts of mercury sulphocyanate. *H. Grossman. Zeit. anorg. Chem.*, 43, *356* (*1905*).—Mercurous sulphocyanate dissolves in potassium sulphocyanate solution, forming $K_2Hg(SCN)_4$ and setting free mercury. In dilute solutions some trisulphocyanate may be formed. At ordinary temperatures the sulphocyanate has the greater tendency to form complex ions and the bromide at higher temperatures. *W. D. B.*

The constitution of neutral zirconium sulphate. *R. Ruer. Zeit. anorg. Chem.*, 42, *87* (*1904*).—Ammonium oxalate precipitates zirconium oxalate at once from zirconium chloride or nitrate solutions but not from neutral zirconium sulphate solutions. It seems probable that the so-called neutral zirconium sulphate is really the free dibasic acid, zircon sulphuric acid having a formula $ZrOSO_4.SO_4H_2$. *W. D. B.*

On metazirconic acid. *R. Ruer. Zeit. anorg. Chem.*, 43, *282* (*1905*).—In aqueous solution zirconium chloride hydrolyzes slowly at ordinary temperatures, rapidly at 100°. The hydrolysis product apparently changes over into another hydroxide standing in the same relation to zirconium hydroxide that metastannic acid does to stannic acid. When dried at 100° zirconium hydroxide has the formula $ZrO_2.2H_2O$ while the metazirconic acid appears to have the formula $3ZrO_2.2H_2O$. Metazirconic acid and its compounds with acids form colloidal solutions only. It is believed that zirconium hydroxide and metazirconic acid derive from different oxides, that for the zirconium hydroxide not being known. *W. D. B.*

The chemical reactions of nickel carbonyl. *J. Dewar and H. O. Jones. Jour. Chem. Soc.*, 85, 203, 212 (*1904*).—Chlorine, bromine and iodine change nickel carbonyl to the corresponding halide. In chloroform solution the reaction with iodine is of the second order. Cyanogen gas does not react with nickel carbonyl but an alcoholic solution does. Iodine monochloride, trichloride and cyanide behave like mixtures. Sulphur, hydrogen sulphide and sulphuric acid react very slowly. Nickel carbonyl does not react with aluminum chloride or with aromatic hydrocarbons. Hydrochloric acid is evolved however if the three are brought together. At low temperatures an aldehyde is formed and practically no nickel chloride. At 100° an anthracene derivative is formed and much nickel chloride. *W. D. B.*

The decomposition of chloral hydrate by sodium hydroxide and by certain salts. *E. A. Werner. Jour. Chem. Soc.*, 85, *1376* (*1904*).—Chloral hydrate is decomposed very rapidly by caustic soda but is very stable in neutral or acid solutions. At higher temperatures sodium formate and some other sodium salts decompose chloral hydrate. Though the author does not so state, this is undoubtedly due to the hydrolysis of the sodium salts. When chloral hydrate is heated to 190° in a sealed tube, two liquid layers are formed which disappear on cooling. [Butyl chloral hydrate behaves similarly in open vessels.] *W. D. B.*

Reduction of perchlorate by the wet way. *B. Sjollema. Zeit. anorg. Chem.*, 42, *127* (*1904*).—If potassium perchlorate be boiled with excess of a ferrous sulphate solution and caustic soda be added in amount insufficient to precipitate all the iron, the perchlorate will be reduced quantitatively to chloride. Before determining the chloride, the ferric hydroxide should be dissolved by nitric acid. *W. D. B.*

Estimation of hydrogen peroxide in the presence of potassium persulphate by means of potassium permanganate. *J. A. N. Friend. Jour. Chem. Soc.*, 85, *597*, *1533* (*1904*).—To obtain approximately accurate results in the titration of hydrogen peroxide in the presence of potassium persulphate, the rapidity with which the titration is effected should be as great as possible, the volume of the solution titrated should be reduced to a minimum, and great excess of sulphuric acid should be employed. The error appears to be due to a reaction between the potassium persulphate and hydrogen peroxide which is accelerated by the manganous sulphate formed during the titration. *W. D. B.*

On weathered silicates in clay, volcanic and lateritic soils. *J. M. van Bemmelen. Zeit. anorg. Chem.*, 42, *265* (*1904*).—A very complete statement of what we now know about the way in which silicates weather and a plea for a careful study of the process. It is made clear that nothing can be accomplished merely by theorizing on the subject. *W. D. B.*

On yellow and red arsenic trisulphide. *H. Winter. Zeit. anorg. Chem.*, 43, *228* (*1905*).—When a yellow colloidal solution of arsenic trisulphide is frozen the trisulphide precipitates as a red modification which does not redissolve in water. Boiling the solution gives the same red modification. On passing hydrogen sulphide into an arsenic solution, small amounts of a golden-yellow amorphous precipitate are sometimes obtained. *W. D. B.*

Solubility of metal hydroxides in glycerol. *A. Müller. Zeit. anorg. Chem.*, 43, *320* (*1905*).—No precipitation is observed when glycerol and ammonia are added to solutions of aluminum nitrate, chrome alum, ammonium ferrous sulphate, ferric chloride, ammonium cerous nitrate and magnesium neodymium nitrate. On diluting these solutions with water the hydroxide precipitates more or less rapidly. When the solutions are heated, precipitation occurs with aluminum hydroxide, ferrous hydroxide and ferric hydroxide, but not in the chromium, cerium and neodymium solutions. The failure to precipitate appears to be due to the formation of a colloidal solution. *W. D. B.*

Colloidal tellurium. IV. *A. Gutbier. Zeit. anorg. Chem.*, 42, *177* (*1904*).—When phenyl hydrazine hydrochloride is added gradually to a solution of tellurium dioxide in dilute hydrochloric acid heated to 70°, a moderately stable gray-blue hydrosol is formed. When *gummi arabicum* is dissolved in a solution of tellurium dioxide in dilute hydrochloric acid heated to 95° and hydrazine hydrate is then added, a brown hydrosol is obtained. If the preceding solution be neutralized at 70° with ammonia and then hypophosphorous acid be added, we get a brown hydrosol changing into a deep-blue one, the intermediate color being violet. *W. D. B.*

Action of hydrogen sulphide on selenous acid, I. *A. Gutbier and J. Lohmann. Zeit. anorg. Chem.*, 42, *325* (*1904*).—When the yellow hydrosol of selenium sulphide is boiled with hydrochloric acid a brilliantly red gel is precipitated. This change of color has been supposed to be due to the rise of temperature. The authors find that the change takes place slowly at ordinary temperatures and that it is accelerated by ultra-violet light and by increased partial pressure of hydrogen sulphide. *W. D. B.*

Action of hydrogen sulphide on selenous acid. II. *A. Gutbier and J. Lohmann. Zeit. anorg. Chem.*, 43, *384* (*1905*).—It is shown that the deposit of selenium and sulphur obtained by the action of hydrogen sulphide and selenous acid contains no compound of the two elements. Treatment of the yellow hydrosol with carbon bisulphide dissolves the sulphur, leaving the pink hydrosol of selenium. *W. D. B.*

On chlorine in colloidal solutions of metal hydroxides. *R. Ruer. Zeit. anorg. Chem.*, 43, *85* (*1905*).—Dialyzed colloidal ferric hydroxide is apt to contain chloride which is not precipitated by silver nitrate until after the solution has been heated with nitric acid. It was believed that the chloride must be present as part of a complex acid, but the author shows that it is merely a case of the action of a colloid causing the silver chloride to remain in solution as a colloid. *W. D. B.*

The preparation and properties of colloidal mixtures. *A. A. Noyes. Jour. Am. Chem. Soc.*, 27, *85* (*1905*).—An experimental lecture constituting the address of the retiring president of the American Chemical Society.

W. D. B.

Velocities

Chemical dynamics of the alkyl iodides. *K. A. Burke and F. G. Donnan. Jour. Chem. Soc.*, 85, *555*(*1904*).—The reaction between an alkyl iodide and silver nitrate in absolute alcohol is apparently of the second order but with marked disturbing influences due chiefly to the silver nitrate. In *n*/40 solutions the reaction velocity decreases in the following order with changing alkyl iodide: isopropyl, ethyl, propyl, methyl, butyl, isoamyl, isobutyl. The authors consider that their results are not in harmony with the views of Nef but they make the unfortunate mistake of discussing Nef's first paper only.

W. D. B.

The chemical dynamics of the reactions between sodium thiosulphate and organic halogen compounds. I. *A. Slator. Jour. Chem. Soc.*, 85, *1286* (*1904*).—The author has studied the reaction between sodium thiosulphate and alkyl halides. This reaction is bimolecular with methyl and ethyl iodides, bromides and chlorides; with ethylene iodide and bromide; and with ethylene bromoiodide. With ethylene chloro-iodide the reaction is of the first order when thiosulphate is present in excess and approximates the second order when the halide is in excess. With ethylene chlorobromide the reaction is of the first order. The active mass of the sodium thiosulphate appears to be proportional to the concentration of thiosulphate as ion. *W. D. B.*

The decomposition of ethylene iodide under the influence of the iodide ion. *A. Slater. Jour. Chem. Soc.*, 85, *1697* (*1904*).—1. Ethylene iodide in aqueous alcoholic solution decomposes quantitatively in the presence of potassium iodide, yielding ethylene and iodine.

2. The velocity of reaction is proportional to the concentration of ethylene iodide and that of the I'-ion, showing that the potassium iodide takes some direct (or catalytic) part in the reaction. The temperature quotient for 10° is 2.5.

3. This reaction is quite distinct from that between ethylene iodide and sodium thiosulphate, for on carrying out the two reactions in the same solution the rate of disappearance of the thiosulphate is approximately equal to that calculated from the velocity of the two single reactions.

4. The rate of liberation of iodine from solutions of methyl iodide, isopropyl iodide, and ethyl iodoacetate is accelerated by the addition of potassium iodide.

5. Ethylene bromoiodide in presence of potassium iodide liberates iodine according to the equation: $C_2H_4IBr + KI = C_2H_4 + I_2 + KBr$.

6. The velocity of the preceding reaction is proportional to the concentration of the bromoiodide and to that of the potassium iodide, and the temperature quotient for 10° is 2.45. Ethylene iodide is probably not an intermediate product in this reaction. The iodide decomposes about three times as fast as the bromoiodide. *W. D. B.*

The acid esters of methyl substituted succinic acids. *W. A. Bone, J. J. Sudborough and C. H. G. Sprankling. Jour. Chem. Soc.*, 85, *534* (*1904*).—The authors have determined the electrical conductivity and the rates of saponification for the acid ester of a number of methyl substituted succinic acids. *W. D. B.*

The decomposition of methylcarbamide. *C. E. Fawsitt. Jour. Chem. Soc.*, 85, *1581* (*1904*).—1. In its decomposition on treatment with acids, alkalis, and water alone, methylcarbamide behaves very similarly to carbamide.

2. The decomposition of methylcarbamide by acids is due to its transformation into methylamine cyanate, this salt being then decomposed by the acid. This transformation is a reaction of the first order.

3. The method of destroying the reaction products in a case of dynamic

isomerism may be used with advantage in certain reactions to obtain the velocity-coefficient of the transformation in one direction.

4. The equilibrium $\frac{C_{CON_2H_3.CH_3} \times C_{HCl}}{C_{CON_2H_3.CH_3,HCl}} = K$ is established by the experiments on the velocity of decomposition, as it is only the free methylcarbamide which gives the active concentration of substances decomposing at any instant.

5. A direct hydrolysis of methylcarbamide is brought about only very slightly even by very concentrated alkali. *W. D. B.*

The kinetics of the permanganate, oxalic acid reaction. *A. Skrabal. Zeit. anorg. Chem.*, 42, *1* (*1904*).—In acid solution permanganate oxidizes a manganous salt to a manganic salt. On addition of oxalic acid there is decomposition, carbon dioxide being set free and a manganous salt formed. To account for this reaction being monomolecular, the author assumes that it takes place in two stages:

$$[Mn(OH)_3.C_2O_4H_2] \longrightarrow Mn^{\cdots}$$
$$Mn^{\cdots} + C_2O_4H_2 \longrightarrow Mn(OH)_2 + CO_2,$$

the second reaction taking place immeasurably fast while the first is the one that is really measured. While the author makes out a strong case for his point of view, it seems hardly possible that it can be right. The problem is left entirely unsolved how it is possible to form $Mn(OH)_3.C_2O_4H_2$ in the manner described since the manganic salt and the oxalic acid should react instantaneously according to the second equation. Even though one may reject the conclusions, one must recognize that this is a very creditable piece of work and that the author tests every postulate but one with admirable thoroughness.
W. D. B.

Rate of self-heating. *G. Bredig and F. Epstein. Zeit. anorg. Chem.*, 42, *341* (*1904*).—The authors deduce an approximate relation between temperature and time for a reaction taking place in an adiabatic shell. *W. D. B.*

The contact sulphuric acid process. *F. W. Küster. Zeit. anorg. Chem.*, 42, *453* (*1904*).—Platinum, vanadium pentoxide and iron oxide at the same temperatures bring about the same equilibria between sulphur dioxide, oxygen and sulphur trioxide. The platinum is the most effective catalytic agent of the three and the only one with which equilibrium is reached under technical conditions. The best amount of moisture is that which is given by ordinary concentrated pure sulphuric acid. With either more or less moisture the yield falls off, especially with vanadium pentoxide and with iron oxide. Vanadium pentoxide does not seem to deteriorate at all while iron oxide is a very sensitive and uncertain catalytic agent. The usefulness of iron oxide decreases rapidly as arsenic is added. *W. D. B.*

The decomposition of ammonia at high temperatures. *A. H. White and W. Melville. Jour. Am. Chem. Soc.*, 27, *373* (*1905*).—Ammonia, either pure or mixed with other gases, was passed at definite rates of speed through glass tubes heated to different temperatures. The apparent result is that the nitrogen and hydrogen behave like inert gases as far as the decomposition of ammonia is concerned. The authors conclude that there is therefore no reaction between nitrogen and hydrogen. They made no determinations to find out whether ammonia would be completely decomposed if time had been given to reach equilibrium. Some experiments by Ramsay and Young are cited however, in which 100 percent decomposition was obtained. The rate of decomposition is largely a matter of the extent and nature of the solid surfaces. These factors were kept as nearly constant in this work as could be done under the circumstances. *W. D. B.*

The intermediate oxide theory of the oxidation process. *A. Skrabal. Zeit. anorg. Chem.*, 42, *60* (*1904*).—The author discusses the behavior of iron, manganese and chromium on the basis that there is always formed an intermediate oxide which then decomposes spontaneously into two products, one of a higher and the other of a lower valency. *W. D. B.*

The effect of colloidal platinum on mixtures of Caro's persulphuric acid and hydrogen peroxide. *T. S. Price and J. A. Friend. Jour. Chem. Soc.*, 85, *1526* (*1904*).—When colloidal platinum is added to mixtures of Caro's acid and hydrogen peroxide, there is a rapid evolution of oxygen. It was hoped that a study of the reaction velocity would throw some light on the formula of Caro's acid. No satisfactory constant could be calculated and it was impossible even to make a guess at the order of the reaction. *W. D. B.*

The slow combustion of ethane. *W. A. Bone and W. E. Stockings. Jour. Chem. Soc.*, 85, *693* (*1904*).—In the slow combustion of ethane, acetaldehyde and water are the first intermediate products to be recognized readily. The next stage is the formation of formaldehyde, carbon monoxide and water, while the oxidation of the formaldehyde is the last stage. Hydrogen and methane may be formed by the heating of formaldehyde and acetaldehyde respectively, but they are not true combustion products of ethane. Alcohol is not found as an intermediate product because it reacts with oxygen much more readily than does ethane. Its combustion products are the same as those of ethane. *W. D. B.*

The combustion of ethylene. *W. A. Bone and R. V. Wheeler. Jour. Chem. Soc.*, 85, *1637* (*1904*).—The experiments confirm the hypothesis "that the combustion of a hydrocarbon is essentially a process of hydroxylation." Formaldehyde is easily obtained as one of the intermediate products in the combustion of ethylene. While it was not possible to show the existence of vinyl alcohol as an intermediate product, traces of the isomeric acetaldehyde could be detected. *W. D. B.*

Electrolysis and Electrolytic Dissociation.

Electrostenolysis and Faraday's law. *T. W. Richards and B. S. Lacy. Jour. Am. Chem. Soc.*, 27, *232* (*1905*).—A cracked glass tube is placed between the anode and the cathode in a silver nitrate solution. When the current passes, metallic silver and silver peroxide are deposited in the cracks. The authors find that the electrostenolysis has no effect on the amount of silver deposited at the cathode. If this conclusion is not wrong, it should be possible to dispense with the diaphragm in the silver voltameter, using a silver peroxide anode. It seems quite as probable that the experiments were not carried on long enough to show the disturbing effect. *W. D. B.*

Material and form of the rotating cathode. *H. E. Medway. Am. Jour. Sci.* (4), 18 *180; Zeit. anorg. Chem.*, 42, *110* (*1904*).—For the precipitation of copper a silver crucible may be substituted for a platinum crucible, but a nickel crucible is distinctly less satisfactory. The author has obtained bad results with an aluminum cathode. He finds a rotating crucible much better than a rotating disc, part of the difference being due to an injudicious arrangement of the anode in the latter case. *W. D. B.*

Further work with the rotating cathode. *H. E. Medway. Am. Jour. Sci.*, (*4*) 18, *56; Zeit. anorg. Chem.*, 42, *114* (*1904*).—Data are given for the electrolytic precipitation of cadmium, tin, zinc and gold, using a rotating cathode. When one reflects that the rotating cathode is certainly better than the rotating anode, it is a little depressing to read the following statement: "No attempt was made to find the minimum time required for these depositions." *W. D. B.*

Electrolytic determination and separation of antimony and tin. *A. Fischer. Zeit. anorg. Chem.*, 42, *363* (*1904*).—A study of the conditions for quantitative electrolytic precipitation of antimony and tin from sulphide solutions. The electrodes were not rotated. Through the paper there runs the characteristic assumption that no electrolytic method is of any value or has ever existed as a method until it has been tested in the Aachen laboratory. This is rather amusing when one reflects that many of the real advances in this subject come from the laboratory of the University of Pennsylvania. *W. D. B.*

The electrolytic estimation of minute quantities of arsenic. *H. J. S. Sand and J. E. Hackford. Jour. Chem. Soc.*, 85, *1018* (*1904*).—Arsenates and arsenites are reduced completely to arsine by electrolytic methods only when a cathode of lead or zinc is used. The authors recommend the use of lead electrodes. *W. D. B.*

Studies on the electrolytic oxidation of the phenols, I. *A. G. Perkin and F. M. Perkin. Jour. Chem. Soc.*, 85, *243* (*1904*).—An aqueous solution of pyrogallol and sodium sulphate was electrolyzed in a cell without a diaphragm using a rotating platinum anode. When the temperature is kept down, a 40 percent yield of purpurogallin is obtained. The yield is much less if a lead anode be substituted for the platinum one, or when sodium acetate is used instead of sodium sulphate. It is not clear from the text whether the authors use the term current density in the ordinary sense or in some other. Some experiments were also made on the electrolytic oxidation of gallic acid. *W. D. B.*

An analytical study on the deposition of aluminum from ethyl bromide solution. *H. E. Patten. Trans. Am. Electrochem. Soc.*, 6, I, *9* (*1904*).—Abstract of a paper published 8, 548.

Electrolytic purification of cobalt and nickel. *W. D. Bancroft. Trans. Am. Electrochem. Soc.*, 6, I, *39* (*1904*).—Abstract of a paper by Root, published 9, 1.

The aluminum rectifier. *W. D. Bancroft. Trans. Am. Electrochem. Soc.*, 6, I, *13* (*1904*).—Abstract of a paper by Charters, published 9, 110.

Blue aluminum compounds at the aluminum anode. *F. Fischer. Zeit. anorg. Chem.*, 43, *341* (*1905*).—When a well-cooled aluminum tube is made anode in a sulphate solution, the portion of the film next the tube is found to be a bright blue. The author did not succeed in finding out much of anything about this blue substance. He notes that Winkler obtained traces of a blue substance by the action of magnesium on alumina. The author inclines to the view that the blue substance is a suboxide. *W. D. B.*

Ionization and chemical combination. *J. W. Walker. Jour. Chem. Soc.*, 85, *1082* (*1904*).—It is believed that, in some cases at least, chemical combination due to potential valencies is the cause of ionization. When aluminum chloride and benzoyl chloride are added to anisol, the mixture conducts pretty well after the reaction. Aluminum chloride was also found to make ethyl iodide and carbon tetrachloride react with formation of iodoform. On adding aluminum chloride to a solution of benzene in ethyl bromide, the conductivity passed through a maximum value followed by a minimum value. *W. D. B.*

Ionization and chemical combination in liquefied halogen hydrides. *J. W. Walker, D. McIntosh and E. H. Archibald. Jour. Chem. Soc.*, 85, *1098* (*1904*).—Experiments were made on the conductivity of a number of substances when dissolved in liquid hydrogen sulphide or in the liquefied halide acids. Four substances which conduct well in hydrogen sulphide are pyridine, piperidine, nicotine and quinoline—all basic substances. All substances containing oxygen, nitrogen or sulphur are fairly good conductors in one or more of the halide acids. So also are thiophene and pyrrol. "The conclusion that we feel justified in drawing from these observations is that in at least a great number of cases, if not in all, combination with the solvent is the necessary precursor of ionization, although such combination does not necessitate ionization." *W. D. B.*

The electrical conductivity of liquid ammonia solutions, II. *E. C. Franklin and C. A. Kraus. Jour. Am. Chem. Soc.*, 27, *191* (*1905*).—"The specific conductivity of liquid ammonia at its boiling-point, —33°, is below 0.01×10^{-6} Kohlrausch units." The acid amides are conductors of electricity in ammonia solutions, some conducting very well and others only slightly. Many nitro compounds conduct well and some form highly-colored solutions. With the cyanides of the heavy metals the molecular conductivity first decreases with increasing dilution and then begins to increase after the dilution has passed a certain value. Data are given in the paper for thirty-seven substances not included in the previous paper. *W. D. B.*

The nature of a solution of iodine in aqueous potassium iodide. *C. H. Burgess and D. L. Chapman. Jour. Chem. Soc.*, 85, *1305* (*1904*).—In an aqueous solution of potassium iodide and iodine we believe that we have a reversible equilibrium between KI, KI_3, I_2, $K^{\cdot}$, I' and I'_3. The authors show that the ratio of the dissociation constants of KI_3 and I'_2 must be equal to the ratio of the electrolytic dissociation constants or ionization constants of KI_3 and KI. Combining this result with the formula of Jakowkin they find that the dissociation constants of KI_3 and I'_3 must be the same and be equal to

Jakowkin's *k*. The ionization constants of KI_3 and KI are consequently also equal. By transference experiments the authors find 0.556 for the ratio of the velocities of I'_3 and I' as ions while a value of 0.553 was obtained from conductivity determinations. *W. D. B.*

The determination of the neutralization point by means of conductivity measurements. *F. W. Kuster, M. Grüters and W. Geibel. Zeit. anorg. Chem.*, 42, *225* (*1904*).—It is shown that by the conductivity method it is possible to titrate sulphuric acid in presence of potassium bichromate or permanganate. The organic acids can also be titrated if they are added to caustic soda instead of adding the soda to them. Magnesia and the alkaloids can also be determined with accuracy. *W. D. B.*

The constitution of phenolphthaleine. *A. G. Green and A. G. Perkin. Jour. Chem. Soc.*, 85, *398* (*1904*).—If enough alkali be added to a phenolphthaleine solution to decolorize it, the color does not come back at once on neutralizing the excess of alkali but does come back if the solution be heated. Further quantitative experiments confirmed the authors in the belief that the color changes are best explained on the basis of the quinonoid theory. It was shown that quinol-phthaleine behaves like phenolphthaleine and the authors therefore suggest the ortho-quinonoid structure for the colored salts of quinolphthaleine. *W. D. B.*

Dielectricity and Optics

The action of radium rays on the halides of the alkali metals and analogous heat effects. *W. Ackroyd. Jour. Chem. Soc.*, 85, *812* (*1904*).—1. The color changes produced by radium rays in chlorides of the alkali metals divide these elements into their two sub-groups: I. LiCl, NaCl; II. KCl, RbCl, CsCl; and the changed chlorides conform to the constitutive-color law.

2. The division into these sub-groups is also indicated by their difference of molecular aggregation as expressed by the coefficient 1/mol. vol.

3. There is relative stability of the colors produced while they remain in darkness and their rate of disappearance or decay in daylight varies with the intensity of the light.

4. The amount of energy expended by the radium rays in effecting the color changes decreases as the molecular weight increases, or, in other words, the sensibility to the action of the radium rays increases with the molecular weight.

5. When the induced phosphorescence has decayed so as to be no longer visible, it can be revived by invisible heat.

6. In many respects, these phenomena are analogous to the thermal effects produced in other substances, and the whole of the evidence points to the conclusion that they are physical changes. *W. D. B.*

The comparison of the rotation-values of methyl, ethyl, and *n*-propyl tartrates at different temperatures. *T. S. Patterson. Jour. Chem. Soc.*, 85, *765* (*1904*).—1. It is shown that methyl tartrate is capable of existence in a solid form melting at 61.5°.

2. Data for the variation of rotation with change of temperature of methyl, ethyl, and *n*-propyl tartrates are given.

3. It is shown that comparisons of these data at identical temperatures are of little value, especially at low temperatures.

4. Since the rotations of methyl, ethyl, and *n*-propyl tartrates vanish at 0°, −34°, and −60° respectively, it may be assumed that these substances are in corresponding optical conditions at these temperatures, and in general that at T°, (T − 34°), and (T − 60°) the methyl, ethyl, and *n*-propyl esters will also be in corresponding conditions as regards rotation.

5. It is shown that comparisons effected at corresponding temperatures are much more satisfactory than those obtained at identical temperatures.

6. If the rotations are taken at corresponding temperatures, the increment of $2CH_2$, in passing from methyl to ethyl tartrate rather more than doubles the rotation, while the next increment of $2CH_2$ in passing to *n*-propyl tartrate increases the rotation 1.41 times. The rotation of *n*-propyl tartrate is therefore almost three times that of methyl tartrate.

7. These regularities persist within wide limits of temperature.

W. D. B.

The influence of solvents on the rotation of optically active compounds, V. *T. S. Patterson. Jour. Chem. Soc.*, 85, *1116* (*1904*).—On raising the temperature the values for the molecular rotation in aqueous solution pass through maxima with sodium tartrate, potassium tartrate, potassium methyl tartrate, potassium ethyl tartrate and potassium propyl tartrate, the maxima being only slightly marked in the case of the first two substances. With methyl, ethyl and propyl tartrates the molecular rotation of concentrated solutions increase with rising temperature while the reverse is the case for dilute solutions.

W. D. B.

The influence of solvents on the rotation of optically active substances. VI. *T. S. Patterson. Jour. Chem. Soc.*, 85, *1153* (*1904*).—The author has determined the densities at 20° of the solutions studied in the preceding paper. With methyl, ethyl and propyl tartrates, the contraction appears to pass through a maximum with increasing dilution; but no such phenomenon could be detected with potassium methyl tartrate, potassium ethyl tartrate, or potassium propyl tartrate.

W. D. B.

Crystallography, Capillarity and Viscosity

The viscosity of liquid mixtures. *A. E. Dunstan. Jour. Chem. Soc.*, 85, *817* (*1904*); 87, *11* (*1905*).—All mixtures of hydroxyl compounds have viscosities differing markedly from those to be expected from the viscosities of the pure components: Both maxima and minima occur in the curves and the author makes assumptions in regard to compounds, which he does not check in any way.

W. D. B.

THE TENSILE STRENGTH OF COPPER-TIN ALLOYS

E. S. SHEPHERD AND G B. UPTON

I. Introductory

In metallurgy, as in most other applied sciences, the practice has usually preceded the theory. Rule of thumb methods have been developing since man began to take an interest in metals, and it ought not to be surprising that these empirical methods should have been brought to a high state of perfection. We have only to recall that the fundamental theory of steel was first presented in 1900, in order to see how little the theory has had to do with the real development of this subject. On the other hand, it must not be forgotten that before this theory was presented, it required a great deal of experience before the mechanic could impart to a steel a given quality. It was only with the greatest difficulty that the skilled mechanic could reproduce a certain quality even in the same piece of metal, and often the product was far from being uniform. A familiar instance of this lack of uniformity, is to be found in the variable quality of razor blades. The advent of the theory has changed this very markedly.

By controlling the temperatures in accordance with the equilibrium diagram, it is possible for even an inexperienced person to produce a very satisfactory temper in any given steel, and a little experience will enable a beginner to produce even more uniform products than the old methods would permit. The reason for this, is that the methods have been systematized and referred to definite fixed standards.

Although steel is our most important alloy, it is also the most complex, and least suited to preliminary investigations. It has been five years since the provisional diagram was published, but we are by no means certain what many of the changes in physical properties really mean. It seems reasonable, therefore, that we should have begun our investigations with more easily studied bronzes. It was thought, at the time this investigation was begun, that the constitution of the bronzes had been sufficiently established. We soon found that we would have to revise Heycock and Neville's diagram, and that work has been done, under the grant to Professor Bancroft. We have now succeeded in clearing up the constitution of the bronzes, and also in obtaining some interesting results as to the relation between the constitution and the tensile strength.

Because of the great difference of properties produced in steel by heat treatments, this metal has always been regarded as a very special material. That similar changes might be produced in other alloys has been suspected, but the method of investigation has been to subject them to the same kind of treatments that are given to steel, and if the metal did not show similar differences it was then regarded as possessing none of the changes which steel shows. It is, of course, obvious that such a method of experimentation will fail to detect important relations in metals other than steel, unless said relations occur at temperatures nearly the same as those in steel. Unfortunately for this method of investigation, most metals possess their own peculiar properties, and where they show transformations similar to steel, they are apt to occur at temperatures widely different, so that the same treatment which is given steel, will fail to produce the similar transformations in another metal, for no other reason than that the changes occur at some different temperature. An intelligent study of the nature of each series of alloys will detect these transformations where the empirical methods will miss them entirely.

For example, heating a piece of steel to a red heat and quenching it in water will harden it. A similar treatment softens bronze. This quenching strengthens both steel and bronze. It softens, but does not strengthen brass. Annealing renders steel more ductile; it renders brass more ductile; it greatly diminishes the ductility of bronze. The reason for these very different results of heat treatment is easily explained by a study of the constitution of the alloys. It seems rational, therefore, to begin the study of the constitution of alloys, before wasting time in trying to determine their physical properties. Engineers have been determining the properties of materials for many years without being able to give to their results any general significance. It is the duty of the physical chemist to point out the general relationships which exist between the constitution and the physical properties.

It might be thought that technical men would gladly support investigations of this nature, so directly are the results applicable to technical problems. A review of the literature will show that such is not the case. Few technical men have the patience to pay for the results which do not have an immediate practical application, however necessary they may be to the theory. In France, where most of the work on the nature of special steels has been done, the investigators confine themselves to a very few selected alloys. Usually only two different concentrations of carbon are tried, and instead of determining the equilibrium diagram, they have to content themselves with the microstructure of the particular compositions examined. What the general relations are they do not attempt to determine. Such investigations can only be regarded as a make-shift.

We have been speaking altogether of the necessity of more complete work for the development of the practical side of the science, it is even more necessary for the pure science. The subject of geophysics is now absorbing the attention of a number of scientists, and such men find themselves seriously handicapped for lack of more exact information as to what happens in fused magmas. The methods which are being used in the investigation of rock magmas are precisely the same as the methods used in the study of alloys, with the difference, that the alloys are much the simpler case. Every discovery which the student of alloys makes, will be of direct assistance to the student of geophysics. For that reason also, it seems that alloy studies should be amplified as much as possible.

The investigation here reported on has been under way for the past year at Cornell University, under a Carnegie grant to Mr. Shepherd. Parallel work has been done in the department of chemistry by Messrs. Shepherd and Blough, and in the experimental engineering laboratory of Sibley College, by Messrs. Upton, Shepherd and Blough.

Except for the experiments of Thurston, there has been little previous work on the engineering strengths of the bronzes. Records of tests are scanty. In 1842, Mallet[1] reported upon the strengths, color and character of fracture, order of hardness, order of malleability, and order of fusibility of the bronzes. He used sixteen pieces to cover the range from copper to tin, and of these half lie in the useful end of the series. Wade,[2] Dean, 1868-1869, and Uchatius[3] all experimented with bronze for cannon, but they worked over very small ranges of composition, and were concerned chiefly with methods of increasing strengths by mechanical manipulation.

The experiments which have become classic in this line are those of the U. S. Board for Testing Materials, conducted by the Committee on Alloys, under the chairmanship of Dr. R. H. Thurston.[4] This work was very extensive, ultimately covering with transverse, tension, and torsion tests the whole of the ternary alloys of copper-tin-zinc. Because of its extensiveness, no part of this investigation could be gone into in great detail, and thus we find that only twenty pieces were tested for all the tensile properties of the copper-rich bronzes, a range of composition from 100 down to 65 percent of copper, which includes all bronzes of industrial importance.

The preceding investigations were all handicapped in one point; the internal chemical and physical constitution of the alloys tested was unknown. This must not be taken superficially to mean that analysis for the ultimate percentage composition was not readily made, although there was not then a method of separating copper and tin that gave a probable error much less than one-half of 1 percent. It is to be understood rather in the sense that no one knew whether the elements in the alloy were combined in chemical compounds, or solid solutions, or mere mechanical mixture, or in other ways. The rise of physical chemistry in the last ten years, the gain in knowledge

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[1] Phil. Mag., 21, 66 (1842).

[2] Report of experiments on metals for cannon, Phila., 1856.

[3] U. S. Ordnance Notes, No. 40, Wash., 1875.

[4] Report on properties of Copper-Tin Alloys, Washington, 1879.

of the changes in constitution of alloy series with heat treatment and composition, have made advisable and necessary the repetition of the tests of engineering properties not only of the bronzes, but of practically all of the metallic materials of engineering.

It is evident that the engineering properties of alloys, such as tensile strength and ductility, transverse strength, shearing strength, etc., must be closely connected with the internal chemical and physical structure. The equilibrium diagram shows, by its boundary lines of regions, where such structure changes; the regions or fields it outlines have each a definite structure characteristic. The investigation of tensile strengths with which this report is concerned is believed to be one of the first sets of tests to be made with the use of the freezing-point diagram, and shows how well that diagram can be relied upon in the prediction of the critical points in such research.

In Fig. 1 is given that portion of the copper-tin freezing-point diagram which includes the alloys containing more than 50 percent copper. The diagram is taken from the data of Heycock and Neville,[1] as modified by the more recent work of Shepherd and Blough.[2]

The coordinates are temperature and concentration, or percentage composition. The lines of the diagram mark the places where some physical or chemical change occurs in the alloy. The upper full line is the "liquidus," above which the alloys are completely molten. At the liquidus, crystals begin to separate out from the melt. The round-dotted line is the "solidus," below which the alloys are completely solid. Between the liquidus and the solidus the alloy is in a partially frozen state and consists of a "mother-liquor" more or less filled with a network of solid crystals. The region marked α means that anywhere within that area the alloy, if in a normal and stable condition, exists only in the form of α crystals. These crystals are composed of a solid solution of tin in copper; with

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[1] Phil Trans., 202 A, (1903).

[2] The complete diagram for the copper-tin alloys forms the subject of a subsequent paper by Messrs. Shepherd and Blough.

anything between 100 and 87 percent of copper the form of crystallization is the same. So β and γ are other solid solutions having definite crystal forms; and what was called Cu_4Sn by Heycock and Neville, is another, δ, with a narrow range of concentration, instead of being as long supposed a chemical compound. The only chemical compound in bronzes containing more than fifty 50 percent copper is Cu_3Sn. Besides the idea of a definite crystalline form being characteristic of a solid solution over a considerable range of concentration and temperature, one must grasp the conception that chemical changes in the solid are of frequent occurrence. Thus below 500° β is an instable form, and if cooled slowly past that temperature, it rapidly breaks down to δ crystals. How complicated the changes in the solid may be can be seen from the fields for β, β + γ, γ, γ + δ, β + δ etc., Fig I.

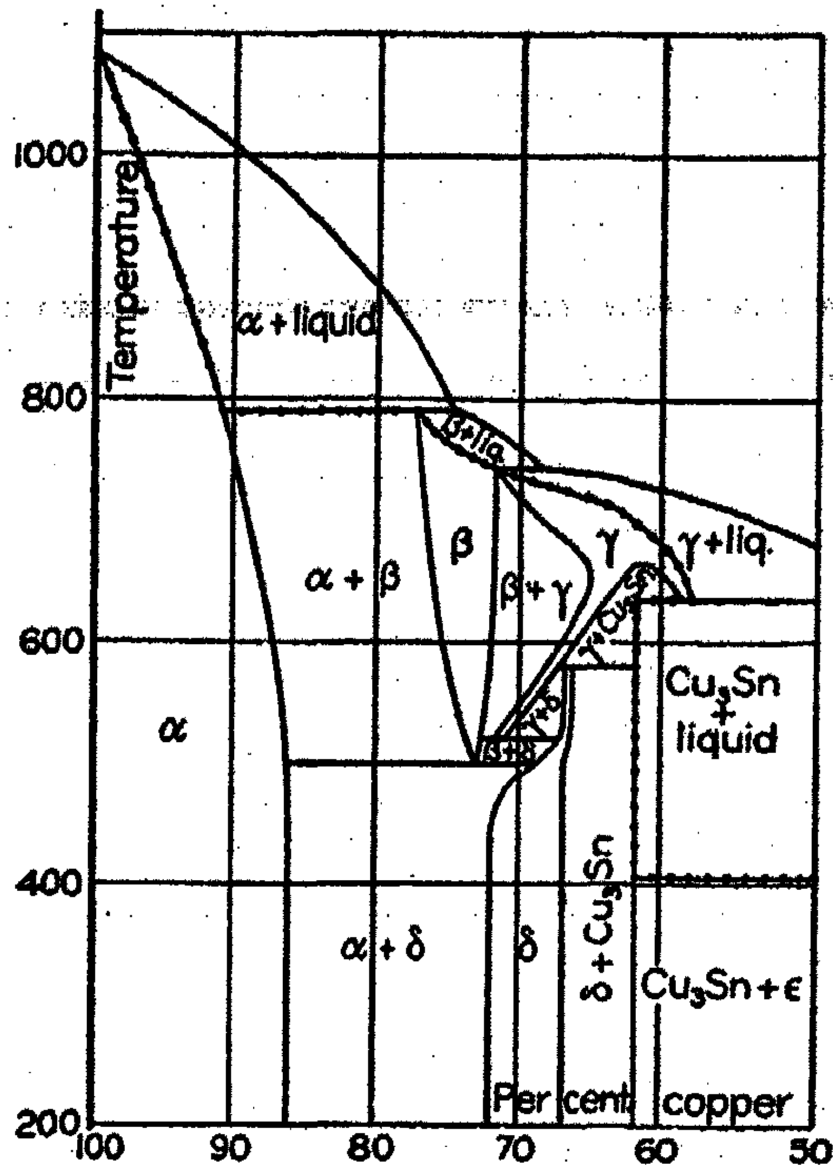

Fig. 1

Let us trace the freezing of a 95 percent alloy. Follow down the 95 percent line; freezing is seen to begin at 1050° C. At that point α crystals begin to form and separate, the mother-liquor becomes richer in tin. As cooling progresses, more and more freezes out, and the mother-liquor composition follows down the liquidus (the upper curve) so that at 950°, for instance, the mother-liquor contains 86 percent of copper. The α has meanwhile built up a crystalline network all through the freezing mass. The 95 percent line cuts the solidus at 910°, meaning that at that temperature the whole alloy becomes solid. The first α crystals contained more than 98 percent of copper; but diffusion and interchange are quite rapid, so that the final cold mass will be uniform α crystals of 95 percent composition. If we had started with an 85 percent alloy, freezing would have begun at 955°, and been complete at 790°. The product would in this case have been a mixture of two forms of crystals, α of about composition of 92 percent, and β of 75 percent, the β coming from the final freezing of the mother-liquor. As cooling progressed there would be a breakdown "in the solid" of β to δ and the final cold alloy would be a mixture of α and δ crystals.

The reaction velocities of internal change in alloys are very small or zero at ordinary temperatures, and do not become rapid until temperatures approach or exceed a red heat. This fact makes it possible to raise a specimen to a certain temperature, hold it there a sufficient time for it to obtain equilibrium, and then by sudden cooling, usually water quenching, to fix the structure normal to that temperature so that the structure is held indefinitely and can be studied or utilized at leisure. The hardening of steel is an example of such treatment, retaining and using at ordinary temperatures characteristics of the metal which are thermally normal at low red heat.

Thus the above description of what occurs in the freezing and cooling of a bronze is true only if the rate of cooling is low enough to enable the mass to maintain throughout, a condition of thermal equilibrium. Suppose one let the 85 percent alloy cool slowly to 650°, and then quenched it in water. He would then fix in the solid the α-β composition and properties the piece had before the quenching. If one desires to know the strength, hardness, ductility, or any other properties of pure β crystals he takes a 75 percent bronze and quenches it from between 600° and 700°. This power of fixing properties by quenching is a fact of the highest importance. The growth of crystals with time at high temperatures, changes of composition due to diffusion, and control of the cooling rate, are the means which underlie and bring about all modifications of the strengths of materials by heat treatment.

The best way to develop the structure and properties normal at a given temperature is first to chill-cast the specimen, then to anneal, holding it at the desired temperature for such a time as is found necessary, and to fix by quenching. Chill-casting gives a very uniform piece with minimum crystal size. Because of this small crystal size, meaning a very close and intimate mixture of components, equilibrium is far more readily reached when heat treatment is made, for diffusion need occur only through very small distances. The more rapid the chilling the better. Chill-casting has been shown to be so effective in securing close mixture of components that even copper and lead, the alloys of which normally separate into two liquid layers, can be obtained in fairly uniform ingots. If there be any tendency to liquation it is checked by chill-casting.

Keeping the preceding discussion in mind, the plan used in carrying out the present investigation was as follows: (1) Chill-casting, to get a very uniform test-piece, with minimum crystal size; for it is generally thought that the smaller the crystal, the higher the strength of the material. (2) The pieces to be given prolonged heating at various temperatures; in order to fully attain the crystallization and structure normal to those temperatures; the heating followed by fixation of properties through control of cooling rate. (3) Testing.—It was decided to carry through certain series—(1) one series of alloys was tested as cast; (2) one series was heated for a week at 540° C, and water quenched, giving the properties of α, β, γ, etc., as shown by following the 540° ordinate through the freezing-point diagram; (3) a third series was heated for one week at 400°

and furnace-cooled, in order to find the properties normal to slow-cooled bronzes, of compositions α, $\alpha + \delta$, ∂, $\delta + Cu_8Sn$, etc.; (4) to show how the heat treatment might be used commercially, a series was carried through where the pieces were simply heated up to a low full red and then quenched, corresponding to about 650° heating and quenching. In addition to these regular series there were many miscellaneous heat treatments, with various times of heating and various temperatures.

II. Making the test-pieces

For the purpose of studying the effects of changes of composition and heat treatment, it is essential that the test-pieces be perfectly uniform in composition. The best way to avoid the effects of liquation, is to chill-cast the test-piece. For the same reason it is desirable to cast the test-piece in the form in which it is to be tested. Machining the test-pieces might change their composition, and will have some mechanical effect which could not be neglected without a special investigation for each particular alloy. In chill-cast copper-rich bronzes the liquation is negligible.

The temperature of pouring, has only one effect on an alloy. The excess heat imparted to the mould determines the rate of cooling, and thereby, the grain size. In the present research, the temperature of pouring was very uniform and, owing to the nature of the alloy and to the process of chilling, would have a minimum effect.

The materials used for making the test-pieces were electrolytic copper, of 0.9998 purity, and tin, 0.999 pure. Thus the influence of even minute quantities of other metals was avoided. For convenience of operation, the original 20-pound copper pigs were recast into 0.75-pound pieces or smaller. The tin was already in narrow bar form.

The melting was done in a gas furnace which was placed at our disposal by the chemical department. This was an air blast-furnace which proved well able to reach and hold the necessary temperature, about 1200° C being desired in the melt of pure copper, requiring a furnace temperature somewhat higher.

The heat was such as to cause the fire-clay furnace lining to soften and flow slowly. This fluxing of the furnace lining is partly due to oxide of copper. At 1200° C copper has a very appreciable vapor tension. Three linings have been used in a year and a half. To increase the efficiency and reduce the amount of gas used, the furnace was fitted with a thick non-conducting jacket, and the valves were calibrated.

Graphite crucibles were used, and 1900 grams (4.25 pounds) of copper constituted a maximum charge. Ordinary "Hessian" crucibles would not last in the service more than two or three melts, while the graphite is good for thirty to fifty.

The original melt for casting a given composition totaled around 1800 grams, or somewhat less than 4 pounds. The weighing out was accurate to 1 gram, or 0.06 of 1 percent. After being broken in the testing machine, the castings were remelted and recast, and this was done with some metal nearly a dozen times. With zinc, as in brasses, this would be impossible without analysis for composition of each melt. No appreciable error is introduced in the bronzes. The greatest shift of composition, due to oxidation or burning out of tin, occurs in the lowest melting bronzes tested, 70 percent of copper, and there it was only 1/10 of 1 percent in 7 or 8 remeltings; that is, it was not large enough to need consideration. With higher copper to start on, the shift was much less; in a 98 percent alloy it could not be detected. After a number of recastings mentioned, the metal was analyzed, and tin added to correct the composition. The compositions used for the tests were in percents of copper 100, 98, 96, 94, 92, 90, 87, 84, 81, 78, 75, 70. These compositions were thought sufficient to cover the ground thoroughly.

(*a*) *Preparation of the Mould.*—Because of the rapid chilling desired it was at first thought that a copper mould would be the best to use. Copper was preferred to iron because of the gases which iron evolves when heated. A copper mould was made, but was found impracticable. The chill was so rapid that the mould would not fill, or if heated so that it would fill, the castings were defective in being full of bubbles of trapped air.

Sand casting was given a trial. The surface of the castings was then very bad, and machining difficult, while the pieces themselves were imperfect. The sand pile available was small, and burned out. Compare Thurston, report on the properties of the copper-tin alloys, page 296: "The first casting was made in dry sand moulds, but so much trouble was given by irregular surfaces and blow-holes that recourse was had to a cast iron mould, with better results." Thurston cast straight bars of uniform cross section. In this form of casting a metal mould can be used.

When the metal was poured at too low a temperature into the cold mould it was sometimes slightly chilled, giving an irregular surface. This was remedied by heating the mould to a temperature somewhat below the melting-point of the alloy, the highest temperature being given it in casting alloys containing the largest percentage of copper. In all cases the mould was placed in a vertical position while the metal was being poured and cooled.

Then trials were begun with a material which has been found ideal—artificial graphite. The graphite is easily worked, and takes a beautiful surface; the cast pieces come out so smooth and accurate that machining is unnecessary. The mould can be made to cast the shape and size desired for the finished test-piece. The moulds are relatively durable; one is good for 75 to 200 castings. They fail finally in three ways: by flaking off of the surface, due to a crack in the original plate; by breaking off of small corners or thin walls, if a piece is left too long to contract in the mould; and by a gradual softening and powdering off of the surfaces against which the hot metal comes.

The evolution of the form of mould finally adopted was gradual. The first form, I in Fig. 2, was a simple sprew running down to a test-piece, with a vent at the other end of the piece. The halves were matched with dowel pins. Difficulty was found with the mould not filling, and was obviated by enlarging the sprew and heating the mould. The greater trouble was trapped air, which made one likely to cast pipes instead of solid test-pieces. The rather sharp tapers on the test-piece made breakage in the mould from cooling strains frequent. In II these tapers were made more gradual, and the air vent was made larger, becoming a small riser. The catching of air bubbles in the cast piece still occurred, and therefore in III, a vented air trap was put into the sprew. A projecting fin along the top of the test-piece was also tried, in the hope that the air bubbles would rise into the fin, and leave the test-piece itself sound. The fin idea was worthless. Finally, it was reasoned that the air bubbles must get into the metal as it splashed in pouring into the sprew, and that the best cure was prevention. Therefore the "centrifugal sprew" (IV) was invented, shown in Fig. 3. The diagram is self-explanatory; the metal was gently caught and sent down, flowing smoothly down the outside of the sprew cavity from the action of centrifugal force. With splashing stopped, the trouble from trapped air bubbles largely ceased. The air trap in the sprew was still retained, as a good precaution.

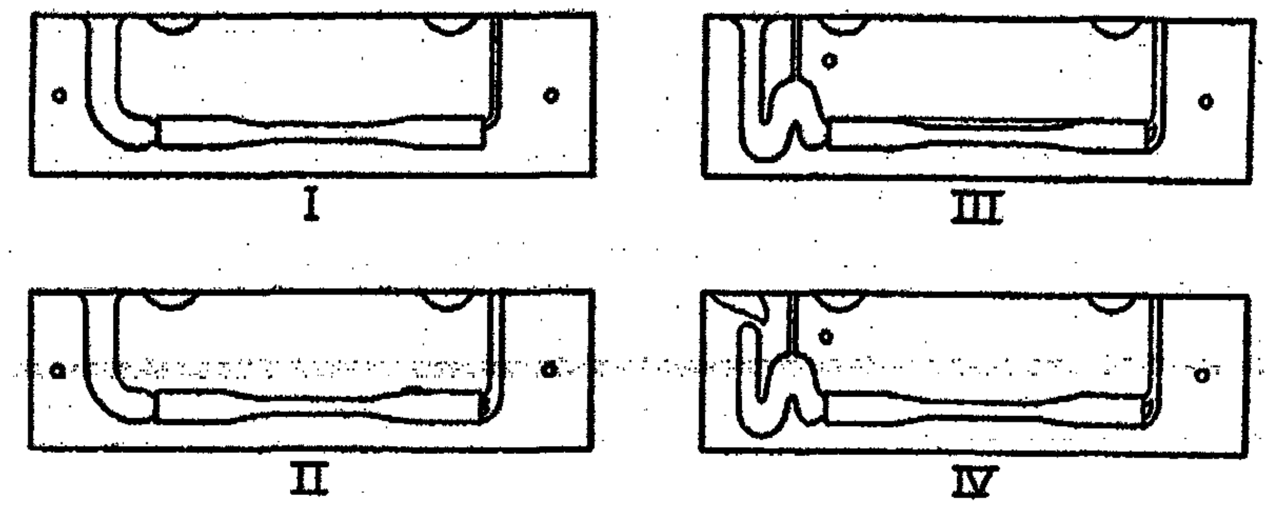

Fig. 2

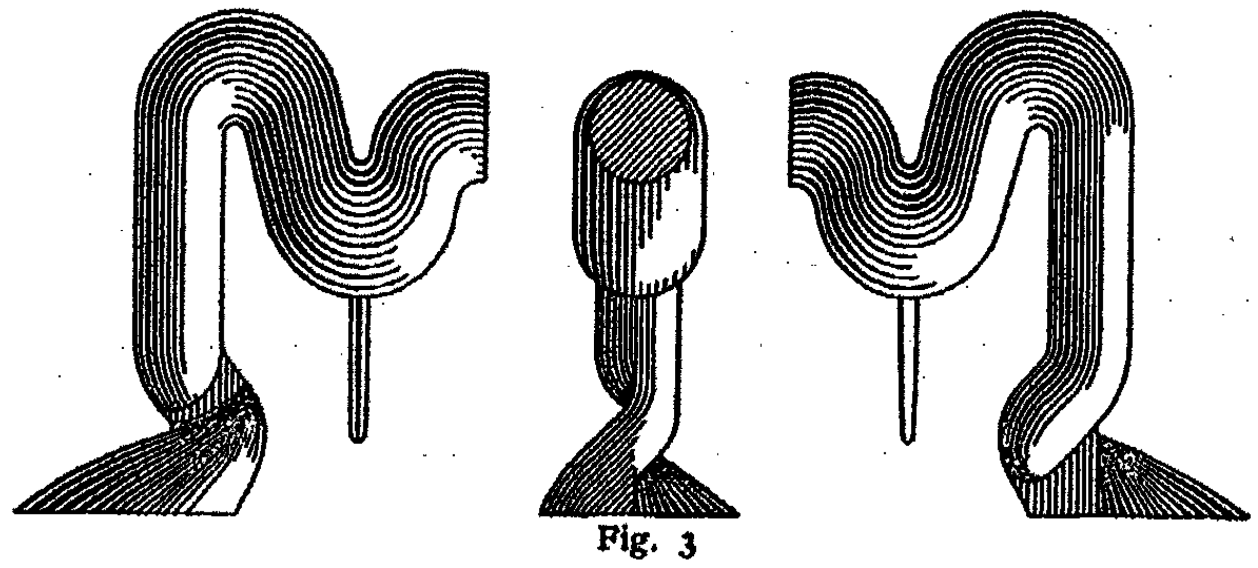

Fig. 3

The halves of the mould were clamped together between two plates of $^3/_8$-inch iron, which were hinged at one end and fitted with a wedge lock at the other. Thus the whole combination could be lifted into or out of an improvised furnace, built of bricks and heated by blast-lamps. In operation, the mould was clamped together, put into the furnace and heated; and when the desired temperature (black or low red heat) was reached, the lid of the furnace was removed, and the pouring made. Then the mould was lifted out of the furnace, unclamped, the casting taken out and quenched in water. The test-piece, before quenching, was usually at or just below a red heat.

The mould heating furnace was shortly done away with, as the form of mould had become such that the heat kept in the graphite from previous castings was sufficient to insure filling. Not having to lift the mould, the iron clamping strips were left off. The mould was simply set up on the cement floor, and the halves held together by three or four bricks laid at each side. This method also did away entirely with breakage of pieces in the mould from cooling strains, because the contracting piece readily spread the mould by means of the long tapers. The contraction in a test-piece 22 cm. long amounts to about 2 mm.

A casting trouble that no variation of mould can rectify is the pinholing, or sponginess, which is due to gases occluded in the molten metal. Molten copper, and molten bronzes down to 85 percent copper, have the power of absorbing gases. When freezing begins these gases are set free with the result that the mass of the casting is filled with tiny bubbles of sizes from a pin-point to a pinhead. The only way to avoid this is by proper treatment of the melt in the furnace. The absorption of gases is roughly proportional to the time the metal is held molten. Hence the furnace was run hot and the time of melting kept as short as possible. The metal must be gotten hot, for if poured too cold, it is practically certain to trap air bubbles. It was found also that the occluded gas was much worse in the top of the melt, and therefore the practice was adopted of pouring off the top portion of the metal in the crucible into an ingot mould, and then pouring the test-piece casting. The little ingot froze, rejected its gas, and while still red hot was returned to the crucible, so that not much heat need be lost by this precaution. The waste gases of the furnace were used to reheat the metal about to be put into the crucible; by thus avoiding the direct introduction of cold metal the furnace temperature was kept high.

Molten, or even hot copper has a great affinity for oxygen. In the crucible, if air has access to the melt, the oxidation is so rapid as to make the metal simmer and bubble. Copper oxide is much weaker than copper, and renders a casting in technical language "rotten," *i. e.*, absolutely worthless. The remedy for the oxidation is exclusion of the air, which was readily done in this case by filling the top of the crucible with an atmosphere of illuminating gas, brought in through the furnace lid by a porcelain tube. Commercially some flux, such as charcoal, would be used to stop oxidation. Its inefficiency is shown by the necessity for poling.

For the original melt of any composition, the copper was always put in first. Usually a piece of soft graphite was put in with the copper, and would be floating on the top when the copper melted down. When it had become thoroughly hot, the molten copper was stirred or "poled" with a rod of graphite or carbon. Then the tin was added, and well stirred in. This stirring with a graphite rod was mainly to make sure that there should be no copper oxide in the melt.

The difficulty of casting pieces varies considerably with the composition. Occluded gases are worst above 90 percent and below that rapidly cease to make trouble. Indeed, it seems that below 85 percent the melt no longer has the power of occluding gas. Oxidation goes out the same way; though it may be severe in an 87, it is rarely found in an 84 percent, and never at all in any percent below 84. The trouble with air holes, from trapped air, has its main cause removed when the mould is properly formed. It may occur in any composition if the metal is poured too cold. It is not likely to occur below 84 percent, because the melting-points are then so low that there is little chance that the metal will be poured cold. To sum up then, there is not much difficulty at or below 84 percent in getting any desired number of good castings. The worst compositions to cast are in the range 94 to 87 percent. There every trouble must be met and in avoiding one, another is almost sure to be increased. The result was an average in this range of less than 60 percent of good castings.

After the casting came the heat treatment. In order to give the prolonged heating at high temperatures, two annealing furnaces were built. Each furnace consisted of a fire-clay muffle about 15 inches long, so built in with tile brick that the gases from a triple or quadruple Bunsen burner passed along the bottom of the muffle, back along the sides and back again along the top. The test-pieces, 20 to 25 at a time, were put into the muffle and sealed in with clay. To prevent oxidation a stream of illuminating gas was passed constantly through the muffle, in at one end and out the other. A tube for a platinum platinum-rhodium thermocouple was sealed in, so that the thermocouple could at any time be used to get the temperature in the middle of the muffle. Temperature regulation was made by adjusting the gas supply. These furnaces were quite satisfactory; they could be kept within 20° C each side of the desired temperature, and usually within 10°.

Two temperatures were used for runs. One series of compositions of test-pieces was put in and run for one week at 540° C, and water quenched when taken out. Another series was run at 400° C one week and allowed to cool in the furnace. Theoretically, furnace-cooling the 400° series would not differ in effect from quenching.

Many shorter heat treatments were made, where pieces were heated for three hours or less. These heatings were made in a regular gas-fired assay muffle furnace. The muffle was partially filled with fine sand and the pieces pressed down into that. One regular series of heat treatment was made thus, where the pieces were simply brought up to a heat between low and full red and then water-quenched. With the compositions below 90 percent, especially 81 and 78, several different combinations of temperature and time were tried.

Very little machining of test-pieces was done, because few were made before the development of the graphite mould made turning up unnecessary.

III. Testing

While it might in some ways have been desirable to make the test-pieces of the same size as the standard for wrought iron and steel, the great expense of the chemically pure materials used made this impossible. Therefore the size of the graphite plates available for the moulds and the capacity of the furnace which had to be used for melting were allowed to control the test-piece size. The dimensions chosen were roughly one-half those of a standard tension piece—more definitely 9 inches long over all, with the cylindrical test portion in the center about 0.42 inch in diameter and 3 inches long. The grips at the ends were 3/4 inch in diameter. A few of the first test-pieces made, those which were turned, had smaller diameters.

When a wrought iron or steel piece is tested, the elongation is made up of two parts: first, a fairly uniform stretch throughout the whole length of the cylindrical portion; and second, for a length of 1/2 inch to 1 inch on each side of the break, there is superposed on the first a greater local elongation in what is called the "neck" of the break. Obviously, then, if the length under observation be shortened so that the neck forms a larger part of the whole, the ultimate elongation found will be much increased. Hence in testing these materials it is absolutely essential in order that tests may be comparable with each other that the same ratio of diameter to length of observed portion of the cylinder be maintained. This is the reason for the existence of standard forms in iron and steel test-pieces. It is not necessary that pieces be of the same size, if their forms are similar; that is, a piece 8 inches long and 1/2 inch in diameter will give the same results as one 4 inches long and 1/4 inch in diameter, or 16 inches long and 1 inch in diameter, barring the fact that the working of the material in manufacture affects the outer part of a rod more than it does the center.

In the bronzes the local effect of necking does not occur, or it is very small. The cylinder draws down straight and uniformly to the break. Hence the great care about the ratio of length to diameter of test-piece is unnecessary, for with the same diameter of piece the length observed may be changed at pleasure and the percent elongation found will be practically unaffected. Therefore, these tests made upon half-size pieces, though the ratio of length to diameter is less than the standard, are yet perfectly typical and are just as good as if made upon standard size. The only disadvantage of measuring a short length of cylinder is, that to get the same accuracy in the percentage extensions greater accuracy of absolute measurement is necessary.

Just as in the iron test-piece the center is filed down to insure the locality of the break, the bronze pieces were cast with the center of the cylinder about 0.01-inch smaller in diameter than the ends. They never broke elsewhere unless there was some internal flaw.

The testing machine used was the 100,000 pound Riehlé which is by far the most convenient of the smaller machines in the Experimental Engineering Laboratory of Sibley College. It is a double screw machine, power driven. A very wide range of testing speeds is available. The scale on the beam is 1000 pounds per inch, reading to 10 pounds by vernier on the sliding weight. The sector is graduated to pounds. Some years ago the machine was tested for accuracy by loading with dead weights, and was found unusually good. As the weighing apparatus is carried on knife edges, and the machine has always been well kept up, it should now be as accurate as it ever was.

The machine was found subject to one peculiar phenomenon. If the beam was set for a load, say, of 3000 pounds total and run till it floated that, and at the instant the motion cut out, the beam would fall, and to get balance it would be necessary to run back about 175 pounds. Investigation disclosed the fact that this action is zero at 500 pounds total load and thence is directly proportional to the load up to about 12,000 pounds where it becomes practically constant. The "throwback" is also slightly greater with higher speeds of the screws. It reaches at 9000 pounds the rather serious value of 600 pounds. It was found also that the test-piece shortened as the throwback occurred; whether the shortening was proportional to the throwback was not determined.

The question was how the throwback would affect the tests. The usual method of carrying out such tests is to set the beam for certain predetermined total loads, run to each till the beam floats, then cut out the motion and take the extensometer readings. But under these circumstances, when the extensometer reading is taken the actual load on the piece is about 6 percent less than that which the beam in motion floated; and the extension recorded for the floating load is accordingly 6 percent less than it should be. To get true and accurate results some method must be adopted which will record observations of extension and load which are read simultaneously. The best way is to take the extensions with moving load as the beam picks up the load in motion. The next best way is to stop the machine, and take both load and extension under static load. This is less accurate than taking under motion, but far better than the usual method. Both of these methods, mainly the latter, have been used in these bronze tests; lately all observations have been taken under motion. Under any conditions, the breaking load recorded is necessarily a floating load. Errors of operation and method have always, if possible, been thrown against, not for, the test-pieces.

Before starting tests, the beam was always balanced at zero. There was a small zero drift in the course of a day, so that the possible zero error of load may be put at 10 pounds. While testing, the error of balancing a given load may be also 10 pounds. The net result is a possible error in the total recorded load of 20 pounds, and a probable error of 10. The reciprocal of area of test-pieces was about 7, so that the possible error of reading in pounds per square inch was ± 140, and probable error ± 70. This work was at least as accurate as ordinary testing machine operation; and the unreasonableness of giving figures in pounds per square inch computed closer than to hundreds is apparent.

The diameters of the test-pieces were measured with a micrometer to the nearest thousandth of an inch. Due to variable separation of the halves of the mould, the castings had elliptical rather than circular sections, and hence a large and a small diameter were taken and the area computed as an ellipse. Allowing an error of 0.001 inch in each diameter, the possible error in area is one percent, and probably about ¼ of one percent. The net result of all probable errors in area and in load is that the breaking loads computed are in error not more than one percent, even in the worst cases.

Because of the shortness of the bronze pieces an extensometer could not be used. Elongations were taken between prick punch marks at the ends of the cylindrical portion of the test-piece, by very fine pointed dividers (drafting instruments) and lengths read off to thousandths of an inch, using a lens and a flexible steel rule graduated to hundredths. Considerable facility was soon acquired at this, and less than one reading in ten was in error 0.001 of an inch. With a length under observation of 3 inches, the extension per inch is then accurate to 0.00035. The greatest objection to this method of taking extensions is that bending of the test-piece cannot be detected and may introduce errors. The probability of this error being serious is small; the prick punch marks were so placed as to minimize the effect of the bending; and where a test-piece was noticeably bent the data on extensions were either not taken or were taken and not used.

After the breaking of a piece in the testing machine the halves were removed from the jaws and examined. The recorded data of tests[1] tell for each piece whether the fracture showed the piece to be "good" or if not good, what the trouble was—trapped air, oxide, occluded gas, flaw from too cold casting, etc. A piece was considered good if it had the proper color for its composition and the right crystallization if it had stood up well for strength; it was called good even when there were one or two pin points of occluded gas visible.

The typical colors and character of fracture were as follows: The color grades from the familiar red of copper through

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[1] Given in Mr. Upton's thesis but not published in this paper.

red tinted grays to a yellow gray at 92 percent, to pure gray at 84 and 81 percent. Fractures are sometimes cup shaped with 94 or more percent of copper, but are generally, and below 94 percent always square across. From medium sized fibrous in pure copper the material changes gradually to very minutely fibrous in 84 and below, where the surfaces of break are almost smooth planes. From 78 percent down the surface depends on the heat treatment. β shows up in long prismatic needle crystals, δ gives a vitreous fracture, light yellow in color. A 75 percent or 70 percent alloy breaks exactly like glass. On cut surfaces the color is decidedly unlike that on fracture. In pure copper it is light yellow, red-tinged. The red is entirely lost at 90 percent or 87 percent; below that the yellow grows whiter, but always remains yellow.

IV. Results of tests

It has not seemed desirable to publish all the data obtained. In Table I is given a summary of the final results. The first column shows the heat treatment, *Aqua* being used as an abbreviation for quenched in water. In the second column G (good) denotes that the casting showed no flaws at the fracture, while B (bad) denotes that the casting was imperfect for some reason or other. In the third column the ultimate tensile strength is given in pounds per square inch. In the last column is given the ductility, expressed in percentage elongation. These same

Table I.—Summary of Tests.

Percentage of copper, 100

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	19650	12.0
Tested as cast	G	17990	—
Tested as cast	G	23740	17.0
Tested as cast	G	19630	22.5
Tested as cast	B	20000	8.0?
Tested as cast	B	15120	7.0?
540° one week, aqua	G	24540	28.0
540° one week, aqua	G	22600	18.5
540° one week, aqua	G	24100	21.5

TABLE I.—SUMMARY OF TESTS—*Continued*

Percentage of copper, 100

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
540° one week, aqua	G	22740	24.5
540° one week, aqua	G	24470	21.5
540° one week, aqua	B	14990	16.0[1]?
540° one week, aqua	B	9090	—
540° one week, aqua	B	21580	25.0
Heated to red, aqua	G	25560	28.5
Percentage of copper, 98			
Tested as cast	G	27380	20.0
Tested as cast	G	27700	23.5
540° one week, aqua	G	31670	31.0
540° one week, aqua	B	26940	20.0?
540° one week, aqua	B	24860	15.0?
540° one week, aqua	B	29150	—
540° one week, aqua	B	24780	—
Heated to red, aqua	B	24330	—
Percentage of copper, 96			
Tested as cast	G	31130	20.5
Tested as cast	B	29630	15.0?
540° one week, aqua	G	38000	22.0
540° one week, aqua	G	33460	20.5
540° one week, aqua	G	36600	27.0
540° one week, aqua	B	28830	—
540° one week, aqua	B	24570	—
Heated to red, aqua	G	32140	18.5
Percentage of copper, 94			
Tested as cast	G	32800	8.0
Tested as cast	G	31470	11.0
Tested as cast	G	33440	24.0
Tested as cast	G	37500	18.0
540° one week, aqua	G	34030	24.5
540° one week, aqua	G	32210	24.5
540° one week, aqua	G	34490	16.5
540° one week, aqua	B	24500	5.0?
540° one week, aqua	B	30220	—
540° one week, aqua	B	33000	—
400° one week, furnace-cooled	B	31390	7.0?
400° one week, furnace-cooled	B	28630	8.0?
400° one week, furnace-cooled	B	30630	14.0?
Heated to red, aqua	G	34350	19.5
Heated to red, aqua	G	33760	21.5
Heated to red, aqua	B	30940	—

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[1] Broke in grips.

TABLE I.—SUMMARY OF TESTS—(*Continued*)

Percentage of copper, 92

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	41020	11.5
Tested as cast	B	23230	—
Tested as cast	B	27620	—
Tested as cast	B	24560	—
540° one week, aqua	G	32990	33.0
540° one week, aqua	G	38870	22.5
540° one week, aqua	G	31930	18.5
540° one week, aqua	G	39110	28.5
540° one week, aqua	G	34470	23.0
540° one week, aqua	B	27720	—
540° one week, aqua	B	29560	14.0?
540° one week, aqua	B	24800	—
540° one week, aqua	B	29830	—
540° one week, aqua	B	34930	18.0?
540° one week, aqua	B	30000?	—
540° one week, aqua	B	33440	—
Heated to red, aqua	G	39190	21.0
Heated to red, aqua	G	34440	20.0
Heated to red, aqua	B	36510	—

Percentage of copper, 90

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	44580	17.0
Tested as cast	G	44280	12.0
Tested as cast	G	40140	9.0
Tested as cast	B	30830	6.0?
Tested as cast	B	31040	10.0?
Tested as cast	B	32090	10.0?
Tested as cast	B	30420	5.0?
540° one week, aqua	G	46920	47.5
540° one week, aqua	G	42900	35.0
540° one week, aqua	G	45790	37.5
540° one week, aqua	G	37240	25.5
540° one week, aqua	B	35630	20.0?
540° one week, aqua	B	34580	20.0?
540° one week, aqua	B	30390	—
540° one week, aqua	B	33080	25.0?
540° one week, aqua	B	26180	—
540° one week, aqua	B	20440	—
400° one week, furnace-cooled	G	40040	26.0
400° one week, furnace-cooled	G	39120	19.5
400° one week, furnace-cooled	G	43130	28.5
Heated to red, aqua	G	44670	21.0
Heated to red, aqua	B	34570	—

TABLE I.—SUMMARY OF TESTS—(*Continued*)

Percentage of copper, 90

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Heated to red, aqua	B	38220	—
Brought to 630°, aqua	B	27830	—
Brought to 620°, aqua	B	30590	—
Brought to 630°, aqua	B	28080	—

Percentage of copper, 87

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	46430	8.5
Tested as cast	G	38130	4.5
Tested as cast	G	32950	4.0
Tested as cast	G	46440	5.0
Tested as cast	G	42840	3.5
Tested as cast	G	42080	6.0
Tested as cast	G	39600	4.5
Tested as cast	B	35640	—
Tested as cast	B	37940	—
Tested as cast	B	37280	—
540° one week, aqua	G	42000	26.5
540° one week, aqua	G	48200	39.0
540° one week, aqua	B	32080	—
540° one week, aqua	B	29500	—
540° one week, aqua	B	29310	—
540° one week, aqua	B	25210	—
540° one week, aqua	B	38180	—
540° one week, aqua	B	36230	—
540° one week, aqua	B	36320	—
540° one week, aqua	B	24970	—
400° one week, furnace-cooled	G	37530	8.5
400° one week, furnace-cooled	G	38770	11.5
400° one week, furnace-cooled	B	35670	12.0?
Heated to red, aqua	G	44080	7.0
Heated to red, aqua	G	39740	9.5
Heated to red, aqua	B	41790	7.0?
Brought to 620°, aqua	G	47370	17.5

Percentage of copper, 84

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	35210	1.0
Tested as cast	G	35930	1.3
Tested as cast	G	36140	1.7
Tested as cast	G	50760	2.0
Tested as cast	G	39900	—
Tested as cast	B	29080	1.0?
Tested as cast	B	43800	1.0?
540° one week, aqua	G	38570	16.0

TABLE I.—SUMMARY OF TESTS—(*Continued*)

Percentage of copper, 84

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
540° one week, aqua	G	37400	19.0
540° one week, aqua	G	52250	—
540° one week, aqua	G	43990	20.5
540° one week, aqua	G	58030	20.5
540° one week, aqua	G	51410	—
540° one week, aqua	G	56170	17.7
540° one week, aqua	G	58700	21.5
540° one week, aqua	G	56710	22.0
540° one week, aqua	B	35520	1.0?
540° one week, aqua	B	46030	—
540° one week, aqua	B	43860	—
540° one week, aqua	B	46240	—
400° one week, furnace-cooled	G	45740	2.0
400° one week, furnace-cooled	G	43430	1.4
400° one week, furnace-cooled	G	32720	2.5
Heated to red, aqua	G	57220	8.0
Heated to red, aqua	G	60680	11.0
Heated to red, aqua	B	58220	—
Brought to 620°, aqua	G	56300	11.0
Brought to 620°, aqua	G	52680	7.0
Percentage of copper, 81			
Tested as cast	G	54140	2.9
Tested as cast	G	53200	—
Tested as cast	B	20830	—
540° one week, aqua	G	49940	—
540° one week, aqua	G	49360	—
540° one week, aqua	G	48360	—
540° one week, aqua	G	60960	—
540° one week, aqua	G	61650	—
540° one week, aqua	G	60260	—
540° one week, aqua	B	48160	5.0?
540° one week, aqua	B	38300	—
400° one week, furnace-cooled	G	42200	0.4
400° one week, furnace-cooled	G	33000	—
400° one week, furnace-cooled	G	41260	0.6
400° one week, furnace-cooled	G	45900	0.6
400° one week, furnace-cooled	B	31200	—
400° one week, furnace-cooled	B	37500	0.5?
400° one week, furnace-cooled	B	32500	0.5?
Heated to red, aqua	G	65750	7.3
Heated to red, aqua	G	61720	8.0

TABLE I.—SUMMARY OF TESTS—(*Continued*)

Percentage of copper, 81

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Heated to red, aqua	G	60670	3.5
Brought to 620°, aqua	G	61320	—
Brought to 620°, aqua	G	72340	6.5
Cast, air-cooled	G	37430	0.3
Cast, air-cooled. Cast, cold	G	32740	0.2
720° three-fourths hour, aqua	G	68630	6.5
720° three-fourths hour, aqua	G	61480	5.0
Percentage of copper, 78			
Tested as cast	G	39520	0.35
Tested as cast	G	49260	—
Tested as cast	B	41150	—
Tested as cast	B	23750	—
Tested as cast	B	36110	—
540° one week, aqua	G	55530	—
540° one week, aqua	G	62930	—
540° one week, aqua	G	51950	—
540° one week, aqua	G	52200	—
540° one week, aqua	B	10000?	—
400° one week, furnace-cooled	G	23980	—
400° one week, furnace-cooled	G	29380	—
400° one week, furnace-cooled	G	21780	—
400° one week, furnace-cooled	B	27910	—
Heated to red, aqua	G	67600	1.3
Heated to red, aqua	G	58940	1.2
600°-620° one hour, aqua	G	56750	4.0
600°-620° one hour, aqua	G	49880	—
600°-620° one hour, aqua	G	64170	6.6
Brought to 700° and air-cooled	G	17630	0.05
Brought to 700° and air-cooled	B	15080	—
700° three-fourths hour, aqua	G	52240	0.6
700° three-fourths hour, aqua	G	52260	0.5
700° three-fourths hour, aqua	G	60400	1.2
400° one hour, air-cooled	B?	14260	—
400° one hour, air-cooled	B	16970	—[1]
400° one hour, air-cooled	B	5450	—
Brought to 700°, aqua	G	51350	1.6
Brought to 700°, aqua	G	56260	—
Brought to 700°, aqua	G	62720	—

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[1] All developed large cracks in cooling.

TABLE I.—SUMMARY OF TESTS—(*Continued*)

Percentage of copper, 75

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	10390	0
Tested as cast	G	16810	—
Tested as cast	G	15180	—
Tested as cast	B	6510	—
540° one week, aqua	G	34060	—
540° one week, aqua	G	30870	—
540° one week, aqua	G	10730	—
400° one week, furnace-cooled	G	22340	—
400° one week, furnace-cooled	G	15490	—
400° one week, furnace-cooled	G	14190	—
400° one week, furnace-cooled	B	6900	—
630° one hour, aqua	G	35640	1.1
630° one hour, aqua	G	27450	0.4
600° one hour, aqua	G	36730	0.35
700° one hour, aqua	G	27860	0.3
700° one hour, aqua	G	34970	0.75
700° one hour, aqua	G	38730	2.1

Percentage of copper, 70

Heat treatment		Strength. Pounds per square inch	Ductility. Percent elongation
Tested as cast	G	0	—[1]
Tested as cast	G	15780	—
Tested as cast	B	3320	—
400° one week, furnace-cooled	G	3490	—
400° one week, furnace-cooled	B	0	—[2]
400° one week, furnace-cooled	B	0	—

results are given in a more condensed form in Table II only the sound castings being included.

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[1] Broke while being placed in jaws.

[2] Broke while being gripped.

TABLE II.—STRENGTHS AND DUCTILITIES OF "GOOD" PIECES IN REGULAR SERIES.

	540°, 1 week, Aqua		Tested as cast		400° 1 week furnace cooled		Brought to red, Aqua	
	Ultimate		Ultimate		Ultimate		Ultimate	
Cu percent	Strength lbs/sq in	Elongation percent	Strength lbs/sq in	Elongation percent	Strength lbs/sq in	Elongation percent	Strength lbs/sq in	Elongation percent
	24500	28.0	19600	12.0			25600	28.5
	22600	18.5	23700	17.0				
100	24100	21.5	19500	22.5				
	22700	24.5	18000					
	24500	21.5						
98	31700	31.0	27400	20.0				
			27700	23.5				
	38000	22.0	31100	20.5			32100	18.5
96	33500	20.5						
	36600	27.0						
	34500	16.5	32800	8.0			34400	19.5
	34000	25.5	31500	11.0			33800	21.5
94	32200	24.5	33400	24.0				
			37500	18.0				
	33000	33.0	41000	11.5			39200	21.0
	38900	22.5					34400	20.0
92	31900	18.5						
	39100	28.5						
	34500	23.0						
	46900	47.5	44600	17.0	40000	26.0	44700	21.0
	42900	35.0	44300	12.0	39100	19.5		
90	45800	37.5	40100	9.0	43100	28.5		
	37200	25.5						
	48200	39.0	46400	8.5	37500	8.5	44100	7.0
	42000	26.3	32900	4.0	38800	11.5	39700	9.+
			38100	4.5				
87			39600	4.5				
			42100	6.0				
			42900	3.5				
			46400	5.0				
	52200	—						
	38600	16.0	35200	1.0	45700	2.0	57200	8.0
	56200	17.7	35900	1.3	43400	1.4	60700	11.0
	37400	18.0	36100	1.7	32700	2.5		

TABLE II.—STRENGTHS AND DUCTILITIES OF "GOOD" PIECES IN REGULAR SERIES

	540°, 1 week, Aqua		Tested as cast		400° 1 week furnace cooled		Brought to red, Aqua	
	Ultimate		Ultimate		Ultimate		Ultimate	
Cu percent	Strength lbs/sq in	Elongation percent	Strength lbs/sq in	Elongation percent	Strength lbs/sq in	Elongation percent	Strength lbs/sq in	Elongation percent
84	58700	21.5	50800	2.0				
	44000	20.5	39900	—				
	56700	22.0						
	58000	20.5						
	51410	—						
	49900	—						
	61000	—						
	49400	4.3	54100	2.9	42200	0.4	65700	7.3
81	48400	3.2	53200	—	41300	0.6	61700	8.0
	60200	4.3			45900	0.6	60700	3.5
	55500	—	39400	0.35	24000	—	67600	1.3
	62900	—	49300	—	29400	—	58900	1.2
78	51900	—			21800	—		
	52200	—						
	34000	—	10400	0.0	22300	—		
75	30900	—	16800	—	15500	—		
	10700	—	15200	—	14200	—		
			0	—	0	—		
70			15800	—	3500	—		

The curves for the tensile strengths are plotted in Fig. 4, the abscissas being percentages of copper and the ordinates pounds per square inch. Until we reach 87 percent copper, there is practically no effect due to heat treatment. This was to be expected because the bronzes richer in copper are homogeneous α-crystals and have no inversion-point. The difference between the test-pieces would, therefore, be due primarily to size of crystals and to possible strains. From 87 percent down to 76 percent copper we get marked differences due to heat treatment. The alloys which have been held at 400° (curve D in Fig. 4) are below the inversion temperature and consist of a mixture of α and δ crystals, while the alloys which have been held at 540° or which have been heated to low red (curves B and A in Fig. 4) are above the inversion-point and consist of a mixture of α- and β-crystals. These alloys are much stronger than the preceding set, a breaking strength of 67,000 pounds per square inch having been obtained with a 78 percent bronze consisting of α- and β-crystals, while about 45,000 pounds is the maximum for a bronze consisting of α- and δ-crystals. The 78 percent bronze brings out the effect of heat treatment very markedly, the tensile strength being well over 60,000 pounds for a bronze quenched from above the inversion temperature and only 30,000 pounds for a bronze annealed below this temperature. The differences between the bronzes which have been held fifteen minutes at a low red and those which have been held a week at 540° are undoubtedly due to a coarer crystallization in the latter.

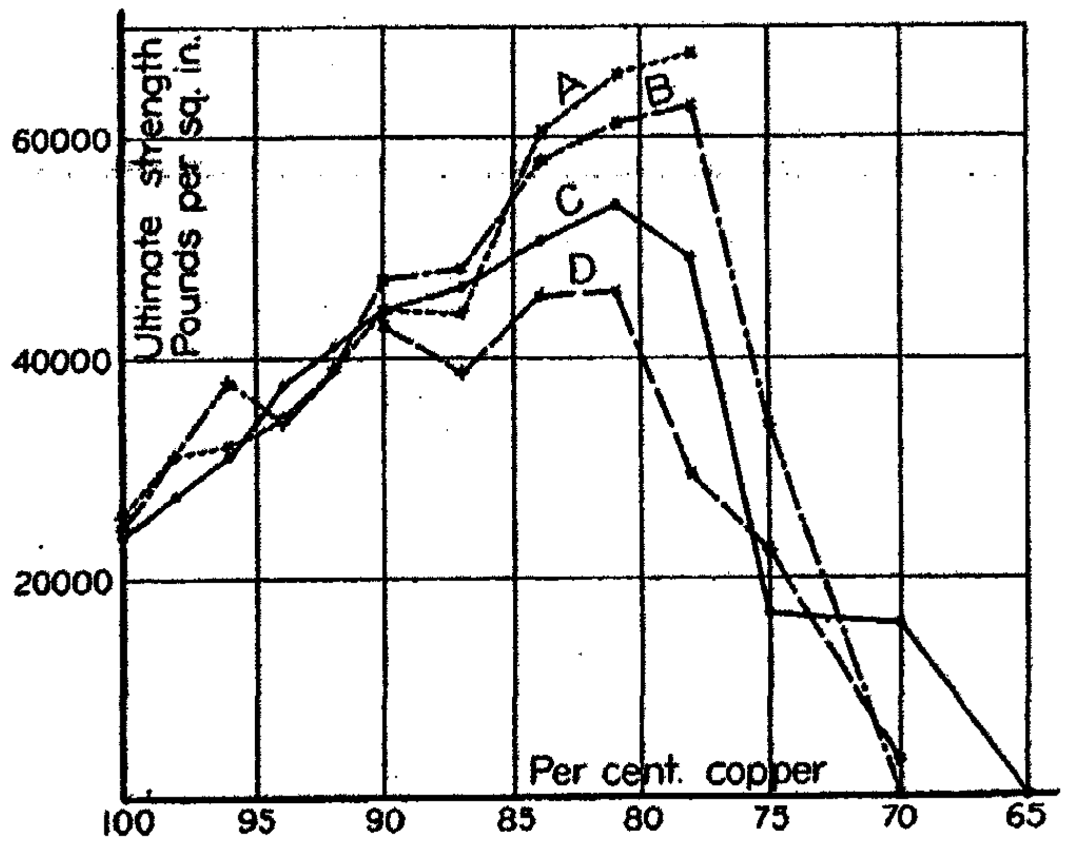

Fig. 4

A. Heated to low red, water-quenched.
B. Held one week at 540°, water-quenched.
C. Tested as cast.
D. Held one week at 400°, furnace-cooled.

Between 86 percent and 76 percent copper, the curve for the bronzes as cast, lies between those for bronzes annealed above and below the inversion temperature. This was to be expected because the cooling was too rapid to permit a complete change into the δ crystals and yet not rapid enough to prevent any change. These bronzes are, therefore, a mixture of α-, β- and δ-crystals.

Since a bronze containing α- and β-crystals is much stronger than one consisting of α-crystals alone, it might reasonably have been expected that pure β would give us the strongest of the copper-tin bronzes. This is not the case experimentally and the maximum strength occurs at 77-78 percent copper[1] which is about the maximum content for pure β at any temperature though well above the maximum content of pure β at the temperatures of the experiments. Why this should be so, cannot be explained until we have more data on other and simpler alloys. As the copper content falls below 77 percent there is a rapid decrease in the strength of the bronzes annealed above the inversion-point. The alloy with 70 percent copper has practically no strength whether annealed above or below 500°. Of two 70 percent bronzes tested as cast, one broke while being placed in the jaws of the testing-machine while the other had a tensile strength of nearly 16,000 pounds per square inch. Such a bronze may contain α, β, γ and δ crystals in varying amounts depending on the rate of cooling. It is, therefore, entirely uncertain what the actual composition or properties of any given casting might be.

In the bronzes annealed at 400° the first admixture seems to have no effect on the strength. As soon as the δ crystals become more than 30 percent of the whole, the strength decreases rapidly.

Some comparisons with the results of previous investigations on the strengths of cast bronzes, unworked, may be made. The only investigations covering the same wide range of compositions are by Mallet[2] and by Thurston[3]. Their results, with those of the present investigation (called Shepherd-Upton on the curve) are given in Fig. 5. Mallet's strength of pure copper

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[1] One 81 percent bronze gave 72,000 pounds when quenched from 620°.

[2] Phil. Mag. 21, 66 (1842.)

[3] Report on the Properties of Copper-Tin Alloys. Washington, 1879.

was undoubtedly taken from a test on a wire and is therefore not comparable. His results for castings agree well with those of Thurston. The Shepherd-Upton curve is curve C from Fig. 4 and represents the results as obtained from pieces as cast without any heat treatment. The differences between the Shepherd-Upton curve and the Thurston curve are very marked for bronzes containing less than 96 percent copper. In fact Thurston's curve lies below that of the authors for bronzes annealed at 400°. The slow cooling in Thurston's castings evidently gave time for a complete change of the β phase into the δ phase. In addition Thurston's castings were by no means sound. Thurston wished to get the commercial strengths and therefore employed a brass founder, who used the current practice of that time in the melting and pouring of the metal. Practice has since changed somewhat for the better. The Shepherd-Upton curve was made with the deliberate idea of finding the maximum value and any commercial practice that interfered with obtaining such a result was either discarded or changed. That does not make the results "laboratory" strengths. The methods and means used can all be applied commercially either directly or in modified form. An instance of this is the centrifugal sprew and air-trap combination.

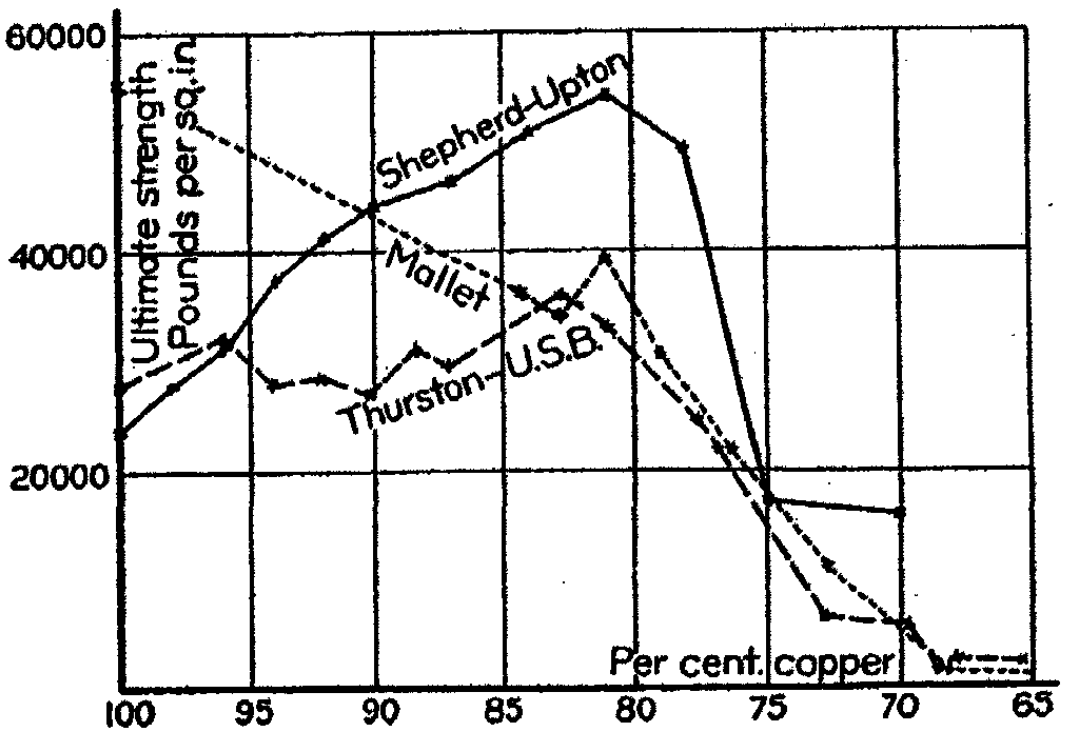

Fig. 5

Another instance is the well-known high strength of phosphor bronze. As usually used, it is doubtful whether any phosphorus is left in the final casting. The part it plays is the prevention of oxidation and of occluded gases. If more than enough phosphorus for this purpose is used, the alloy becomes weaker and so brittle as to be useless.

In Fig. 6 are plotted the tests on ductility, the abscissas being percentage copper and the ordinates percentage elongation. In these results the time factor is a very important one. While increased size of crystal is a disadvantage as far as the strength is considered, it appears to be favorable to ductility, presumably because the crystals slip more readily. In the bronzes as cast there is a slight maximum of ductility at about 97.5 percent copper which probably means nothing. Except for this the ductility decreases with decreasing copper content. The bronzes that have been held fifteen minutes at a dull red and then quenched show a decreasing ductility with decreasing copper content. Down to 80 percent copper the ductility is approximately 5 percent higher than in the cast bronzes. When the bronzes are held for a week at 540° and then quenched we get a most remarkable curve. There is a maximum ductility at about 88-90 percent copper, very close to the limiting maximum concentration of the α-crystals. This maximum ductility repre-

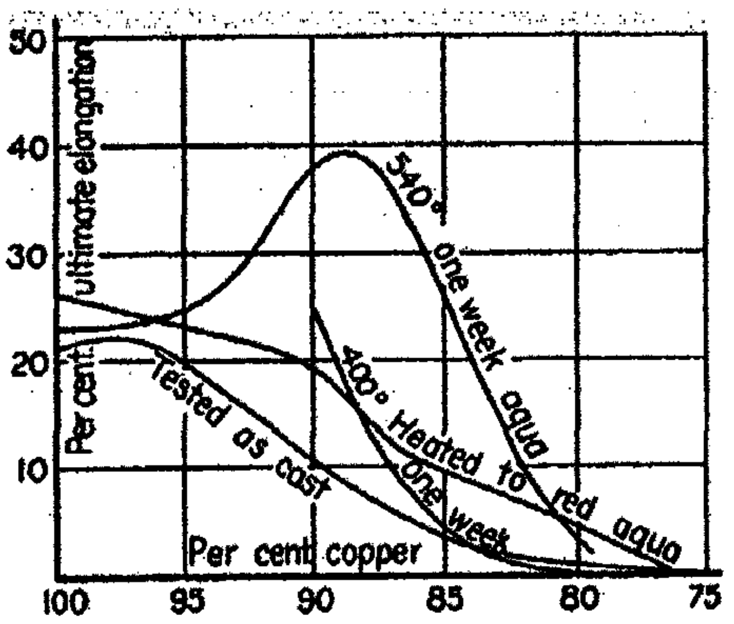

Fig. 6

sents in round numbers a 39 percent elongation.[1] So far as we can see, this can only be due to a change in the size of the crystals, since the tensile strength experiments showed that equilibrium was reached in fifteen minutes at a low red heat, about 650°.

The ductility of the bronzes annealed for one week at 400° does not differ appreciably from that of the cast bronzes so long as we have a mixture of the two crystals, α and δ. As soon as the copper content exceeds 85 percent the ductility of the bronzes annealed at 400° increases very rapidly cutting the curve for the bronzes quenched from a low red at 88 percent copper. The experiments were not carried beyond 90 percent copper because the tensile strength of a bronze containing 90 percent and upward of copper is practically independent of the heat treatment. Since the 88 percent bronze consists of pure α both at 400° and at 540°, the two must have the same ductility, giving the same size of crystals. It seems reasonably certain that the reason for the difference between the two is merely a difference in the rate of growth of the crystals. If the 88 percent bronze had been held two, three, or, if necessary, four weeks at 400°, it would eventually have shown the same ductility as the same bronze held for one week at 540°.

In Fig. 7 are given stress-strain curves for 100 percent copper, for a bronze containing 90 percent copper, for a bronze containing 81 percent copper and two for ordinary wrought iron. The ordinates are percentage elongations with a special zero for each metal. The abscissas are pounds per square inch. The numbers at the ends of the curves give the ultimate percentage elongation. Whatever the composition or heat treatment the copper and the bronze curves do not lose their similarity in shape. They have no elastic line or limit. A yield point might be arbitrarily selected, but its location would depend almost entirely on the horizontal scale to which the curve was drawn. Indeed a yield point is in general hard to place at all. The bronzes have no maximum load in the sense that iron and

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[1] One 90 percent bronze gave 47 percent.

steel do. A bronze runs up to its break without the curve ever turning over.

When considering the shape of the curve it must be kept in mind that these are tests of cast bronzes and that the pieces had never previously been under load or worked in any way. Working the metal would have made it have an elastic line because it would have been strained. With bronzes containing 87 percent to 92 percent copper, it should be possible to get a large increase of strength by cold working. If in testing one of these cast bronzes the load be run up to one-half or two-thirds of the ultimate strength and then removed, a set line is found; only from such lines can the modulus of elasticity be derived. Connected with this is the interesting phenomenon that some of the test-pieces can easily be bent nearly double by hand; but it is quite impossible to bend them back again.

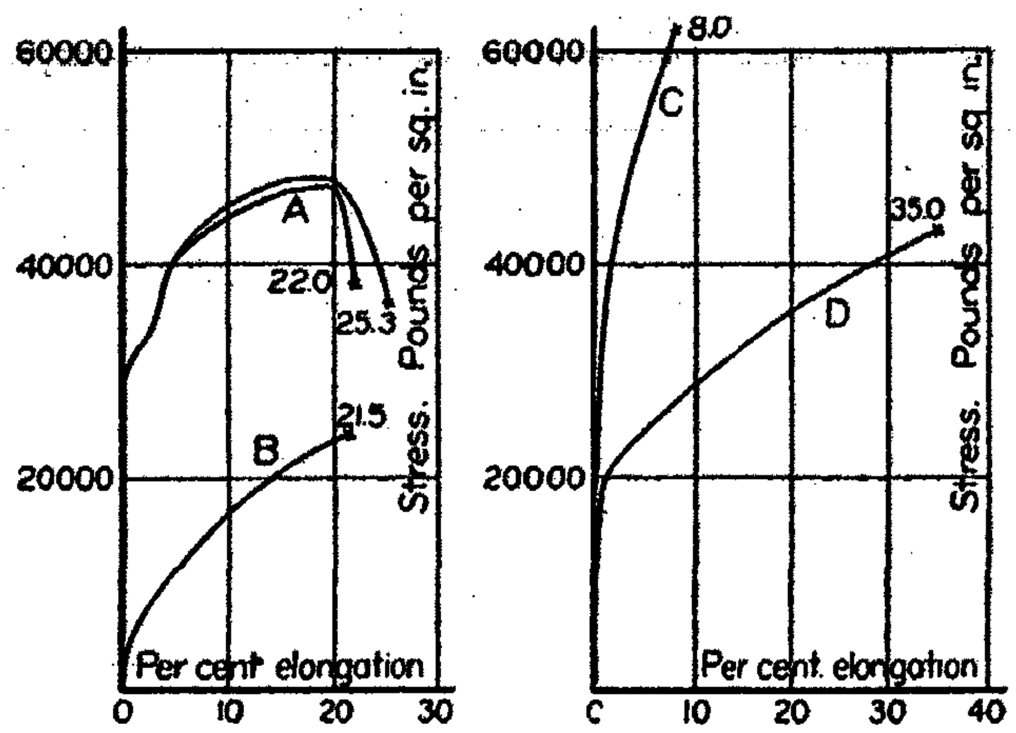

Fig. 7

A. Wrought iron.
B. Copper—100; 540° one week, aqua.
C. Copper—90, tin—10; 540° one week, aqua.
D. Copper—81, tin—19; heated to red, aqua.

The ultimate resilience of bronzes containing more than 95 percent copper is low because the breaking strengths are low. With bronzes containing less than 85 percent copper, the resilience is low because the elongation is small. The maximum resilience occurs between 90 percent and 87 percent copper; it is some 15 percent higher than that of the wrought iron curve.

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

1. A study has been made of the effect of heat treatment on the tensile strength and ductility of cast copper-tin alloys containing more than 70 percent copper.

2. The tensile strength of bronzes consisting of pure α is affected but slightly by heat treatment.

3. Bronzes containing 74-87 percent copper are much stronger if annealed above the inversion temperature (510°) than if annealed below.

4. Prolonged annealing tends to coarsen the crystalline structure, to decrease the tensile strength, and to increase the ductility.

5. The tin-rich α crystals are stronger than those low in tin.

6. The strongest bronzes contain 78-81 percent copper and are mixtures of α and β crystals.

7. The strongest of the bronzes annealed below 510° consist of mixtures of α and δ crystals.

8. Bronzes containing no α crystals have very low tensile strengths.

9. When tested as cast, the ductility of bronzes decreases with decreasing copper content.

10. The ductility of cast bronzes can be increased about 5 percent by bringing to a red heat and then quenching in water. With bronzes containing less than 88 percent copper, this treatment increases the strength markedly.

11. Annealing at 540° for one week causes an enormous increase in the ductility especially of bronzes containing 88-90 per cent copper.

12. Annealing the 85-90 percent Cu bronzes at 400° for one week causes an effect on ductility similar to, but less than that due to annealing for the same time at 540°.

13. It is possible to make a cast bronze with an ultimate tensile strength of over 60,000 pounds per square inch and an ultimate elongation of about 1.5 percent or a bronze with an ultimate tensile strength of 45,000 pounds per square inch and an ultimate elongation of 39 percent.

14. By suitable heat treatment it is possible to vary the ultimate elongation of a bronze containing 90 percent copper from 10 percent to 37 percent without affecting the tensile strength materially.

15. The bronzes have no maximum load in the sense that iron and steel do.

This work was made possible by grants from the Carnegie Institution and has been carried out under the direction of Professor Bancroft.

Cornell University, January, 1905.

CONCENTRATION CELLS IN LIQUID AMMONIA

BY HAMILTON PERKINS CADY

In continuing the investigation of the properties of solutions in liquid ammonia that have been carried on at this University, it seemed desirable to study the electromotive forces of concentration cells with this substance as solvent.

From the striking similarity in the behavior of aqueous and ammonia solutions, so far as investigated, it was expected that the laws that hold in water solutions would also apply here. Of all the formulas that have been proposed for the calculation of the electromotive forces of concentration cells the Helmholtz formula[1] is doubtless the most rigid for the reason that this formula involves no assumptions with regard to the degree of dissociation, etc., but calculates the electromotive force from the vapor pressures of the two differently concentrated solutions. All the other formulas are approximations only, and involve assumptions which are realized only in infinitely dilute solutions where the salts are completely dissociated. For solutions of ordinary concentrations the calculated electromotive force obtained by using the approximate formulas must necessarily be in error, and the more so as the degree of dissociation of the salt decreases.

The degree of dissociation of salts in ammonia solutions is much lower than that of the same salts at similar concentrations in water. Consequently the calculated electromotive forces would deviate more widely from the observed values than if the solvent had been water. It is true that ammonia solutions are better conductors than the corresponding aqueous solutions but this is due to the high ionic velocities and not to the greater degree of dissociation.

The experimental difficulties in the way of the application of the Helmholtz formula are so great that it was thought best not to attempt it at this time. Hence the approximate formulas were chosen for the following work. On account of the small

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[1] Ges. Abh. I, 840 and II, 979.

degree of dissociation of the salts, the calculated values in many cases, do not agree well with the observed, however the agreement is sufficiently good to show clearly that the same laws apply to ammonia solutions as have been found to govern aqueous solutions. With these results the main objects in view in undertaking this investigation have been realized.

The measurements were made at temperatures below —33°C., the boiling-point of liquid ammonia. After considerable preliminary work the form of apparatus shown in Fig. 1 was devised and used for making most of the measurements.

Description of apparatus and method of manipulation

Ammonia is drawn from the cylinder A, which contained the liquefied gas, until the desired amount of liquid is obtained in the reserve tube B, in the bath D′ around D, in that around E and in the bath C′ around the receptacle C. The tube B, and that around D and E, are vacuum jacketed, while that around C is air jacketed. The small cylinder I contained especially purified ammonia standing over calcium oxid to absorb the last traces of water. On opening the valve I′ ammonia gas passes from I into C and is there condensed by ammonia boiling in the bath C′ under lower pressure. From C the liquid is drawn down into D, whence it could be run either to waste or into the measuring cell E through the tube H. When the apparatus is clean and free from moisture as shown by the high resistance of the solvent as measured between the electrodes *d d′* in D, a weighed amount of salt is introduced and the solution made up to the pointer F. Uniformity of concentration is secured by blowing purified air through the solution by means of the tube H H′ which also acts as a delivery tube for the solution. After determining the resistance of the salt solution it is ready to be transferred by means of compressed air introduced through D″ to the outer part of the measuring cell E. Inside of the cell E is a tube J for the dilute solution. Communication between the two solutions is established through a hole in J packed with cotton, as shown at K. When amalgam electrodes are used one is put in the bottom of J and the other is run through L into the horn shaped cup L′ at the bottom of E. Electrical contact with these amalgams is made by platinum wires sealed into glass tubes, Pt and Pt′.

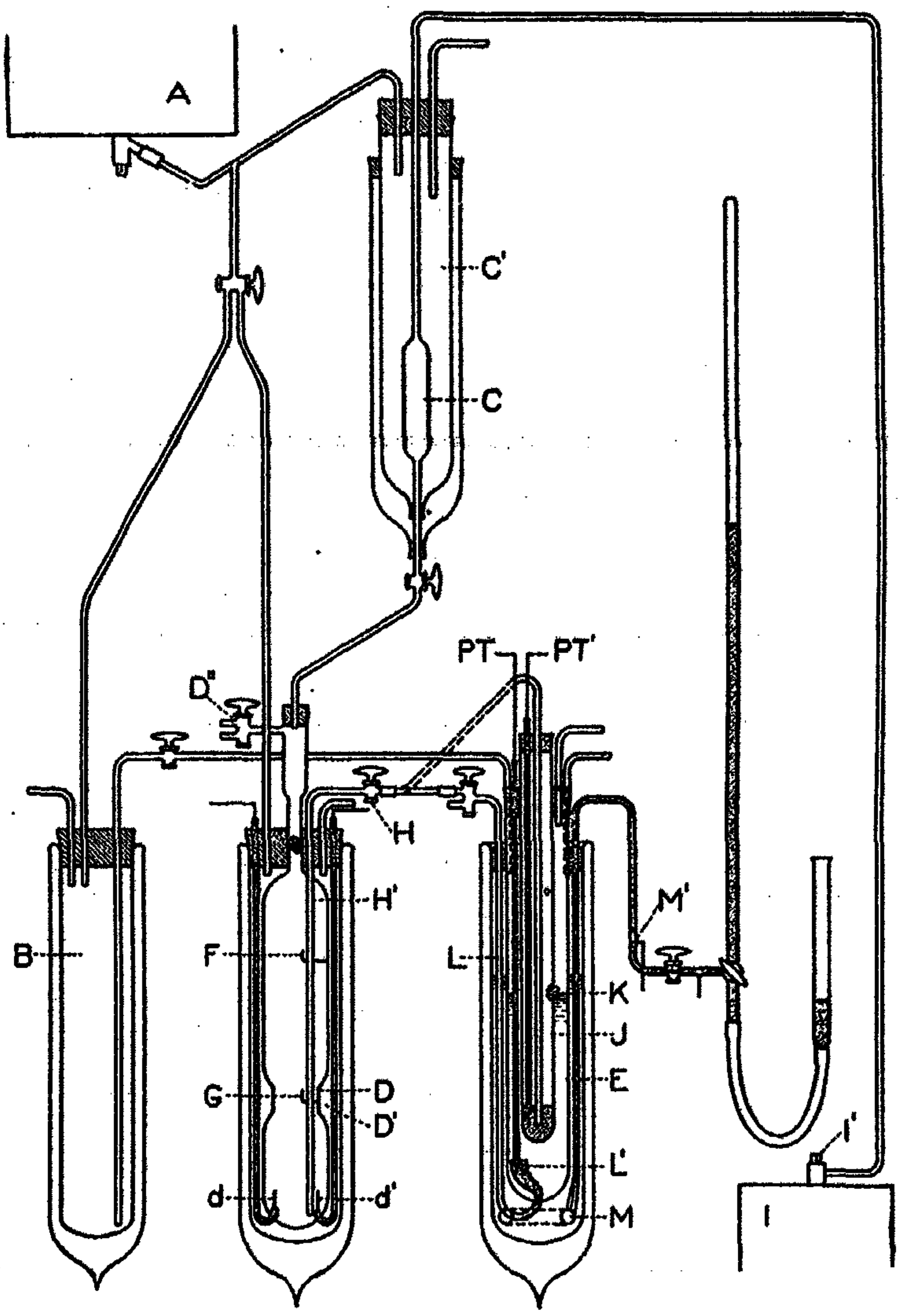

Fig. 1

After the outside compartment E is filled up to the cotton plug with the more concentrated solution made up in D (Fig. 1) the remainder is blown to waste by disconnecting H from L, until the meniscus touches the pointer G. The solution left in the tube is then diluted to the point F. The volume up to the pointer F and that to G being known the concentration of the two solutions may be calculated. After thorough stirring, the resistance of the dilute solution is measured, thus giving the necessary data for the calculation of the electromotive forces from the approximate formulas involving the concentration of the solutions and that of the ions.

The dilute solution is then run over into the tube J and after the insertion of the electrodes the cell is ready for measurement.

In order to hold the cell EJ at some constant temperature below the boiling-point of ammonia, use was made of the temperature regulator used by Franklin and Cady in the measurement of the absolute velocities of ions in ammonia. The cell E J is surrounded by liquid ammonia boiling under diminished pressure produced by a Bunsen pump. In the bath is placed the bulb M of an air thermometer so arranged that when the temperature falls too low the air contracts and brings the confining mercury column into contact with the platinum point M′ thus making circuit through a relay and sounder. The latter is so arranged that it closes down on a rubber tube in the gas exit train, thus shutting off the connection between the pump and the bath until the rising temperature of the latter expands the air in the thermometer bulb and again breaks the circuit through the relay and sounder, thus setting the bath to boiling again. This cycle of operation occurs every few seconds and keeps the bath very nearly at constant temperature.

The space around the cell E J was too small and too much taken up with other things to admit of a thermometer being placed in the bath. This difficulty was overcome by the use of a nickel-iron thermocouple and galvanometer for obtaining the temperature. The second of the two junctions of the couple is kept at 0° by immersion in a bath of melting ice. The thermocouple was calibrated by comparison with a toluene thermometer standardized by the Reichsanstalt, and the constancy of the calibration was controlled by noting from time to time the freezing-point of mercury.

The volume of the tube D up to the pointer F was determined by weighing when empty and when filled with water and found to be 54.76 cc. The volume up to the pointer G, when the delivery tube was filled to the stop-cock, was 8.94 cc. The ratio between these volumes is the ratio between the concentrations of the solutions when made up as described above, viz. 6.124.

Theory

If two solutions so dilute that the gas laws apply to their osmotic pressures are separated by a movable semi-permeable membrane, work may be obtained in the amount indicated by the following equation:

$$A = \int_{v}^{v'} pdv$$

in which A represents the work, v and v' the volumes of the solutions containing one gram molecule of the solute, and p the osmotic pressure of the solution. Since p and v are dependent upon each other as shown by the gas law equation

$$pv = RT$$

or,

$$P = \frac{RT}{v};$$

then by substituting this value of p in the above equation and placing the constants before the integral sign the expression

$$A = RT \int_{v}^{v'} \frac{dv}{v}$$

is obtained; this equation contains one variable and is easily integrated, giving

$$A = RT\, ln \frac{v'}{v}.$$

From Boyle's law $pv = p'v'$

or,

$$\frac{p}{p'} = \frac{v'}{v}$$

therefore

$$A = RT\, ln \frac{p}{p'} = \frac{RT}{0.4343} \log \frac{p}{p'}$$

in which *ln* represents the natural logarithms and log the Briggsian. A is the work done by the passage from the dilute into the concentrated solution of such a quantity of water that in effect one gram molecule of solute has been transferred from the concentrated to the dilute solution. R is the gas constant, T the absolute temperature, p and p' the osmotic pressure of the concentrated and dilute solutions respectively.

If the apparatus be so arranged that the equalization of the concentrations of the two solutions takes place electrically, a condition which is easily realized by placing in each solution an electrode of the same metal as the cation of the salt, bringing the solutions into contact with each other through a porous wall and connecting the electrodes (metallically). The cation will precipitate from the concentrated solution upon the cathode while the anode will simultaneously dissolve in the dilute solution. The anion will go through the porous wall into the dilute solution, while the cation passes into the concentrated, and electricity will flow from one electrode to the other. The work obtained by the passage of one gram molecule of the solute from the concentrated to the dilute solution, must of course be equal to that obtained osmotically as calculated above, *i. e.*

$$\text{Electrical energy} = \frac{RT}{0.4343} \log \frac{p}{p'}.$$

The transfer of one gram molecule of a salt of a monovalent cation is accompanied by the movement of 96,540 coulombs. Hence

$$96540 \times E\ (\text{volts}) = \frac{RT}{0.4343} \log \frac{p}{p'}$$

or

$$E = \frac{RT}{96540 \times 0.4343} \log \frac{p}{p'}.$$

In order to express E in volts R must be given in electrical units. R = 1.98 calories; one calorie = 4.18 Joules, consequently

$$E = \frac{1.98 \times 4.18 \times T}{96540 \times 0.4343} \log \frac{p}{p'}$$

or

$$E = 0.000198T \log \frac{p}{p'}.$$

If the solutions are sufficiently dilute the salts will be completely dissociated and the osmotic pressures will be proportional to the concentrations, then p and p' may be replaced by the known values c_1 and c_2, the concentrations of the two solutions, and

$$E = 0.000198 \text{ T} \log \frac{c_1}{c_2}. \qquad \text{(I)}$$

But even in aqueous solutions this formula does not apply to any but very dilute solutions because in solutions of ordinary concentrations the osmotic pressure is not proportional to the concentration. This is due to incomplete dissociation. Because of the moderate dissociating power of ammonia, the formula is more inaccurate when applied to ammoniacal than to aqueous solutions. That it is not strictly applicable to aqueous solutions is shown by the following example. Nernst[1] measured the electromotive force of the cell: silver, silver nitrate solution (0.1 normal), silver nitrate solution (0.01 normal), silver; and found E = 0.055 volts at 18°. The calculated value of this cell is

$$E = 0.00198 \times 291 \log \frac{10}{1} = 0.058 \text{ volt.}$$

The difference between the calculated and the observed value is about 6 percent, but becomes greater as the solution becomes more concentrated and the osmotic pressure becomes less nearly proportional to the concentration, that is as the degree of dissociation decreases. The 0.1 normal silver nitrate solution of the above cell is about 80 percent dissociated while the degree of dissociation of many of the ammonia solutions used in the measurements given below is less than 40 percent. Hence the electromotive

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[1] Zeit. phys. Chem., 4, 129 (1889).

forces calculated by means of the above formula should be expected to differ considerably from those observed. That this is true is shown by the following table, in which is compared the calculated with the observed electromotive forces for the cells (1) sodium amalgam, sodium nitrate solution (conc. c_1), sodium nitrate solution (conc. c_2); sodium amalgam (2), sodium amalgam, sodium chloride solution (conc. c_1), sodium chlorid solution (conc. c_2), sodium amalgam; (3), silver, silver nitrate solution (conc. c_1), silver nitrate solution (conc. c_2), silver.

In these cells c_1 and c_2 represent the concentrations of the solutions in gram molecules per liter.

TABLE I.—$NaNO_3$ Cells

Abs. temp.	Conc. of solution		$\frac{C_1}{C_2}$	Log $\frac{C_1}{C_2}$	E calc.	E obs.
	C_1	C_2				
234.0	0.0458	0.00748	6.124	0.7870	0.0364	0.0236
234.0	0.0458	0.00122	37.49	1.5740	0.0728	0.0465
234.6	0.0117	0.001910	6.124	0.7870	0.0365	0.0276
234.6	0.0117	0.000312	37.49	1.5740	0.0730	0.0572
236.5	0.002245	0.000367	6.124	0.7870	0.0368	0.0307
236.5	0.002245	0.000060	37.49	1.5740	0.0738	0.0603
NaCl cells						
236.8	0.01093	0.00179	6.124	0.7870	0.0369	0.0276
236.8	0.01093	0.00029	37.49	1.5740	0.0738	0.0562
236.8	0.01093	0.0000475	229.7	2.3611	0.1108	0.0832
235.6	0.003084	0.000503	6.124	0.7870	0.0367	0.0290
235.6	0.003084	0.000082	37.49	1.5740	0.0734	0.0621
233.8	0.00906	0.000039	229.7	2.3611	0.1088	0.0832
234.7	0.0276	0.0000197	1406.4	3.1481	0.1463	0.1150
$AgNO_3$ cells						
235.3	0.00182	0.000298	6.124	0.7870	0.0366	0.0308
235.3	0.00182	0.0000487	37.49	1.5740	0.0732	0.0592
235.3	0.00182	0.0000080	229.7	2.3611	0.1100	0.0845
235.0	0.00454	0.000743	6.124	0.7870	0.0366	0.0341
235.3	—	—	6.124	0.7870	0.0366	0.0341
235.3	—	—	37.49	1.5740	0.0732	0.0664

Inspection of the last two columns of this table shows that the observed values are only 80 to 90 percent of those calculated. Something like this variation was to be expected from what has been said above. The results show very clearly though that the electromotive force is governed by a logarithmic law, because when the ratio of the concentration is squared or cubed the electromotive force is only doubled or trebled.

The electromotive force of a concentration cell may also be calculated by making use of the conception of solution pressure that was introduced by Nernst.[1] Just as every substance has a tendency to give off vapor, which tendency may be measured in terms of the pressure of the vapor when it is just great enough to balance the tendency to evaporate, so every substance has a tendency to dissolve which may be measured in terms of the osmotic pressure necessary to balance it. This is complicated by the fact that when metals dissolve in water they go into solution as positively charged ions. The ions taking on a positive charge leave the metal negatively charged while the solution containing the ions becomes positive. This produces an electrostatic attraction between the metal and its ion which opposes the solution pressure. Therefore the metal ceases to dissolve when the electrostatic attraction between the ions and the electrode plus the osmotic pressure of the ions in solution balances the solution pressure or tension of the metal. Because of this electrostatic attraction there exists a difference of potential between the metal and its solution. This potential difference varies inversely as the osmotic pressure of the cations.

If positive electricity be supplied to the metal it will continue to dissolve, and for a metal that forms a monovalent ion 96,540 coulombs will cause one gram ion to go into solution. The electrical energy involved in this equals the potential difference times 96540.

$$\text{Electrical energy} = E \times 96540.$$

The value of E may be found by equating the electrical energy to the work that can be produced by one gram ion of the metal dissolving at its solution pressure P against the osmotic pressure of its ions p. This for dilute solutions will be the same as the work done by one gram molecule of a gas in passing from the pressure P to the pressure p at constant temperature.

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[1] Zeit. phys. Chem., 4, 129 (1889).

$$\text{Work} = \text{electrical energy} = \text{RT}\, ln\, \frac{\text{P}}{p},$$

$$\text{E} \times 96540 = \text{RT}\, ln\, \frac{\text{P}}{p},$$

$$\text{E} = \frac{\text{RT}}{96540}\, ln\, \frac{\text{P}}{p}.$$

From this it will be seen that E depends upon the osmotic pressure of the cation. The more concentrated the solution the smaller will E become.

If a cell be made up of two electrodes of the same metal dipping each into solutions of different concentrations of a salt of a metal the electromotive force of the cell will be, neglecting the potential difference at the point of contact of the solution, the difference between the potential differences in the concentrated solution and that in the dilute solution. Since the metal is the same, P is the same in each solution. Let p' be the osmotic pressure of the cations in the dilute solutions, and p that of the cations in the concentrated solution, and let E′ be the potential difference for the dilute solution and E″ be that for the concentrated solution.

Then
$$\text{E}' = \frac{\text{RT}}{96540}\, ln\, \frac{\text{P}}{p'},$$

$$\text{E}'' = \frac{\text{RT}}{96540}\, ln\, \frac{\text{P}}{p},$$

For the whole cell

$$\begin{aligned} \text{E} &= \text{E}' - \text{E}'' = \frac{\text{RT}}{96540}\, ln\, \frac{\text{P}}{p'} - \frac{\text{RT}}{96540}\, ln\, \frac{\text{P}}{p}, \\ &= \frac{\text{RT}}{96540}\left(ln\, \frac{\text{P}}{p'} - ln\, \frac{\text{P}}{p}\right), \\ &= \frac{\text{RT}}{96540}\, ln\, \frac{p}{p'}. \end{aligned}$$

But the osmotic pressure of the cations is proportional to their concentrations, hence

$$\text{E} = \frac{\text{RT}}{96540}\, ln\, \frac{c_2}{c_1}.$$

in which $\frac{c_1}{c_2}$ represents the ratio of the concentrations of the cations. The concentrations of the ions is proportional to the conductivity of the solutions, which in turn is inversely proportional to the resistance (R) of the solutions, and

$$E = \frac{RT}{96540}\, ln \frac{x_1}{x_2} = \frac{RT}{96540}\, ln \frac{\frac{1}{R_1}}{\frac{1}{R_2}} = 0.000198\, T \log \frac{R_2}{R_1}. \qquad (II)$$

At infinite dilutions the formula used in the previous calculations (I), agrees with this last one (II) and both agree with the exact Helmholtz formula, excepting that they neglect the potential difference at the contact of the two solutions which usually is small. For solutions of ordinary concentration, however, formulas (I) and (II) do not agree with each other, but of the two, formula (II) might be expected to give calculated values agreeing more nearly with the observed than those calculated with (I). Formula (II) however cannot be exact because it entirely neglects the undissociated part of the salt, although the latter affects the vapor pressure of the solution and consequently the work obtained from the cell.

In order to apply this formula, the resistance of the solutions of different concentrations is determined by measurement between the electrodes *d* and *d'* sealed into the bottom of the tube D (Fig. 1). The results for sodium nitrate, sodium chlorid, and silver nitrate cells are given below in Table II.

It will be seen by comparison of the last two columns in Tables I and II that the electromotive forces as calculated by Formula II agree much better with those observed than do those calculated by Formula I, as was to be expected. Absolute agreement cannot be looked for because Formula II is only an approximation.

From the conceptions upon which this formula is founded the nature of the anion should have no effect upon the electromotive force of the cell. That this is true will be seen by comparing the observed electromotive forces at corresponding concentrations of sodium nitrate and sodium chlorid. See Table III.

TABLE II.—$NaNO_3$ cells.

Abs. temp.	Conc. of solutions		Res. of solutions		$\frac{R_2}{R_1}$	Log $\frac{R_2}{R_1}$	E calc.	E obs.
	c_1	c_2	Conc. R_1	Dil. R_2				
234.0	0.0458	0.00748	14.1	58.5	4.15	0.6180	0.0286	0.0236
234.0	0.0458	0.00122	14.1	227.0	16.10	1.2068	0.0559	0.0465
234.6	0.0117	0.001910	41.0	177.0	4.32	0.6355	0.0295	0.0276
234.6	0.0117	0.000312	41.0	855.0	29.83	1.3187	0.0613	0.0572
236.5	0.002245	0.000367	150.5	705.0	4.68	0.6702	0.0314	0.0307
236.5	0.002245	0.000060	150.5	3855.0	25.60	1.4082	0.0659	0.0603
NaCl cells								
236.8	0.01093	0.00179	48.5	196.0	4.04	0.6064	0.0284	0.0273
236.8	0.01093	0.00029	48.5	870.0	17.95	1.2541	0.0588	0.0562
236.8	0.01093	0.0000475	48.5	4500.0	92.90	1.9680	0.0923	0.0830
235.6	0.003084	0.000503	122.0	535.0	4.38	0.6415	0.0300	0.0290
235.6	0.003084	0.000082	122.0	2810.0	23.05	1.3626	0.0637	0.0621
233.8	0.00906	0.000039	60.5	6067.0	100.3	2.0012	0.0926	0.0832
234.7	0.0276	0.0000197	23.5	8520.0	362.0	2.5587	0.1190	0.1150
$AgNO_3$ cells								
235.3	0.00182	0.000298	170.0	772.0	4.54	0.6571	0.0306	0.0308
235.3	0.00182	0.0000487	170.0	3505.0	20.62	1.3139	0.0612	0.0592
235.3	0.00182	0.0000080	170.0	1150.0	67.7	1.8306	0.0853	0.0845
235.0	0.00454	0.000743	82.5	389.0	4.72	0.6739	0.0314	0.0348
235.3	—	—	100.5	492.0	4.89	0.6893	0.0321	0.0341
235.3	—	—	100.5	2690.0	26.76	1.4275	0.0664	0.0664

TABLE III

Salt	C_1	C_2	E Obs.
$NaNO_3$	0.0117	0.001910	0.0276
	0.0117	0.000312	0.0572
NaCl	0.01093	0.00179	0.0273
	0.01093	0.00029	0.0562

When a concentration cell with diffusion is in operation, the current usually flows from the dilute to the concentrated solution in the cell itself. This passage of electricity must necessarily be accompanied by the movement of the cation in the direction of the current and of the anion against the current. The transfer of the cations from the dilute solution where they have an osmotic pressure of p_1 to the concentrated solution where their pressure is p can only be made through the expenditure of work. The value of this work for one gram ion is

$$A = RT \, ln \frac{p}{p'_1}.$$

At the same time the movement of the anions against the current and hence from the concentrated to the dilute solution will yield work. For one gram ion this work will be the same as for the cation.

$$A = RT \, ln \frac{p}{p'_1}.$$

If in a given time the same number of cations and anions pass from the one solution to the other (that is if their velocities are equal) the work done by the anion just equals that expended upon the cation, and no correction need be added to the electromotive force as calculated above. But if the velocities of the two ions are different a correction must be made. The magnitude of this correction may be readily determined if the relative velocities of the two ions is known. Let u represent the velocity of the cation and v that of the anion. Then $\frac{u}{u + v}$ represents the fraction of the current carried by the cation $\frac{v}{u + v}$ that by the anion.

Now the passage of 96,540 coulombs through the cell is not accompanied by the transfer of one gram cation from the dilute to the concentrated solution, but by the passage of the fraction $\frac{u}{u+v}$ of a gram ion. Hence the work done upon the cation is

$$A = \frac{u}{u+v} RT \, ln \frac{p}{p'},$$

for each 96,540 coulombs. The electrical energy is then

$$E \times 96540 = \frac{u}{u+v} RT \, ln \frac{p}{p'}$$

or

$$E = \frac{u}{u+v} \times R \frac{RT}{96540} ln \frac{p}{p'}.$$

Similarly the work done by the anion during the passage of 96,540 coulombs equals

$$E \times 96540 = \frac{v}{u+v} RT \, ln \frac{p}{p'}$$

$$E = \frac{v}{u+v} \times \frac{RT}{96540} ln \frac{p}{p'}$$

The difference between the work done by the anion and that absorbed by the cation represents the gain in energy at this point during the operation of the cell.

$$A_{an} - A_{cat} = E \times 96540 = \frac{v}{u+v} RT \, ln \frac{p}{p'} - \frac{v}{u+v} RT \, ln \frac{p}{p'}.$$

$$E = \frac{v-u}{u+v} \times \frac{RT}{96540} ln \frac{p}{p'}$$

This is the correction which must be applied in the calculation of the electromotive force of a cell with diffusion. It is the potential difference at the point of contact of the two solutions and becomes zero when $v = u$ as said above. Therefore the electromotive force of such a concentration cell applying this correction should be

$$E = \frac{RT}{96540} ln \frac{p}{p'} + \frac{v-u}{v+u} \times \frac{RT}{96540} ln \frac{p}{p'}$$

$$= \frac{2v}{u+v} \times \frac{RT}{96540} ln \frac{p}{p'} \qquad (111)$$

But $\frac{RT}{96540} ln \frac{p}{p'} = 0.000198 \, T \log \frac{R'}{R}$ See Formula (11)

Whence it follows that the calculated electromotive forces corrected for the potential differences of the two solutions may be obtained for the cells discussed above by multiplying the numbers under the heading ('calculated') in Table (II) by the fraction $\frac{2v}{u + v}$

This fraction may be obtained from the absolute velocities of the ions as determined by Franklin and Cady.[1] These are as follows in centimeters per second: Sodium 0.00130, silver 0.00111, nitrate 0.00175, chlorin 0.00180. The value of the fraction for sodium nitrate then is 1.14, for sodium chlorid 1.156, and for silver nitrate 1.22. These corrected calculated electromotive forces are given in the following table, together with the uncorrected calculated values and those observed. The consecutive order of the data is the same as that in Table II.

TABLE IV.—$NaNO_3$ cells

$\frac{2v}{u + v}$	E Calc. Uncor.	E Obs.	E Calc. Corrected
1.14	0.0286	0.0236	0.0323
	0.0559	0.0465	0.0637
	0.0295	0.0276	0.0346
	0.0613	0.0572	0.0699
	0.0314	0.0307	0.0358
	0.0659	0.0603	0.0750
	NaCl cells.		
1.156	0.0284	0.0273	0.0328
	0.0590	0.0562	0.0683
	0.0923	0.0830	0.1068
	0.0300	0.0290	0.0347
	0.0637	0.0621	0.0737
	0.0926	0.0832	0.1071
	0.1190	0.1150	0.1378
	$AgNO_3$ cells		
1.22	0.0306	0.0308	0.0373
	0.0612	0.0592	0.0746
	0.0853	0.0845	0.1041
	0.0314	0.0348	0.0383
	0.0321	0.0341	0.0392
	0.0664	0.0664	0.0810

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[1] Jour. Am. Chem. Soc., 26, 499 (1904).

The cells so far considered have involved monovalent cations only. If the cell involves a bivalent cation, 2×96540 coulombs will be required for the solution or precipitation of one gram ion. Hence the electrical energy obtained during the transfer of one gram ion from the concentrated to the dilute solution is

$$E \times 2 \times 96540 = RT\, ln \frac{c'}{c''}$$

$$E = \frac{RT}{2 \times 96540}\, ln \frac{c'}{c''}$$

$$E = \frac{RT}{2 \times 96540}\, ln \frac{p}{p'}$$

$$E = \frac{RT}{2 \times 96540 \times 0.4343} \log \frac{R_2}{R_1} \qquad \text{(IIIA)}$$

That is the electromotive force of such a cell will be approximately half that of a cell involving monovalent cations.

Several bivalent metals including copper, mercury, zinc and lead were tried, but only the lead could be used because of the fact that all the mercury salts tried "hydrolyzed" and the potential of the other metals against their salt solutions was too variable. For instance, when several copper electrodes are placed in the same solution of copper nitrate in ammonia, in general no two of them will show the same potential. There is usually a large and rapidly changing difference of potential which in extreme cases amounts to as much as 0.075 volt, and often changed sign several times in half an hour. Zinc showed a similar behavior though not so marked, while lead was fairly regular. The behavior of copper and zinc may be due to the combined action of oxygen and ammonia on the metal. The results for the cell; lead amalgam, lead nitrate solution (conc.), lead nitrate solution (dil.) lead amalgam are given below in Table V.

TABLE V.

Abs. temp.	Concentrations		Resistance		$\frac{c_1}{c_2}$	$\frac{R_2}{R_1}$	E for $\frac{c_1}{c_2}$	E for $\frac{R_2}{R_1}$	E obs.
	c_1	c_2	R_1	R_2					
235.0	0.0129	—	105.0	418.0	—	3.99	—	0.0140	0.0138
238.0	0.0312	—	59.0	217.0	—	3.68	—	0.0133	0.0129
238.0	0.0312	—	59.0	825.0	—	14.00	—	0.0270	0.0227
234.0	0.0430	0.00702	43.2	160.0	6.124	3.72	0.0183	0.0133	0.0138
238.0	0.0538	0.00879	37.6	142.0	6.124	3.76	0.0185	0.0136	0.0106
238.0	0.0538	0.00144	37.6	560.0	37.49	14.80	0.0370	0.0278	0.0273

It will be seen from the table that the values of the electromotive forces calculated from the ratio of the resistances agree very well with the observed, and that the cells show approximately one-half the electromotive force of monovalent cation cells; thus proving that the cells obey the same law as that which governs the behavior of aqueous cells. Since neither the absolute velocity nor the transference number of the lead ion is known, no correction can be applied for the difference of potential at the junctions of the solutions.

Concentration cells without diffusion

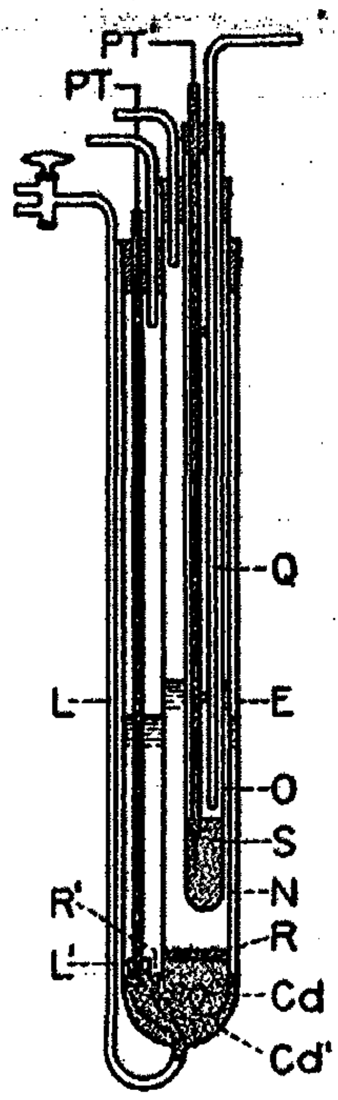

Fig 2

Concentration cells may be so arranged that there will be no diffusion from one solution to the other, by making what is practically two calomel[1] cells. Such a cell was arranged as follows: Sodium amalgam, sodium chlorid solution (conc. c_1), cadmium chlorid, cadmium amalgam; cadmium amalgam, cadmium chlorid, sodium chlorid solution (conc. c_2), sodium amalgam. Mercurous chlorid was not available as a depolarizer because it hydrolyzes in ammonia. Cadmium chlorid is easily obtained anhydrous, and since it is insoluble in ammonia it was chosen as the depolarizer. The arrangement of the essential parts of the apparatus is shown in Fig. 2.

In order to make the measurements, the concentrated solution is placed in the outer part of the cell E, the dilute in the inner tube N. The sodium amalgam electrodes are placed at S and L′ and the cadmium amalgams at Cd and Cd′. The cadmium chlorid is shown at R and R′. Electrical connection between the cadmium amalgams is made by a wire sealed into the bottom of N and with the sodium electrodes by the wires Pt and Pt′ sealed in tubes as shown.

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[1] Zeit. phys. Chem., 13, 577 (1894).

The operation of the cell during electrolysis is as follows: Upon the passage of 96,540 coulombs, one gram equivalent of sodium dissolves and one gram equivalent of cadmium separates in the dilute solution. Since this cadmium comes from the practically insoluble cadmium chlorid it follows that when one gram equivalent of the metal separates one gram equivalent of chlorin as ion passes into solution. At the same time in the concentrated solution this 96,540 coulombs precipitates one gram equivalent of sodium and causes one gram equivalent of cadmium to go into the form of ion and this takes up one gram ion of chlorin to form the insoluble cadmium chlorid. Hence in effect one gram equivalent of sodium and of chlorin have been transferred from the concentrated to the dilute solution. The work which may be obtained from this transfer is for the sodium ion

$$A = RT\, ln \frac{p_{na}}{p'_{na}},$$

in which p and p' are the osmotic pressures of the sodium ions in the concentrated and dilute solutions respectively. For the chlorin ion the work is

$$A' = RT\, ln \frac{p_{cl}}{p'_{cl}}$$

where p and p' are the osmotic pressures of the chlorin ion in the concentrated and in the dilute solutions. The total work will be the sum of these two, or

$$A'' = RT\, ln \frac{p_{na}}{p'_{na}} + RT\, ln \frac{p_{cl}}{p'_{cl}}$$

But the concentration of the sodium ion is the same, as that of the chlorin ion, hence $p_{na} = p_{cl}$ and $p'_{na} = p'_{cl}$, and the total work equals

$$A'' = 2RT\, ln \frac{p}{p'}$$

or

$$E \times 96540 = 2RT\, ln \frac{p}{p'}$$

$$E = \frac{2RT}{96540}\, ln \frac{p}{p'}$$

but $\frac{p}{p'} = \frac{R'}{R}$ in which R′ represents the resistance of the dilute solution and R that of the concentrated solution.

$$\therefore E = \frac{2RT}{96540} \ln \frac{R'}{R} = \frac{2 \times 2 \times 4.18\,T}{96540 \times 0.4343} \log \frac{R'}{R} =$$

$$2 \times 0.000198 \times T \times \log \frac{R'}{R} \qquad \text{(IV)}$$

From this it will be seen that the electromotive force of such a cell is approximately twice that of the same cell when diffusion is possible. The variation from double the value is caused by the difference in the migration velocity of the cation and anion.

In performing the experiments with these cells considerable annoyance was caused by the fact that the electromotive force of the cells falls off as they stand until finally the electromotive force is only from 85–90 percent of that at the beginning. The cause of this behavior is unknown but it may be an exaggerated case of the phenomenon that is generally observed with calomel cells that their electromotive force is higher immediately after being shaken than when they have remained quiet for some time. Neither is it known which value is correct. For the present purpose, however, this makes practically no difference, for either the highest or the lowest figures will give results which show that the electromotive force is about double that of the simpler cell with diffusion. The results given in the following table are the mean of the measurements made during the first half hour after the cell was prepared.

Calculation of transference number

By comparison of Formulas III and IV it will be seen that by determining the electromotive force of a cell with and without diffusion one should be able to calculate the transference number of the anion. Since with diffusion

$$E = \frac{2v}{u + v} \frac{RT}{96540} \ln \frac{p}{p'},$$

TABLE VI.—NaCl CELLS WITHOUT DIFFUSION.

Abs. temp.	Conc. C	Conc. C′	R	R′	$\frac{R'}{R}$	E Calc.	E Obs.	E with diffusion
237.0	—	—	43.5	175.0	4.03	0.0568	0.0548	—
239.8	—	—	65.5	267.0	4.08	0.0579	0.0523	—
234.9	0.1035	0.00169	50.2	206.0	4.10	0.0571	0.0520	—
236.1	0.1092	0.00178	48.3	196.0	4.07	0.0569	0.0527	0.0273

and without diffusion

$$E' = \frac{2RT}{96540}\, ln \frac{p}{p'};$$

$$\frac{E}{E'} = \frac{\frac{2v}{u+v} \times \frac{RT}{96540}\, ln \frac{p}{p'}}{\frac{2RT}{96540}\, ln \frac{p}{p'}} = \frac{v}{u+v}.$$

It is just here that the variability of the cell without diffusion introduces the greatest element of doubt.

The last cell given in the table above is comparable with the first under NaCl in Table II.

$$\frac{E}{E'} = \frac{0.0273}{0.0527} = \frac{v}{u+v} = 0.528$$

Taking the highest value of E' obtained shortly after setting up the cell and the final value and calculating therefrom the transference number of chlorin in sodium chlorid solution the values 0.504 and 0.605 are obtained. That, calculated from the absolute velocities is 0.579. It is fortunate that there are other methods of determining the transference number.

Amalgam cells

The cells so far considered have had to do with the electromotive forces produced by different concentrations of the ions, but cells may be prepared in which different concentrations of the ion-forming material comes into play.[1] For instance two amalgams of different concentrations of the same metal in contact with a solution of a salt of the metal that is dissolved in the mercury show a difference of potential against each other. The numerical value of this difference of potential may be calculated from the work which may be obtained by the osmotic transfer of one gram equivalent of metal from the concentrated to the dilute amalgam, in the same manner as was done above. Then

$$A = RT\, ln \frac{c_1}{c_2},$$

in which c_1 and c_2 represent the concentrations of the concen-

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[1] G. Meyer: Zeit. phys. Chem., 7, 447 (1891).

trated and of the dilute amalgam respectively. When the salt in solution has a monovalent cation then

$$E \times 96540 = RT\, ln \frac{c_1}{c_2},$$

or

$$E = \frac{RT}{96540}\, ln \frac{c_1}{c_2}$$

and for a bivalent cation

$$E = \frac{RT}{2 \times 96540}\, ln \frac{c_1}{c_2}$$

This formula is based upon the assumption that the molecular weight and the atomic weight of the metals are the same when dissolved in mercury; an assumption that is justified by the results for most metals[1]. The formula contains no term for the solvent and the electromotive force is independent of the solvent[2].

The electromotive force between amalgams of the alkaline and alkaline earth metals is far higher than that calculated upon the above assumption. This can only be accounted for either by assuming that the molecule has half the weight of the atom, or that the heat of dilution produces a great effect upon the electromotive force of the cell. That the latter is more probable is shown by the measurements of Cady (*l. c.*) in which it was shown that the heat of dilution would almost account for the difference between the observed and the calculated values for one pair of analyses. From this it follows that the heat of dilution for that pair of amalgams must be independent of the temperature and that the difference between the calculated and the observed electromotive forces must be constant. This latter point was tested over a limited range of temperatures and found to hold. That this can not be the case with all amalgams of sodium is shown by the variation in the value of the difference between the observed and the calculated electromotive forces for

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[1] Zeit. phys. Chem. 7, 447 (1891).

[2] Cady : Jour. Phys. Chem., 2, 551 (1898).

a pair of amalgams having a concentration of 0.346 percent and 0.0346 percent respectively. These amalgams are more dilute than those previously measured. (See Table VII).

In making these measurements the apparatus shown in Fig. 3 was used. The two sodium amalgams of different concentrations and the sodium chlorid solution were sealed up in the glass tube X. The dilute amalgam was placed in a small tube *u* and the concentrated amalgam was put in the bottom of X. Electrical connection was made with these amalgams by means of platinum wires sealed through the glass at *w* and *y*. The wire running down from *w* into the dilute amalgam was sealed into a small glass V-tube to prevent it coming into contact with the sodium chlorid solution. The electromotive force of this cell was determined over a considerable range of temperatures. The results obtained are abnormally high but they are nevertheless in entire accord with what had been previously found with pyridine as solvent[1], as is shown by the following figures.

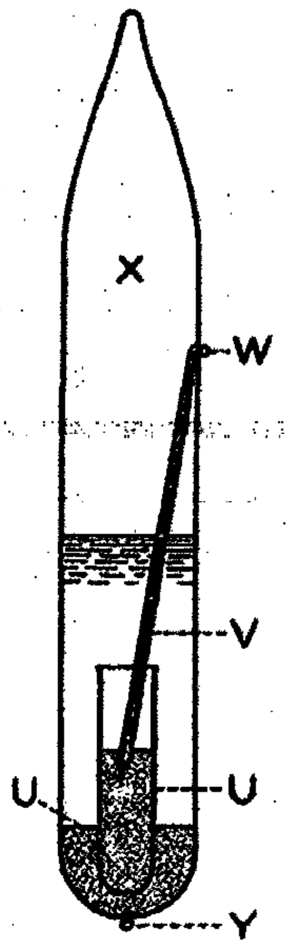

Fig. 3

Solvent	Temp.	Percent conc. of amal. c	c	E obs.	E calc.	$\frac{\text{E obs.}}{\text{E calc.}}$
Ammonia	291.5	0.346	0.0346	0.0817	0.0577	1.42
Pyridine	292.0	0.460	0.0321	0.0950	0.0674	1.41

The agreement between the ratios of the observed and the calculated electromotive forces shows very clearly that the nature of the solvent has nothing to do with the abnormal results. The results of the measurements on this cell at various temperatures are given in Table VII.

That the electromotive force is a function of the absolute concentrations as well as of the ratios of the concentrations of the amalgams is shown by the results recorded in Table VIII.

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[1] Cady: l. c.

TABLE VII.

Abs. temp.	E calc.	E obs.	Difference
291.8	0.0579	0.0817	238
291.5	0.0578	0.0817	239
291.3	0.0577	0.0816	239
286.0	0.0567	0.0805	238
285.5	0.0566	0.0803	237
273.0	0.0542	0.0768	226
239.0	0.0474	0.0682	208
236.5	0.0469	0.0674	205
234.9	0.0466	0.0668	202
233.7	0.0463	0.0659	196
233.7	0.0463	0.0656	193

It will be noticed that the ratio of the observed to the calculated electromotive force decreases as the amalgams become more dilute.

These measurements were made with the apparatus shown in Fig. 1. The most concentrated amalgam was placed in E, a less concentrated one in J and a still more dilute amalgam in a tube that is not shown on the drawings but which was placed inside the tube J. All these parts of the cell were in free communication with each other through openings blown in the sides of the tubes. A sodium chlorid solution was then made up in the tube D and transferred to the cell EJ. The electromotive force was then determined for all possible combinations of these three amalgams which gives three pairs. This gave three determinations in the time that would otherwise have been occupied by one. The results are given in Table VIII.

Oxidation and reduction cells[1]

The electromotive force of three oxidation and reduction cells was determined in very much the usual manner. The oxidizing agent, potassium permanganate, in solution was made up in the tube D (Fig. 1) and run over in the outer part of E. The reducing agent was then dissolved in D and run into J, communication between the two solutions being established

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[1] Bancroft: Zeit. phys. Chem., 14, 193 (1894).

TABLE VIII.—SODIUM AMALGAM CELLS

Abs. temp.	Percent of conc. amal.	Percent of dil. amal.	E calc.	E obs.	$\frac{\text{E obs.}}{\text{E calc.}}$
236.0	0.3460	0.03140	0.0487	0.0697	1.43
236.0	0.0314	0.00461	0.0388	0.0430	1.11
236.0	0.3460	0.00461	0.0875	0.1105	1.26
236.3	0.3460	0.03140	0.0488	0.0682	1.40
235.8	0.3460	0.03460	0.0465	0.0575	1.24
235.8	0.0346	0.00346	0.0465	0.0593	1.27
235.8	0.3460	0.00346	0.0930	0.1163	1.25
236.5	0.3460	0.03460	0.0466	0.0667	1.43
236.5	0.0346	0.00347	0.0466	0.0493	1.05
236.5	0.3460	0.00346	0.0932	0.1167	1.25
238.0	0.4960	0.19600	0.0188	0.0299	1.58

through the cotton plug K (Fig. 1) as in the cells with diffusion. Platinized electrodes were used. The results are given below.

Oxidizing agent	Reducing agent	E obs.
$\frac{M}{50}$ $KMnO_4$	$\frac{M}{10}$ $HCOONH_4$	0.35
$\frac{M}{50}$ $KMnO_4$	$\frac{M}{10}$ KI	0.24
$\frac{M}{50}$ $KMnO_4$	$\frac{M}{x}$ $Na_2S_2O_8$	0.31

SUMMARY

The electromotive forces of concentration cells, with diffusion, involving the monovalent metals, sodium and silver, and the bivalent metal lead, were determined and compared with the calculated values obtained by the approximate formulas.

$$E = \frac{RT}{n \times 96540} \ln \frac{c_1}{c_2}$$

$$E = \frac{RT}{n \times 96540} \ln \frac{p}{p'}$$

$$E = \frac{2v}{u + v} \frac{RT}{96540} \ln \frac{p}{p'}$$

The calculated electromotive force agrees well enough with the observed to show that the laws which have been shown to apply to aqueous solutions also apply to ammonia solutions.

The electromotive force of concentration cells without diffusion was determined for sodium chlorid cells. The observed values agree fairly well with those calculated from the formula

$$E = \frac{2RT}{96540} \ln \frac{p}{p'}$$

The transference number of chlorin in the sodium chlorid solution was calculated from the ratio of the electromotive force with diffusion to that without for a sodium chlorid cell.

The electromotive force between two differently concentrated sodium amalgams was determined and found to agree with that previously obtained with pyridine as solvent, showing again that the electromotive force of an amalgam cell is independent of the nature of the solvent. It was shown too that the electromotive force of an amalgan cell is a function of the absolute concentration of the amalgams as well as of the ratio of their concentrations.

The electromotive forces of three oxidation and reduction cells were determined.

This work was done under the direction of Prof. E. C. Franklin and I am glad of this opportunity to express my appreciation of his kindness.

Lawrence, Kansas, May 1903.

ALUMINUM-ZINC ALLOYS

BY E. S. SHEPHERD

Certain of the alloys of the aluminum-zinc series have found a more or less extensive use as light alloys for certain kinds of foundry work. Under the name of Alzine, and Sibley Casting Metal, they have been suggested for making castings, for which pure aluminum is unsuited. They are said to expand on freezing, and to thereby yield sharper castings. While no exact determination of the question of whether or not the alloys expand on freezing has been made, it seems probable that the greater fluidity, and lesser surface tension are the real explanation of their superior casting properties. An examination of the shape assumed by drops of the alloys shows that with increasing amount of zinc there is a marked flattening of the shape of the drops. Thus pure aluminum, when cast in an ingot mould, gives a surface which is dome-shaped rather than flat, while, with more than twenty percent of zinc, the upper surface becomes concave, and the edges quite sharp. The alloy with twenty-five percent of zinc evidently adapts itself more readily to the effect of gravity and gives fairly sharp edges, while those of the pure metal are very much rounded. It does not seem necessary, therefore, to adopt any hypothesis as to expansion on freezing, to account for the sharper castings given by the alloy.

It is also stated that these alloys are much more stable than most of the aluminum alloys, a fact which finds its explanation in the fact that the two metals are quite near each other in the voltaic series, and that therefore there is less difference of potential and consequently less tendency to corrosion by galvanic action.

There has been but little work done on the constitution of this series of alloys. Gautier[1] made an approximate determination of the freezing-point curve. Heycock and Neville[2] determined the curve accurately, using the resistance pyrometer, and taking the necessary precautions as to supercooling, etc. Their data are given in Table I.

TABLE I

Percent Al	F. P.	Percent Al	F. P.
	418.6°	43.6	542.2°
2.0	401.0°	46.3	548.5°
3.2	392.0°	50.9	560.2°
5.4	(380.6°)	55.8	571.1°
7.6	(380.9°)	61.6	584.5°
7.6	404.9°	68.9	598.7°
9.7	418.4°	74.8	613.0°
14.5	447.3°	81.8	623.2°
18.8	466.1°	88.1	634.4°
25.0	492.6°	91.3	639.5°
30.3	508.4°	94.2	644.9°
36.2	525.4°	100.0	654.0°

Louguinine and Schukareff[3] attempted to get at the constitution by a study of the heat of formation of the various alloys. Unless the alloys examined had reached equilibrium at the temperature at which their determinations were made, it is obviously impossible to deduce any exact conclusions from the data obtained. Since we know that they took no precautions to enable the alloys studied to reach equilibrium, it necessarily follows that their results can have only a qualitative significance, although they made the determinations with the greatest care.

Recently H. Pecheux[4] has stated that he obtained the following definite alloys of aluminum and zinc. Zn_3Al, Zn_2Al, ZnAl, $ZnAl_2$, $ZnAl_3$, $ZnAl_4$, $ZnAl_6$, $ZnAl_{10}$, and $ZnAl_{11}$. It is difficult to determine, from what the author says, just what he means by a definite alloy. Certain of his statements would indicate that he regarded the above symbols as expressing a definite combination between the aluminum and zinc in the above proportions. This is so obviously in error, that one is inclined to assume that he means that the two metals can be melted together in the above proportions. If the latter supposition is correct, then an apt comment would be, that the publication of the freezing-point curve, as far back as 1897, had demonstrated that point perfectly.

Both Louguinine and Schukareff, and Pecheux have used fire-clay crucibles in which to melt the alloys but it has been shown many times that molten aluminum attacks all kinds of clay, absorbing silicon and thus rendering the material too impure for experimental work.

We may accept Heycock and Neville's freezing-point determinations as sufficiently exact, and from it we see that there are only two possible solid phases. Whether these be pure zinc, and pure aluminum can only be determined by other methods, but the existence of compounds is positively excluded. The present investigation began with the determination of the density curve for this series of alloys.

The metals were melted up in crucibles made of artificial graphite. The temperature was watched so that it never rose above 700°. At this temperature graphite is but very slightly, if at all, absorbed by aluminum, and as the graphite was free from silicon this enabled us to obtain a very pure alloy. An atmosphere of coal gas was maintained, thereby avoiding oxidation.

The densities of the ingots were determined by weighing the ingots in benzene and subsequently recalculating the values to the basis of water at 20° = 1. Since it was possible to weigh accurately to within two-tenths of a milligram, and the samples weighed twenty-five grams, the determinations of density were considered to be sufficiently accurate. They were,

TABLE II

Percent Al	No.	Density	Sp. vol.	Percent Al	No.	Density	Sp. vol.
90	1	2.865	0.3490	30	1	4.670	0.2140
	2	2.847	0.3512		2	4.687	0.2133
80	1	3.031	0.3299	20	1	5.228	0.1912
	2	3.025	0.3305		2	5.280	0.1894
70	1	3.249	0.3077	10	1	6.078	0.1645
	2	3.230	0.3096		2	6.087	0.1643
60	1	3.498	0.2858	100	1	2.687	0.3721
	2	3.487	0.2867		2	2.693	0.3713
50	1	3.752	0.2665	0	1	7.136	0.1401 Mean of 5
	2	3.785	0.2641				
40	1	4.160	0.2404				
	2	4.168	0.2398				

in fact, more accurate than the variations in the ingots would require. The results obtained are given in Table II, and the results plotted in Fig. 1. It appears that while the observed (solid curve) and calculated (dotted curve) values for the density do not agree, there is no marked variation, and we are therefore led to the plotting of the results in terms of specific volumes. This is also shown in Fig. 1, and, as is seen, the specific volume curve consists of two branches which meet at about the composition fifty percent aluminum. Since the specific volume curve must consist of straight lines joining the volumes of the phases which make up the alloy, these results would indicate that the composition of the phases present were approximately pure zinc, and a solid solution of zinc in aluminum with a limiting concentration of about fifty percent. Precisely the same shaped curves would result if there were present three phases, as, for example, a compound of zinc and aluminum, which contained fifty percent of each, and which did not form solid solutions with either. But the freezing-point curve has shown that no compounds exist, consequently the explanation that there is a solid solution whose limiting concentration is

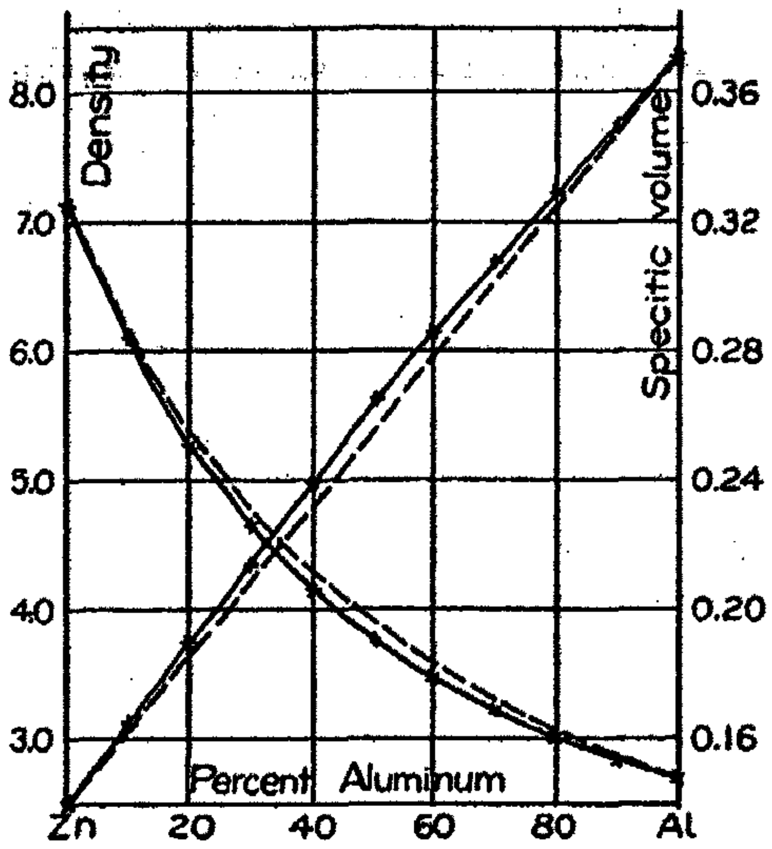


Fig. 1

fifty percent, is probably the correct one. Necessarily, we must make certain that the densities in question are obtained on ingots in which equilibrium has been reached, and this was done. To bring about equilibrium the alloys were annealed for a week by boiling in naphthalene. After this annealing it would be expected that the ingots would have reached equilibrium, or if not, that they would show some change indicating that they were approaching it. As a result of such an annealing, it was found that there was too little change in density to affect the results above given, and we are therefore justified in assuming the above determinations to be sufficiently correct to warrant the deductions which we have based upon them.

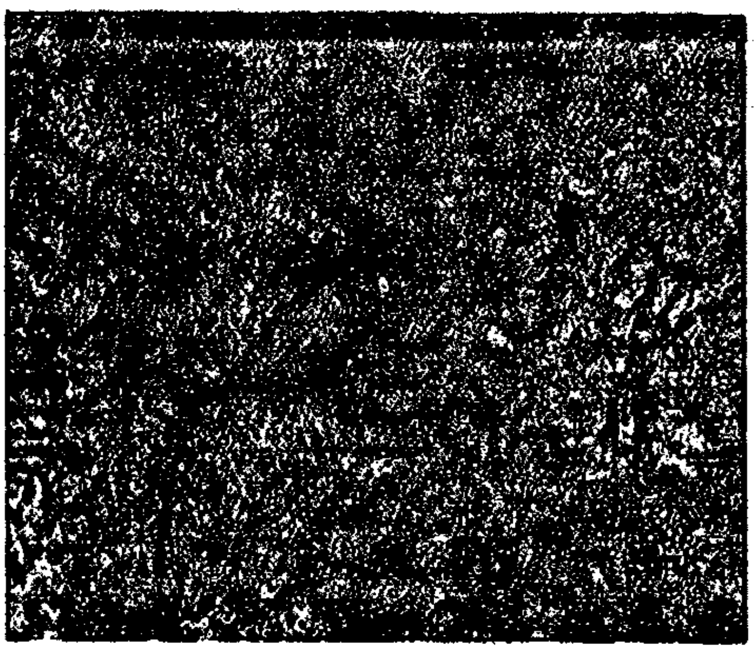
Since Heycock and Neville did not examine the alloys for other than the freezing-point evolutions of heat, it was desirable to establish the presence or absence of such secondary changes. It was also necessary to ascertain whether the existence of the solid solution was indicated by the absence of the eutectic temperature in the cooling of alloys containing more than fifty percent of aluminum. Alloys containing sixty and fifty percent of aluminum were examined by means of the recording pyrometer. The freezing-point was marked but there was no evolution of heat at 381°, as would be the case if the limiting concentration of the solid solution were more than sixty percent aluminum, or if a compound with a composition of fifty percent were present. On the other hand, the alloy containing forty percent of aluminum did show the evolution of heat at the eutectic temperature. Thus it is shown, that the hypothesis of a solid solution containing fifty percent aluminum, as suggested by the specific volume curve, is borne out by the pyrometric evidence.

There remain two other methods of attacking this problem, the analytical method suggested by Bancroft and the microscopic. The analytical method is barred out because of the volatility of the zinc, and by the difficulty of keeping the aluminum melted for any length of time without it becoming contaminated with impurities.

Microscopically, all alloys with more than sixty percent of aluminum are homogeneous whether chill-cast or annealed. At

I. 60 Percent Al

II. 40 Percent Al



III. 30 Percent Al

IV. 1 Percent Al cast

V. 4 Percent Al cast

sixty percent the cast alloy shows a trace of intercrystalline material. This intercrystalline material is ill-defined, as is shown by photograph 1. It amounts to a difference in composition of the large crystals rather than to a definitely crystallized mass. In this respect it resembles the chill-cast bronzes of more than ninety-two percent copper. When this alloy is annealed, this inhomogeneity disappears entirely, leaving the homogeneous solid solution.

The alloy containing forty percent aluminum is not homogeneous either cast or annealed, photograph 2. Here the presence of a true eutectic is easily seen, though the softness of the metals does not allow the granular nature of the eutectic to be well shown in the photograph. Since the composition of the eutectic is at five percent aluminum, it is seen that on any other assumption than that there is present a solid solution of about fifty percent aluminum, we would be unable to account for the small amount of eutectic in alloys of only forty percent aluminum. At thirty percent of aluminum, the fern-like crystals of the solid solution appear surrounded by eutectic, photograph 3.

Photograph 4 shows the alloy containing one percent of aluminum as cast. The structure is quite unlike that of zinc, showing that a certain amount of intercrystalline material was present. This eutectic, however, disappears on annealing, leaving a homogeneous ingot. Similarly, the four percent alloy cast (photograph 5) is nearly homogeneous after annealing. The extreme softness of these alloys renders polishing difficult, but after repeated trials, we were able to show that the four percent alloy is nearly homogeneous.

From the microscopic examination in conjunction with the other data, we are enabled to draw the equilibrium diagram for the series. The pyrometric evidence shows that the solidus for the aluminum-rich crystals crosses the eutectic isotherm at a little over fifty percent of aluminum. The microscopic examination shows that at the annealing temperature, isotherm 217°, the solidus approaches forty-five percent.

At the zinc end of the series the solidus crosses the 381° isotherm at about two percent aluminum, and at the 217°

isotherm at nearly four percent. The equilibrium diagram is shown in Fig. 2.

The solidus is drawn as a dotted line between the melting-point of pure aluminum and forty-five percent aluminum. At present we have no method of determining with any accuracy what course it may take. The usually adopted method of considering the temperature at which the freezing of the alloy ceases to effect the cooling curve markedly is very faulty and leads to erroneous conclusions. So greatly is the determination of this so-called point influenced by the rate of cooling and the personal judgment of the observer as to which temperature to select, that one finds in the literature flat contradictions due solely to this method of determining the solidus. Heycock and Neville have tried, with little success, to determine by mechanical tests the temperature at which liquid first appeared in the alloy. Roberts-Austen has tried the method of squeezing out the mother-liquor, but his results could have been predicted from the work of Joule,[5] where it is found that pressures as high as one hundred thousand pounds to the square inch, continued for relatively long periods of time, would not remove the excess of mother-liquor. It is true that Joule did not draw this conclusion from his results, but a comparison of his data with the recent determinations of the constitution of the alloys with

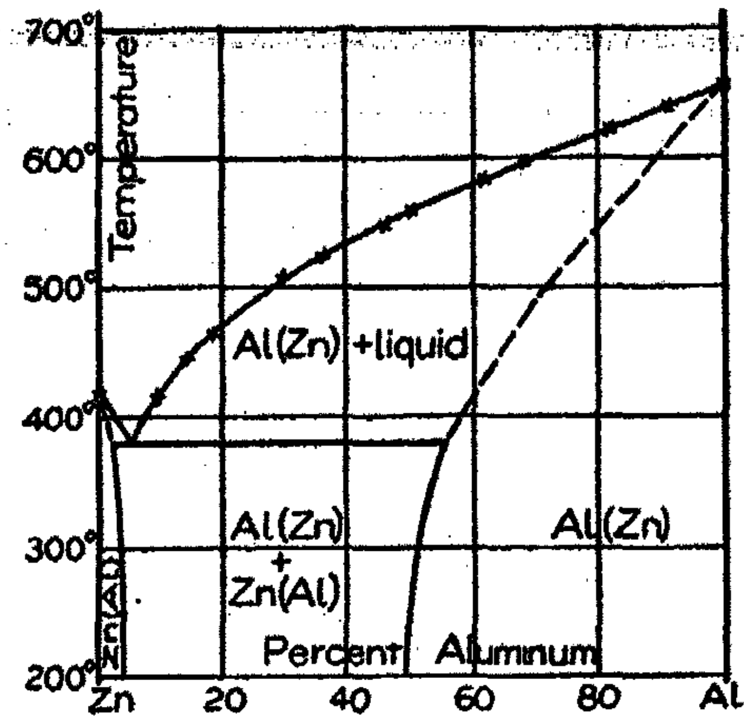


Fig. 2

which he experimented shows how futile are the efforts to solve the problem in this way. Since it is impossible to locate the solidus accurately by means of the pyrometric and mechanical methods (analytical), it would seem rather bold to attempt to draw in this line. In the solid alloy, quenching allows us to follow the course of the solubility curve with comparative ease. The same method has been applied to the location of the curve for solid-liquid, and with fair success, but for soft alloys like the present series, the method does not allow of any great precision.

In conclusion, it may be said that the pyrometric and microscopic data are in perfect agreement with the deductions based on the specific volume relations. We are led to conclude that this series of alloys presents no so-called definite compounds. There are two series of solid solutions, that of zinc in aluminum having a limiting concentration of about fifty percent zinc, and that of aluminum in zinc of about four percent aluminum, at the temperature of 217°. Below this temperature the reaction proceeds too slowly to permit of accurate determination, and it follows that the above concentrations are those which are present in the alloys as met in practice.

Theoretically, the specific volume curve should consist of three parts: the first, between pure zinc and four percent aluminum; the second, a straight line from four percent aluminum to about fifty percent aluminum; and the third from fifty percent to pure aluminum. Owing to the very slight expansion of the alloys between zero and four percent aluminum, it is not possible to determine this branch of the curve. The variation is within the limits of experimental error.

This investigation was intended as a preliminary to a study of the mechanical properties, and was finished in the spring of 1904. A change of circumstances has made it advisable to publish this portion separately. In so far as we may predict them, the mechanical properties will not show any great difference between the cast and annealed alloys. This is due to the fact that the alloys apparently reach equilibrium readily, and any but very rapid chilling will allow the metal to come to equilibrium. Annealing increases the size of the crystals very greatly indeed, and renders them more brittle. It is a fact well known to technical men, that these alloys become crystalline under repeated shock, and break. It is for this reason that they have been largely displaced by the Al-Sn alloys, and are now used chiefly for ornamental castings, and for meter cases.

The aluminum used was an especially pure one, for which we are indebted to Mr. Wm. Hoopes, of the Pittsburgh Reduction Company, to whom we wish to express our appreciation. The writer wishes also to express his gratitude to Prof. Bancroft, who kindly supervised the work, and to the Carnegie Institution of Washington, which furnished the funds necessary for the research.

Cornell University.

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NEW BOOKS

Marceli Nencki Opera Omnia. *Gesammelte Arbeiten von M. Nencki. Erster Band, 1869-1885, pp. xlii + 840; Zweiter Band, 1886-1901, pp. xiv + 894. 17 × 25 cm.; Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, 45 marks.*—These two magnificent volumes, most carefully edited by Professors Sieber and Zaleski, of St. Petersburg, contain all of the published researches of the late Professor Nencki and of work carried on under his direction. To workers in the field of physiological chemistry this collection of Nencki's publications, mainly in the German language, will prove of inestimable value since now for the first time all of his work is made readily accessible. Through a very active life Professor Nencki had published widely, but in the German, French, Russian and Polish languages, and frequently in journals and in monographs not easily accessible except in large libraries.

The range of subjects—directly and indirectly connected with physiological chemistry—represented in these volumes is very great and the collection as a whole constitutes a most striking testimonial of the untiring activity and brilliant achievement of a man who contributed largely to the development of modern physiological chemistry.

It is an interesting fact that the first paper published by Nencki, in 1869, dealt with the antecedents of urea in the organism, for in the last years of his life some of the most important work that came from Nencki's laboratory was concerned with questions in metabolism in which the *modus operandi* of urea formation and the locality of its production in the animal body were successfully solved. This is not the place, however, to enter into any detailed description of the work embodied in these two volumes. It will suffice to say that every one interested in the subject of physiological chemistry will find this complete record of the achievements of a master mind indispensable for a comprehensive knowledge of the development of this department of chemistry.

Russell H. Chittenden

Hypochlorite und elektrische Bleiche. *By Emil Abel. Theoretischer Teil: Theorie der elektrochemischen Darstellung von Bleichlauge. (Monographien über angewandte Elektrochemie. XVII. Band). 16 × 24 cm; pp. 110. Halle: Wilhelm Knapp, 1905. Price: paper, 4.50 marks.*—This book is intended to give the theory of the formation of hypochlorites and the author discusses in detail the properties of hydrogen, hydroxyl, oxygen, chlorine, hypochlorite and chlorate as ions. The literature references are complete and the book is valuable on this account. The presentation of the subject is not very satisfactory. From the first chapters one gets the impression that hypochlorite is formed by direct oxidation of sodium chloride. This is abandoned later; but the unfortunate reader has a hard time trying to learn just what the author's view is as to the formation of hypochlorite. It would have been much better if the author had given a brief statement of the theory and had then cited the data for and against that view.

So far as we know hypochlorite is formed electrolytically only by the action of chlorine on water or alkali. We can have direct decomposition of hypochlorite into chlorate or into chloride and oxygen. When hypochlorite as ion is discharged at the anode we get chlorate and oxygen. In strongly alkaline solutions, chlorate may perhaps be formed without hypochlorite being an intermediate stage. Such a statement as this sums up our knowledge in a clear and condensed form. The author, however, looks upon the discharge of hypochlorite ions as hypothetical, though no other satisfactory explanation has ever been offered for the oxygen evolution when the concentration of hypochlorite becomes high.

The literary quality of the book may be judged from the following sentence:

"Indessen giebt die auch dem ClO'-Ion selbstverständlich notwendig zukommende Entladungsfähigkeit dem von Foerster und Müller in seine Einzelvorgänge zerlegten Chlorat-Mechanismus etwas derart Bestechendes, dass auch wir, schon der Einfachheit des Ausdruckes halber und aus Anschaulichkeitsgründen, uns die Chloratbildung nach 5 mit der Entladung der ClO'-Ionen in Zusammenhang denken wollen—unbeschadet der vorstehenden Bemerkungen, die nur die Schwierigkeit aufdecken sollen, welcher mit dieser Annahme verknüpft ist, und den Zweck haben, den Anschluss der Foersterschen Gleichung an eine Reihe anderer denkbarer, unten kurz erwähnter Chlorat-Mechanismen zu ermöglichen, bei denen von einer tatsächlichen Entladung der Hypochloritionen schon deshalb keine Rede sein könnte, weil hier die Anzahl der reagierenden ClO'-Ionen von der (+) verschieden ist, die aber—in ihrer Form allerdings vorerst willkürlich—mit Schema 5 zumindest bezüglich ihrer unmittelbaren experimentallen Grundlage gleichwertig wären; diese beruht vorzugsweise darauf, dass in der betreffenden Chloratformel qualitativ und quantitativ der Mechanismus der Sauerstoffentwicklung zum Ausdruck gelangt." *Wilder D. Bancroft*

Practical Methods of Electro-Chemistry. *By F. Mollwo Perkin. 14 × 22 cm; pp. x + 322. New York: Longmans, Green and Co., 1905. Price: $1.60.*—The book consists of three sections: an introductory part; a section on electrochemical analysis; and one on electrolytic preparation. "The book has been some years in preparation, owing to the fact that I did not wish to include any experimental work which had not been personally tested or supervised." While this spirit is commendable, the result has been a bit unfortunate because the analytical methods are largely obsolete. The use of the rotating electrode has revolutionized electrochemical analysis but this is not recognized as it should be. It is hardly conceivable that anyone would now use the flag electrode for instance in the determination of copper.

The section on electrolytic preparations is very satisfactory; the directions are clear and complete. It may be questioned whether the actual preparation of substances is as important as the study of conditions but it must be admitted that the student enjoys it more.

A few slips in the text should be corrected in the next edition. On p. 10, the student should be warned that a nickel anode does not dissolve well in a sulphate solution and that he will not get a quantitative deposition of nickel for any length of time. On p. 24, if the resistance of the main circuit be one ohm and of the shunt circuit ten ohms, 1/11 of the current will flow through the shunt and not 1/10. On p. 37, massive nickel will not replace copper to any appreciable extent in a solution acidified with sulphuric acid. On p. 40 the chemical energy of the Clark cell is not represented by the equation $Zn + Hg_2SO_4 \rightleftarrows ZnSO_4 + 2Hg$. On p. 41 the concentration of the amalgam in the Weston cell should be given. On p. 57 the word "resistance" is used in an unusual and rather slipshod way. "By connecting the cells up in parallel, the internal resistance of the system is lowered, being very little more than that of only one cell." On p. 73 it may be all right to calculate the resistance of a solution of sodium sulphate between lead electrodes, but the result would be very inaccurate if platinum electrodes were used. In the preparation of chlorates, p. 211, satisfactory results are obtained when calcium salts alone are used; but the addition of a calcium salt to a solution of a potassium salt does not work well. Under white lead, p. 217, it might have been well to make reference to the unsatisfactory physical properties of electrolytic white lead.

Wilder D. Bancroft

Kristallinische Flüssigkeiten und flüssige Kristalle. *By Rudolf Schenck. 15 × 23 cm.; pp. viii + 156. Leipzig: Wilhelm Engelmann. 1905. Price: paper, 3.60 marks.*—This book gives a general outline of what is known in regard to liquid crystals, special stress being laid on the physical-chemical side. As a great deal of this work has been carried out in the author's laboratory, we get a clear and readable account. The general point of view is that of Lehmann. When a general crystalline form can still be seen, the author speaks of crystalline liquids; and he calls an anisotropic drop a liquid crystal. As a matter of fact he is not very consistent in his nomenclature. The subject is treated under the following heads: experimental material; properties of the triple points; comparative measurements on crystalline and isotropic liquids; microscopic investigations of O. Lehmann.

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

A revision of the atomic weights of sodium and chlorine. *T. W. Richards and R. C. Wells. Jour. Am. Chem. Soc.*, 27, *459* (*1905*).—Taking silver as 107.92, sodium becomes 23.006 and chlorine 35.470. With silver as 107.93 the values are 23.008 and 35.473, respectively. The discrepancies between these results and those of Stas are due chiefly to the latter's habit of adding *solid* sodium chloride to a silver nitrate solution and to the presence of oxygen in his silver. *W. D. B.*

One-component Systems

Note on the formation of solids at low temperature. *M. W. Travers. Proc. Roy. Soc.*, 73, *181* ; *Zeit. phys. Chem.*, 49, *224* (*1904*).—When liquid hydrogen is allowed to boil under a sufficiently low pressure, the liquid solidifies to a pasty mass. While no crystals could be detected, the sharpness with which the solid hydrogen is formed and the constancy of the apparent melting pressure lead the author to believe that solid hydrogen is a crystalline substance and not a pseudo solid. *W. D. B.*

The specific heats of metals and the relation of specific heats to atomic weight, III. *W. A. Tilden. Phil. Trans.* 203A, *139* (*1904*).—It is found that the observed specific heats of tin telluride, nickel telluride and a silver-aluminum alloy containing 92.3 percent silver can be calculated fairly accurately from the atomic heats of the elements concerned. This is not the case with the silver-aluminum alloy containing 24.9 percent silver. Although the author does not so state, it is evident that an additive relation cannot exist if the alloy contains two phases either of which changes in composition with changing temperature. It is really a waste of time to make careful measurements of the specific heats of silver-aluminum alloys until the constitution of these alloys is known. *W. D. B.*

On the compressibility of solids. *J. Y. Buchanan. Proc. Roy. Soc.*, 73, *296* (*1904*).—The author has determined the compressibility of platinum, gold, copper, aluminum and magnesium, using the method devised by him thirty years ago. With these five metals the compressibility increases as the density and atomic weight diminish ; but it is not believed that this relation is general. *W. D. B.*

The most probable value for the gas constant. *D. Berthelot. Zeit. Elektrochemie*, 10, *621* (*1904*).—The most probable value for the volume of one molecular weight of an ideal gas at 0° under one atmosphere pressure, at sea-level, latitude 45°, is 22.412 liters. The most probable value for the temperature of melting ice is 273.09°. From these two values we deduce R = 0.08207 liter-atmospheres per degree. *W. D. B.*

The numerical values of some important physical chemical constants. *W. Nernst. Zeit. Elektrochemie*, 10, *629* (*1904*).—The author calculates the following values for the gas constant:

$R = 0.832 \times 10^{8}$ ergs $= 0.0821$ liter-atmospheres $= 1.985$ g cal $= 0.861 \times 10^{-4}$ watts. The watts are calculated on the assumption of 96540 coulombs per equivalent instead of 96580 as found by Richards. *W. D. B.*

Tantalum, its preparation and properties. *W. von Bolton. Zeit. Elektrochemie*, 11, *45* (*1905*).—The colored oxides of vanadium, niobium, and tantalum can be formed into sticks similar to the Nernst glowers, and electrolyzed. If this electrolysis takes place in vacuo, the oxygen is pumped off, leaving the pure metal. Vanadium melted at 1680°, while niobium melted at 1950°. Both of these metals disintegrate at high temperatures staining the vessel walls. Metallic tantalum does not so disintegrate. Since its oxides are more volatile and melt lower than the metal, it is possible to free the metal completely from oxides by electrolyzing in vacuo. The melting-point is between 2550° and 2360°. Specific heat 0.0365. Atomic heat 6.64. Density 16.64, that of the wire less. Coefficient of linear expansion 0.0000079. Electrical resistance for a column 1 meter long and 1 mm in cross section 0.165. Temperature coefficient from 0-100° 30/00 and from 0-350° 2.60/00. Electronegative to Pt, and positive to Ag, passive when anode. Modulus of elasticity 1900 kg/mm². Tensile strength 93 kg/sq. mm. Heated to red heat and hammered, it is so hard that a diamond drill is destroyed by it. Can be drawn into very fine wire. Glowing tantalum decomposes water. Heated to red heat in oxygen it still does not burn like magnesium. If the pressure is less than 20 mm it does not combine with oxygen, in fact the oxide is decomposed. It combines with sulphur, selenium, and tellurium to form products which decompose water, evolving the hydrides of these metalloids. Iron containing 5-10 percent of tantalum is hard and ductile. It does not alloy with silver, or mercury, but does with molybdenum and tungsten. It is not attacked by boiling nitric, sulphuric, or hydrochloric acids, nor does aqua regia affect it. It is attacked by fused alkalies. As cathode, as when in contact with platinum in a solution, it is attacked. Hydrofluoric acid dissolves it slowly, but in contact with platinum the metal dissolves rapidly. *E. S. S.*

Two-Component Systems

The application of the phase rule to mixtures of iron and carbon. *H. W. B. Roozeboom. Zeit. Elektrochemie*, 10, *489* (*1904*).—The upper temperature limit for cementite appears to be 1050°. The transition point at 800° found by Carpenter and Keeling may be due to the appearance of a second modification of cementite. It is not known what change takes place at 600° though it seems to be a change in the iron. The author admits the possibility of cementite never being a stable phase. *W. D. B.*

Labile and metastable equilibria in iron-carbon alloys. *E. Heyn. Zeit. Elektrochemie,* 10, *491* (*1904*).—The author considers that iron and graphite are the only stable phases and that all the others are merely metastable phases due to rapid cooling from the melt. This is a point which ought not to be difficult to decide. *W. D. B.*

Some physical constants of saturated solutions. *The Earl of Berkeley. Phil. Trans.,* 203A, *189* (*1904*).—The author has determined the density and concentration of saturated solutions of nineteen salts over a wide range of temperatures. *W. D. B.*

The electrical conductivity and other properties of sodium hydroxide in aqueous solution as elucidating the mechanism of conduction. *W. R. Bousfield and T. M. Lowry. Phil. Trans.,* 204A, *253* (*1904*).—The authors have made very accurate determinations of the conductivity, viscosity and density of caustic soda solutions over a wide range of concentrations and temperatures. It is proposed to determine the vapor pressures as well. If the authors will also determine the heats of dilution at different temperatures we shall then have a mass of data which will be of extraordinary value for the future theory of concentrated solutions. *W. D. B.*

On lead-tin alloys. *O. Sackur. Zeit. Elektrochemie,* 10, *522* (*1904*).—Tin precipitates lead almost completely from an acid solution of lead acetate while lead precipitates tin from a nitrate solution. The author decides from some experiments with chloride solutions that tin can take up nearly ten percent of lead as solid solution. Starting from this premise he discusses the behavior of lead-tin alloys. The premise is false and the reasoning must be inaccurate or it would have led him to a contradiction. *W. D. B.*

Some results of cryoscopy in medicine. *H. Schröder. Zeit. Elektrochemie,* 10, *649* (*1904*).—A brief sketch of what can be told from the freezing-points of secretions from different organs. *W. D. B.*

Multi-Component Systems

Calcium sulphate in ammonium sulphate solution. *E. C. Sullivan. Jour. Am. Chem. Soc.,* 27, *529* (*1905*).—The first additions of ammonium sulphate to calcium sulphate solutions decreases the solubility of calcium sulphate by about the theoretical amount, but this ceases to hold even before the solubility begins to increase. Isohydric calcium sulphate and ammonium sulphate solutions have the calculated conductivity when mixed, though theoretically this should not be true. It is believed that the concentration of undissociated calcium sulphate in a saturated solution does not remain constant when ammonium sulphate is added. *W. D. B.*

On potassium magnesium carbonate. *F. Auerbach. Zeit. Elektrochemie,* 10, *163* (*1904*).—The author has determined portions of 15°, 20° and 25° isotherms for the system, $KHCO_3$, $MgCO_3$ and H_2O. The solid phases were $MgCO_3.3H_2O$ and $MgCO_3.KHCO_3.4H_2O$. The double salt is decomposed by water. *W. D. B.*

The molecular state of anhydrous and hydrated salts in organic solvents. *G. Bruni and A. Manuelli. Zeit. Elektrochemie,* 10, *601* (*1904*).—

1. Manganese, cobalt and copper chlorides have the formulas $MnCl_2$, $CoCl_2$ and $CuCl_2$ when dissolved in urethane solution.

2. In urethane solution $MnCl_2$, $CoCl_2$, $NiCl_2$ and $CuCl_2$ hold part of their water of crystallization.

3. In accordance with the high dielectric constant, acetamide is a strong ionizing medium, potassium iodide being completely dissociated in it.

4. Anhydrous $MnCl_2$, $CoCl_2$ and $CuCl_2$ are markedly dissociated in acetamide solution.

5. When $MnCl_2 4H_2O$, $CoCl_2 6H_2O$ or $NiCl_2 6H_2O$ is dissolved in acetamide, the whole of the water is set free. *W. D. B.*

The reciprocal replacement of metals in aqueous solutions. *G. McP. Smith. Jour. Am. Chem. Soc.*, 27, *540* (*1905*).—Copper precipitates zinc from a concentrated potassium zinc cyanide solution. Mercury precipitates iron from a potassium ferricyanide solution. Platinum precipitates mercury from a potassium mercury cyanide solution, as does also gold. Gold precipitates silver from a potassium silver cyanide solution. *W. D. B.*

The application of the laws of chemical equilibrium to mixtures of toxine and antitoxine. *W. Nernst. Zeit. Elektrochemie*, 10, *377* (*1904*).—The author criticizes the paper of Arrhenius and Madsen (8, 366), giving reasons for believing that no true equilibrium is reached between toxine and antitoxine. *W. D. B.*

The formation, constitution and uses of slags. *Mathesius. Zeit. Elektrochemie*, 10, *839* (*1904*).—The author distinguishes four kinds of slags: sulphides, spinels, silicates and phosphates. The silicate slags are now worked up into cement and the phosphate slags into fertilizers. *W. D. B.*

New views on colloids. *E. Jordis. Zeit. Elektrochemie*, 10, *509* (*1904*).—It is believed that a colloidal solution can only exist in presence of impurities and that both hydrogels and hydrosols are normal products of dissociation and hydrolysis in aqueous solution. *W. D. B.*

The preparation of so-called crystalline zirconium in the electric furnace. *E. Wedekind. Zeit. Elektrochemie*, 10, *231* (*1904*).—When potassium zirconium fluoride is heated with aluminum in an electric furnace and the excess aluminum dissolved in hydrochloric acid, there is left behind an alloy which appears to have the formula $ZrAl_2$. This alloy is apparently not acted on by anything except hydrochloric acid and fused alkali. When the potassium zirconium fluoride is reduced by magnesium, the resulting metal is 94 percent pure. An alloy of titanium and aluminum has the formula $TiAl_3$ and seems to have all the good properties of the zirconium aluminum alloy. *W. D. B.*

Pyrogenic reactions and dissociation processes. *W. Löb. Zeit. Elektrochemie*, 10, *504* (*1904*).—It is assumed that reactions take place only between substances with free valences and that the change of benzene into diphenyl and hydrogen is conceivable only when C_6H_5 and H are intermediate products. The author then discusses the dissociation phenomena for a number of organic reactions. *W. D. B.*

Osmotic Pressure and Diffusion

On the rate of diffusion of water through a semipermeable membrane. *J. Sebor. Zeit. Elektrochemie,* 10, *347* (*1904*).—The author finds that the rate of diffusion of water through a copper ferrocyanide membrane into a solution is proportional to the osmotic pressure of the solution. There is no apparent reason why this should be the case and it seems quite as probable that the author has interpreted his results wrongly and that the rate is proportional to the difference between the vapor pressures of the solvent. It would take fairly accurate experiments to distinguish between these two cases. *W. D. B.*

Velocities

Studies on enzyme action, II, III. *E. F. Armstrong. Proc. Roy. Soc.,* 73, *500, 516* (*1904*).—The author believes that the enzyme combines with the sugar, the active mass of the sugar being that in combination with the enzyme. The following cases are to be distinguished:

1. Whatever the amount of sugar, the quantity of enzyme is relatively small.
2. The quantity of enzyme is relatively considerable.
3. The amount of enzyme diminishes as the action proceeds.
4. The amount of sugar is varied.

In the third paper it is shown that "the only hexoses which retard hydrolysis by any given enzyme are those derived from the hexosides which undergo hydrolysis under the influence of that enzyme.

"A more absolute proof of the close correlation in configuration between enzyme and hydrolyte cannot well be imagined: it is difficult to interpret such behavior in any other way than as evidence that the enzyme combines with the hexose in some special, peculiarly intimate manner and is thereby withdrawn from the sphere of action. The retardation cannot well be due to reversion, as in the case of milk-sugar the retardation is effected chiefly by glucose when emulsin is the active agent but by galactose alone when lactase is used to effect hydrolysis." *W. D. B.*

Studies on enzyme action, IV. *E. F. Armstrong and R. J. Caldwell. Proc. Roy. Soc.,* 73, *526* (*1904*).—"It is shown that, within certain limits, milk-sugar is hydrolyzed in accordance with the logarithmic law; but that in somewhat concentrated solutions there is a marked tendency for 'reversion' to take place, so that the course of change in the later stages of hydrolysis departs from this law." Enzymes hydrolyze milk-sugar very much more rapidly than does hydrochloric acid. *W. D. B.*

Enzyme action as bearing on the validity of the ionic-dissociation hypothesis and on the phenomena of vital change. *H. E. Armstrong. Proc. Roy. Soc.,* 73, *537* (*1904*).—The author considers it as proved that the first step in the hydrolysis of sugars by enzymes is a combination between enzyme and sugar. This is believed to be a proof that the dissociation theory is untenable. He contends "that an association hypothesis is preferable and of far wider application" although admitting "that the dissociation hypothesis is often susceptible of numerical treatment in a way which places it at a great advantage."
W. D. B.

The theory of saponification. *F. Goldschmidt. Zeit. Elektrochemie*, 10, *221* (*1904*).—In alcoholic solution sodium ethylate is said to react instantaneously with $(CH_2OF)_2CHOF$, where F is the radical of a fatty acid. The products are sodium glycerate and the ethyl ester of a fatty acid. Since the reaction takes place so rapidly, the author concludes that it must be a reaction between ions with the acid radical as the cation and the alkoxy radical as the anion. This is a necessary consequence if reactions between ions are the only ones that take place rapidly. *W. D. B.*

On the theory of reaction velocity in heterogeneous systems. *F. Haber. Zeit. Elektrochemie*, 10, *156* (*1904*).—It is pointed out that the action of water on glass is not a case in which one can assume that equilibrium is reached instantaneously at the surface between glass and water. *W. D. B.*

On vitrification and devitrification. *G. Tammann. Zeit. Electrochemie*, 10, *532* (*1904*).—If a liquid be cooled suddenly to a temperature below that at which crystal nuclei form or grow, a glass is obtained. If a glass be heated to a temperature at which crystalline nuclei form readily, the glass will change to a crystalline mass. If this temperature at which crystallization begins is at all sharply marked, it is called the temperature of devitrification. The author discusses: spontaneous crystallization; rate of crystallization; devitrification; the relation between spontaneous crystallization; rate of crystallization and viscosity; stability of amorphous substances; volume and energy changes. *W. D. B.*

The succession of changes in radio-active bodies. *E. Rutherford. Phil. Trans.*, 204A, *169* (*1904*).—The author considers that the following stages in the decomposition of radium have been established, the time given being that for 50 percent change: radium, 800 years; radium emanation, 4 days; radium A, 3 minutes; radium B, 21 minutes; radium C, 28 minutes; radium D, 40 years; radium E, 1 year; etc. Polonium and radio-active tellurium are merely radium E. Helium is the α-particle. *W. D. B.*

Further experiments on the production of helium from radium. *W. Ramsay and F. Soddy. Proc. Roy. Soc.*, 73, *346*; *Zeit. phys. Chem.*, 48, *682* (*1904*).—The experiments tend to show that only one α-particle is expelled from the atom at each disintegration; that the greater part of the energy of disintegration appears in the form of kinetic energy of α-radiation; and that the emanation is a monatomic gas. *W. D. B.*

Electromotive Forces

The carbon cell. *F. Haber and L. Bruner. Trans. Am. Electrochem. Soc.*, 6, II, *27*; *Zeit. Elektrochemie*, 10, *697* (*1904*).—The authors look upon the passive iron in the Jacques cell as an oxygen electrode, the sodium manganate in the caustic soda facilitating reaching equilibrium. The carbon electrode reacts with the caustic soda to a certain extent, setting free hydrogen and forming a hydrogen electrode. From this point of view the cell is merely an oxyhydrogen gas cell.

W. D. B.

On the concentration of mercury ions at the calomel electrode and on the solubility of calomel. *H. Ley and C. Heimbucher. Zeit. Elektrochemie*, 10, *301*

(*1904*).—The authors have measured a calomel electrode against a mercuric perchlorate, mercury electrode. From the data they calculate 0.8×10^{-6} for the solubility of calomel while Ogg obtained 1.0×10^{-6} by measurement of a chloride-nitrate cell. *W. D. B.*

Anodic evolution of oxygen. *F. Foerster and A. Piguet. Zeit. Elektrochemie*, 10, *714* (*1904*).—The anode potential was determined for electrodes of platinum, iridium, palladium, iron and nickel in caustic potash solution and for electrodes of platinum, palladium, and iridium in sulphuric acid solution. The authors adopt Haber's view that the difference in the potentials is due to differences in oxygen absorption. *W. D. B.*

The construction of some mercury standards of resistance. *F. E. Smith. Phil. Trans.*, 204A, *57* (*1904*)—"The difficulty of defining and constructing a practical invariable mercury standard of resistance has been shown to be rather under- than over-estimated. The possibility that the axis of the tube may be undulating seems difficult to remove, though the final results indicate that its effect is small. The presence of films of moisture and of air is disconcerting, though again the results indicate the constancy of these under definite conditions. Of the methods chosen to measure the resistance of mercury standards, that of the Kelvin double bridge is certainly best. . . . As already mentioned, for permanent work all rubber may be removed, the tubes themselves being ground as stoppers. The temperature of observations is advisably that of melting ice, for while there is little uncertainty concerning the equality of temperature of the mercury and a well-stirred liquid, the thermometry then plays a considerable part in the determinations. The change in resistance is determinable to 0.0001 percent, equivalent to one-thousandth of a degree on the centigrade scale.

"The primary objects in view have, it would appear, been achieved with a fair measure of success. The eleven mercury standards constructed from theoretical considerations enable a resistance to be evaluated in international ohms with an accuracy of at least 0.001 percent."

"Some information respecting the stability of the tubes may be gleaned from ice-point determinations of thermometers. The permanency of the mercury resistances depends entirely on the freedom of the glass from strain, or, if in a strained condition, the maintenance of that strain. Now the walls of a mercury tube are much thicker than the walls of a thermometer bulb. Probably, therefore, complete recovery from strains will be more difficult in the former case than in the latter. On the other hand, the distorting forces to which a thermometer bulb is subject are much greater and more variable than those acting on a mercury standard. Under similar conditions, therefore, a mercury tube is probably not more liable to change than the bulb of a thermometer; also, the condition of a tube when a measurement of its resistance is being made is very similar to that of a thermometer which has been raised to the steam-point shortly before an observation of its zero. The constancy of such zero readings should therefore be comparable with the constancy of the resistance measurements. In the case of well-annealed *Verre dur* thermometers, Dr. J. A. Harker, of the Thermometric Department of the Laboratory, assures the writer that the difference between such zero readings, spread over

a considerable number of years, will not average, in the general case, more than a few hundredths of a degree centigrade. Since a change of 0.1° C corresponds to an alteration in the capacity of the bulb of 0.002 percent, changes of considerable magnitude in the standards of resistance are not anticipated."
W. D. B.

The high temperature standards of the National Physical Laboratory. *J. A. Harker. Phil. Trans.*, 203A, *343* (*1904*).—A comparison of platinum resistance thermometers with thermocouples and with the nitrogen thermometer shows that Callendar's parabolic formula holds well over the whole range from —200° to +1100°. *W. D. B.*

Electric resistance thermometry at the temperature of boiling hydrogen. *J. Dewar. Proc. Roy. Soc.*, 73, *244* (*1904*).—At the boiling-point of liquid hydrogen no resistance thermometer gives true readings, the error being 30° in the case of copper. The author feels certain that the parabolic curve of Callendar is purely an interpolation formula. *W. D. B.*

Electrolysis and Electrolytic Dissociation.

The preparation of calcium. *W. Rathenau. Zeit. Electrochemie*, 10, *508* (*1904*).—Calcium is now made electrolytically on a commercial scale by means of a contact electrode such as is used in the Rathenau and Suter process for making sodium. In the discussion Muthmann stated that he had made 600g calcium in a forenoon, using a current of 80 amperes. A slight calculation shows that the forenoon must begin in Munich soon after midnight.
W. D. B.

The preparation of metallic sodium by electrolysis of a fused mixture of sodium hydroxide and carbonate. *C. F. Carrier, Jr. Zeit. Elektrochemie*, 10, *568* (*1904*).—Laboratory experiments on Becker's process for sodium. The electrolyte is a mixture of fused caustic soda and sodium carbonate. The author finds that practically no carbon dioxide is set free and he looks upon the process consequently as a poor imitation of the Castner process. While this is probably true, it seems a pity that the question of water vapor should not have been considered a little more in detail. *W. D. B.*

The use of the rotating anode in electro-analysis. *E. F. Smith. Jour. Am. Chem. Soc.*, 26, *1595* (*1904*).—Details are given in regard to precipitation of nickel and cobalt from a number of different solutions. Very valuable time diagrams are given. At the end of the paper it is stated that 0.5g copper or nickel can be precipitated completely in fifteen minutes using a rotating anode and a mercury cathode. *W. D. B.*

Electrolytic analysis using rotating electrodes. *R. Amberg. Zeit. Elektrochemie*, 10, *385* (*1904*).—The author states that "no satisfactory explanation has yet been given for the extraordinarily beneficial effect of stirring the liquid" during electrolytic analyses. He seems to think that some further explanation is necessary than the simple and obvious one that stirring keeps the solution at the cathode more nearly equal to the mean concentration. *W. D. B.*

Electrolysis with rapidly moving electrodes. *H. J. S. Sand. Zeit. Elektrochemie*, 10, *452* (*1904*).—The author criticizes the statement of Amberg (preceding review) that no satisfactory explanation has been given for the beneficial effect of rotating electrodes. *W. D. B.*

Electrolytic precipitation of palladium. *R. Amberg. Zeit. Elektrochemie,* 10, *386* (*1904*).—Palladium is precipitated quantitatively when a chloride solution or a chloride solution plus sulphuric acid is electrolyzed at 60°-65° with a current density of 0.04 amp/dcm² using a rapidly rotating anode to keep the solution stirred. *W. D. B.*

Electrolytic determination of manganese. *J. Koster. Zeit. Elektrochemie,* 10, *553* (*1904*).—Manganese can be precipitated satisfactorily from a solution containing ammonium acetate, chrome alum and alcohol. The current density is 4-4.5 amp/dcm² and the temperature about 75°. The anode is a roughened platinum iridium dish and the cathode is rotated rapidly. *W. D. B.*

Note on the determination of transference numbers in the electrolysis of fused salt-pairs. *R. Lorenz and G. Fausti. Zeit. Elektrochemie,* 10, *630* (*1904*).—In a fused mixture of potassium and lead chlorides, containing fifty percent or over of potassium chloride, lead moves to the anode. Two determinations of the transference number of potassium gave 0.36 and 0.19. *W. D. B.*

Experiments on electrolysis of alkali chlorides with mercury flowing over iron cathodes. *W. Kettembeil and C. F. Carrier, Jr. Zeit. Elektrochemie,* 10, *561* (*1904*).—Laboratory experiments on a process patented by Gurwitsch. The cathode consists of an inclined grooved iron sheet over which mercury flows. The best yield was obtained with a current density of 34-50 amp/dcm². Unless a diaphragm is used, the chlorine dissolved in the water cuts down the yield to about 50 percent. [This is due to the fact that no attempt is made to remove the chlorine. The experiments are therefore not carried on under the conditions prevailing in technical work.] *W. D. B.*

Studies on the so-called bell process for the electrolysis of aqueous solutions of alkali chlorides. *O. Steiner. Zeit. Elektrochemie,* 10, *317* (*1904*).—With the bell process there can be obtained a current efficiency of 85 to 94 percent, a solution containing 120 to 130g KOH per liter, and a 97 to 100 percent chlorine. The current density should be 2-4 amp/dcm² which calls for a potential difference of 3.7 to 4.2 volts. Acheson graphite anodes are not attacked but carbon anodes are. The position of the anode and dimensions of the bell have a marked effect on the position and effectiveness of the neutral zone.

W. D. B.

Comments on a paper by Mr. O. Steiner. *G. Adolph. Zeit. Elektrochemie,* 10, *449* (*1904*).—The author claims that Steiner (preceding review) has contributed nothing new in regard to the bell process for making caustic soda and chlorine. *W. D. B.*

Reply to the remarks of G. Adolf. *O. Steiner. Zeit. Elektrochemie,* 10, *713* (*1904*).—A reply to Adolf (preceding review). *W. D. B.*

The significance of the cathode material in the reduction of *m*- and *p*-nitrotoluene. *W. Löb and J. Schmitt. Zeit. Elektrochemie,* 10, *756* (*1904*).—In the reduction of *m*-nitrotoluene a current efficiency of 62, 90 and 100 percent is obtained with nickel, zinc, and copper cathodes respectively. The product is chiefly *m*-azoxytoluene with nickel and zinc, while *m*-toluidine preponderates with copper. With *p*-nitrotoluene, 100 percent efficiency is obtained with all three cathodes in the first part of the run but this falls off more quickly with nickel than with zinc while the copper cathode gives the highest total efficiency. *W. D. B.*

Experiments on the electrochemical preparation of hydrosulphites. *K. Elbs and K. Becker. Zeit. Elektrochemie*, 10, *361* (*1904*).—Dilute solutions of sodium bisulphite can be reduced to hydrosulphite, $Na_2S_2O_4$, using a platinum or aluminum cathode. A saturated solution can also be obtained by starting from zinc sodium bisulphite. For making concentrated solutions of hydrosulphites or for making the solid salts chemical methods are superior to electrochemical ones. *W. D. B.*

Electrolytic preparation of sodium and calcium hydrosulphites. *A. R. Frank. Zeit. Elektrochemie*, 10, *450* (*1904*).—In 1897-99 the author obtained concentrations of 30-40g $Na_2S_2O_4$ per liter by avoiding the presence of free sulphurous or free hydrosulphurous acid in the cathode chamber. He also made solid calcium hydrosulphite electrolytically. The reasons Elbs and Becker failed in this (preceding review) is that they started with too dilute a solution of calcium bisulphite. *W. D. B.*

Anodic behavior of zinc, antimony and bismuth. *K. Elbs and H. Thümmel. Zeit. Elektrochemie*, 10, *364* (*1904*).—In sodium chloride, sodium sulphate, hydrochloric acid, and sulphuric acid, a tin anode dissolves chiefly as bivalent tin. In chloride solutions bismuth and antimony dissolve only as trivalent metals. *W. D. B.*

Anodic pulverization of copper. *F. Fischer. Zeit. Elektrochemie*, 10, *421* (*1904*).—With a high anode current density in an acidified copper sulphate solution, copper dust is formed at the anode owing to the formation and decomposition of cuprous sulphate. If the solution is neutral, cuprous oxide is formed. The higher the temperature the greater the amount of cuprous sulphate. In some cases it was one-half of the total. If an oxidizing agent is present, it may be reduced at the anode by cuprous sulphate. *W. D. B.*

The electrolysis of copper sulphate solutions. *F. Foerster and G. Coffetti. Zeit. Elektrochemie*, 10, *736* (*1904*).—A discussion of the equilibrium between cupric and cuprous sulphate at copper anode and cathode. It is shown that the anode loss should be greater than the theoretical but the authors seem to think that the cathode gain should be the theoretical even when much cuprous sulphate is present. An interesting series of experiments was made with neutral copper sulphate at 70°-90° with a potential just under that of copper. The precipitate consists of practically pure cuprous oxide. If the solution is acid there is no precipitate. The formation of cuprous oxide is referred to hydrolysis, $Cu_2SO_4 + H_2O = Cu_2O + H_2SO_4$. *W. D. B.*

The electrolysis of potassium acetate. *F. Foerster and A. Piguet. Zeit. Elektrochemie*, 10, *729* (*1904*).—When aqueous potassium acetate is electrolyzed, we may have an evolution of oxygen at the anode, an oxidation of acetic acid to carbon dioxide or monoxide, and a formation of ethane. The last requires the highest potential and takes place chiefly with smooth anodes and high current densities. The presence of free acetic acid seems also to be necessary. With iron or palladium anodes, the evolution of oxygen takes place readily. When the solution is slightly alkaline, the oxidation increases at the expense of the ethane formation. The authors are inclined to believe that ethane is formed according to the reaction

$$2CH_3CO_2H + O = C_2H_6 + 2CO_2 + H_2O$$

and not according to the reaction

$$2CH_3CO'_2 + 2F = C_2H_6 + 2CO_2.$$

The fluctuations in the potential difference during electrolysis are due chiefly to the presence of bicarbonate. This paper is an admirable illustration of the way a problem of this sort should be attacked. *W. D. B.*

On the electrolytic oxidation of sulphites and on the electrochemical formation of dithionates. *A. Friessner. Zeit. Elektrochemie,* 10, *265* (*1904*).—A neutral or alkaline solution of sodium sulphite is oxidized to sulphate and dithionate, $Na_2S_2O_6$. A high anode potential and high temperature increases the yield of dithionate. In acid solutions sulphate is the only anode product while some thiosulphate is formed at the cathode. Electrolysis of pure dithionate solutions resulted in no reduction at the cathode and less than three percent oxidation at the anode. *W. D. B.*

Electrolytic preparation of azo dye-stuffs. *W. Löb. Zeit. Elektrochemie,* 10, *237* (*1904*).—Starting with sodium sulphanilate, β-naphthol, sodium nitrite and water in the anode compartment, Orange II is obtained. With benzidine, sodium salicylate, sodium nitrite and water, the product is chrysamine G. An anode density of 0.5–6.0 amp/dcm^2 may be used and efficient stirring must be provided. Further details will be given in a later paper. *W. D. B.*

Note on the electrolysis of tetra-ethyl ammonium iodide. *E. Goecke. Zeit. Elektrochemie,* 10, *249* (*1904*).—When an aqueous solution of tetra-ethyl ammonium iodide is electrolyzed between platinum electrodes, some tetra-ethyl ammonium tri-iodide is formed and some iodoform. *W. D. B.*

Effect of indifferent ions on the electrolytic formation of periodic acid salts. *E. Müller. Zeit. Elektrochemie,* 10, *753* (*1904*).—The beneficial effect of chlorides, chlorates or sulphates on the electrolytic formation of periodates might have been connected with a change in these salts. Addition of potassium fluoride is found to have an equally beneficial effect and to increase the anode potential 0.2 volt. We can therefore make periodates using a platinum anode and adding potassium fluoride, or using a lead peroxide anode and adding no fluoride. *W. D. B*

Electrolysis of alkali chlorides in presence of fluorides. *F. Foerster and E. Müller. Zeit. Elektrochemie,* 10, *781* (*1904*).—Siemens and Halske have patented the addition of fluorides to the solution when making chlorates. Experiments by the authors show that the addition of neutral fluorides has no effect and that the addition of acid fluorides has a good effect which, however, is due to the acid and not to the fluoride. *W. D. B.*

The action of bromine on alkalies and the electrolysis of alkali bromides. *H. Kretschmar. Zeit. Elektrochemie,* 10, *789* (*1904*).—The reaction between

NaBrO and 2HBrO takes place 100 times as fast as the corresponding reaction with hypochlorite. Electrolysis of a hypobromous acid solution gives no bromate and practically no bromide. In other respects the formation of bromate follows the same lines as the formation of chlorate. *W. D. B.*

A method of preparing persulphates. *E. Müller. Zeit. Elektrochemie,* 10, *776* (*1904*).—Addition of hydrofluoric acid to a solution of potassium bisulphate plus sulphuric acid increases the anode potential and the yield of persulphuric acid. This beneficial effect is interfered with if potassium persulphate crystallizes on the anode. *W. D. B.*

Formation of oxyhydrogen gas with alternating currents. *R. G. Van Name. Zeit. Elektrochemie,* 10, *303* (*1904*).—No electrodes will withstand for any great length of time the corroding effect of an alternating current either in caustic potash or sulphuric acid solution. While a mixture of hydrogen and oxygen gas can be obtained with an alternating current, the yield is never more than half what could have been obtained with a direct current. *W. D. B.*

Time values for formation of complexes, constants for complexes and atomic dimensions. *F. Haber. Zeit. Elektrochemie,* 10, *433* (*1904*).—"The dissociation constant of a complex may be considered as the ratio of the time of formation to the time of composition for unit concentrations." In the case of potassium silver cyanide, the equilibrium constant for the equation $[Ag^{\cdot}][CN']^3 = k\ Ag(CN)_3''$ has the value 1.13×10^{-21}. If we assume a time of 0.0001 second for the formation of $Ag(CN)_3''$ we get an infinitely slow time of decomposition and we cannot account for the chemical precipitation of silver by zinc or for the electrolytic phenomena so long as we postulate only ion reactions. If, on the other hand, we assume a time of 10^{-3} seconds for the decomposition of $Ag(CN)_3''$ we obtain a value of 10^{-24} seconds for the time of formation. If we assume that we are working at atomic distances, a reaction taking place with the speed of light or of electricity would require 10^{-18} seconds. Starting from a kinetic basis, with these assumptions stated clearly, we find that the decomposition of $Ag(CN)_3''$ then involves a velocity at least a million times as great as that of light. As the author says, this is absurd. He is inclined to think that these infinitely low concentrations such as that of silver as ion in cyanide solution are mythical. This may well be so because these calculations involve the assumption that the solution pressure of silver is the same in cyanide solutions as in nitrate solutions. We know that the addition of alcohol to a nitrate solution changes the solution pressure and the burden of proof is on the man who maintains that the addition of cyanide has no effect. *W. D. B.*

Time values for formation of complexes, constants for complexes, and atomic dimensions. *G. Bodländer. Zeit. Elektrochemie,* 10, *601* (*1904*).—The author suggests getting round the difficulty raised by Haber (preceding review) by assuming that the actual concentration of silver as ion is not proportional to its active mass in cyanide solutions. He thinks it preposterous to doubt the existence of incredibly low concentrations of ions. He thinks it possible that the actual reaction in the electrolysis of silver cyanide solutions does not pass through the stage of metal as ion. Thus we might have

$$Ag(CN)_3'' + F = Ag(CN)_3'''$$
$$Ag(CN)_3''' = Ag + 3(CN)'.$$

W. D. B.

Time values for formation of complexes, constants for complexes, and atomic dimensions. *H. Danneel. Zeit. Elektrochemie*, 10, *609* (*1904*). — The author claims that Haber is wrong in assuming that the distance between two reacting substances is necessarily of atomic dimensions. If it may approximate zero, Haber's whole reasoning falls to the ground. The point is also made that if there are no atoms there are no atomic dimensions. *W. D. B.*

Electrode reactions and potential formation with very low concentrations of ions. *R. Abegg. Zeit. Elektrochemie*, 10, *607* (*1904*).—Attention is called to the fact that a good deposit of copper can be obtained from a potassium copper cyanide solution while the potential difference between copper and a very dilute solution of copper sulphate cannot be measured. The experiments of Baker on the effect of traces of moisture on certain reactions is cited as an argument for the dissociation theory, though it is not clear what bearing this has on anything. The actual existence of infinitely low concentrations is also deduced from the results with the acid-alkali cell. *W. D. B.*

On low concentrations. *F. Haber. Zeit. Elektrochemie*, 10, *773* (*1904*). — A reply to Bodländer, Abegg and Danneel (preceding review). The author sums up his review in the statement that when there is marked dissociation we have a reaction between ions but that the reaction takes place direct between the undissociated substances when the dissociation is very slight. The author's point of view seems to be both saner and sounder than that of his opponents. *W. D. B.*

The electrochemical determination of the corrosion of glass. *F. Haber and H. Schwenke. Zeit. Elektrochemie*, 10, *143* (*1904*).—It is shown that a fair estimate of the quality of a commercial glass bottle can be obtained by filling it with water, holding it at 80° for five hours, and measuring the conductivity every hour. *W. D. B.*

Indicators for acidimetry and alkalimetry, I. *W. Salessky. Zeit. Elektrochemie*, 10, *204* (*1904*).—The author has determined the potential difference between a normal hydrogen electrode and hydrogen electrodes dipping in solutions just neutral to different indicators. The concentrations of hydrogen as ion were calculated: $10^{-6.9}$ with curcuma; 10^{-7} with phenolphthaleine when colorless, and $10^{-4.5}$ with phenolphthaleine when red; $10^{-8.8}$ with methyl orange when red and $10^{-5.3}$ with methyl orange when yellow; 10^{-7} with litmus when violet. *W. D. B.*

Indicators for acidimetry and alkalimetry, II. *B. Fels. Zeit. Elektrochemie*, 10, *208* (*1904*).—This is a continuation of Salessky's work (preceding review). Known concentrations of hydroxyl as ion were prepared by adding ammonium chloride to ammonia solutions. Known concentrations of hydrogen as ion were obtained by adding sodium *p*-nitrophenolate to a saturated solution of *p*-nitrophenol. The values check pretty well with those of Salessky. *W. D. B.*

Determination of hydrogen ions by means of indicators. *E. Salm. Zeit. Elektrochemie*, 10, *341* (*1904*).—A table is given showing the colors of sixteen indicators in a number of solutions in which the concentration of hydrogen as ion decreases according to powers of ten. The table brings out well both the relative and the absolute sensitivenesses of the different indicators.

W. D. B.

Mixed indicators. *M. Scholtz. Elektrochemie*, 10, *549* (*1904*)—When two indicators are added to a solution, the more sensitive one will change color first. The author gives a table showing the color changes for a number of pairs of indicators. *W. D. B.*

Dielectricity and Optics

On the resistance and electromotive forces of the electric arc. *W. Duddell. Phil. Trans.*, 203A, *305* (*1904*).—The true resistance of an arc, 3 mm long, between 11 mm solid "Conradty Noris" carbons is 3.81 ohms when a current of 9.91 amperes is flowing. There is a real back electromotive force of about 12 volts. The counter-electromotive force appears to be the difference between a value of about 17 volts at one electrode and a value of about 6 volts in the opposite direction at the other electrode. Introducing any impurity into the carbons lowers the resistance and increases the back electromotive force. *W. D. B.*

A study of the radio-activity of certain minerals and mineral waters. *R. J. Strutt. Proc. Roy. Soc.*, 73, *191* (*1904*).—Radium emanation could be detected in samarskite, fergusonite, pitch-blende, malacone, zircon, and in monazite from three different localities. A meteorite from Augusta Co., Virginia contained argon and helium but no radium emanation. Radium emanation was found in the salt deposit from the King's Well at Bath.

W. D. B.

On gasolene burns. *G. Just. Zeit. Elektrochemie*, 10, *202* (*1904*).—When woolen cloths are rubbed with gasoline in contact with a metal, sparks may easily be generated which will cause damage. *W. D. B.*

The refractive indices of the elements. *C. Cuthbertson. Phil. Trans.*, 203A, *323* (*1904*).—It was noticed that the refractivities of helium, neon, argon, krypton, and xenon are in the proportion of 0.25, 0.5, 2, 3 and 5. The corresponding values for fluorine, chlorine, bromine and iodine are in the proportion of 0.5, 2, 3 and 5. The data for fluorine were determined by the author who also measured mercury, phosphorus and sulphur. "The indices of fourteen elements have been measured in the gaseous state. Of these, two, mercury and hydrogen, are not related to any other whose indices have been determined. The remaining twelve all conform to the rule [that the refractivities of the different members of the same chemical family are related in the ratios of small integers]." *W. D. B.*

The optical properties of vitreous silica. *J. W. Gifford and W. A. Shenstone. Proc. Roy. Soc.*, 73, *201* (*1904*).—Two prisms of fused quartz seem to differ less from each other than two prisms of glass. The refractive index for the D line is 1.458480. A table is given showing the refractive indices for twenty-six different wave-lengths. *W. D. B.*

On flame spectra. *C. de Watteville. Phil. Trans.*, 203A, *139* (*1904*).—This is a study of the spectra obtained by injecting the spray from saline solutions into the gas to be burned. These flame spectra are similar to the arc spectra and to the 'oscillatory spark' spectra; but "none of the characteristic lines of the spark spectrum are ever seen in the flame spectrum." It is believed that these differences are due to temperature differences. *W. D. B.*

New luminescence phenomena. *M. Trautz. Zeit. Elektrochemie*, 10, *593* (*1904*)—Fused anhydrous sodium acetate glows when the first crystals appear from a supercooled melt. A supersaturated solution of barium chlorate or bromate gives out flashes when crystallization begins. Presence of other substances may interfere with the phenomenon which seems to be connected only with the appearance of the first crystals. A glow is to be seen when perchloric acid acts on calcium hydroxide. *W. D. B.*

Crystallography, Capillarity and Viscosity

Internal friction of solutions. *G. Rudorf. Zeit. Elektrochemie*, 10, *473* (*1904*).—In the experiments on solutions of urea (7, 491), the author used a spiral tube and this is probably responsible for the 'negative' friction then found. All the measurements in the preceding paper are probably wrong as far as absolute values go, though they are probably comparable among themselves. *W. D. B.*

DINERIC EQUILIBRIA

BY J. M. BELL

It has been shown by Professor Bancroft[1] that the general exponential expression

$$(1) \qquad \frac{x^{\alpha}.y^{\beta}}{z^{\alpha+\beta}} = \mathrm{K},$$

where α, β, K are constants, describes the equilibrium between the concentrations x, y and z of two non-miscible liquids dissolved in a consolute liquid. This general group will be called Group I. Two equations of the form (1) are usually necessary, for in general the constants α, β, K change abruptly in passing from the curve representing the compositions of the upper layer to that representing the compositions of the lower layer. Of the large number of combinations actually tried, only one was found which could not be described by the formula. In the second group (Group II) one of the two non-miscible substances has a limited solubility in the third substance and a general case is that in which there is a solid having a limited solubility in the common solvent (*i. e.*, not miscible in all proportions at the temperature of the experiment). To express this limited solubility a constant was introduced into equation (1), which then became

$$(2) \qquad \frac{(x + \mathrm{A})^{\alpha}.y^{\beta}}{z^{\alpha+\beta}} = \mathrm{K}.$$

This equation was found to describe the equilibrium in the cases for which data were available. The results of Bodländer,[2] Gérardin,[3] and Schiff[4] on the solubility of different alkali salts in aqueous alcohol can be classified fairly well by means of this formula. In a third group (Group III) both of the non-miscible

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[1] Phys. Rev. 3, 21 (1895); Jour. Phys. Chem. 1, 34, 760 (1896-7).

[2] Zeit. phys. Chem. 7, 308 (1891).

[3] Ann. Chim. Phys. (4), 5, 129 (1865).

[4] Liebig's Ann. 118, 362 (1861).

substances are soluble to a limited extent in the common solvent. The formula was then modified by the introduction of two constants for the two limited solubilities. It then becomes

$$\frac{(x+A)^{\alpha}(y+B)^{\beta}}{z^{\alpha+\beta}} = K. \tag{3}$$

This formula describes fairly well the conditions obtaining when two electrolytes, such as potassium chloride and potassium nitrate, are dissolved in water. Of course, there will be two equations of this type, one to describe the curve of solutions saturated with respect to potassium chloride, and the other to describe the curve of solutions saturated with respect to potassium nitrate.

In groups II and III the constant or constants expressing the limited solubility of the solids vary with the temperature and, of course, vary with the nature of the substances entering into the physical reaction. The constants, α and β, however, depend in all cases only on the nature of the substances and not on the temperature. The constant K depends on both factors.

The first of these three equations has been very carefully tested by Lincoln for the system benzene-alcohol-water[1] and for the system benzene-acetic acid-water,[2] and he comes to the conclusion that "*the formula represents the facts absolutely.*"

The correction for the limited solubility when a salt is precipitated by alcohol is a purely empirical one. A formula

$$\frac{(x+y)^{\alpha}y^{\beta}}{z^{\alpha+\beta}} = K$$

would introduce the same limitation that the miscibility of one substance with the common solvent shall be finite while that of the other shall be infinite. Other formulations are also possible. There are a number of cases known in which the addition of a liquid to a solution of a solid in a liquid precipitates a second liquid phase instead of a solid phase. Since the two-liquid

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[1] Jour. Phys. Chem. 4, 161 (1900).

[2] Ibid. 8, 248 (1904).

phases or dineric system can be followed beyond the point at which the solid phase becomes stable, there is no certainty that there is any limiting solubility and this case might really come under Group I, though the dineric system could not, of course, be followed over a very wide range owing to the spontaneous crystallization of the solid at some concentrations. In any event these systems formed a transition from Group I to Group II and therefore called for careful study. Assuming for the moment that these systems belong under Group I we can write equation (1) in the form

$$\frac{z^{\frac{\alpha+\beta}{\beta}}}{y} = \frac{x^{\alpha/\beta}}{K}, \tag{4}$$

where x denotes the concentration of the solid, y the concentration of the precipitating liquid, and z the concentration of the common solvent, the three concentrations being expressed in any desired units. If we express the concentrations of the precipitating liquid and of the common solvent in terms of a constant quantity of the solid, the right-hand side of the equation becomes constant. Replacing $(\alpha + \beta)/\beta$ by n we have

$$z^n/y = K, \tag{5}$$

where K has not the same value as in equation (4).

This formula was first applied to some data of Linebarger's[1] on the solubility of acetone or an alcohol in aqueous salt solutions. In the experiments Linebarger added acetone or an alcohol to an aqueous solution of an electrolyte until the solution became cloudy owing to the formation of minute globules of a second liquid phase. In this way the compositions of solutions in equilibrium with a second liquid phase at that temperature are determined synthetically. The calculations are given in Tables I–XIII, in which z denotes the grams of water per gram of salt and y the grams of acetone or alcohol per gram of salt. Under the heading "calc" are given the grams of water necessary to satisfy equation (5) when assuming the value of log K given at the head of each table. This gives a more satisfactory

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[1] Am. Chem. Jour. 14, 380 (1892).

idea of the possible applicability of the formula than does the constancy of log K. It should also be remembered that Linebarger does not claim any great accuracy for his results.

TABLE I

$$\frac{z^{1.52}}{y} = K \qquad \text{Log } K = 0.615$$

Potassium carbonate, one gram
z = water, y = ethyl alcohol

C_2H_5OH	H_2O calc.	H_2O found	Log K
26.9	22.2	22.7	0.631
53.3	34.8	34.7	0.614
83.6	46.7	45.5	0.598
107.8	58.2	55.6	0.620
134.5	63.1	65.3	0.630
161.7	71.3	73.8	0.630

TABLE II

$$\frac{z^{1.62}}{y} = K \qquad \text{Log } K = 0.865$$

Potassium carbonate, one gram
z = water, y = propyl alcohol

C_3H_7OH	H_2O calc.	H_2O found	Log K
8.9	13.2	13.3	0.872
44.3	35.5	35.3	0.862
66.7	45.7	45.1	0.855
70.0	47.1	47.2	0.867
137.2	71.9	71.9	0.868

TABLE III

$$\frac{z^{1.54}}{y} = K \qquad \text{Log } K = 0.806$$

Potassium carbonate, one gram

z = water, y = acetone

$(CH_3)_2CO$	H_2O calc.	H_2O found	Log K
4.8	9.2	9.2	0.803
11.4	16.2	16.1	0.802
18.8	22.1	22.1	0.806
30.8	31.0	31.1	0.810
43.0	38.4	38.5	0.808
5.4	10.0	10.2	0.820
14.4	18.8	18.8	0.808
28.2	29.2	28.7	0.794
50.0	41.4	38.7	0.746
89.7	61.8	49.9	0.662

TABLE IV

$$\frac{z^{1.66}}{y} = K \qquad \text{Log } K = 0.935$$

Sodium carbonate, one gram

z = water, y = ethyl alcohol

C_2H_5OH	H_2O calc.	H_2O found	Log K
23.6	30.8	30.4	0.925
30.4	36.3	37.8	0.968
49.7	49.8	50.86	0.948
66.7	59.4	57.7	0.905

TABLE V

$$\frac{z^{1.74}}{y}\ \mathrm{K} \qquad \mathrm{Log\ K} = 1.210$$

Sodium carbonate, one gram

z = water, y = propyl alcohol

C_3H_7OH	H_2O calc.	H_2O found	Log K
6.5	14.6	16.4	1.301
20.0	27.6	27.8	1.212
29.2	34.5	33.9	1.197
56.9	50.7	50.2	1.204
71.0	57.5	57.5	1.211
90.7	66.2	66.9	1.217
30.4	35.2	37.4	1.252
102.0	70.0	72.7	1.236
140.7	85.3	89.7	1.243

TABLE VI

$$\frac{z^{1.58}}{y} = \mathrm{K} \qquad \mathrm{Log\ K} = 1.087$$

Sodium carbonate, one gram

z = water, y = acetone

$(CH_3)_2CO$	H_2O calc.	H_2O found	Log K
9.2	19.9	19.8	1.085
16.8	29.1	28.8	1.080
27.7	39.9	39.8	1.086
38.4	49.2	49.9	1.099
51.3	58.9	59.1	1.089
63.1	67.2	67.5	1.090
74.8	74.8	74.8	1.087
16.8	28.8	28.85	1.087
43.5	53.2	57.55	1.121
46.9	55.6	60.4	1.141
76.7	72.3	78.8	1.152
98.0	88.3	105.4	1.202

TABLE VII

$\frac{z^{1.60}}{y} = K \qquad \text{Log } K = 0.570$

Ammonium sulphate, one gram
z = water, y = ethyl alcohol

C_2H_5OH	H_2O calc.	H_2O found	Log K
1.5	3.14	3.8	0.694
4.3	6.35	6.5	0.585
6.8	8.61	8.7	0.577
12.1	12.65	12.3	0.552
24.7	20.4	19.3	0.536
33.3	24.8	24.3	0.557
78.5	43.9	43.4	0.561

TABLE VIII

$\frac{z^{1.88}}{y} K \qquad \text{Log } K = 1.220$

Ammonium sulphate, one gram
z = water, y = propyl alcohol

C_3H_7OH	H_2O calc.	H_2O found	Log K
2.8	7.69	10.7	1.488
15.0	19.3	19.0	1.227
22.0	23.1	23.0	1.218
41.6	32.36	32.2	1.216
61.8	39.9	40.2	1.224
71.4	43.2	43.5	1.227

TABLE IX

$\frac{z^{1.54}}{y} = K \qquad \text{Log } K = 0.800$

Ammonium sulphate, one gram
z = water, y = acetone

$(CH_3)_2CO$	H_2O calc.	H_2O found	Log K
2.4	5.85	6.4	0.860
10.0	14.8	14.5	0.786
21.2	24.0	24.2	0.804
39.0	35.8	35.0	0.805
58.0	46.2	45.5	0.787

TABLE X

$\frac{z^{1.632}}{y} = K \qquad \text{Log } K = 0.840$

Sodium sulphate, one gram
z = water, y = propyl alcohol

C_3H_7OH	H_2O calc.	H_2O found	Log K
20.8	26.2	28.5	0.896
44.1	42.9	44.5	0.864
76.8	61.7	61.2	0.835
102.4	74.6	78.6	0.844
136.6	90.2	88.6	0.828
182.5	108.9	108.1	0.835

TABLE XI

$\frac{z^{1.46}}{y} = K \qquad \text{Log } K = 0.670$

Manganous sulphate, one gram
z = water, y = ethyl alcohol

C_2H_5OH	H_2O calc.	H_2O found	Log K
3.1	6.24	6.2	0.665
15.3	18.9	18.7	0.672
23.7	25.1	24.9	0.663
46.7	39.8	40.2	0.675
68.2	51.9	52.0	0.671

TABLE XII

$\frac{z^{1.77}}{y} = K \qquad \text{Log } K = 1.170$

Manganous sulphate, one gram
z = water, y = propyl alcohol

C_3H_7OH	H_2O calc.	H_2O found	Log K
6.8	13.5	12.9	1.131
16.8	22.5	24.0	1.203
42.7	38.2	36.7	1.136
55.1	44.1	47.0	1.213

TABLE XIII

$$\frac{z^{1.35}}{y} = K \qquad \text{Log } K = 0.730$$

Manganous sulphate, one gram

z = water, y = acetone

$(CH_3)_2CO$	H_2O calc.	H_2O found	Log K
4.1	9.9	10.7	0.776
14.8	25.5	26.4	0.727
27.0	39.8	39.2	0.714
38.1	51.5	53.2	0.749
58.5	70.8	71.2	0.733
69.4	80.2	80.2	0.729
93.0	100.0	99.1	0.725
106.8	110.7	109.9	0.726

It should be pointed out that it is very likely that some of the data given by Linebarger describe the concentrations of solutions of the lower layer and some describe those of the upper layer in the same table. In such case the formula at the head of the table does not in general describe the concentrations of both layers. Such a circumstance as this may be the cause of the deviation of the constants in Tables VII, VIII, X, and XIII.

By means of the same method which was adopted by Linebarger, Krug and McElroy[1] determined the amount of acetone necessary to cause a sugar solution of known strength to cloud. Their results at 25°, recalculated on the basis of the exponential formula, are given in Table XIV.

TABLE XIV

$$T = 25^\circ \qquad \frac{z^{2.237}}{y} = K$$

z = water, y = acetone

Sugar	Acetone	Water	Log K
40	92.76	60	0.029
45	68.81	55	0.009
50	48.13	50	0.017
55	33.81	45	0.015
60	24.18	40	0.001
65	17.68	35	$\bar{1}.965$
70	12.82	30	$\bar{1}.914$

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[1] Jour. anal. Chem. 6, 153 (1892).

The values of log K for temperatures 20° and 30° show the same general variations.

In another paper, Krug[1] has given the solubility of acetone in aqueous solutions of other carbohydrates at 15°, 25° and 35°. The curves for the three temperatures are approximately parallel and lie very close together. The results for dextrose, maltose and sucrose at 25° have been recalculated on the basis of the exponential formula with the following results:

TABLE XV

$$T = 25^\circ \qquad \frac{z^{2.158}}{y} = K$$

z = water, y = acetone

Dextrose	Acetone	Water	Log K
10	747.86	90	0.180
20	247.71	80	0.203
30	149.83	70	0.095
40	79.57	60	0.065
50	33.02	50	0.180

TABLE XVI

$$T = 25^\circ \qquad \frac{z^{1.085}}{y} = K$$

z = water, y = acetone

Maltose	Acetone	Water	Log K
10	348.09	90	0.065
20	181.17	80	0.047
30	115.99	70	0.033
40	74.73	60	0.011
50	42.95	50	0.066

TABLE XVII

$$T = 25^\circ \qquad \frac{z^{1.76}}{y} = K$$

z = water, y = acetone

Sucrose	Acetone	Water	Log K
10	581.84	90	$\bar{1}.914$
20	263.19	80	$\bar{1}.940$
30	162.55	70	$\bar{1}.915$

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[1] Jour. anal. Chem. 6, 188 (1892).

The values for Log K for the cases of sugar, maltose and sucrose are found to be fairly constant and in the case of dextrose there is still the explanation that compositions may have been found for both upper and lower layers, and it has been pointed out that in such case two formulas are necessary to describe the facts for different layers. Further, it was found that two such exponential formulas will describe well all the data which Krug and McElroy give for sugar.

The results of Linebarger, and Krug and McElroy seem to indicate that if the data had been obtained over a much greater range of concentration, the exponential formula might describe the conditions throughout the whole range. With this object in view, data for several cases studied by Linebarger, and for the case studied by Krug and McElroy were redetermined over a much greater range of concentration.

Purification of Compounds

The acetone used was boiled over fused calcium chloride for twelve hours in a flask provided with a return condenser. On cooling, small crystals separated on the walls of the flask, owing to the slight solubility of calcium chloride in acetone at higher temperatures. The acetone was poured off from these crystals which adhered to the glass into another flask and it was fractionated with a long Hempel column. The first fraction was rejected and the main portion distilled over within 0.2°. The residue was a yellow, oily material insoluble in water. The density of the acetone was 0.79179 at 19.8° corresponding to 100 percent acetone. The alcohol was boiled over quicklime for twelve hours and was then distilled from the lime. The density at 25° C was 0.78990 corresponding to 99.14 percent alcohol. The potassium and sodium carbonates were fractionally crystallized from hot aqueous solution and were then ignited to drive off the water of crystallization. The naphthalene and benzophenone used in the work were crystallized from alcohol and acetone solutions, and gently warmed to drive off the solvent adhering to the crystals. The anethol was fractionally distilled and gave a boiling-point on the second fractionation of 230°–231° C at 735 mm.

Method of Working

The modus operandi was in all cases the same. The solid, or in the case of anethol, the liquid, was weighed in a small flask of known weight. Then the solvent for the substance was added and the flask was again weighed. The flask was then immersed in an Ostwald thermostat to acquire the desired temperature and the second liquid was added from a burette in small portions from time to time. In this way the temperature of the flask and its contents was kept constant. The point at which globules of a second liquid could be distinguished floating around, or at which the liquid suddenly went cloudy due to the formation of minute globules of a second phase, was in most cases sharply defined, and especially so in the region of the critical point, at which the compositions of the two phases are the same, *i. e.*, the upper and lower liquid become identical. At this point a drop too much of the second liquid divides the homogeneous solution into two layers of which the masses are about the same. At extreme concentrations it is more difficult to determine the end-point sharply as the quantity of the second phase appearing is very minute. Under these circumstances by holding the flask before an incandescent lamp it was possible to discern whether or not minute globules of the new phase had appeared and with a little practice these globules could be distinguished easily from air-bubbles. After arriving at the end-point the flask was again weighed.

Calculation of Results

It was hoped that formula (5) would describe all cases but it was found that for some cases at least the formula must be modified. To show the agreement with, or deviation from, the formula, a graphical method was employed. Formula (5) was written

$$\frac{z^n}{y} = K.$$

Taking logarithms of both sides, we have

$$n \log z - \log y = \log K.$$

It follows from this that if log y and log z are plotted, the curve will be a straight line if the formula holds and it will not be a straight line in case the formula fails. In the cases where the formula was found to describe the facts, the agreement is further shown by calculations of log K. Log K is the negative intercept of the straight line on the axis log y; and as it is the distance from a fixed point (the origin), the absolute values of log K are not to be taken as a criterion of the constancy of log K, but the values of K are the test of the constancy. For instance, in Table XXI, the values of log K range between 0.012 and 0.027 while the values of K range between 1.028 and 1.064.

System I. Potassium Carbonate, Water, Acetone

Linebarger's results, when calculated on the basis of the exponential formula, give a fairly good constant over a considerable range of concentrations, but when very dilute solutions of the salt in water are clouded with acetone, the value of log K falls very perceptibly. It was thought that this might be due to experimental error which is quite large on account of the difficulty of determining the exact point at which the solution clouds. The following table gives the data over a much greater range of concentration; z denotes the number of grams of water per gram of carbonate, and y the number of grams of acetone per gram of carbonate.

TABLE XVIII. T = 25° C

	K_2CO_3	H_2O	$(CH_3)_2CO$	Log *z*	Log *y*
1	1.456	34.41	26.36	1.374	1.258
2	1.924	35.67	23.64	1.268	1.089
3	2.257	35.57	21.49	1.196	0.978
4	2.251	36.10	19.494	1.205	0.938
5	2.746	37.92	20.645	1.140	0.876
6	2.694	39.94	19.153	1.171	0.852
7	3.016	37.87	19.510	1.099	0.811
8	3.380	39.25	19.001	1.065	0.750
9	3.984	40.13	17.303	1.003	0.639
10	4.571	42.89	17.426	0.972	0.581
11	4.981	42.81	16.173	0.935	0.509
12	6.022	45.17	14.602	0.875	0.385
13	7.349	45.00	11.078	0.787	0.178
14	8.093	49.91	12.339	0.790	0.183
15	9.060	50.05	10.[illegible]46	0.742	$\underline{0}.053$
16	9.765	50.17	8.940	0.710	$\bar{1}.961$
17	11.076	49.99	6.802	0.655	$\bar{1}.789$
18	12.396	50.87	5.572	0.613	$\bar{1}.653$
19	14.509	50.40	3.656	0.540	$\bar{1}.401$
20	15.744	51.03	2.966	0.511	$\bar{1}.275$
21	17.820	50.53	2.143	0.452	$\bar{1}.079$
22	19.670	50.48	1.563	0.409	$\bar{2}.900$
23	22.602	50.38	0.940	0.348	$\bar{2}.619$

System II. Potassium Carbonate, Water, Alcohol

The results of Lobry de Bruyn[1] are not suitable for calculation, as the percentage error is very large. The mass concentrations of this system are given in the following table.

TABLE XIX. T = 25° C

	K_2CO_3	H_2O	C_2H_5OH	Log *z*	Log *y*
1	1.596	25.140	22.478	1.198	1.149
2	2.116	26.358	20.252	1.095	0.981
3	2.750	27.614	18.718	1.002	0.833
4	3.829	29.376	15.870	0.885	0.618
5	5.011	31.114	13.929	0.793	0.443
6	6.549	32.459	11.351	0.695	$\underline{0}.239$
7	8.916	33.446	7.288	0.574	$\bar{1}.912$
8	10.576	33.893	5.140	0.506	$\bar{1}.687$
9	12.034	34.077	3.705	0.452	$\bar{1}.488$
10	13.533	33.655	2.425	0.396	$\bar{1}.253$

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[1] Rec. Trav. Chim. Pays.-Bas, 18, 87 (1899).

System III. Sodium Carbonate, Water, Acetone

Table XX gives the mass concentrations of the layers in the system sodium carbonate-water-acetone.

TABLE XX. T = 25° C

	Na_2CO_3	H_2O	$(CH_3)_2CO$	Log z	Log y
1	1.038	25.68	11.690	1.394	1.052
2	1.228	25.63	10.928	1.319	0.949
3	1.530	25.79	9.626	1.227	0.799
4	1.817	25.67	8.338	1.151	0.652
5	2.201	26.15	7.520	1.075	0.534
6	2.403	25.35	6.560	1.023	0.436
7	2.819	25.67	5.823	0.960	0.315
8	3.180	25.55	5.026	0.900	0.199
9	3.597	25.41	4.138	0.849	0.061
10	4.549	29.55	4.200	0.813	$\bar{1}.965$
11	4.204	25.55	3.197	0.784	$\bar{1}.881$
12	8.653	44.65	3.916	0.713	$\bar{1}.655$
13	5.233	27.01	2.365	0.713	$\bar{1}.655$
14	5.187	26.48	2.257	0.708	$\bar{1}.639$
15	10.068	51.10	4.170	0.705	$\bar{1}.617$
16	6.151	26.53	1.339	0.635	$\bar{1}.348$
17	7.174	26.95	0.945	0.575	$\bar{1}.120$

A graphical representation of the data from Tables XVIII and XX will be found further on in the paper (Fig. 1) in connection with some of the other results.

The curve representing log z and log y in all three systems is not two straight lines but a smooth curved line. Theoretically, there are two distinct curves intersecting in the critical point, at which the composition of the upper layer is the same as that of the lower layer. Curve II actually shows a rather abrupt break, indicating the presence of two curves which in this case intersect at a small angle, while curves I and III show no apparent abrupt change in direction. In these cases the angle of intersection of the two curves is too small to show in the diagram. It will be seen that the extreme points on the curves are nearly on straight lines and as Linebarger was working mainly at these dilutions, his data naturally fell very nearly on a straight line. My own experiments prove, however, that the exponential formula does not describe the facts for these three systems.

The exponential formula has been found to describe a large number of cases of dineric equilibria, especially organic liquids, over very wide ranges of concentration. Lincoln has found that it describes the facts absolutely in the case of benzene-alcohol-water and in the case of benzene-acetic acid-water. The question now arises—what is the difference between the cases for which the formula holds and the cases given above which the formula fails to describe? Two explanations present themselves. The deviation may be due to the different degree of electrolytic dissociation of the salts, a degree which depends on the dilution and also on the other substances present in the solution; or the deviation may be ascribed to the fact that in these cases we are using a substance which is solid at ordinary temperature and in the other cases all the substances are liquid. It is quite possible, too, that both of these factors may influence the equilibrium conditions. In order to test the validity of these possible explanations, several cases were studied in which a non-electrolyte was the solid.

It was observed quite accidentally that at the extreme ends of the curve the solutions were supersaturated with respect to solid sugar. The flasks containing the mixtures were left at room temperature over night and next morning a considerable crop of sugar crystals had separated. These crystals did not dissolve after the flasks had been kept at the temperature of the thermostat for a long time. Minute crystals of sugar were added to the other solutions to induce crystallization and it was found that in solutions 4 to 18 inclusive, the minute crystals disappeared while in the other solutions, either sugar crystals had appeared on standing or else the crystal formed a nucleus for a larger crystal. Herz and Knoch[1] have recently determined the solubility of sugar in aqueous acetone by adding solid sugar to different water-acetone mixtures and shaking at constant temperature until equilibrium was reached. For certain of the

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[1] Zeit. anorg. Chem. 41, 315 (1904).

System IV. Sugar, Water, Acetone

TABLE XXI. T = 25°C

$$\frac{z^{1.745}}{y} = K_1,\ \log K_1 = \bar{1}.950;\quad \frac{z^{2.281}}{y} = K_2,\ \log K_2 = 0.020$$

z = water per gram sugar
y = acetone per gram sugar

Upper Layer

	Sugar	Acetone	Water calc.	Water found	Log K_1
1	1.10	41.70	8.27	8.30	$\bar{1}.953$
2	2.20	50.80	12.44	12.60	$\bar{1}.954$
3	3.99	83.15	21.29	21.42	$\bar{1}.955$
4	4.13	51.68	16.44	16.37	$\bar{1}.946$
5	9.95	106.47	36.21	35.95	$\bar{1}.945$
6	5.50	43.28	16.36	16.50	$\bar{1}.936$
7	3.86	25.00	10.62	10.41	$\bar{1}.946$
8	4.07	22.02	10.01	10.03	$\bar{1}.951$
9	5.02	19.31	10.18	10.08	$\bar{1}.943$
10	6.12	16.27	10.04	10.00	$\bar{1}.943$

Lower Layer

					Log K_2
11	7.00	16.53	10.02	10.42	0.012
12	7.07	14.90	10.14	10.14	0.026
13	8.00	12.91	10.12	10.09	0.017
14	9.03	11.07	10.01	10.08	0.018
15	10.05	10.08	10.26	10.25	0.018
16	20.02	18.93	19.93	19.89	0.017
17	22.45	16.31	19.86	19.91	0.023
18	24.90	14.78	20.12	20.20	0.023
19	27.50	13.07	20.13	20.23	0.025
20	32.47	12.25	21.54	21.29	0.014
21	37.51	11.96	23.60	23.15	0.007
22	35.01	10.39	20.75	20.69	0.016

mixtures they found that two liquid layers appeared, and with excess of solid sugar the mass-ratio of water to sugar was 55/45 for the lower layer and about 20/80 for the upper layer. This agrees with the present experiments which show that above the ratio 55/45 and below 20/80 the solutions were supersaturated with respect to sugar.

TABLE XXII. T = 40°

$$\frac{z^{1.715}}{y} = K_1, \log K_1 = \bar{1}.970; \quad \frac{z^{2.337}}{y} = K_2, \log K_2 = 0.060$$

z = water per gram sugar
y = acetone per gram sugar

Upper layer

	Sugar	Acetone	Water calc.	Water found	Log K_1
1	24.13	68.69	42.23	42.00	$\bar{1}.966$
2	26.12	64.18	41.98	41.98	$\bar{1}.970$
3	28.28	59.83	41.60	42.18	$\bar{1}.978$
			Lower layer		Log K_2
4	30.08	56.70	42.50	42.20	0.054
5	32.05	52.25	42.45	42.15	0.054
6	36.12	44.59	42.26	42.11	0.057
7	40.27	39.37	42.39	42.54	0.063
8	44.05	34.48	42.01	42.26	0.067
9	48.14	33.27	43.33	43.41	0.062

It will be noticed that the same exponent gives very good constants for both temperatures while the values of log K_1 and log K_2 both increase with increase of temperature.

The results indicate quite definitely that in this case, at least, the exponential formula holds with a very gratifying degree of accuracy. Other cases have been tried in which the common solvent is not water, but acetone or alcohol and where water is one of the two non-miscible components.

System V. Naphthalene, Acetone, Water

The system naphthalene-acetone-water has been studied by Cady[1] with the object of finding the limiting concentrations for homogeneous mixtures. This was accomplished by making up mixtures of the three components at a temperature at which the mixtures were homogeneous and by allowing them to cool very slowly. The temperature at which a second phase appeared was determined. This gives not only the limiting concentrations for homogeneous solutions but also the limiting concentrations

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[1] Jour. Phys. Chem. 2, 168 (1898).

which divide into two liquid layers. No work, however, was done on the compositions of two liquid phases in equilibrium.

The composition of such phases is given in Table XXIII and here, as in the system sugar-water-acetone, it is very probable that the end solutions of the table are supersaturated with respect to naphthalene. The exponential formula describes accurately the conditions obtaining at 35°, a temperature well below the melting-point of naphthalene. For any lower temperature than 35° it was found that the range of concentrations between which two liquid phases appear, was very small. The temperature coefficient of solubility of naphthalene in acetone at 35° is very great and any minute temperature change in the thermostat produces a very great change in the amount of water necessary to cause the appearance of a second liquid phase.

TABLE XXIII. T = 35°

$$\frac{z^{1.573}}{y} = K_1,\ \log K_1 = 0.718;\ \frac{z^{2.184}}{y} = K_2,\ \log K_2 = 1.112$$

z = acetone per gram naphthalene

y = water per gram naphthalene

	Naphthalene	Water	Acetone calc.	Acetone found	Log K_1
			Upper layer		
1	1.790	36.74	34.95	35.53	0.728
2	2.777	29.51	35.57	35.57	0.718
3	3.824	24.85	35.85	35.70	0.713
4	4.751	21.97	35.80	35.50	0.708
5	5.723	19.71	35.81	35.66	0.713
6	6.717	17.50	35.35	35.35	0.718
			Lower layer		Log K_2
7	8.789	14.364	35.57	35.64	1.114
8	9.825	12.801	35.82	35.63	1.106
9	10.785	11.438	35.76	35.40	1.102
10	11.730	10.381	35.75	35.57	1.106
11	12.944	9.182	35.74	35.56	1.108
12	13.545	8.695	35.56	35.56	1.112
13	14.880	7.747	35.70	35.72	1.114
14	15.968	6.970	35.67	35.67	1.112

System VI. Anethol, Acetone, Water

In Table XXIV are given the compositions of phases for the system anethol-acetone-water. The anethol used was in a liquid condition although the temperature is below its melting point.

TABLE XXIV. T = 25°

$$\frac{z^{1.481}}{y} = K_1,\ \log K_1 = 0.662; \quad \frac{z^{2.112}}{y} = K_2,\ \log K_2 = 1.085$$

z = acetone per gram anethol
y = water per gram anethol

	Upper Layer				
	Anethol	Water	Acetone calc.	Acetone found	Log K_1
1	1.055	22.48	23.23	23.26	0.664
2	1.055	19.68	21.22	21.22	0.662
3	1.055	15.72	18.20	18.20	0.661
4	1.055	11.19	14.50	14.50	0.661
5	1.055	8.92	12.46	12.46	0.661
6	1.055	6.85	10.46	10.46	0.662
7	1.055	5.00	8.48	8.48	0.663
8	1.055	3.53	6.29	6.83	0.676
	Lower Layer				Log K_2
9	1.055	1.55	4.06	4.23	1.088
10	1.055	0.98	3.25	3.38	1.079
11	1.055	0.38	2.08	2.18	1.088

System VII. Benzophenone, Alcohol, Water

In the case of benzophenone-alcohol-water it was necessary to raise the temperature of the thermostat to 40° in order to get a sufficient range of concentrations on which to base any conclusions. As benzophenone is much more soluble in acetone than in alcohol, for the system benzophenone-acetone-water determinations over a sufficient range could be made at the lower temperature 25°.

TABLE XXV. T = 40.05° C

$\frac{z^{1.489}}{y} = K_1$, log $K_1 = 0.457$; $\frac{z^{1.348}}{y} = K_2$, log $K_2 = 0.400$

z = alcohol per gram benzophenone

y = water per gram benzophenone

	Upper layer				
	Benzophenone	Water	Alcohol calc.	Alcohol found	Log K_1
1	1.147	20.41	16.07	16.09	0.458
2	2.127	15.88	16.61	16.61	0.457
3	3.149	15.25	16.32	16.36	0.459
4	3.187	12.18	15.88	15.86	0.456
5	4.111	10.88	16.26	16.06	0.444
6	5.124	10.01	16.28	16.30	0.458
7	6.074	9.07	16.11	16.11	0.457
	Lower layer				Log K_2
8	7.106	8.679	16.33	16.33	0.400
9	8.117	8.179	16.03	16.07	0.396
10	8.160	7.991	15.93	15.955	0.401
11	10.146	7.571	16.18	16.18	0.400
12	12.08	7.285	16.42	16.42	0.400
13	12.11	7.277	16.45	16.49	0.402
14	15.16	6.813	16.50	16.54	0.397
15	15.04	6.672	16.24	16.18	0.395
16	21.97	6.011	16.48	16.52	0.396
17	34.97	6.025	16.30	16.33	0.397

Some of these data are represented graphically in Fig. 1, together with the data for the systems, carbonate-acetone-water.

The results as given thus far seem to imply that for non-electrolytes, the dineric equilibria can be represented by equation (1). This is not the case, however. Equation (5) does apply, but no constant can be obtained when the quantity of the solid is allowed to vary. The complete equation for this group of systems must therefore have the general form

$$(6) \qquad \frac{f(x).y^{\beta}}{z^{\gamma}} = K'$$

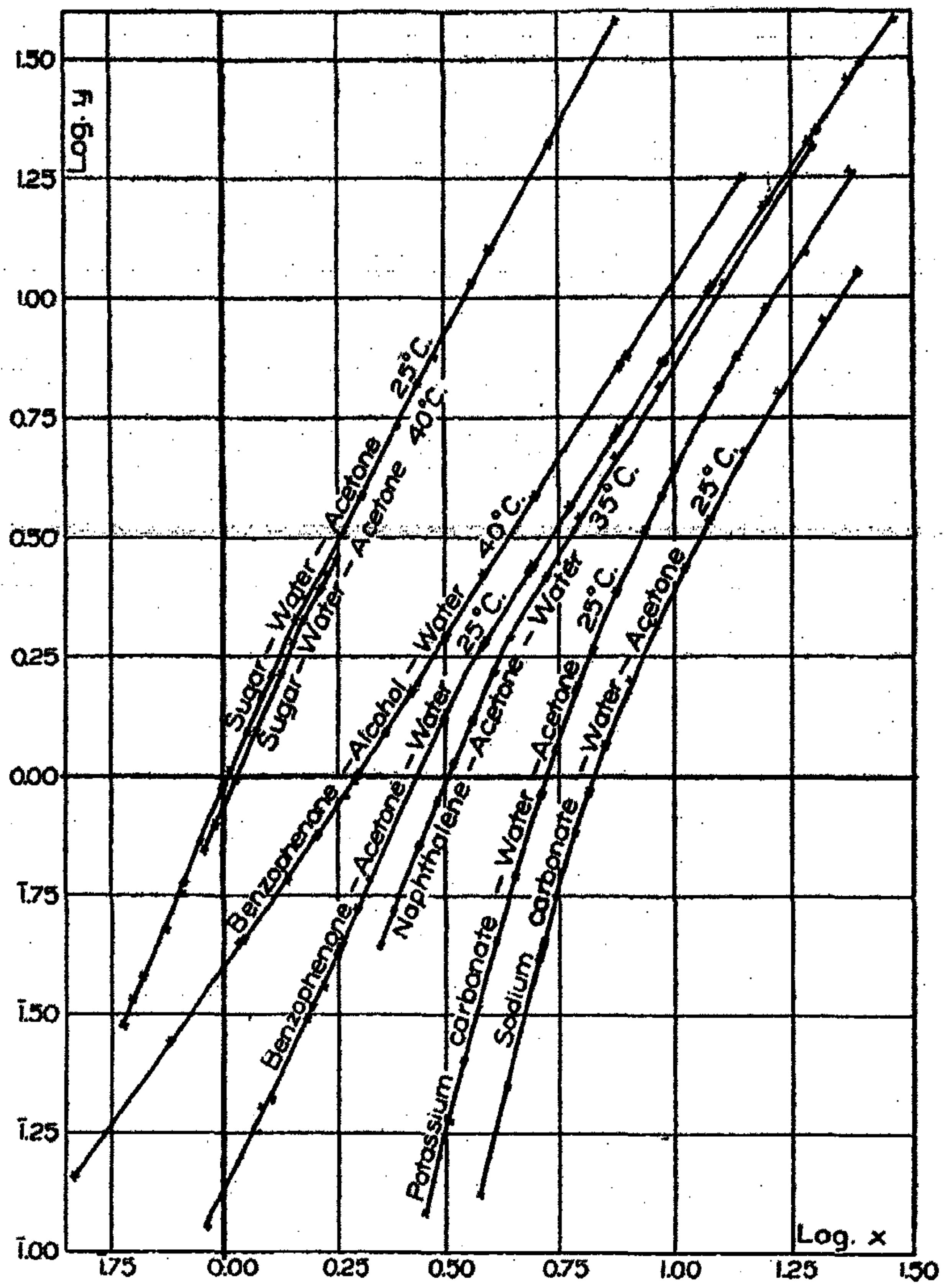

Fig. 1

which may be transformed into

$$z^n/y = K$$

when x is kept constant. The form of $f(x)$ is not yet known and will have to be determined later. That we have such a function and that the formula does not apply to electrolytes make it seem probable that we have not yet worked out the final form

System VIII. Benzophenone, Acetone, Water

TABLE XXVI. T = 25°

$$\frac{z^{1.407}}{y} = K_1,\ \log K_1 = 0.600;\ \frac{z^{1.966}}{y} = K_2,\ \log K_2 = 0.860$$

z = acetone per gram benzophenone

y = water per gram benzophenone

	Benzophenone	Water	Acetone calc.	Acetone found	Log K_1
			Upper Layer		
1	0.498	19.04	14.32	14.60	0.614
2	0.634	19.27	15.61	15.89	0.611
3	0.620	17.55	14.55	14.55	0.600
4	0.725	16.08	14.46	14.67	0.609
5	1.000	20.95	19.20	19.46	0.607
6	1.048	21.61	19.93	20.11	0.606
7	1.232	19.36	19.53	19.60	0.603
8	1.312	19.77	20.50	20.41	0.596
9	2.036	21.21	24.56	24.63	0.603
10	2.032	20.74	24.17	24.24	0.603
11	2.531	18.88	24.10	24.23	0.606
12	2.621	19.11	24.94	24.74	0.596
13	3.201	16.79	24.39	24.18	0.595
14	3.275	16.61	24.34	24.30	0.599
15	4.028	15.03	24.05	24.25	0.595
16	4.085	14.82	24.05	24.20	0.597
17	5.032	13.71	24.73	24.76	0.601
18	5.017	13.40	24.28	24.18	0.597
19	6.255	11.79	24.06	24.29	0.606
20	6 227	11.58	24.70	23.86	0.604
			Lower Layer		Log K_2
21	7.87	10.28	24.68	24.82	0.866
22	11.11	6.686	23.50	23.24	0.851
23	15.16	7.934	23.26	29.53	0.851
24	11.14	5.057	20.02	20.24	0.852
25	11.21	4.881	20.15	20.13	0.861
26	13.03	5.510	23.03	23.14	0.864
27	15.06	5.411	24.50	24.72	0.868
28	15.69	5.482	24.67	24.65	0.859
29	13.16	4.292	20.36	20.58	0.868
30	13.10	4.029	19.68	19.68	0.860
31	16.08	3.354	20.07	20.05	0.859
32	16.13	3.125	19.49	19.76	0.871
33	20.12	2.265	18.12	18.35	0.869

of the equation representing the precipitation of a solid by a liquid. It should be kept in mind, however, that the conditions are somewhat different in the two cases. In the case of equilibrium between two liquid phases the chemical potentials of all three components change with changing concentration. The chemical potential of one of the components does not vary with changing concentration when the solution is in equilibrium with a solid component.

It is evident from the experimental data that the mass law equation does describe satisfactorily the conditions when all three of the components are non-electrolytes, but when one is an electrolyte the formula seems to fail. This can properly be ascribed to the fact of different degrees of electrolytic dissociation at different dilution. An apparent exception to this is the case studied by Lincoln,[1] benzene-acetic acid-water, in which it was found that the mass law described the condition. At one extreme of concentration there is a very strong solution of acetic acid in water and a little benzene. The high concentration of the acetic acid and the presence of the benzene will both tend to reduce the degree of dissociation of the acid. At the other extreme there is a strong solution of acetic acid in benzene and a little water. At this end, too, the degree of dissociation will be very low, so that at all equilibrium concentrations there are two factors: strength of solution and presence of benzene, tending to drive back the dissociation of acetic acid, a dissociation which, even in moderately dilute solution, is low. In the present cases, both these factors, it is true, tend to drive back the dissociation of potassium and sodium carbonates, but these are quite highly dissociated salts and hence the dissociation will not be depressed so far as to be neglected.

While dissociation seems to cause the mass law equation to fail, yet association does not seem to play any part. Such substances as water and alcohol usually considered to be in a more or less associated molecular condition seem to have no influence whatever on the validity of the formula, although it seems very

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[1] Jour. Phys. Chem. 8, 248 (1904).

probable that just as the presence of alcohol changes the degree of dissociation of salts in water, the presence of alcohol should change the degree of association of the water molecules.

Finally it should be noted that many different types of compounds, water, alcohol, acetone, naphthalene, benzophenone, sugar, and anethol, have been employed in these experiments and that their behavior seems to be subject to the mass law equation.

In this paper the following general results have been obtained:

1. The dineric equilibria for two liquids and a solid may be represented by the mass law equation when the components are not electrolytes and when the mass of the solid component is kept constant.

2. If z and y are the mass concentrations of the common solvent and of the precipitating liquid with reference to a constant mass of the solid component, the ratio of the changes of concentration are proportional to the ratio of the concentrations, or $dy/dz = ny/z$, where n is a constant.

3. The complete equation for this case is $\frac{f(x).y^{\beta}}{z^{\gamma}} = K$ where β, γ and K are constants and $f(x)$ is an undetermined function of the concentration of the solid component.

4. The equilibrium equations are, in general, not the same for the upper and lower liquid phase.

5. In some cases the equations have been tested well beyond the point at which the solutions become saturated with respect to the solid phase.

6. The mass law equation does not describe the dineric equilibria for salts in aqueous solution.

In conclusion, I express my sincerest thanks to Professor Bancroft, at whose suggestion the work was undertaken, for his kindly criticism and advice; also to Dr. H. R. Carveth for his numerous valuable suggestions.

Cornell University.

ON INDIFFERENT POINTS

BY PAUL SAUREL

The following properties of an indifferent point of a bivariant or multivariant system are well known:

The temperature of the indifferent point which corresponds to a given pressure is a maximum or a minimum of the temperatures at which the system can be in equilibrium under the given pressure; the pressure of the indifferent point which corresponds to a given temperature is a maximum or a minimum of the pressures under which the system can be in equilibrium at the given temperature.

In certain cases, however, it is possible to assert that the temperature of the indifferent point is a maximum and again in other cases it is possible to assert that the pressure of the indifferent point is a minimum.

Let us consider first a bivariant or multivariant system consisting of a liquid phase of variable composition and of solid phases of invariable composition, and let us suppose that in a reversible change at the temperature and under the pressure of the indifferent point an increase of entropy is accompanied by an increase in the mass of the liquid phase. It follows from this supposition[1] that the system formed by removing the liquid phase cannot be in equilibrium at temperatures higher than that of the indifferent point. It follows, further, that the original system cannot be in equilibrium at temperatures higher than that of the indifferent point, for if it could be in equilibrium, this equilibrium would not be destroyed by the removal of the liquid phase. Thus, in the case under consideration, the temperature of the indifferent point is a maximum. It is to be noticed that if the solid phases were of variable composition the above conclusion could not be drawn.

Let us next consider a bivariant or multivariant system consisting of a vapor phase of variable composition and of solid

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[1] Jour. Phys. Chem. 8, 488 (1904).

phases of invariable composition, and let us suppose that in a reversible change at the temperature and under the pressure of the indifferent point an increase of volume is accompanied by an increase in the mass of the vapor phase. It follows from this supposition that the system formed by removing the vapor phase cannot be in equilibrium under pressures lower than that of the indifferent point. It follows, further, that the original system cannot be in equilibrium under pressures lower than that of the indifferent point, for if it could be in equilibrium, the equilibrium would not be destroyed by the removal of the vapor phase. Thus, in the case under consideration, the pressure of the indifferent point is a minimum. It is to be noticed that if the solid phases were of variable composition the above conclusion could not be drawn.

New York, May 15, 1904.

INDIRECT ANALYSIS IN MULTI-COMPONENT SYSTEM

BY WILDER D. BANCROFT

In a paper by Browne[1] an algebraical method was given for indirect analysis in multi-component systems. Such a method really requires absolute accuracy in the analyses, a state of things which can never be realized. As I shall show, the method can be applied in a much easier way, which allows one to estimate the probable error. In 1898, Morozewicz published some data which we can use for this purpose.[2] He fused his materials in a glass furnace, allowed them to cool, dissolved the glassy part in hydrochloric acid, and analyzed both the crystals and what had been dissolved. By adding together these two analyses he obtained the initial concentration of the magma. While the data thus given are not the direct results of experiment, we can take them as though we did not already know it. This has seemed better than inventing purely arbitrary numbers to illustrate the method. Although Morozewicz's actual analyses did not add up one hundred percent, he has recalculated the mother-liquor to that basis. We shall therefore not come back exactly to Morozewicz's composition of the solid phase and some of the variations are thereby introduced which would occur in actual practice.

In Table I are given one set of data. In the upper part of the table the second column is the initial composition of the melt; in the third is the composition of the mother-liquor after crystallization has taken place. In the last column are given the ratios of the concentrations in the solution after crystallization has taken place to the corresponding concentrations in the

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[1] Jour. Phys. Chem., 6, 311 (1902).

[2] Tschermak's Mineralogische und petrographische Mittheilungen (2), 18, 1 (1898).

TABLE I

	Melt	Mother-liquor	Calculated[1]	$\frac{\text{Mother-liquor}}{\text{Melt}}$
SiO_2	27.0	38.9	38.9	1.44
Al_2O_3	54.9	35.9	35.9	0.65
Fe_2O_3,FeO	3.0	4.3	4.3	1.43
CaO	4.3	6.3	6.2	1.46
MgO	0.4	0.5	0.6	1.25
K_2O	2.6	3.7	3.7	1.42
Na_2O	7.2	10.4	10.4	1.45
Total	99.4	100.0	100.0	—

	SiO_2	Al_2O_3	Fe_3O_4	CaO	MgO	K_2O	Na_2O
Melt	100.0	203.3	11.1	15.9	1.5	9.6	26.7
Mother-liquor	100.0	92.3	11.1	16.2	1.3	9.5	26.7
Crystals	0.0	111.0	0.0	—0.3	0.2	0.1	0.0

original melt. The ratios for silica, iron, lime, potash and soda are practically constant, showing that none of these substances has crystallized or that all of them have separated in the same relative proportions that they were present in the original melt. While the ratio for magnesia is not the same as that for the other substances cited, the total quantity of magnesia is small and a slight error in the analysis would account for the discrepancy. We have then only one ratio which changes materially, that for alumina, which has decreased. The presumption, therefore, is that pure alumina has crystallized. In the lower part of Table I the assumption is made that no silica has crystallized and the concentrations of the melt and the mother-liquor are expressed in grams per hundred grams of silica instead of grams per hundred grams of solution. By subtracting the concentrations of the mother-liquor from the concentrations of the melt, we get the apparent concentration of the solid phase. The slight variation from pure alumina falls well inside the experimental error. Now 111g Al_2O_3 per 100g SiO_2 is equal

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[1] On the assumption that 30 percent Al_2O_3 crystallized.

to 9.7g Al_2O_3 per 27g SiO_2. The column entitled "calculated" is obtained by subtracting 30 percent Al_2O_3 from the original melt and changing the resulting solution to a percentage basis.

In Table II we have a similar calculation for a different melt. It is clear that the ratios of silica, lime, potash and soda are practically identical, while those for alumina, iron and magnesia are less than unity. Assuming again that no silica has crystallized we calculate the composition of the solid phase as before, finding it to consist of 44.1 parts of alumina to 5.2 parts of iron oxide and to 18.7 parts magnesia. These data when referred back to 37.8g SiO_2 instead of 100g SiO_2 show that 16.7g Al_2O_3, 1.97g Fe_3O_4 and 7.07g MgO crystallized. The column entitled "calculated" is obtained on this assumption. The percentage composition of the spinel which crystallized is 64.8 percent Al_2O_3, 7.7 percent Fe_3O_4, 27.5 percent MgO. These data only show the apparent composition of the solid phase and do

TABLE II

	Melt	Mother-liquor	Calculated[1]	Mother-liquor. Melt
SiO_2	37.8	51.1	51.2	1.352
Al_2O_3	35.9	26.0	26.0	0.72
Fe_2O_3. FeO	3.6	2.2	2.2	0.61
CaO	5.6	7.6	7.6	1.354
MgO	9.8	3.7	3.7	0.38
K_2O	1.8	2.5	2.4	1.389
Na_2O	5.1	6.9	6.9	1.353
Total	99.6	100.0	100.0	

	SiO_2	Al_2O_3	Fe_3O_4	CaO	MgO	K_2O	Na_2O
Melt	100.0	95.0	9.5	14.8	25.9	4.8	13.5
Mother-liquor	100.0	50.9	4.3	14.7	7.2	4.9	13.5
Crystals	0.0	44.1	5.2	0.1	18.7	—0.1	0.0

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[1] On the assumption that 16.7g Al_2O_3, 1.97g iron oxides, and 7.07g MgO crystallized. Composition of spinel: 64.8 percent Al_2O_3, 7.7 percent iron oxides, 27.5 percent MgO.

not give any clue whether we are dealing with one or more solid phases. This difficulty can easily be obviated by making a series of measurements with varying initial concentrations.

Whether this method will really be of value in dealing with fused silicates is a matter that can only be determined experimentally. If the viscosity of the melt is so great that no separation can be effected, the method is useless. On the other hand, it is not necessary to be able to pipette off the mother-liquor. If we can hold the mass at the desired temperature and then quench rapidly so as to convert the fluid mass into a glass, it might then be possible to break up the mass with a hammer and select pieces of glass under the microscope. For aqueous solutions there would be no such difficulty, and the only question then would be the accuracy of the analysis. The general error is the same as in three-component systems and will be apt to be greater the smaller the field in which a given solid phase occurs.

In this paper it has been shown that the indirect analysis of solid phases can be performed easily in systems containing any number of components provided one can effect a partial separation of mother-liquor from crystals and provided one can analyze accurately for all components.

Cornell University.

ON THE CONDITION WHICH DETERMINES THE CHEMICAL SIMILARITY OF ELEMENTS AND RADICLES

BY GEOFFREY MARTIN

We propose to show in this paper that chemically similar elements attract the same radicles with *proportional* intensities of force, whereas chemically unlike elements attract them with *unlike* intensities. Mathematically this may be expressed thus: If we denote the attractions which an element A exerts on the various radicles A, B, C, D .... by $f_1, f_2, f_3 \ldots . f_n$; and the corresponding attractions which an element B exerts by $f'_1, f'_2, f'_3 \ldots . f'_n$. Then, if the elements A and B are chemically similar, the following relation holds:

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \ldots . = \frac{f_n}{f'_n} = \mathrm{K}. \qquad (1)$$

Further we will show that the closer K approaches unity, the closer the elements approach each other in their chemical properties. When $\mathrm{K} = 1$ the forces the two elements exert are equal and this is obviously the condition that the elements A and B may be perfectly chemically similar, for in this case one may replace the other in any chemical reaction without altering the nature and direction of the reaction which is determined by these forces.

When $\mathrm{K} = n$ the one element possesses the same chemical properties as the other, but intensified n-fold. For example for the system fluorine and chlorine, K has the value 1.7 as the following thermal data shows (see later):

$\left(\mathrm{F}, \mathrm{Si}\,\frac{1}{4}\right) = 67.3 = f_1 \qquad \left(\mathrm{Cl}, \mathrm{Si}\,\frac{1}{4}\right) = 39.4 = f_1'$

$(\mathrm{F}, \mathrm{H}) \quad = 37.6 = f_2 \qquad (\mathrm{Cl}, \mathrm{H}) \quad = 22.0 = f_2'$

where

$$\frac{f_1}{f_1'} = \frac{67.3}{39.4} = 1.71$$

$$\frac{f_2}{f_2'} = \frac{39.4}{22.0} = 1.70.$$

This means that fluorine possesses the same chemical properties as chlorine, but intensified 1.7-fold.

In general, the relationship (1) is not satisfied by the affinities of any two elements A and B selected at random. We find, however, that the more closely their affinities conform to this law, the closer is their chemical resemblance. And conversely, the more widely their affinities depart from this law, the remoter is their chemical resemblance, so that in the case of elements which behave in a quite different way chemically, this relationship is not even remotely satisfied, as we will presently show.

No two elements are perfectly chemically similar. All exhibit certain chemical peculiarities which distinguish one from the other. Therefore the relation (1) is never *exactly* satisfied by the affinities of two elements, but is the limiting condition which is more and more exactly fulfilled as the elements approach more and more exactly to perfect chemical similarity. For atoms of the same element alone is the condition exactly fulfilled, K here taking the value unity since the forces are now of the same intensity.

It may be noted that many of the so-called radicles play the part of elementary atoms, although quite incapable of existing separately (for example NH_4—, —N_3, —CN), simply because they are arrangements of atoms so combined together as to exert forces of the same intensity as the elementary atoms, of which they play the part.

The best way to make the above law evident, is to contrast the quantities of heat evolved when equivalent quantities of like and unlike elements combine with the same radicles. Of course, it must be remembered that the heat evolved in the formation of a compound, does not exactly measure the force driving the atoms together, except perhaps, at the absolute zero of temperature. Further, the heats of formation of compounds as given in the text-books are not the *true* heats of formation, but are merely *difference* effects which may be positive or negative—where the true heats of formation must be always positive. For example, when hydrogen combines with iodine, the change is not simply

$$H + I = HI$$

but is a double decomposition; thus:

$$\left.\begin{matrix}H\\H\end{matrix}\right\} + \left.\begin{matrix}I\\I\end{matrix}\right\} = \left.\begin{matrix}H\\I\end{matrix}\right\} + \left.\begin{matrix}H\\I\end{matrix}\right\}.$$

Now, if the heat required to effect the separation of H from H, and I from I, is greater than the amount of heat generated when 2H combines with 2I, then the result will be negative.

Hence it is apparent that even in those cases of chemical action in which an evolution of heat is actually observed, this heat represents only the surplus energy remaining over after the breaking up of the molecules of the original substances employed in the experiment. In fact it is only when the heat evolved in the formation of a compound is very great, that it can be taken as measuring approximately the attractive forces, for in this case the incidental errors become small in comparison with the quantity of heat evolved. Bearing these limitations in mind, the conformance to the above law which appears (as we will immediately show) when we contrast the quantities I have evolved when the atoms of chemically similar elements unite with the same radicle, must be regarded as nothing else than surprising.

1. Chemically Unlike Elements

When we contrast chemically unlike elements the relations

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \ldots\ldots = \frac{f_n}{f_n'} = K$$

are not even remotely satisfied, and K varies widely and irregularly for every different ratio.

As typical pairs of unlike elements, we will contrast H with Cl, on the one hand, O with I on the other. In neither case are the relations satisfied.

Hydrogen and Chlorine

$(\mathrm{H}, \mathrm{Li}) = 21.6 = f_1'$	$(\mathrm{Cl}, \mathrm{Li}) = 94 = f_1$
$(\mathrm{H}, \mathrm{Na}) = 13 = f_2'$	$(\mathrm{Cl}, \mathrm{Na}) = 98 = f_2$
$(\mathrm{H}, \mathrm{C}^{1}/_{4}) = 5.4 = f_3'$	$(\mathrm{Cl}, \mathrm{C}^{1}/_{4}) = 13.5 = f_3$
$(\mathrm{H}, \mathrm{Si}^{1}/_{4}) = 8.2 = f_4'$	$(\mathrm{Cl}, \mathrm{Si}^{1}/_{4}) = 39 = f_4$
$(\mathrm{H}, \mathrm{N}^{1}/_{3}) = 4.0 = f_5'$	$(\mathrm{Cl}, \mathrm{N}^{1}/_{3}) = -13 = f_5$
$(\mathrm{H}, \mathrm{P}^{1}/_{3}) = 3.86 = f_6'$	$(\mathrm{Cl}, \mathrm{P}^{1}/_{3}) = 25 = f_6$
$(\mathrm{H}, \mathrm{As}^{1}/_{3}) = -12.2 = f_7'$	$(\mathrm{Cl}, \mathrm{As}^{1}/_{3}) = 24 = f_7$
$(\mathrm{H}, \mathrm{Sb}^{1}/_{3}) = -28.1 = f_8'$	$(\mathrm{Cl}, \mathrm{Sb}^{1}/_{3}) = 30.46 = f_8$
$(\mathrm{H}, \mathrm{O}^{1}/_{2}) = 34.2 = f_9'$	$(\mathrm{Cl}, \mathrm{O}^{1}/_{2}) = -9 = f_9$
$(\mathrm{H}, \mathrm{S}^{1}/_{4}) = 2.3 = f_{10}'$	$(\mathrm{Cl}, \mathrm{S}^{1}/_{4}) = 6 = f_{10}$

Whence

$$\frac{f_1}{f_1'} = \frac{94}{21.6} = 4.3$$

$$\frac{f_2}{f_2'} = \frac{98}{13} = 7.5$$

$$\frac{f_3}{f_3'} = \frac{13.5}{5.4} = 2.3$$

$$\frac{f_4}{f_4'} = \frac{39}{8.2} = 4.7$$

$$\frac{f_5}{f_5'} = \frac{-13}{4.0} = -3.2$$

$$\frac{f_6}{f_6'} = \frac{25}{3.86} = 6.5$$

$$\frac{f_7}{f_7'} = \frac{24}{-12.2} = -1.9$$

$$\frac{f_8}{f_8'} = \frac{30.46}{-28.1} = -1$$

$$\frac{f_9}{f_9'} = \frac{-9}{34.2} = -0.26$$

$$\frac{f_{10}}{f_{10}'} = \frac{6}{2.3} = 2.6$$

Hence K takes in succession each of the following values: 4.3, 7.5, 2.3, 4.7, —3.2, 5.5, —1.9, —1, —0.26, 2.6.

The ratio is in no case constant but varies widely and irregularly. The varying of K would be very much greater if we only knew the H.F. of all the corresponding compounds; but as a matter of fact experimental difficulties limit the determination of the H.F. of compounds only to those which are stable enough to exist at an ordinary temperature. Many compounds of chlorine are known of great stability, whereas the corresponding hydrides are too unstable to exist at ordinary temperatures, *e.g.*, $\mathrm{PbCl_2}$ and $\mathrm{PbH_2}$.

Iodine and Oxygen

$(\mathrm{H}, \mathrm{I}) = -6 = f_1'$ $\qquad (\mathrm{H}, \mathrm{O}^{1}/_{2}) = 34.2 = f_1$

$(\mathrm{I}, \mathrm{Cu}) = 17.6 = f_2'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Cu}^{1}/_{2}) = 18.6 = f_2$

$(\mathrm{I}, \mathrm{Ag}) = 14 = f_3'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Ag}) = 3 = f_3$

$(\mathrm{I}, \mathrm{Li}) = 64 = f_4'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Li}) = 70.6 = f_4$

$(\mathrm{I}, \mathrm{Mg}^{1}/_{2}) = 42.4 = f_5'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Mg}^{1}/_{2}) = 70.0 = f_5$

$(\mathrm{I}, \mathrm{Na}) = 69 = f_6'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Na}) = 45.5 = f_6$

$(\mathrm{I}, \mathrm{Hg}^{1}/_{2}) = 11.1 = f_7'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Hg}^{1}/_{2}) = 11.0 = f_7$

$(\mathrm{I}, \mathrm{K}) = 80.1 = f_8'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{K}) = 47.4 = f_8$

$(\mathrm{I}, \mathrm{Ca}^{1}/_{2}) = 53.6 = f_9'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Ca}^{1}/_{2}) = 72.4 = f_9$

$(\mathrm{I}, \mathrm{Sr}^{1}/_{2}) = 71.7 = f_{10}'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Sr}^{1}/_{2}) = 64.2 = f_{10}$

$(\mathrm{I}, \mathrm{Cl}) = 2.1 = f_{11}'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Cl}) = -9 = f_{11}$

$(\mathrm{I}, \mathrm{S}) = 5.0 = f_{12}'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{S}^{1}/_{4}) = 17.7 = f_{12}$

$(\mathrm{I}, \mathrm{As}^{1}/_{3}) = 9.5 = f_{13}'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{As}^{1}/_{3}) = 25.27 = f_{13}$

$(\mathrm{I}, \mathrm{Si}^{1}/_{4}) = 14.5 = f_{14}'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Si}^{1}/_{4}) = 54.8 = f_{14}$

$(\mathrm{I}, \mathrm{Pb}^{1}/_{2}) = 22.1 = f_{15}'$ $\qquad (\mathrm{O}^{1}/_{2}, \mathrm{Pb}^{1}/_{2}) = 25.1 = f_{15}$

Whence

$\frac{f_1}{f_1'} = \frac{34.2}{-6} = -5.7$ $\qquad \frac{f_8}{f_8'} = \frac{47.4}{80.1} = 0.59$

$\frac{f_2}{f_2'} = \frac{18.6}{17.6} = 1.06$ $\qquad \frac{f_9}{f_9'} = \frac{72.4}{53.6} = 1.35$

$\frac{f_3}{f_3'} = \frac{3}{14} = 0.21$ $\qquad \frac{f_{10}}{f_{10}'} = \frac{64.2}{71.7} = 0.89$

$\frac{f_4}{f_4'} = \frac{70.6}{64} = 1.10$ $\qquad \frac{f_{11}}{f_{11}'} = \frac{-9}{2.1} = -4.3$

$\frac{f_5}{f_5'} = \frac{70.0}{42.4} = 1.65$ $\qquad \frac{f_{12}}{f_{12}'} = \frac{17.7}{5.0} = 3.54$

$\frac{f_6}{f_6'} = \frac{45.5}{69} = 0.66$ $\qquad \frac{f_{13}}{f_{13}'} = \frac{25.77}{9.5} = 2.7$

$\frac{f_7}{f_7'} = \frac{11}{11.1} = 0.99$ $\qquad \frac{f_{14}}{f_{14}'} = \frac{54.8}{14.5} = 3.78$

$$\frac{f_{15}}{f_{15}'} = \frac{25.1}{22.1} = 1.14$$

K, therefore, takes any of the following values: —5.7, 1.06, 0.21, 1.10, 1.65, 0.66, 0.99, 0.59, 1.35, 0.89, —4.3, 3.54, 2.7, 3.78, 1.14, and hence is not even remotely constant.

An examination of the corresponding compounds of any two dissimilar elements will reveal the same peculiarity.

2. Chemically Similar Elements

When, however, we contrast chemically similar elements, a very different relationship is observed. K remains approximately constant.

Chlorine and Bromine

$(Cl, Cu) = 32.9 = f_1$	$(Br, Cu) = 25 = f_1'$
$(Cl, Ag) = 29.2 = f_2$	$(Br, Ag) = 22.7 = f_2'$
$(Cl, Li) = 93.8 = f_3$	$(Br, Li) = 80 = f_3'$
$(Cl, Na) = 97.7 = f_4$	$(Br, Na) = 85.8 = f_4'$
$(Cl, K) = 105.6 = f_5$	$(Br, K) = 95.3 = f_5'$
$(Cl, Ca^1/_2) = 84.6 = f_6$	$(Br, Ca^1/_2) = 70.4 = f_6'$
$(Cl, Sr^1/_2) = 92.3 = f_7$	$(Br, Sr^1/_2) = 78.8 = f_7'$
$(Cl, Ba^1/_2) = 97.3 = f_8$	$(Br, Ba^1/_2) = 85.0 = f_8'$
$(Cl, Zn^1/_2) = 48.6 = f_9$	$(Br, Zn^1/_2) = 40.0 = f_9'$
$(Cl, Hg^1/_2) = 27.2 = f_{10}$	$(Br, Hg^1/_2) = 20.3 = f_{10}'$
$(Hg, Cl) = 32.6 = f_{11}$	$(Br, Hg) = 24.5 = f_{11}'$
$(Cl, Al^1/_3) = 53.66 = f_{12}$	$(Br, Al^1/_3) = 41.0 = f_{12}'$
$(Cl, As^1/_3) = 23.8 = f_{13}$	$(Br, As^1/_3) = 19.7 = f_{13}'$
$(Cl, Sb^1/_3) = 30.46 = f_{14}$	$(Br, Sb^1/_3) = 25.63 = f_{14}'$
$(Cl, Pb^1/_2) = 41.0 = f_{15}$	$(Br, Pb^1/_2) = 36.0 = f_{15}'$

Whence

$$\frac{f_1}{f_1'} = \frac{32.9}{25} = 1.32$$

$$\frac{f_2}{f_2'} = \frac{29.2}{22.7} = 1.29$$

$$\frac{f_3}{f_3'} = \frac{93.8}{80} = 1.17$$

$$\frac{f_4}{f_4'} = \frac{97.7}{85.8} = 1.14$$

$$\frac{f_5}{f_5'} = \frac{105.6}{95.3} = 1.11$$

$$\frac{f_6}{f_6'} = \frac{84.6}{70.4} = 1.20$$

$$\frac{f_7}{f_7'} = \frac{92.3}{78.8} = 1.18$$

$$\frac{f_8}{f_8'} = \frac{97.3}{85.0} = 1.15$$

$$\frac{f_9}{f_9'} = \frac{48.6}{40.0} = 1.21$$

$$\frac{f_{10}}{f_{10}'} = \frac{27.2}{20.3} = 1.34$$

$$\frac{f_{11}}{f_{11}'} = \frac{32.6}{24.5} = 1.33$$

$$\frac{f_{12}}{f_{12}'} = \frac{53.66}{71.0} = 1.30$$

$$\frac{f_{13}}{f_{13}'} = \frac{23.8}{19.7} = 1.21$$

$$\frac{f_{14}}{f_{14}'} = \frac{30.46}{25.63} = 1.19$$

$$\frac{f_{15}}{f_{15}'} = \frac{41}{36} = 1.14$$

K is here throughout the series approximately constant, never becoming greater than 1.34 nor less than 1.11.

When we contrast these values of K with the previous values, we see how closely constant K remains. The values of K range in the case of H and Cl from 7.5 to —3.2 and in the case of O and I, from —5.7 to 3.78.

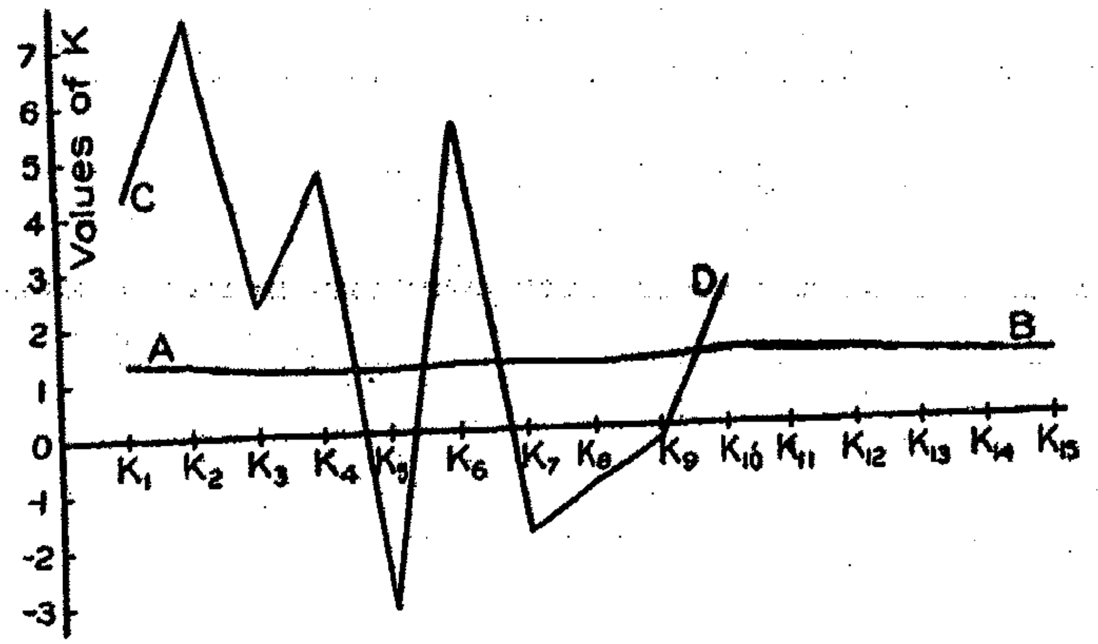

Fig. 1

Showing the approximate constancy of K for similar elements (Cl and Br) and its variation for dissimilar elements (Cl and H).

The erratic line CD records the successive values of K for the system Cl and H. The nearly straight line AB records the successive values of K for the system Cl and Br.

The approximate constancy of K for similar elements, and its variation for dissimilar elements is best demonstrated graphically. Writing K_1 for $\frac{f_1}{f_1'}$; K_2 for $\frac{f_2}{f_2'}$; . . . . . . K_n for $\frac{f_n}{f_n'}$; and taking K_1, K_2, K_3, K_4 . . . . . K_n as abcissae, and the successive numerical values as ordinates, we find for the system Cl and H an erratic line, for the system Cl and Br an almost straight line parallel to the axis of *x* (Fig. 1).

Fluorine and Chlorine

The only data available is the following:

$(\mathrm{F}, \mathrm{Si}^{1}/_{4}) = 67.3 = f_1$ $(\mathrm{Cl}, \mathrm{Si}^{1}/_{4}) = 39.4 = f_1'$

$(\mathrm{F}, \mathrm{H}) = 37.6 = f_2$ $(\mathrm{Cl}, \mathrm{H}) = 22 = f_2'$

Whence:

$$\frac{f_1}{f_1'} = \frac{67.3}{39.4} = 1.71$$

$$\frac{f_2}{f_2'} = \frac{37.6}{22} = 1.70$$

The ratio is, therefore, constant even for such different elements as H and Si.

The large value of K shows, that F possesses the same chemical properties as Cl, but intensified 1.70 times.

Sodium and Potassium

The only data available is the following:

$(K, Cl) = 105.6 = f_1$ $(Na, Cl) = 97.7 = f_1'$
$(K, Br) = 95.3 = f_2$ $(Na, Br) = 85.8 = f_2'$
$(K, I) = 80.1 = f_3$ $(Na, I) = 69.1 = f_3'$
$(K, O^{1/2}) = 47.4 = f_4$ $(Na, O^{1/2}) = 45.5 = f_4'$
$(K, NH_3) = 6.3 = f_5$ $(Na, NH_3) = 5.2 = f_5'$

Whence:

$$\frac{f_1}{f_1'} = \frac{105.6}{97.7} = 1.08 \qquad \frac{f_3}{f_3'} = \frac{80.1}{69.1} = 1.16$$

$$\frac{f_2}{f_2'} = \frac{95.3}{85.8} = 1.11 \qquad \frac{f_4}{f_4'} = \frac{47.4}{45.5} = 1.05$$

$$\frac{f_5}{f_5'} = \frac{6.3}{5.2} = 1.21$$

It will be seen, that here also K is constant and very nearly equal to unity—a fact, which explains the great chemical resemblance of Na and K.

Potassium and Caesium

The only available data is the following:

$(K, Br) = 95.3 = f_1'$ $(Cs, Br) = 99.8 = f_1$
$(K, I) = 80.1 = f_2'$ $(Cs, I) = 86.6 = f_2$

Whence:

$$\frac{f_1}{f_1'} = \frac{99.8}{95.3} = 1.05$$

$$\frac{f_2}{f_2'} = \frac{86.6}{80.1} = 1.08$$

Here again, K is constant and very nearly equal to unity. In the case of all the alkali metals this is so, and this is the reason why there exists such a close resemblance between them.

Zinc and Cadmium

The only data available is the following:

$$(Zn, Cl_2) = 97.2 = f_1 \qquad (Cd, Cl_2) = 93.0 = f_1'$$
$$(Zn, O) = 85.4 = f_2 \qquad (Cd, O) = 75.5 = f_2'$$

Whence:

$$\frac{f_1}{f_1'} = \frac{97.2}{93} = 1.04$$
$$\frac{f_2}{f_2'} = \frac{85.4}{75.4} = 1.13$$

Here again K is constant and nearly equal to unity, which accounts for the close resemblance of Zn and Cd.

Boron and Silicon

The case is of great interest, inasmuch as B and Si possess a great degree of chemical similarity, and yet B is trivalent and Si tetravalent. The chemical similarity of elements does not, in fact, depend upon their valence but solely upon their attractive forces.

The following data—the only available—shows, that K is nearly equal to unity, a fact which explains the remarkable chemical resemblance of these two elements.

$$(B^1/_3, Cl) = 34.70 = f_1' \qquad (Si^1/_4, Cl) = 39.4 = f_1$$
$$(B^1/_3, O^1/_2) = 52.8 = f_2' \qquad (Si^1/_4, O^1/_2) = 54.8 = f_2$$

Hence:

$$\frac{f_1}{f_1'} = \frac{39.4}{34.7} = 1.13$$
$$\frac{f_2}{f_2'} = \frac{54.8}{52.8} = 1.04$$

Calcium and Strontium

$$(Ca^1/_2, Cl) = 84.6 = f_1' \qquad (Sr^1/_2, Cl) = 92.3 = f_1$$
$$(Ca^1/_2, Br) = 70.4 = f_2' \qquad (Sr^1/_2, Br) = 78.8 = f_2$$
$$(Ca^1/_2, I) = 53.6 = f_3' \qquad (Sr^1/_2, I) = 71.7 = f_3$$
$$(Ca^1/_2, O^1/_2) = 65.5 = f_4' \qquad (Sr^1/_2, O^1/_2) = 64.2 = f_4$$
$$^1/_4(Ca, O^2) = 37.6 = f_5' \qquad ^1/_4(Sr, O^2) = 35.5 = f_5$$

Whence:

$$\frac{f_1}{f_1'} = \frac{92.3}{84.6} = 1.09 \qquad \frac{f_3}{f_3'} = \frac{71.7}{53.6} = 1.33$$

$$\frac{f_2}{f_2'} = \frac{78.8}{70.4} = 1.12 \qquad \frac{f_4}{f_4'} = \frac{64.2}{65.5} = 0.98$$

$$\frac{f_5}{f_5'} = \frac{35.5}{37.6} = 0.94$$

Here again K is nearly equal to unity, a fact which explains the chemical resemblance of Ca and Sr.

Strontium and Barium

$$\begin{array}{rr}
(\text{Sr}^1/_2, \text{Cl}) = 92.3 = f_1' & (\text{Ba}^1/_2, \text{Cl}) = 97.3 = f_1 \\
(\text{Sr}^1/_2, \text{Br}) = 78.8 = f_2' & (\text{Ba}^1/_2, \text{Br}) = 85.0 = f_2 \\
(\text{Sr}^1/_2, \text{I}) = 71.7 = f_3' & (\text{Ba}^1/_2, \text{I}) = 72.3 = f_3 \\
(\text{Sr}^1/_2, \text{O}^1/_2) = 64.2 = f_4' & (\text{Ba}^1/_2, \text{O}^1/_2) = 62.1 = f_4 \\
{}^1/_4(\text{Sr}, \text{O}_2) = 35.5 = f_5' & {}^1/_4(\text{Ba}, \text{O}_2) = 34.0 = f_5
\end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{97.3}{92.3} = 1.05 \qquad \frac{f_3}{f_3'} = \frac{72.3}{71.7} = 1.01$$

$$\frac{f_2}{f_2'} = \frac{85.0}{78.8} = 1.08 \qquad \frac{f_4}{f_4'} = \frac{62.1}{64.2} = 0.97$$

$$\frac{f_5}{f_5'} = \frac{34.0}{35.5} = 0.96$$

Here again K is nearly equal to unity, which accounts for the great chemical similarity of Sr and Ba.

Nickel and Cobalt

The only available data is the following:

$$\begin{array}{rr}
(\text{Ni}^1/_2, \text{Cl}) = 37.2 = f_1' & (\text{Co}^1/_2, \text{Cl}) = 38.2 = f_1 \\
(\text{Ni}^1/_2, \text{Se}^1/_2) = 9.21 = f_2' & (\text{Co}^1/_2, \text{Se}^1/_2) = 9.64 = f_2 \\
(\text{Ni}^1/_2, \text{Te}^1/_2) = 7.55 = f_3' & (\text{Co}^1/_2, \text{Te}^1/_2) = 7.65 = f_3
\end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{38.2}{37.2} = 1.02$$

$$\frac{f_2}{f_2'} = \frac{9.64}{9.21} = 1.05$$

$$\frac{f_3}{f_3'} = \frac{7.65}{7.55} = 1.01$$

Here again K is constant and very nearly equal to unity, as we should expected from the remarkable chemical resemblance of Co to Ni.

Antimony and Bismuth

The data available is meagre:

$(Sb^1/_3, Cl) = 30.46 = f_1$ $(Bi^1/_3, Cl) = 30.21 = f_1'$
$(Sb^2, O^3, 3H_2O) = 167.52 = f_2$ $(Bi^2, O^3, 3H_2O) = 137.74 = f_2'$

Whence:

$$\frac{f_1}{f_1'} = \frac{30.46}{30.21} = 1.01$$

$$\frac{f_2}{f_2'} = \frac{167.4}{137.4} = 1.21$$

The preceding pages contain practically all the available thermal data for comparing the corresponding compounds of chemically similar elements. In every case where elements possess a great degree of similarity, K is approximately constant, and very often nearly unity. And in every case where elements differ widely in their chemical properties, precisely the reserve holds true.

University of Kiel.

ON THE USE OF THE DIFFERENTIAL EQUATION IN CALCULATING THE RESULTS OF KINETIC MEASUREMENTS; THE REACTION BETWEEN ARSENIC ACID AND POTASSIUM IODIDE NEAR THE EQUILIBRIUM

BY W. C. BRAY

Introduction

I. The Method

According to the present view that the rate of a reaction is proportional to the concentration of the "reacting" substances, the fundamental equation[1] in kinetics is

$$\frac{dx}{dt} = K(A-x)^n (B-x)^m \ldots \qquad \text{I}$$

To test the correctness of the formula assumed in any special case, it is customary to calculate K from the derived integral equation.

Many rates have, however, been measured which cannot be expressed by any simple form of Equation I. (On account of the large number of reactions which do obey this law it has been concluded in such cases that complicated reactions take place, not that the fundamental equation has ceased to be of general application.) When, for example, two independent reactions take place at the same time, the differential equation is the sum of two simple terms; and in the neighborhood of an equilibrium the rate measured is a difference of two rates. The differential equation will, therefore, have the following form,

$$\frac{dx}{dt} = \frac{dx_1}{dt} \pm \frac{dx_2}{dt} = K_1(A_1-x_1)^{n_1}(B_1-x_1)^{m_1} \ldots \pm K_2(A_2-x_2)^{n_2}(B_2-x_2)^{m_2} \ldots \qquad \text{II}$$

In the majority of such cases[2] the integrated expression will

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[1] A, B, x, t, have their usual meaning, cf. p. 574.

[2] For methods of finding the law governing complicated reactions see Mellor: "Chemical Statics and Dynamics," p. 55 (1904).

be so complicated that it will be difficult and often impossible to obtain values for the constants of the single reactions. In these cases it is convenient to use the differential equation directly. In the following paper a method of doing so has been described, and examples of its application given.

Especial attention has been paid to the calculation of the constant in the neighborhood of the equilibrium, when the rate of the reverse reaction is not negligible. A detailed example is given in the second part of this paper (see p. 578).

The determination of $\frac{dx}{dt}$

From the form of the fundamental equation (I), it is evident that K may be calculated if $\frac{dx}{dt}$ is known, assuming of course that A, B, . . the initial concentrations, and x the amount of change in time t are given. When the differential equation is more complicated, as in (II), it is only a question of obtaining a sufficient number of rate measurements for varying concentrations of the reacting substances to be able to calculate the different K's accurately. The problem then is to determine $\frac{dx}{dt}$ at any time.

The formula $\frac{dx}{dt} = \frac{x_2 - x_1}{t_2 - t_1}$ where t_1, x_1, and t_2, x_2 are the results of two successive measurements, is not of general application, as it is only in exceptional cases that the rate is practically constant between the measurements. But by taking a sufficiently large quantity of the reacting mixture for each analysis, so that the actual change of concentration is small while the total change is large enough to measure accurately, it is often possible to obtain an accurate measure of the rate with this formula. From a series of such measurements it is easy to determine the order of a reaction.[1] The name "Method of constant rates" which I used in a former paper in describing this method[2] was suggested by Professor W. Lash Miller.

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[1] See Mellor: Loc. cit. Van't Hoff was the first to point out how this could be done.

[2] Bray. Jour. Phys. Chem. 7, 92 (1903).

The rate $\frac{dx}{dt}$ can always be obtained graphically. When the results are plotted in the (t, x) diagram, the ratio $\frac{dx}{dt}$ may be obtained by drawing the tangent at the point (t, x). The accuracy of the determination depends upon the number of measurements and on the care with which the diagram is constructed. This method is very simple, but has seldom been used.

The corresponding analytical method is to obtain by trial *any* simple function of A, B, x, t, which represents the course of the curve in the neighborhood of the point (t, x) and to obtain $\frac{dx}{dt}$ by differentiation. The simplest case is when this function is closely related to the more-complicated final function, *e. g.*, when it is the integral of a differential equation of the form $\frac{dx}{dt} = k(A - x)^n$, where n is a small integer.

The method. A simple example

Let the course of a reaction be expressed by the formula

$$\frac{dx}{dt} = K(A - x)\ (B - x)^2. \qquad \text{(III)}$$

In the simple case, when B is large compared with A, the equation $\frac{dx}{dt} = k_1(A - x)$ may also be used to represent the course of the reaction; k_1 may be easily calculated from the equation,

$$k_1 = \left(\frac{1}{t}\right) \mathit{ln\ nat}\ \frac{A}{(A - x)};\ \text{and } K = \frac{k_1}{B^2}.$$

The method used in the following calculations is merely an extension of the principles used in this well-known example. A preliminary "constant" k is calculated from as simple an equation as possible, and the final constant is derived from it by means of the differential equation. It is not necessary that this preliminary k be constant; in general it will show a decided tendency to decrease or increase. But the rate, $\frac{dx}{dt}$ at a given time can *always be accurately calculated* when the value of k at this time is accurately known. It is evident that k must be calculated from pairs of consecutive measurements, and not, as is the usual way, by comparing each measurement with the initial measurement. On account of the increased error in k resulting from this calculation it is advisable to plot the values of k and t, and to replace the zigzag curve by a continuous one.

To illustrate the method let us consider that B in the above example is only three times as large as A. The "constant" k will decrease rapidly as the reaction progresses. Let k_1 be the value of the constant at the point $(t_1, {}_1x)$, k_2 at the point (t_2, x_1), ... Then at the time t_1, $\frac{dx}{dt} = k_1 (A - x_1)$, and $= k_2(A - x_2)$ at the time t_2. But at these times $\frac{dx}{dt} = K (A - x_1) (B - x_1)^2$, and $K(A - x_2) (B - x_2)^2$, respectively. Hence

$$K = \frac{k_1}{(B - x_1)^2} = \frac{k_2}{(B - x_2)^2}.$$

Thus K is obtained in a much simpler manner than if the values of t and x had been substituted in the integral of Equation III.

$$Kt = \frac{1}{(B - A)^2}\left(ln\frac{A}{A - x} - ln\frac{B}{B - x}\right) - \frac{1}{B - A}\left(\frac{1}{B - x} - \frac{1}{B}\right).$$

It is evident that practically the same results for K would have been obtained if the preliminary constants had been calculated from the integral of the formula $\frac{dx}{dt} = k(A - x)^2$. In this case K would have been equal to $\frac{k(A - x)}{(B - x)^2}$.

An application of the method

The method may be used to test if the course of the reaction can be better expressed by another formula than the one used in calculating the results. As an example, let a set of values of K, calculated on the assumption that

$$\frac{dx}{dt} = K(A - x) (B - x)^2,$$

be given. If we wish to test the formula $\frac{dx}{dt} = K'(A - x)^2(B - x)$, then the values of K′ may be obtained from the values of K by means of the equation

$$K' = \frac{K(B - x)}{(A - x)}.$$

In general the use of this method in such cases will lessen the labor of calculation very considerably. It is scarcely necessary to repeat that the values of K must be calculated from pairs of consecutive measurements.

The calculation of the constant in the neighborhood of an equilibrium

The rate of a reaction approaching an equilibrium is equal to the difference of two rates. In simple cases, as in the reaction between alcohol and acetic acid, where

$$\frac{dx}{dt} = k(1 - x)^2 - k'x^2$$

and $\frac{k}{k'} = 4$, or in the same reaction in an alcohol-water mixture, where $\frac{dx}{dt} = k_1, (1 - x) - k_1' x$, the equation may be integrated.[1] But when the order of the reactions is greater than the second, the integration is either impossible or gives a very complicated expression. The method described in the following paragraph is of general application, and as the example in Part II shows, is capable of giving accurate results.

In general at least one of the reactions may be measured at such a distance from the equilibrium that the reverse rate is negligible; the order of the reaction and its constant may then be determined in the usual way. The order of the other reaction may be derived from this result and the equilibrium formula, or may itself be determined at a distance from the equilibrium. But when it is necessary to make measurements where the reverse rate is not negligible, the constants, which are calculated

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[1] Nernst. Theor. Chemie, 4th ed. p. 560 (1903).

on this assumption, will decrease more or less rapidly as the reaction proceeds and the error due to the reverse reaction increases. As in the above examples, however, the actual rate at any time, $\frac{dx}{dt}$ measured, may be calculated from the preliminary constants. And when the reverse reaction has already been measured, the correction for the reverse rate, $\frac{dx}{dt}$ correction, may be calculated. The sum of these two rates gives the theoretical rate of the direct reaction, from which the desired constant K may be obtained.

$$K = k\left(\frac{\frac{dx}{dt}\text{ measured} + \frac{dx}{dt}\text{ correction}}{\frac{dx}{dt}\text{ measured}}\right).$$

Here as before the preliminary k's must be calculated from pairs of consecutive measurements.

II. The Reaction between Arsenic Acid and Potassium Iodide Near the Equilibrium

The method has been tested by means of the velocity measurements of the reaction between arsenic acid and potassium iodide in acid solution.[1]

The reverse rate, the reaction between arsenious acid and iodine (see Part I of the original paper), is accurately expressed by the equation

$$\frac{d(\text{Iodine})}{dt} = \frac{k(\text{arsenious acid})\ (\text{tri-iodion})}{(\text{sulphuric acid})\ (\text{potassium iodide})^2} \qquad \text{(IV)}$$

k in the unit chosen = 0.28.

The measurements were made under such conditions that the rate of the arsenic acid reaction was practically negligible throughout the whole series of experiments. I found on calculating the error in the last measurements of each table that it was very small except in the last two measurements of Tables IV, XIII, XIV, and XVI, and that even in these cases it was not large enough to change the results in any way.

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

The concentrations in the above equation (IV) are the analytical, not the ionic concentrations. Under the conditions of the experiments, the concentrations of the ions I_3', $H^{\cdot}$, and I' are practically proportional to the corresponding analytical concentrations, and it is clear that these ions may be considered the "reacting" substances. On the other hand it is the concentration of the undissociated[1] arsenious acid that is proportional to the analytical concentration; and it seems probable that the undissociated acid takes part in the reaction, and not an ion as AsO_3''' or H_2AsO_3'.

The formula found for the equilibrium and the theory of the intermediate formation of hypoiodite, advanced to explain the results, required the reaction between arsenic acid and iodine ion to follow the law:

$$\frac{d(\text{iodine})}{dt} = k_6(\text{arsenic acid})\ (\text{potassium iodide})\ (\text{sulphuric acid}) \quad \text{V}.$$

Although the agreement was a remarkable one, the results left much to be desired: the rate was not strictly proportional to the potassium iodide or sulphuric acid concentrations, and the value found for k_5, 0.326×10^{-6}, was smaller than the theoretical value, 1.9×10^{-6}.

The decrease in the constants in Tables XVIII, XIX, XXVIII, and XXIX, which became much more marked when the calculations were made with pairs of consecutive results, led to the discovery that the rate of the arsenious acid reaction in these experiments was not negligible. The results of the recalculation (see following tables), showed that a higher value for k_6 must be assumed, and that in dilute potassium iodide solution the rate is strictly proportional to the first power of the iodine ion concentration.

The numbers of the tables refer to the original paper, and the same nomenclature is used. V is the volume in liters, C, D, E, represent the number of units of potassium iodide, sul-

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[1] The undissociated arsenious acid molecule contains only one combining weight of arsenic. Zawidzki. Ber. chem. Ges. Berlin, 36, 1427 (1903); Brunner and St. Tolloczko: Zeit. anorg. Chem. 37, 455 (1903).

phuric acid, and arsenic acid used in each experiment. One unit arsenic acid in 1 liter gives a 0.01 molar H_3AsO_4 solution; and the other units are chosen so that 1 unit potassium iodide and 1 unit sulphuric acid react with 1 unit arsenic acid according to the following equation,

$$3\,I' + 2H^{\cdot} + H_3AsO_4 = H_3AsO_3 + I_3' + H_2O.$$

The number of units of iodine x formed in the time t, given in the first column, is taken from the original tables.

The second column contains the values for the constant k_1', recalculated from pairs of consecutive measurements. The fact that these values may be used without further correction to obtain the rate, $\frac{dx}{dt}_{\text{measured}}$, is a proof of the accurate nature of the experimental work.

$\frac{dx}{dt}_{\text{measured}}$, (in third column), $= 2.3k_1'(C - x)$ in Tables XVIII and XIX.

$= 2.3k_1'(E - x)$ in the other Tables.

$\frac{dx}{dt}_{\text{correction}}$, (in fourth column), $= \frac{k_3 x_1 2V}{(C - x)^2 (D - x)}$, where $k_3 = 0.28$.

k_1'', (in the fifth column), =

$$k_1' \left(\frac{\frac{dx}{dt}\text{ measured} + \frac{dx}{dt}\text{ correction}}{\frac{dx}{dt}\text{ measured}} \right)$$

k_3, (in the last column), $= \frac{2.3\,k_1''\,V^2}{(E - x)\,(D - x)}$, in Tables XVIII and XIX.

$= \frac{2.3\,k_1''\,V^2}{(C - x)\,(D - x)}$, in the remaining tables.

TABLE XVIII

C, 0.1385; D, 22.85; E, 1.16; V, 0.12

x	$k_1' \times 10^3$ recalculated	$\frac{dx}{dt} \times 10^4$		$k_1'' \times 10^3$ corrected	$k_5 \times 10^6$
		measured	correction		
0.0095	—	—	—	—	—
0.0172	11.1	30.9	0.36	11.2	1.71
0.0255	11.9	30.9	0.80	12.2	1.87
0.0361	10.3	24.2	1.80	11.0	1.71
0.0515	9.87	19.8	5.26	12.5	1.96
0.0594	3.91	7.10	8.2	8.4	1.33
0.0648	3.08	5.22	11.4	9.8	1.93

TABLE XIX

C, 0.1385; D, 22.85; E, 0.580; V, 0.12

x	$k_1' \times 10^3$	$\frac{dx}{dt} \times 10^4$		$k_1'' \times 10^3$	$k_5 \times 10^6$
		measured	correction		
0.0066	—	—	—	—	—
0.0125	6.31	14.6	0.24	6.42	1.56
0.0226	5.52	14.7	0.50	5.71	1.78
0.0361	6.01	14.1	1.80	6.77	2.17
0.0427	3.89	8.6	2.9	5.20	1.69
0.0523	4.28	8.7	5.5	7.15	2.38
0.0575	2.79	5.2	7.5	6.82	2.27
0.0613	1.74	3.1	9.3	6.98	2.34

TABLE XXIII

C, 0.644; D, 22.85; E, 0.136; V, 0.12

x	$k_1' \times 10^3$	$\frac{dx}{dt} \times 10^4$		$k_1'' \times 10^3$	$k_5 \times 10^6$
		measured	correction		
0.00386	—	—	—	—	—
0.0326	7.80	—	—	7.80	2.23
0.0460	5.75	—	—	5.75	1.67
0.0614	8.00	—	—	8.00	2.38
0.0751	7.00	9.70	0.22	7.16	2.19
0.0871	6.06	6.93	0.36	6.38	2.00
0.0989	5.21	4.20	0.48	5.77	1.86
0.1095	5.04	3.07	0.62	6.17	2.02
0.1173	3.37	1.48	0.74	5.06	1.69
0.1206	2.28	0.80	0.79	4.51	1.51

TABLE XXVI

C, 1.88; D, 9.15; E, 0.290; V, 0.13

x	$k_1' \times 10^3$	$\frac{dx}{dt} \times 10^4$		$k_1'' \times 10^3$	$k_5 \times 10^6$
		measured	correction		
0.0085	—	—	—	—	—
0.0140	1.90	—	—	1.90	0.55
0.0309	2.14	—	—	2.14	0.64
0.0517	2.11	—	—	2.11	0.64
0.0689	2.14	10.9	0.058	2.16	0.66
0.0967	—	—	—	—	—
0.123	2.06	7.91	0.198	2.12	0.67
0.141	1.98	6.78	0.26	2.05	0.66
0.166	1.90	5.42	0.38	2.03	0.67
0.191	2.17	4.94	0.52	2.40	0.80
0.212	1.95	3.24	0.65	2.34	0.80

TABLE XXVIII

C, 2.270; D, 2.293; E, 0.310; V, 0.155

x	$k_1' \times 10^4$	$\frac{dx}{dt} \times 10^5$		$k_1'' \times 10^4$	$k_5 \times 10^6$
		measured	correction		
0.00161	—	—	—	—	—
0.0107	2.30	—	—	2.3	0.38
0.0122	2.53	—	—	2.5	0.43
0.0434	2.16	13.2	0.73	2.3	0.40
0.113	1.88	8.42	5.46	3.1	0.56
0.122	1.11	4.50	6.45	2.7	0.49
0.137	1.42	5.65	8.30	3.5	0.65
0.164	1.17	3.70	12.36	5.1	0.97
0.171	0.57	1.70	13.56	5.1	0.98

TABLE XXIX

C, 2.270; D, 1.147; E, 0.310; V, 0.155

x	$k_1' \times 10^4$	$\frac{dx}{dt} \times 10^6$		$k_1'' \times 10^4$	$k_5 \times 10^6$
		measured	correction		
0.00092	—	—	—	—	—
0.00551	—	—	—	—	—
0.0170	0.82	5.75	0.21	0.85	0.29
0.0602	0.99	5.67	2.96	1.50	0.53
0.0680	0.77	4.40	3.84	1.44	0.52
0.0776	0.69	3.70	5.10	1.64	0.60
0.0989	0.40	2.00	8.60	2.14	0.80
0.1020	0.20	0.95	9.37	2.13	0.81

Tables XVIII and XIX, in which the concentration of the potassium iodide is small compared with the sulphuric and arsenic acids, show that the constant *does not decrease* as the reaction progresses, and that under these conditions the rate is proportional to the first power of the iodine ion concentration. The values for k_5, between 1.7 and 2.1×10^{-6}, are in good agreement with the theoretical value calculated from k_3 and the equilibrium constant.

In Table XXIII the initially high value of $k_5 = 2.1 \times 10^{-6}$ appears to decrease as the reaction progresses.

The initial value of k_5 in Table XXVI, 0.6×10^{-6}, is very small. It, however, appears to increase as the reaction proceeds and the equilibrium is approached. In Tables XXVIII and XXIX, where the initial value of k_5 is still smaller, and the error due to the reverse reaction greater, this increase of k_5 is very marked.

In the remaining Tables, XX–XXX, the error due to the reverse rate at the last measurements never exceeds 10 percent, and the constants are practically constant in each table, although different values are obtained in the different tables. The following table gives a summary of the results of the recalculations. The average initial values of k_1 and k_5, and the average final values of k_5 are given. The "percent error" at the last measurement $= 100 \dfrac{\dfrac{dx}{dt}\text{ measured}}{\dfrac{dx}{dt}\text{ correction}}$ is given in the last column. The last column refers to the change in the value of k_5 during the reaction. +, ++, and — mean an increase, a great increase, and a decrease, respectively. In the remaining cases, k_5 is constant.

SUMMARY, TABLES XVIII TO XXX.

Table	C	D	E	V	Initial values		Final value $k_5 \times 10^6$	Per-cent error	Re-marks k_5
					$k_1 \times 10^5$	$k_5 \times 10^6$			
XVIII	0.1385	22.85	1.16	0.12	11.7	1.8	1.7	218	
XIX	0.1385	22.85	0.58	0.12	6.0	1.8	2.3	300	+
XX	5.64	9.4	0.29	0.13	10.4	1.04	—	2	
XXI	3.76	9.4	0.29	0.13	5.6	0.85	1.0	10	+
XXII	1.288	22.85	0.136	0.12	18.1	2.63	—	2	
XXIII	0.644	22.85	0.136	0.12	7.0	2.10	1.6	98	—
XXIV	1.88	18.25	0.29	0.13	9.7	1.52	1.8	10	+
XXV	1.88	13.7	0.29	0.13	5.0	1.01	—	10	
XXVI	1.88	9.15	0.29	0.13	2.08	0.64	0.8	20	+
XXVII	3.76	4.70	0.29	0.13	1.74	0.51	0.7	2	+
XXVIII	2.27	2.293	0.31	0.155	0.238	0.40	0.98	800	++
XXIX	2.27	1.147	0.31	0.155	0.085	0.29	0.81	965	++
XXX	1.88	18.75	0.29	0.26	0.96	1.12	—	3	

The values obtained for k_5 are practically constant in each experiment as long as the error due to the arsenious acid reaction is negligible. This proves that the rate of the reaction is proportional to the first power of the arsenic acid concentration. Owing to the presence of excess of hydrogen ions, the dissociation of the arsenic acid, although very small, remains constant during each experiment; and the reacting substance may be an ion (as H_2AsO_4'), or the undissociated acid. The evidence seems to be in favor of the latter view, although for the present the question must remain an open one.

The initial values of k_5 vary in the different experiments between 0.3×10^{-6} and 2.6×10^{-6}, which shows that the rate is not proportional to the concentration of the sulphuric acid or the potassium iodide in the somewhat concentrated solutions used. (Sulphuric acid is nearly four times normal in Table XXIII.)

The change in the rate produced by varying the initial concentrations is most easily determined by comparing the initial values of k_1 in the different experiments in the above table. As these constants are practically the same as the constants given in the original paper, the relationships given in that paper remain unaltered. The agreement with the theoretical order of the reaction is much better in dilute solutions than in concentrated, and Roebuck concluded that the reaction corresponding to Equation V was a limiting case which could only be realized in dilute solutions. The new result that in a dilute solution of potassium iodide the rate is proportional to the first power of the potassium iodide concentration agrees with this view. The constant k_2 in dilute solutions is, however, smaller than the theoretical value.

No satisfactory explanation why the simple reaction should not show its theoretical order has been found. It is true that these solutions are often fairly concentrated and contain large quantities of neutral salts, but the departure from the theoretical order appears to be too great to be explained by this cause alone. In such cases it is customary to assume that a second independent reaction takes place. It is quite possible that a formula containing two terms might be found to express the results. The second reaction would have to be of the second or higher order with respect to the potassium iodide and sulphuric acid concentrations. Attempts to construct such a formula and speculations on the nature of the second reaction seem at present useless. Here again the small value of the constant does not agree with the explanation. If two independent reactions take place, the constant ought to be greater than the theoretical constant, because the equilibrium measurements were not made under conditions where the second reaction could have much influence.

The possibility suggests itself that the equilibrium constant, and perhaps the function itself used to express the equilibrium, may not be correct. Although this is not probable, further experimental work along this line seems necessary. The effect produced upon the constant by changing the concentrations of the hydrogen and iodine *ions* ought also to be measured. The possibility that an error has been made in determining the equilibrium constant is, however, very much lessened by the following result.

As the reaction approaches the equilibrium, k_5 in each of the experiments tends to assume a limiting value between 0.8×10^{-6} and 2.3×10^{-6}. This means that k_5 in the neighborhood of the equilibrium seems to agree with the thoeretical value calculated from the equilibrium constant, and the constant k_3 of the arsenious acid reaction. The fact that k_5 remains constant in some experiments, in others increases, and in another decreases, is strong evidence that the correction applied for the reverse rate is accurate; in other words, we have no evidence that the formula which was obtained for the arsenious acid reaction at a distance from the equilibrium does not apply near the equilibrium.

It will be interesting to see if further experimental work will confirm this result—that k_5 tends towards the theoretical value. If it proves to be true,[1] then there is a much better agreement with the theory. The theoretical reaction takes place near the equilibrium, and probably at a distance from the equilibrium in dilute solutions. In the latter case it must be assumed that the rate of the reaction is retarded in some yet unknown way. The higher values of the constants in the concentrated solution may mean that this unknown influence ceases to have an effect in the concentrated solutions or that a second reaction is taking place, as explained above. The assumptions that, as the equilibrium is approached, the constant of the reaction can change, or that a complete change can take place in the nature of the reaction, are neither impossible nor improbable.

The final result then of the recalculations is that there is a better agreement with the theory than was claimed in the

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[1] As the equilibrium constant is itself not perfect, it is not to be expected that the limiting value for k_5 will be identically the same in the different experiments.

original paper. The rate is proportional to the first power of the potassium iodide concentration in dilute solution; the theoretical reaction appears to take place in the neighborhood of the equilibrium; and a higher value for k_5 than 0.326×10^{-6} must be assumed. Considering the complicated nature of the reactions, and the fact that the solutions are fairly concentrated and contain large quantities of neutral salts, the agreement is remarkable. It is, however, not a perfect one, and there are a number of difficult problems which can only be solved by further experimental work. Mr. Roebuck has informed me that he has continued his work upon this subject during the past winter and that he expects to publish his results very shortly.

Summary

1. A method had been described for using the differential equation in calculating the results of kinetic measurements. It is of value when the integration is impossible or leads to a very complicated expression.

2. It depends on the determination of $\frac{dx}{dt}$, the rate of a reaction at any time. The methods of determining $\frac{dx}{dt}$ were described.

3. The method was used to calculate the constant in the neighborhood of the equilibrium for the reaction between arsenic acid and potassium iodide in acid solution. The results obtained show that the method is a practical one.

4. It was also pointed out that, when the constants for a set of experimental results have been calculated for one formula, another formula may be tested without integrating the second differential equation. This generally lessens the labor of calculation very considerably.

The calculations on which the above conclusions are based were made in April, 1904.

Leipzig, April, 1905.

NEW BOOKS

Grundzüge der Siderologie. Für Hüttenleute, Maschinenbauer u. s. w. sowie zur Benutzung beim Unterrichte bearbeitet. *By Hanns Freiherr v. Jüptner. 15 × 23 cm. Erster Teil: Die Konstitution der Eisenlegierungen und Schlacken, pp. viii + 315, 1900; Zweiter Teil: Zusammenhang zwischen thermischer und mechanischer Bearbeitung, Konstitution und Eigenschaften der Eisenlegierungen, pp. viii + 408, 1901; Dritter Teil, erste Abteilung: Die Wechselwirkungen zwischen Eisen und verschiedenen Agentien; zweite Abteilung: Die hüttenmannischen Prozesse; pp. xi + 427, 1904. Leipzig: Arthur Felix. Price: paper, I. Band, 13 marks; II. Band, 18 marks; III. Band, 9 marks.*— Vol I. *Constitution of iron alloys and slags.* Part 1. The first book is devoted to the theory of solution as applied to alloys, and in the course of 62 pages the author endeavors to cover the theory necessary to appreciation of the constitution of alloys. This volume, having been issued in 1900, is, of course, considerably out of date. The figures with which the author would illustrate the theory of alloys are, in a number of cases, in error. Apparently the author had grasped only a part of the theory and made rather too great haste to include it in his book. It is scarcely worth while to mention the individual errors which are scattered through the text, such a course requiring practically a complete discussion of the general theory of alloys.

Part 2. Metallography. The microstructure of various iron alloys is given and the author has illustrated the text with many photomicrographs taken from the publications of different investigators. The microstructure of slags is included, the paper being a very brief résumé of Vogt's work on that subject. Vogt's table of slag composition is given, but the discussion of it is too brief to give any idea of what the table means. It is therefore questionable whether there was any advantage in including the table.

Part 3. The chemical composition of iron alloys. We find 130 pages devoted to the discussion of the condition of carbon in iron. We have reviewed the many experiments in which it has been attempted to show the molecular condition of carbon in iron, as well as the experiments where the isolation of the carbides of iron has been undertaken. The results of these various experiments here collected are sufficient to convince any one of the uselessness of the chemical method in attempting to solve such problems. The results are contradictory, though strangely enough, any one author seems to be able to get more or less concordant data. We have also treated the condition of Si, P, S, Cr, Wo, Mo, Cu and O when present in the iron alloys. Needless to state, we know very little more about them than we do about the condition of carbon, and the reader who expects to find the problem illumined will meet with disappointment.

Part 4. The chemical composition of slags. The author has here collected and abstracted the various papers which have been issued on the composition of slags. As a reference to the composition of slags, this part of the book may be of interest. There is, of course, no scientific treatment of the subject, and the writing of hypothetical formulae for the compounds in the slags is scarcely warranted by the data available. In an appendix, the author gives a very valuable index of the literature on the subject.

Vol. II. The author has reviewed Roozeboom's paper on the Constitution of the Iron-Carbon Alloys, and has endeavored by a series of calculations and deductions to show what the constitution of the iron alloys may be. He has very impartially added LeChatelier's criticism of Roozeboom's paper, and has included the evidence obtained by Charpy and others as to the breaking down of cementite with the liberation of graphite. He has then endeavored to give all of the contradictory evidence thus obtained a place in the diagram. Consequently, the author is compelled to make a very large number of assumptions which have not been tested experimentally, and the author's additions to the quite valuable review of current literature on the subject do not assist greatly in the solution of the problem.

In the second part of the book, the author considers the relations between the physical properties and the chemical composition. Here again the work is largely of the nature of an abstract, and as such will be very valuable to those who have not the advantage of a large library readily available.

A discussion of the influence of the various elements on the strength, ductility, elasticity, hardness, etc., completes this part of the book. There is also included a review of Ewing and Rosenhain's work on the development of slipbands in metals under stress. The appendix includes an index of the literature.

Vol. III. *The reactions between iron and the various elements.* After a mathematical statement of the phase rule and the theorem of Le Chatelier, the author reviews the literature which deals with the interaction of iron with oxygen and of iron oxides with various reducing agents. This résumé is very useful as such, but from the reviewer's standpoint, the author has contributed little of value to the discussion. The relation between iron and carbon, phosphorus and sulphur, and between iron and slags is considered. The photomicrographs which are used to illustrate the structure of iron alloys with these various included elements are very good, but were taken largely from papers by other authors. In the final section, the author considers the various reactions of the blast-furnace, the puddling furnace and cementation process. An index of the literature considered may conclude this volume.

In publishing any work on metallurgy, the author is of necessity required to take a large part of his data and many of his conclusions from previous workers in the field, and von Jüptner has here collected all of the most important papers dealing with the subject of iron and steel. In a work of this kind, one can scarcely criticize an author who has collected and abstracted the widely scattered literature on iron and steel. With the author's method of presentation, one may, of course, find fault if one chooses.

Valuable as a book of this kind is to persons denied access to large libraries, it seems a little unfortunate that the author should have taken his data and reprinted them without careful consideration of their relative merits. Thus we find occasional contradictions as to facts, and of course the theories contradict each other frequently. The information gathered has in some cases seemed not to have been digested by the author before including it in his book, and in some cases the desire to outline possible theories which other people may then test experimentally has led the author rather far afield. The student of physical chemistry will find in this book a very satisfactory collection of data on which he may test his ingenuity. From the author's explanation of the physical chemistry of the processes involved, he will probably get very little. The fault is not entirely that of the author. The subject of iron and steel has been worked at from so many points of view and data collected by observers more or less skilful, and for the most part ignorant of the fundamental theory, that it is not surprising that data so gathered should be contradictory, and that many of them should lack the essential qualities necessary to make them of value. Nevertheless, because of the comparatively small compass in which the author has collected so many scattered data, the book is a very desirable one for all physical chemists to possess. *E. S. Shepherd.*

Die Grundlagen der Bewegungslehre von einem modernen Standpunkte aus. *By G. Jaumann. 14 × 22 cm.; pp. vi + 421. Leipzig: Johann Ambrosius Barth, 1905. Price: paper, 11; bound, 12 marks.*—Occasional readers of German scientific periodicals will be surprised at the rapidity with which the vector calculus is superseding all other methods. It has already become bad form to write in Cartesian coördinates, at least if the subject under discussion is treated mathematically at length. The present book is in line with this tendency, and will be welcomed as a self-contained treatise of dynamics in quaternion notation. To assist the reader, chapters on the vector methods are distributed throughout the book, so that the main principles used are developed as they are needed. No doubt the habit of writing a single equation for the three Cartesian equations is an advantage, and if the mind is habituated to the usual polygon interpretation there is a gain of clearness and simplicity. The transformation of such equations is, however, attended with the spice of danger, which induces many cautious or timid people to prefer the more cumbersome methods. Curiously enough it is the vector calculus of J. W. Gibbs, as elaborated in E. B. Wilson's book, which has been largely followed; we say curiously, since it is not so long ago that Prof. Knott, of the Edinburgh school, took the Gibbsian development severely to task. Jaumann, however, introduces modifications of notation of his own—a privilege, it seems, which every adult vector analyst covetously cherishes, but which, nevertheless, has interfered with the general introduction of the vector methods more than any inherent difficulty has done.

Apart from the mathematics, the presentation here given is modern in character in departing from the formal development of Newton's laws. In other words, the endeavor is made to eliminate Newton's irreducible quantity, force, as far as possible. The author shares the belief, which is now quite general, that the newer conquests of physics, like electricity for instance, are much more liable to contribute fundamentally to the development of dynamics, than dynamics will be able to do for the advance of electricity.

The claims of the vector method are well established by the scope of the book, which in about four hundred pages gives a terse account of dynamics, acoustics, hydrodynamics, elastics, viscosity, and even capillarity, in addition to the mathematical notes. It is odd, however, to see figures of highly developed experimental apparatus in a work dealing largely with abstractions.

In conclusion, we cannot too highly recommend this careful treatise to the reader desirous of informing himself on the trend of modern tendencies in dynamics. *Carl Barus.*

The Dynamical Theory of Gases. *By J. H. Jeans. 17 × 27 cm.; pp. vi + 352. New York: The Macmillan Company, 1904. Price: $4.50.*—Some years ago, when questions relating to the equipartition of energy among the molecules of a gas were being actively discussed in the columns of *Nature*, by Boltzmann, Bryan, Burbury, and others, Mr. Jeans took a prominent part. Subsequently there appeared from him a remarkably original treatment relating to this difficult subject, in the *Philosophical Magazine*. Though the results of Jeans's methods have not the assent of Burbury, it seemed obvious to the readers of that article that a strong mind had come forward to assist in rehabilitating the kinetic theory against the severe criticism of some of its assailants and the misgivings of the general body of physicists.

The book before us is in a measure an attempt at a more rigorously logical foundation of the kinetic theory of gases than has hitherto been given, even in Boltzmann's great work. It is Mr. Jeans's fundamental idea to abandon the customary assumption of the theory, that there is no action between ether and matter, believing that to do so is to reach propositions which agree more closely with experiment. Indeed the author has been at great pains to accentuate the experimental side of the discussion. He has been at further pains to reduce the severe mathematics, by which the theory is necessarily approached, to the lowest limits consistent with a clear presentation of the subject. The book is divided into four parts, the first of which treats the law of distribution, giving an account of the statistical method and of the method of general dynamics, with a comparison between the two and an extension to molecules of the most general conservative type. This part and the next follow, in the main, the classical method of development. The second part considers the physical properties of a gas, pressure, temperature, density, etc. The third part, on the theory of a non-conservative gas, embodies the ideas on which Mr. Jeans has put forward his utmost strength. This is an actual approach to the new kinetics originating with him, in which the molecular dynamics of a gas are treated with the admission of dissipation. The last part of the book returns again to the more usual methods, and includes those fascinating applications which originally gave such luster to the kinetic theory, *viz.*, the free path phenomena, embracing the treatment of viscosity, heat conduction, diffusion, propagation of sound, planetary atmospheres, dissociation, size of molecules, etc.

The whole discussion is divided into nineteen chapters, and in none of them is the severity of the mathematical method relaxed. Highly specialized treatises have been put forward before (witness that of Burbury) but none with so broad a scope as Mr. Jeans's book. It will, therefore, be impossible to attempt any adequate discussion here. Suffice it to say that beyond the well-known treatise (of which there is now an English translation) in which O. E. Meyer has embodied an able summary of the subject from the experimental point of view, a systematic account of the furthest advances of the subject regarded from the mathematical standpoint is now available in English.

Carl Barus.

Handbuch der Spectroscopie. *By H. Kayser. Dritter Band. 17 × 25 cm; pp. viii + 604. Leipzig: S. Hirzel, 1905. Price: paper, 38; bound, 42 marks.*

—The third volume of Kayser's great work on spectroscopy follows the second with astonishing promptness, when the immense amount of matter which has been systematized is taken into account. The volume as a whole is more highly specialized and empiric in character, and therefore less interesting, than the two preceding. The phenomena of absorption are exhaustively summarized, and Kayser remarks with dismay that the wealth of available data is such that two volumes will be needed instead of the single one contemplated for this part of the treatise. The present instalment contains a detailed account of the apparatus needed in absorption spectroscopy and a discussion of the relation of absorption to chemical constitution, including all the known data for inorganic and artificial organic bodies. Kayser dwells at length on the extreme laboriousness of the work of the data-gatherer in this field, in view of the dearth of general principles deducible therefrom. He particularly congratulates himself on the co-operation of Prof. W. N. Hartley, of Dublin, to whom the third chapter, dealing with the relations between absorption and chemical constitution, is due.

Of the five chapters which make up the book, the first, in addition to the description of apparatus and methods, contains a summary, nearly free from formal mathematics, of the prominent theories of absorption, due respectively to Angström, Lorentz, Planck, Drude, Hartley, and with the absorption exponentials of Bouguer and Lambert, and of Beer. The second chapter contains an analysis of absorption effects, such as those due to the solvent, to the solute, to concentration, to temperature, etc., together with an interesting discussion of color and atomic weight. The fourth chapter is a systematic catalogue of absorptions; and the fifth an alphabetical list of all known absorption spectra.

The book will probably appeal most directly to chemists. A theory of sufficient scope to serve as a commentary on these complicated phenomena is scarcely to be looked for in the near future. Meanwhile one may note that Kayser's book has already grown from five volumes to six during the period of compilation. *Carl Barus.*

Thermodynamik technischer Gasreaktionen. *By F. Haber. 15 × 23 cm.; pp. xv + 296. München und Berlin: R. Oldenbourg, 1905.*—This book contains seven lectures delivered in Karlsruhe last February. The subjects of the lectures were: the latent heat of chemical reactions and its relation to the energy of reaction; the entropy and its significance in gas reactions; another deduction of the preceding relations together with a statement of their bearing on changes in solids; cases in which the reaction is hylotropic; cases in which the reaction is not hylotropic; determination of the specific heats of gases; determination and general discussion of gas equilibria.

The author has given a very satisfactory presentation of our knowledge of the subject and the value of the book is much increased by the critical analysis to which the data are subjected. So long as one is in doubt as to the accuracy of the experiments, one takes great risks in drawing conclusions from them. The reviewer must confess to having found the remarks on the true and the mean specific heats, p. 29, very obscure. *Wilder D. Bancroft.*

Outlines of Industrial Chemistry. *By Frank Hall Thorp. Second edition, revised and enlarged, and including a chapter on Metallurgy by Charles D. De-*

mond. 14 × 22 cm.; pp. xxv + 618. New York: The Macmillan Company, 1905. Price: bound, $3.50.—As stated in the preface to the first edition, "the object of this book is to furnish an elementary course in Industrial Chemistry which may serve as the groundwork for a more extended course of lectures, if desired. The writer has endeavored to describe briefly, within the limits of one moderate-sized volume, the more important industrial chemical processes, but omitting matters of detail which properly belong in the larger hand-books." The author makes no pretense of giving anything beside facts. Whether this is the best way to teach industrial chemistry is very much open to question; but it is certainly the easiest way.

Some errors have been overlooked. Holding a still-head at a temperature between the boiling-points of two liquids, p. 9, will not enable one to get the lower-boiling liquid off pure. The student will get very little out of the statement, p. 12, that "sublimation is influenced by the pressure within the vessel, and is generally carried on under atmospheric pressure only." On p. 16 we find a statement which is quite wrong. "In the majority of cases, the solubility of a substance increases as the temperature of the liquid rises, until a point is reached at which no more of the substance will dissolve, even though the solution is boiling." As a matter of fact the solubility curve shows no change at the boiling-point of the solution. The reason that the solubility does not become any greater is because the temperature does not rise. On p. 22 density and specific gravity are said to be synonymous. On p. 115 it is implied that the theoretical yield per ampere-hour is a function of the voltage. On this same page we read that "electrolysis in fused baths makes anhydrous caustic directly, but a good deal of fuel is used in heating the cells." No fuel is used in the Acker process which is the only commercial one using fused salt. The remarks on the electrolytic chlorate process, p. 121, do not describe modern practice. In the Readman-Parker phosphorus furnace, p. 234, metallic bars are not used to start the circuit through the furnace. The catalysis of the glycerides by mineral acids, p. 338, might well have been discussed in a less vague manner.

While recognizing the right of the author to select his own point of view, it must also be kept in mind that the author is really advocating a method of teaching applied chemistry. It seems to the reviewer that some of the facts could have been omitted in order to make room for a discussion of the factors determining the use of triple or quadruple effect evaporating systems; for the general theory of fractional distillation and crystallization; for a clearer statement why the Dutch process gives the best white lead; for the reason why there is an increased amount of fused oil formed when alcoholic fermentation takes place above 20°; etc. A few lines here and there suggesting research work for the student would have been a good thing both for the student and for the author. It is not well to teach applied chemistry as though it were history and nothing more.

The subject-matter is treated under the general headings: introduction; fuels; water; sulphur; sulphuric acid; salt; hydrochloric acid and sodium sulphate; soda industry; chlorine industry; nitric acid; ammonia; potash industry; fertilizers; lime, cement, and plaster of Paris; glass; ceramic industries; pigments; boric acid; electric furnace products; arsenic compounds; waterglass; oxygen; sulphates; cyanides; carbon disulphide; carbon tetrachloride;

manganates and permanganates; destructive distillation of wood; destructive distillation of bones; illuminating gas; coal tar; mineral oils; vegetable and animal oils, fats and waxes; soap; candles; glycerine; essential oils; resins and gums; starch, dextrin, and glucose; cane sugar; fermentation industries; explosives; textile industries; paper; leather; glue; metallurgical processes; roasting; iron and steel; copper; lead; zinc; tin; silver; gold; platinum; mercury; aluminum; nickel; arsenic; sodium; antimony; bismuth; cadmium; magnesium; alloys. *Wilder D. Bancroft.*

Cours de Chimie a l'Usage des Étudiants du P. C. N. *By R. de Forcrand. 14 × 22 cm. Tome I: Généralités, Chimie minérale, pp. 325; Tome II: Chimie organique, Chimie analytique, pp. 317. Paris: Gauthier-Villars, 1905. Price: paper, 5 francs each.*—The reviewer is ignorant as to the meaning of the mystic letters P. C. N.; but the student apparently covers the whole of chemistry in three lectures a week for one year. For this reason the book could find but a limited application in this country. After a theoretical introduction, the author takes up inorganic chemistry, organic chemistry and analytical chemistry. The author upholds the principle of maximum work, though he adds a correcting term which gives him plenty of leeway. Even this is not enough so he postulates that all endothermal reactions, taking place spontaneously, are physical reactions. *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

A revision of the atomic weight of iodine. *G. P. Baxter. Jour. Am. Chem. Soc.*, 27, *876* (*1905*).—If silver is 107.930 iodine becomes 126.985 while it is 126.973 if silver is taken as 107.920. Richards and Wells's value of 35.473 for chlorine is confirmed and so is Stas's value of 79.555 for bromine. *W. D. B.*

The unit of the combining weights. *R. Luther. Zeit. Elektrochemie*, 11, *273* (*1905*).—It is urged that the only rational basis for the combining weights is given by the c. g. s. system and Faraday's law. The author does not urge the immediate adoption of the new numbers. *W. D. B.*

A new regulator for thermostats. *O. Dony-Hénault. Zeit. Elektrochemie*, 11, *3* (*1905*).—In order to prevent the toluene in the regulating tube of the Ostwald thermostat from creeping and volatilizing, the author covers the two surfaces with a sodium chloride solution. *W. D. B.*

One-Component Systems

Amorphous sulphur, II. *A. Smith, W. B. Holmes and E. S. Hall. Jour. Am. Chem. Soc.*, 27, *797* (*1905*).—Liquid sulphur occurs in two modifications S_λ and S_μ, the second being what is ordinarily called insoluble sulphur when cold. At 160° there is a triple point, the first of its kind, with two liquid phases and vapor in equilibrium. When melted sulphur saturated with sulphur dioxide is chilled, a large amount of insoluble sulphur is formed. When melted sulphur, saturated with ammonia is chilled, very little insoluble sulphur is formed. This is not due to a displacement of equilibrium at higher temperature but to the catalytic action of ammonia which causes equilibrium to be reached nearly independently of the rate of cooling. Iodine acts in the same way. This is a most creditable piece of work. *W. D. B.*

On the coefficient of expansion of quartz. *H. M. Randall. Phys. Rev.*, 20, *10* (*1905*).—The method of Fizeau was used. The experiments covered a range of 500° and the coefficient of expansion a of quartz can be represented between 0° and 250° by the equation

$$a_t = 10^{-8}(717.0 + 1.620\,t).$$

The values for the ranges 0°–50° and 0°–100° agree very closely with those obtained by Benoit and by Scheel. *W. D. B.*

The coefficient of expansion of nickel at its critical temperature. *H. M. Randall. Phys. Rev.*, 20, *85* (*1905*).—As the author did not determine the critical temperature of his nickel, it is not surprising that he did not succeed in measuring the coefficient of expansion at that temperature. *W. D. B.*

The specific gravities of cadmium chloride and cadmium bromide. *G. P. Baxter and M. A. Hines. Am. Chem. Jour.*, 31, *220* (*1904*).—Anhydrous cadmium chloride, cadmium bromide and silver bromide were fused and then allowed to cool slowly to 25°. A special pycnometer was used and the densities 25°/4° were found to be: $CdCl_2$, 4.049; $CdBr_2$, 5.196; AgBr, 6.478.

W. D. B.

The specific gravity of zinc chloride. *G. P. Baxter and A. B. Lamb. Am. Chem. Jour.*, 31, *229* (*1904*).—Anhydrous zinc chloride was made from the double salt $ZnCl_2.3NH_4Cl$. The density 25°/4° is about 2.907. *W. D. B.*

The specific gravities of lithium chloride, bromide, and iodide. *G. P. Baxter. Am. Chem. Jour.*, 31, *558* (*1904*).—Anhydrous lithium chloride, bromide, and iodide were prepared, fused and allowed to cool slowly. The specific gravities 25°/4° were: LiCl, 2.068; LiBr, 3.464; LiI, 4.061. *W. D. B.*

Boiling-points of ammonia, methyl amine, methyl chloride and sulphur dioxide. *H. D. Gibbs. Jour. Am. Chem. Soc.*, 27, *851* (*1905*).—The following boiling-points were found: ammonia, —33.46° at 760 mm; methyl amine, —6.7° at 755.67 mm; methyl chloride, —24.09° at 760 mm; sulphur dioxide, —10.09° at 760 mm. *W. D. B.*

Tests of some oils suitable for use in air pumps. *P. G. Nutting. Phys. Rev.*, 19, *231* (*1904*).—The vapor-pressures were determined for a number of heavy oils suitable for use with a Geryk pump (Fleuss patent). A little dissolved air was given off at about 3 mm. After this had been removed, the several specimens showed vapor-pressures lying between 0.015 mm. and 0.03 mm. The Standard Gas Engine oil, supplied by the Standard Oil Co., was rather the best of all and is better than the oil supplied by the Pulsometer Co.

W. D. B.

The equilibrium pressure of a vapor at a curved surface. *A. A. Bacon. Phys. Rev.*, 20, *1* (*1905*).—If a capillary tube closed at the lower end be dipped into a liquid, the liquid should distil into the tube filling it to the height that the liquid would rise in the tube if the lower end of the tube were open. This experiment has been tried with ether as the liquid. When sufficient precautions were taken the results were in agreement with the theory, but the rate of condensation is very low. *W. D. B.*

On red phosphorus. *R. Schenck. Zeit. Elektrochemie*, 11, *117* (*1905*).—When white phosphorus changes to red phosphorus the vapor-pressure drops gradually and not suddenly when the last of the white phosphorus has apparently disappeared. The author believes that this is due to an adsorption of the white phosphorus because 100g of white phosphorus will take up 47g of phosphorus tribromide when changing to red phosphorus in presence of the tribromide. *W. D. B.*

Two-Component Systems

Magnesium-lead alloys. *G. Grube. Zeit. anorg. Chem.*, 44, *117* (*1905*).—The difficulty in working with alloys rich in magnesium is in obtaining a suitable crucible. The author thinks he has solved this difficulty by using an iron tube lined with asbestos paper. He found that when the alloys became rich in lead the paper was attacked, and then hard glass tubes were used. The freezing-point curve has a maximum at the composition $PbMg_2$. The eutectic for Mg + $PbMg_2$ is at 76 percent Pb, and 459°. The eutectic for $PbMg_2$ + Pb, is at 247° and 97 percent Pb. The absence of a heat evolution at 459° in the 90 percent Mg alloy, when taken in conjunction with the very small amount of eutectic in the photomicrograph shown, would seem to indicate that there was a possibility of there being a solid solution at the magnesium end of the series. The compound $PbMg_2$ is said to be a brittle, crystalline metal with a specific gravity of 5.54. This observed density is very nearly that which would be calculated from the composition, showing that the combination takes place without appreciable change of volume. In moist air the compound oxidizes to a black powder. It is stable in a desiccator over P_2O_5. In moist air the compound seems to oxidize to the oxide of the formula $(PbO.2MgO)3H_2O$. This hydrate loses all of its water at 280°. *E. S. S.*

Alloys of antimony and bismuth. *K. Huettner and G. Tammann. Zeit. anorg. Chem.*, 44, *131* (*1905*).—The authors are in doubt as to the significance of their results in this series. The freezing-point curve seems to run directly from pure bismuth to pure antimony. There may be a eutectic with about 0.005 gram of antimony in 100 grams of bismuth. The liquidus seems to possess an irregularity at 500° and 50 percent Sb. The heat evolution at the temperature of freezing of bismuth, is found in compositions up to 70 percent Sb. They are inclined to consider it a case of a solid solution with a limiting solubility of about 70 percent Sb. This is in contradiction to the microscopic evidence which shows abundant eutectic at 95 percent Sb. Since practically pure bismuth seems to crystallize from the alloys, and the microscope shows eutectic in the 95 percent alloy we are justified in supposing that the first crystals which separate are practically pure components. Until the authors have annealed the alloys with more than 70 percent Sb, in order to see whether the eutectic is absorbed on prolonged heating at temperatures below the freezing-point, it will be impossible to say just what the constitution of this series may be. It seems certain that antimony is insoluble in bismuth at the melting-point of the latter. There would not seem to be any question as to whether or not the metals form a single series of solid solutions, but rather it is a question whether they form any. *E. S. S.*

The gold-lead alloys. *R. Vogel. Zeit. anorg. Chem.*, 45, *11* (*1905*).—The author has determined the freezing-point curve for the gold-lead alloys and finds reason to believe in the existence of two compounds, Au_2Pb and $AuPb_2$. Lead apparently crystallizes pure, as does also gold, over their respective portions of the freezing-point curve. Neither of these compounds is stable at its melting-point, and their existence was determined by means of the pyrometric examination. The method followed was that which has been described by Tammann previously, and the amount of alloy used in the determination was quite small, about 20 grams. The freezing-point curve consists of four branches. From pure gold to about 45 percent of lead, gold is a solid phase. From 45 percent lead to about 73 percent lead, the compound Au_2Pb

is solid phase. From 73 percent to 86 percent of lead, $AuPb_2$ is stable in contact with the melt. From 86 percent to the melting-point of pure lead, the solid phase is lead. The only eutectic in the series is at 86 percent lead, where the eutectic consists of lead and $AuPb_2$. The author makes the unfortunate mistake of speaking of the inversion temperatures for gold to Au_2Pb and of Au_2Pb to $AuPb_2$ as eutectic temperatures. The mistake is unfortunate, not only because the first essential of an eutectic is that it is at a minimum temperature, but also because reactions occurring at the inversion temperatures are in no way analogous to the reactions which occur at the eutectic, and the microstructure resulting is not similar. The reaction in the case of the inversion temperature is one of re-solution and a simultaneous precipitation of the second solid phase; whereas at the eutectic it is simultaneous precipitation of both solid phases. The structure resulting can be similar only to the extent of giving large primary crystals surrounded by entirely different and perhaps fine-grained structure of the second phase.

There is an inversion temperature for $AuPb_2$ from the α-form into the β, and this occurs at very nearly the temperature of the eutectic. The author found also that, due to hysteresis, the inversion temperature for $AuPb_2$ and the transformation from the α- into the β-compound could be detected 15 percent beyond the composition to which they were presumably limited by the equilibrium condition. This was found to be due to the crystals first formed, being coated over with the second, thus distributing the equilibrium. It was found that by slow cooling, and stirring the melt, this condition could be avoided. No attempt was made to determine whether or not gold might contain small amounts of lead as solid solution in this investigation, nor was such an examination made in the case of the compounds in question. The author has completely disproved Maey's suspicions as to the existence of the compound Au_2Pb_3. Six photomicrographs accompany the paper. The author's success in getting good photographs in the case of such very soft metals is worthy of notice. *E. S. S.*

The gold-thallium alloys. *M. Levin. Zeit. anorg. Chem.*, 45, *31* (*1905*).—The author has taken the freezing-point curve for these alloys at intervals of 20 percent, and finds the curve to consist of two branches with the eutectic at about 25 percent of gold and 131°. There was no evidence of the formation of solid solutions or of any compounds. The author believes in the existence of three allotropic formations of thallium, one of which appeared on the cooling curve at 225°. The author discusses some abnormal appearances of the alloys on sudden cooling, explaining that the simultaneous appearance of large crystals of both gold and thallium in the same alloy may be due to supercooling with the resulting precipitation of the metal which should only appear as eutectic. It is the same as the case discussed years ago by Roberts-Austen for the case of the lead-tin alloys, although the author makes no reference to Austen and apparently does not know of his work. No examination was made of the alloys to see whether or not solid solutions of small limiting concentrations existed. *E. S. S.*

Magnesium-aluminum alloys. *G. Grube. Zeit. anorg. Chem.*, 45, *225* (*1905*).—The author has redetermined the freezing-points of these alloys, and succeeds in disproving the conclusions reached by Boudouard in his examination of this series. This investigation shows that only one compound exists between Mg and Al, namely Al_3Mg_4. The author believes that Al crystallizes pure from all alloys between 0 and 35 percent of magnesium. The eutectic for Al-Al_3Mg_4 occurs at 35 percent of magnesium, and at a temperature of about 450°. The maximum for Al_3Mg_4 occurs at 462.7°. Between 35 percent and 55 percent of magnesium the alloys are apparently homogeneous solid solutions, of the compound and aluminum. The fact that the compound forms a continuous series of solid solutions over a range extending almost to the eutectic, makes it seem a little odd that aluminum should not take up any magnesium as solid solution. While such a condition may readily exist, it must be remembered that this is not an equilibrium diagram which the author presents, but is merely a diagram representing the facts *under the conditions under which he worked.* Only those reactions which took place very rapidly would be noticed working as he did. It may be, therefore, that aluminum does form a limited series of solid solutions with magnesium. In any case the work will have to be repeated before we shall know. Between 55 and 67 percent Mg the series is again eutectic; this time the compound forms the primary crystals with pure magnesium as the other phase in the eutectic. This eutectic is at 67 percent Mg and 440°. There is no reason to suppose that the author has not arrived at nearly the correct conclusions as to this series, but it is to be regretted that he should have been in too great haste to settle the question while he was about it. *E. S. S.*

Gold-nickel alloys. *M. Levin. Zeit. anorg. Chem.*, 45, *238* (*1905*).—The liquidus consists of only two branches, which meet in a eutectic at 22 percent Ni and 950°. The author believes that both components form solid solutions whose limiting concentrations are but a few percent removed from that of the pure components. He did not make any experiments to ascertain the limits of these solid solutions, and until this point has been checked we are not much wiser than we were before. The inversion temperature of the nickel is but slightly affected. *E. S. S.*

Alloys of nickel and of cobalt with iron. *W. Guertler and G. Tammann. Zeit. anorg. Chem.*, 45, *205* (*1905*).—The authors have endeavored to determine the constitution of this important series of alloys. Their first step was to attempt the determination of the freezing-point curves. Ten grams of alloy were thought to be enough for these determinations. The authors then assumed that the true freezing-point lay between the values determined by means of heating and cooling curves, and that if the rate of heating and of cooling were the same, then the freezing-point would be the mean between the values found by means of the two curves; that is, to assume that the degree of superheating and the degree of supercooling are determined entirely and *quantitatively* by the rates of heat transfer. We recall that superheating has been shown only for those very viscous substances such as minerals. It has never been shown to occur in metals. On the other hand, supercooling is not determined quantitatively by the rate of cooling, from which it follows that this "corrected" value bears no more relation to the real value than the above assumptions do to the truth. A large number of determination of heat changes in metals, using a most accurate and carefully verified pyrometric system has shown the reviewer that whereas the points determined by means of the heating curves usually checked to within two microvolts (0.2°) the same points determined by cooling curves varied over *three hundred* microvolts and that irregularly even for the same rate of cooling, from which it would seem that the values determined by means of the heating curves were approximately correct, while the values obtained by cooling curves are in error, and the nature of the case does not permit a correction of the error. That such is the case appears on a close examination of the data given in the paper in question. In many cases only one determination was made for each composition. In some cases two observations are given. Take the example of the freezing-point of pure iron. Three determinations of heating curves gave the point as 1485° on his scale, but the rate in the first two cases was 1.05 while in the last case it was 2.00. By means of the formula the corrected value falls again at 1480°, but here is a difference of 90 percent in the rate which does not affect the result at all, whereas a rate differing by 57 changes the observed value of the 60 percent alloy some 20°. These instances could be multiplied, but it would only emphasize the conclusion that the author's "corrected" data form an entirely artificial curve. Nor does it help matters greatly to take the authors' actual data and plot them. For the nickel steel this leads to three maxima, instead of the authors' two minima. Even the assumption that the data obtained by heating, are the more accurate, fails to bring any regularity out of this chaos. We are forced to conclude that either from using a contaminated thermocouple, or because of a faulty galvanometer, or for some other not so evident a reason, this work on the freezing-points of cobalt-iron and nickel-iron alloys is worthless.

If we examine the equilibrium diagram offered by these authors we find the fields for the various phases undetermined. Thus above 66 percent Ni, and above 600° the authors state that the alloys are a solid solution of βNi and βNi$_2$Fe. If the authors are merely dividing the region into fields for these different phases, then they are trying to make the old distinction between the solvent and solute in a homogeneous phase, the properties of which vary uniformly with the concentration. If the 10 percent alloy differs from the 90 percent when quenched from high temperatures, it would have been worth while to show how. If we have two sets of solid solutions over this range it was the only object of further research to show what relation these phases bore to each other. The maximum in the liquidus as they interpret their results, is unexpected.

It has been known for a long time, that over a part of these concentrations the loss of magnetic properties occurred at different temperatures on heating and upon cooling the alloy. If the present investigation was to add anything to our knowledge, it was certainly to determine why these changes occurred at different temperatures. Since it does not do this, and since the determination of the liquidus is evidently useless, one may well ask: what does this research add to our present information?

The same criticisms apply to the cobalt-iron alloys. The transformations for α- and β-iron are started out into the diagram and left unfinished. The relation between β- and γ-iron in these alloys is left entirely undetermined.

The following statement is an interesting instance of consistency in theoretical reasoning. "Since we found previously that Ni and CO form a continuous series of solid solutions, then β-nickel and β-cobalt as well as α-Ni and α-CO, are to be considered as isomorphous. Since the liquidus for β-Ni and γ-Fe is composed of two branches, these substances are not to be considered as isomorphous, and then β-cobalt and γ-iron should not be isomorphous; *therefore* the liquidus of the CO-Fe series *must* consist of two branches." (The italics are ours.) Now refer to the paper of Grube (preceding review, and work under Tammann's direction). There the compound Al_3Mg_4 forms solid solutions containing some 20 percent of Al, yet it was not even suspected that Al would form solid solutions with the compound. Without doubt the facts are correct, but the reasoning is not. The subject of isomorphism is not nearly well enough known to warrant us in drawing deductions as to the form of the liquidus from the crystalline symmetry of the components.

It is scarcely worth while to examine the paper further except to point out, that this, like all of the other alloy studies emanating from this laboratory, bears the evidences of mad haste. Incomplete, inaccurate and unverified, these papers must come as a keen disappointment to those who have long admired Tammann as one of the most brilliant and conscientious experimentalists of the present time. *E. S. S.*

On the application of thermal analysis in abnormal cases. *G. Tammann. Zeit. anorg. Chem.*, 45, *24* (*1905*).—The author discusses the deduction of the composition of the solid phase from the cooling curves of the alloys, using as illustrations the work of Vogel on the gold-lead alloys. He discusses the disturbing effect of hysteresis and points out the method of correcting for that. As in his previous paper on this subject, it is necessary to assume that equilibrium is reached during the time in which the cooling curve is taken. Experience would seem to indicate that this is usually not the case, especially for solid solutions. *E. S. S.*

The dissociation of the carbonates of the alkaline earths. *O. Brill. Zeit. anorg. Chem.*, 45, *275* (*1905*).—The author has determined the temperatures at which the various carbonates dissociate in an atmosphere of CO_2. The method is to weigh a very small amount of the carbonate on the Nernst 'Mikrowage' and after heating at a given temperature weigh again. The time of heating was ten minutes for each temperature. The small mass of the material allowed the temperature adjustment to take place almost instantly.

Under these conditions it was found that $CaCO_3$ first began to lose weight at 815°, and had lost all of its CO_2 at 900°. $SrCO_3$ decomposed at 1170°, and $BaCO_3$ at about 1400°. The exact point for the barium salt could not be determined because the oxide attacked the crucible. $MgCO_3$ decomposed in steps, leading the author to the compounds; $MgCO_3$, $10MgO.9CO_2$, $9MgO.8CO_2$, $8MgO.7CO_2$, $7MgO.6CO_2$, $6MgO.5CO_2$, $9MgO.7CO_2$ (?), $7MgO.7CO_2$, and finally MgO. The temperatures at which these various products occur are given, and the whole of the CO_2 is evolved by 520°. The pressure in all cases was atmospheric.

The author then shows how this method can be applied quantitatively to the determination of the composition of the mixed carbonates. His results are very interesting, the maximum difference in his determinations being about 0.8 percent.

It is stated that the neutral carbonate of magnesium can be obtained by heating the basic carbonate at 225° in an atmosphere of CO_2. *E. S. S.*

On the nature of concentrated solutions of electrolytes—hydrates in solution. *H. C. Jones and F. H. Getman. Am. Chem. Jour.*, 31, *303* (*1904*).—The authors have determined the freezing-points of moderately concentrated solutions of chlorides, nitrates and sulphates of manganese, nickel, cobalt, copper and aluminum. The general conclusion is that "those substances which crystallize out of solution with the largest number of molecules of water of crystallization, give the greatest molecular lowering of the freezing-point of water in concentrated solution." *W. D. B.*

The existence of hydrates in solutions of certain non-electrolytes and the non-existence of hydrates in solutions of organic acids. *H. C. Jones and F. H. Getman. Am. Chem. Jour.*, 32, *308* (*1904*).—The authors conclude that of the thirteen non-electrolytes studied, glycerol alone shows a marked tendency to form hydrates. Cane-sugar, fructose, methyl alcohol and ethyl alcohol show signs of hydration. None of the organic acids studied showed any appreciable tendency to form hydrates. In many instances it was necessary to assume a polymerization of the solvent. *W. D. B.*

The existence of alcoholates in solutions of certain electrolytes in alcohol. *H. C. Jones and F. H. Getman. Am. Chem. Jour.*, 32, *338* (*1904*).—It had been found that the molecular rise of the boiling-point of ethyl alcohol produced by the five electrolytes—sodium bromide, cadmium iodide, potassium iodide, ammonium iodide, and sodium iodide—is greater at some dilution than the theoretical molecular rise. This pointed to the existence of alcoholates. Similar results are now obtained for lithium chloride, lithium nitrate and calcium nitrate. *W. D. B.*

The approximate composition of the hydrates formed by certain electrolytes in aqueous solutions at different concentrations. *H. C. Jones and H. P. Bassett. Am. Chem. Jour.*, 33, *534* (*1905*).—The authors calculate what hydrates must be formed if the abnormal vapor-pressure phenomena are due solely to a decrease in the amount of free solvent. The salts under discussion are calcium chloride, calcium bromide, strontium bromide, barium bromide, magnesium chloride, magnesium bromide, manganese chloride, manganese nitrate, cobalt chloride, cobalt nitrate, nickel chloride, nickel nitrate, copper chloride, copper nitrate, and sulphuric acid. Over most of the range the apparent compositions of these hypothetical hydrates varies irregularly with increasing concentration. Strontium bromide is believed to combine with about eighteen of water; barium bromide with fifteen; magnesium bromide with from eighty to twenty.

It seems to the reviewer that there is a certain lack of perspective about all this work. If a portion of the solvent is not free, a correction must be made for this; but it does not follow, as Mr. Jones appears to assume, that this is the only factor. If there are any other factors, the calculations as given in this paper are of absolutely no value. *W. D. B.*

A study of the molecular lowering of the freezing-point of water produced by concentrated solutions of electrolytes. *H. C. Jones and F. H. Getman. Phys. Rev.*, 18, *146* (*1904*).—Reviewed (8, 223) from *Zeit. phys. Chem.*, 46, *244* (*1903*).

A lecture experiment on mutual solubilities. *P. Muller. Zeit. Elektrochemie*, 11, *3* (*1905*).—Isobutyl alcohol and water form two liquid layers. The water layer clouds with rising temperature and the lower layer with falling temperature. The amount of the clouding is so marked as to make this a good lecture experiment. *W. D. B.*

Heat of vaporization of liquid air. *R. C. Fenner and F. K. Richtmeyer. Phys. Rev.*, 20, *77* (*1905*).—The heat of vaporization of liquid air is practically independent of the concentration between 19.6 percent oxygen and 95.7 percent oxygen, the average value being 50.9 cal. In discussing the matter the authors seem to ignore the heat of dilution and they speak of the nitrogen in the liquid air as being superheated, which is absurd. *W. D. B.*

Oxides of ruthenium. *A. Gutbier and F. Ransohoff. Zeit. anorg. Chem.*, 45, *243* (*1905*).—The authors have reviewed the work of the older chemists and find, as we have learned to expect, that many of the supposed oxides were really mixtures, and that the real oxides are comparatively few in number. By direct ignition in air ruthenium takes up an almost constant amount of oxygen, namely, 27 percent. It does not under these conditions form the sesquioxide, but a mixture of the dioxide and metallic ruthenium. Alkalies precipitate $Ru_2(OH)_6$ from the chloride, but the alkali can not be entirely removed from the product. The impure hydroxide heated in a stream of CO_2 yields an intermediate product. Neutralization of the alkali ruthenate gives a mixture of the hydroxide and an anhydrous oxide, instead of the sesquihydroxide, or the $Ru_2O_5 2H_2O$ suggested by Debray and Joly. The ruthenate when treated with alcohol gives a mixture.

RuO_2 results partly when ruthenium is heated in O, or quantitatively from the ignition of the sulphate. The hydrate of this oxide described by Claus could not be obtained, while the oxides, Ru_2O_5 and Ru_4O_9 do not exist.

The tetroxide is easily prepared, decomposes readily, forms no hydrate, and in all ways behaves like a true peroxide. The oxides RuO_3 and Ru_2O_7 must be allowed because the salts are known, but they could not be prepared in a pure state. *E. S. S.*

Multi-Component Systems

The solubility of barium and mercuric chlorides. *H. W. Foote and H. S. Bristol. Am. Chem. Jour.*, 32, *246* (*1904*).—Solubility determinations for mixtures of barium and mercuric chlorides show that no double salt is stable at 25°. Below about 17.2° a double salt $BaCl_2.3HgCl_2.6H_2O$, can exist, but is decomposed by pure water with precipitation of mercuric chloride. *W. D. B.*

The solubility of potassium and barium nitrates and chlorides. *H. W. Foote. Am. Chem. Jour.*, 32, *251* (*1904*).—At 25° a double salt, $Ba(NO_3)_2.2KNO_3$, cannot exist, but is decomposed by water with precipitation of barium nitrate. At the same temperature barium and potassium chlorides form no double salts.
W. D. B.

Some determinations in the system copper chloride, ammonium chloride and water. *P. A. Meerburg. Zeit. anorg. Chem.*, 45, (*1905*).—The author has endeavored to determine the number of ternary compounds possible, and finds evidence of only one well-defined salt, *viz.*, $CuCl_2.2NH_4Cl2H_2O$. He has determined the isotherm for 30° and by analyzing the solution and the solid phase, deduces only this one compound. He has also determined the freezing-point curve for $CuCl_2 2NH_4Cl$ and water, finding the cryohydric point to be at 20 percent of the double salt, and at a temperature of —11°. From the continuity of the solubility curve between —11° and 80°, it is evident that for at least this range, no other hydrated salts exist. *E. S. S.*

The solubility of lead sulphate in ammonium acetate solutions. *A. A. Noyes and W. H. Whitcomb. Jour. Am. Chem. Soc.*, 27, *747* (*1905*).—Conductivity measurements showed that lead acetate is only about 22 percent dissociated in *n*/10 solutions, which is an abnormally low value for salts of this type. Migration experiments on solutions of lead sulphate and ammonium acetate showed that the lead remained nearly stationary and that its concentration as ion was therefore low. Solubility determinations showed that the solubility of lead sulphate is approximately the same in sodium acetate and ammonium acetate. The authors conclude that the solubility of 10.1 millimols lead sulphate per liter of 0.414 normal ammonium acetate solution is due chiefly to the formation of undissociated lead acetate by metathesis. *W. D. B.*

Two historical notes. *R. Abegg. Zeit. Elektrochemie*, 11, *2* (*1905*).—In an unpublished Breslau thesis of date 1874, Mikolajczak discusses the reaction between sodium sulphate and barium carbonate. He considers that this is precisely similar to the reaction between two soluble salts because the sparingly soluble salt must dissolve to a certain extent. This is interesting but scarcely justifies the author in saying that Mikolajczak recognizes with all clearness the constant concentration of the saturated solution as the cause of the constancy of the active mass. There is nothing in the passages quoted to show that Mikolajczak knew that the actual solubility of a salt is unchanged by the addition of other salts. This is a later conception and is only approximately accurate at best.

The second note is to the effect that Kekulé, in 1875, predicted that the ratio of the specific heats of diatomic gases would be 1.41. As this was accompanied by the further prediction that the specific heat of mercury at constant volume would be zero, it is not surprising that this paper was promptly forgotten. *W. D. B.*

Copper, tin and oxygen. *E. Heyn and O. Bauer. Zeit. anorg. Chem.*, 45, *52* (*1905*).—The authors have investigated the question of whether or not stannic oxide may exist in bronzes in solution, and whether or not it enters into equilibrium relations with the Cu_2O and copper. As was to have been expected, it was found that both metallic tin and tin dissolved in copper promptly reduced Cu_2O with a formation of stannic oxide and metallic copper. The stannic oxide so formed separates in large crystals in the melt and renders it much less fluid by purely mechanical action. Since stannic oxide occurs held mechanically in bronzes, it is essential, in determining the composition of the bronze analytically, to determine the amount of stannic oxide present as such. This can be done by dissolving the bronze in sulphuric acid with density 1.18, making the bronze anode and using a current of about 0.5 of an ampere. A certain amount of copper is found in this oxide so obtained, but whether it is there as occluded copper or as copper oxide is not known.

Metallic tin does not absorb stannic oxide. The action of phosphorus in rendering bronzes more fluid and stronger is properly explained as being due to the reduction of the Cu_2O and the stannic oxide which may be present. The grayish-yellow spots on the fracture of copper-rich bronzes is said not to be due to segregation, but to result from the orientation of the crystals in freezing. The paper is a very interesting one and is illustrated by 14 excellent photomicrographs. *E. S. S.*

Some cuprammonium sulphates. *D. W. Horn and E. E. Taylor. Am. Chem. Jour.*, 32, *253* (*1904*).—The salt $CuSO_4.4NH_3.H_2O$ has been prepared and found not to lose ammonia readily when dry. The behavior of the salt at 100°, 125°, 149°, 203° and 260° was studied in a purely qualitative way, the conclusion reached being the qualitative one that more than one decomposition product is formed. It is shown that in aqueous solution there is a slow change takes place which may continue for weeks. This affects the conclusions drawn by Dawson and McCrae and by Locke and Forssell. It is rather a pity that no pressure measurements were made. *W. D. B.*

Removal of oxygen by platinum. *R. Lucas. Zeit. Elektrochemie*, 11, *182* (*1905*).—On heating ordinary platinum foil and oxygen to temperatures between 500° and 900°, there is a marked absorption of oxygen. It was shown that this was due to the iridium content of the platinum and that it did not take place when chemically pure platinum was used. *W. D. B.*

The action of ammonia upon copper sulphate solutions. *J. Locke and J. Forssell. Am. Chem. Jour.*, 31, *268* (*1904*).—Attempts have been made to determine the partial pressure of ammonia above ammoniacal copper sulphate solutions. It is believed that only one complex is formed $CuSO_4.4NH_3$ and that the free ammonia has a higher partial pressure than the normal, owing to a precipitating action of the copper sulphate. *W. D. B.*

A study of hydrolysis by conductivity methods. *J. Stieglitz and I. H. Derby. Am. Chem. Jour.*, 31, *449* (*1904*).—Experiments were made on the conductivity of mixtures of potassium chloride and hydrochloric acid, and of aniline and hydrochloric acid to show that in the hydrolysis formula, the term μ_{HCl} means the conductivity of hydrochloric acid at that dilution and not at some other dilution. *W. D. B.*

Some double salts of lead. *J. White. Am. Chem. Jour.*, 31, *1* (*1904*).—The author has prepared and analyzed some double salts of lead iodide with various acetates. No conditions are given, there is no certainty that other double salts have not been overlooked, and the work must be classed as inexcusably bad. *W. D. B.*

Hydrofluorides of anilides and substituted aniline. *R. F. Weinland and H. Lewkowitz. Zeit. anorg. Chem.*, 45, *39* (*1905*).—A descriptive paper giving the preparation and crystalline form of a number of combinations of hydrofluoric acid and the anilides and substituted anilines. It is interesting to note that where the hydroxyl or ethoxyl group is in the para position in the anilide, an excess of hydrofluoride gives the trifluorhydrate. A methyl or methoxy group, or bromine in the para position will yield the monofluorhydrate with an excess of hydrofluoride. If the para position is occupied by a carboxyl or nitro group, the hydrofluoride does not form. *E. S. S.*

On the action of dry hydrochloric acid gas dissolved in anhydrous benzene on dry zinc. *K. G. Falk and C. E. Waters. Am. Chem. Jour.*, 31, *398* (*1904*).—In spite of repeated efforts the authors have not been able to prepare an anhydrous solution of hydrochloric acid in benzene which will not act on dry zinc. *W. D. B.*

Reactions in liquid ammonia. *E. C. Franklin. Jour. Am. Chem. Soc.*, 27, *820* (*1905*).—Attention is called to the striking parallelism between the physical properties of the two electrolytic solvents, water and ammonia. *W. D. B.*

The determination of oxalic acid by permanganate in the presence of hydrochloric acid. *G. P. Baxter and J. E. Zanetti. Am. Chem. Jour.*, 33, *500* (*1905*).—Oxalic acid may be determined with great exactness by titration with permanganate in presence of hydrochloric acid if the temperature of the solution is at least 70° at the start, if the hydrochloric acid and the oxalic acid are not too concentrated, if the permanganate is added slowly, and if the solution is stirred vigorously. *W. D. B.*

Separation of thorium and the cerite earths by means of the neutral sodium sulphite. *A. Batek. Zeit. anorg. Chem.*, 45, *87* (*1905*).—The author claims priority for the application of this method. *E. S. S.*

Ammonium sulphocyanate and thiourea as sources of nitrogen to fungi and micro-organisms. *J. H. Kastle and E. Elvove. Am. Chem. Jour.*, 31, *550* (*1904*).—*Penicillium glaucum*, yeast and nitrifying organisms thrive on ammonium sulphocyanate while they do not act upon thiourea. Both compounds remain unaltered in the animal organism. *W. D. B.*

On colloids. *E. Jordis. Zeit. Elektrochemie*, 11, *285*, *289* (*1905*).—How do colloids behave? How are colloids prepared? What is a colloid? How does a colloid form? From what does a colloid come? What is present in the solution from which a colloid is formed? What is essential and what an impurity in a sol? What takes place in hydrolysis? What is a chemical compound? On what does the existence of the amorphous state depend? The author considers that all these questions and probably many others must be faced by the man who investigates colloids. In the second paper the author states that a silicic acid sol always contains either chloride or sodium salt in excess when made from sodium silicate and hydrochloric acid. He looks upon this as conclusive proof that silicic acid is an amphoteric electrolyte. It is doubtful, however, whether others will take quite this view of it. If barium sulphate is made from barium hydroxide and sulphuric acid, it will carry down one or the other of the components; but it cannot be classed as an amphoteric electrolyte. *W. D. B.*

Velocities

The hydrolysis of ethyl butyrate by lipase. *J. H. Kastle, M. E. Johnston and E. Elvove. Am. Chem. Jour., 31, 521 (1904).*—The hydrolysis of ethyl butyrate by lipase is apparently a monomolecular reaction, though with some disturbing factors. The butyric acid checks the reaction so that within limits the total amount of butyrate hydrolyzed in twenty hours is nearly independent of the initial concentration. The rate of reaction doubles with a 10° rise of temperature. *W. D. B.*

The oxidation of sulphocyanic acid and its salts by hydrogen peroxide. *J. H. Kastle and C. R. Smith. Am. Chem. Jour., 32, 376 (1904).*—The reaction between sulphocyanic acid and hydrogen peroxide is apparently of the third order and the authors suggest that it takes place in two stages, the second one being infinitely short:

$$HCNS + 2H_2O_2 = HCN + 2H_2O + SO_2$$
$$SO_2 + H_2O_2 = H_2SO_4.$$

The rate practically doubles for a 10° rise of temperature. The reaction is much accelerated by chrome alum, copper sulphate or copper nitrate but not by platinum black, manganese dioxide or potassium iodide. *W. D. B.*

The molecular rearrangement of aminophenyl alkyl carbonates. *J. Stieglitz and H. T. Upson. Am. Chem. Jour., 31, 458 (1904).*—The rearrangement of aminophenyl alkyl carbonates in presence of hydrochloric acid has been studied by following the conductivity changes. The active mass is the free base and an excess of acid therefore checks the reaction. *W. D. B.*

On desmotropic compounds. *H. Goldschmidt. Zeit. Elektrochemie, 11, 5 (1905).*—With reference to some experiments by Dimroth it is pointed out that reaction velocity experiments will not permit us to determine whether the active mass of an enol ester having acid properties is the undissociated ester or the ions. *W. D. B.*

On desmotropic compounds. *O. Dimroth. Zeit. Elektrochemie, 11, 137 (1905).*—It is admitted that Goldschmidt is right (preceding review) in saying that reaction velocity experiments will not enable one to determine whether the undissociated enol form is the active mass or whether the ions of the enol form react. Other reasons are given for believing that the former reaction is the one that occurs in the cases studied by the author. *W. D. B.*

Action of platinum on potassium chlorate and hydrochloric acid. *H. Sirk. Zeit. Elektrochemie, 11, 262 (1905).*—The evolution of chlorine from a solution containing potassium chlorate and hydrochloric acid is accelerated by the presence of platinum and still more by platinum black. At best the reaction velocity is not very high. *W. D. B.*

The rate of crystallization of plastic sulphur. *J. H. Kastle and W. P. Kelley. Am. Chem. Jour., 32, 483 (1904).*—The higher the temperature to which sulphur is heated before chilling, the slower the rate of crystallization of the plastic form. Ammonia, alcohol and bromine accelerate the crystallization and so does tension while iodine retards the crystallization. *W. D. B.*

Pure nitrogen from nitrous and nitric oxides and ammonia. *G. P. Baxter and C. H. Hickey. Am. Chem. Jour.*, 33, *300* (*1905*).—In presence of a catalytic agent such as copper gauze or finely-divided platinum, nitrous oxide and nitric oxide react when hot with ammonia according to the equations:

$$3N_2O + 2NH_3 = 4N_2 + 3H_2O$$
$$6NO + 4NH_3 = 5N_2 + 6H_2O.$$

The reaction in the case of nitrous oxide is explosive, so the use of nitric oxide is recommended. *W. D. B.*

On hydration and hardening processes. *P. Rohland. Zeit. Elektrochemie*, 10, *893* (*1904*).—Dry lime does not react with dry carbon dioxide and a very wet mortar takes up carbon dioxide much more slowly than one that is merely moistened. The rate of hydration of anhydrous calcium sulphate is said to depend on its solution pressure in any solution. The hardening is believed to be due to the formation of a solid solution, though the existence of such a phase is not proved. *W. D. B*

On hydration and hardening processes. *E. Jordis. Zeit. Elektrochemie*, 10, *938* (*1904*).—It is claimed that Rohland (preceding review) has not recognized all the changes that take place when Portland cement hardens. The point is made that the effect of salts on the rate of hardening is not a purely catalytic action because the salts react with the cement. *W. D. B.*

Hydration and hardening processes. *P. Rohland. Zeit. Elektrochemie*, 11, *129* (*1905*).—A reply to Jordis (preceding review). *W. D. B.*

Electromotive Forces

Temperature measurements to 1600° C. *A. L. Day and E. T. Allen. Phys. Rev.*, 19, *177* (*1904*).—A description of the precautions taken in establishing a high-temperature thermoelectric scale and a description of a platinum wire resistance furnace which allows a temperature of 1600° C to be reached and held. The melting-points selected for calibration purposes are: cadmium 321.7°; zinc 419°; silver 961.5°; copper 1065°. [The copper-silver eutectic is another good point.] *W. D. B.*

Thermo-electromotive force of nickel nitrate in organic solvents. *J. F. Meyer. Phys. Rev.*, 19, *156* (*1904*).—"The thermo-electromotive force of nickel nitrate in aniline and pyridine with platinum electrodes is zero through a temperature range of about 80° C. In solutions of nickel nitrate in alcohol, the heated electrode is first positive and becomes negative towards the cold electrode, while in acetone solutions the heated electrode is always positive. The thermo-electromotive force is independent of the concentration from one-tenth to one-fiftieth normal." *W. D. B.*

Electromotive behavior of bromine. *F. Boericke. Zeit. Elektrochemie*, 11, *57* (*1905*).—The solubilities of bromine and of bromine hydrate in bromide solutions were determined. By making assumptions as to the concentration of free bromine in bromide solutions, the electrolytic potential of bromine at 25° is calculated to be 1.098 volts. When bromide solutions are electrolyzed, a smooth platinum anode becomes passive though to a less extent than in a chloride solution. *W. D. B.*

Some experiments on the polarization recovery of cadmium cells. *S. J. Barnett. Phys. Rev.*, 18, *104* (*1904*).—The author has polarized cadmium cells in different ways and has then observed the rate of recovery. No conclusions are drawn. *W. D. B.*

On the theory of the electrolytic rectifier. *S. R. Cook. Phys. Rev.*, 18, *23* (*1904*).—A white non-crystalline film is formed on an aluminum anode in a sulphate solution when the impressed voltage is not too high. At higher voltages the film is crystalline and does not rectify. A counter-electromotive force was obtained, running in some cases to thirty volts. Experiments were made with direct current only. *W. D. B.*

On the theory of the electrolytic rectifier. *S. R. Cook. Phys. Rev.*, 20, *312* (*1905*).—An aluminum cell was polarized by a direct current and the counter-electromotive force measured sooner after breaking the circuit than had been possible in the previous set of experiments. So long as the film holds, the initial counter-electromotive force is apparently exactly equal to the impressed electromotive force. The author does not discuss the bearing of these results upon the behavior of the rectifier upon an alternating circuit. *W. D. B.*

Surface resistance and polarization at the aluminum anode. *F. Fischer. Zeit. Elektrochemie*, 10, *869* (*1904*).—By cooling an aluminum tube anode the break-down point in dilute sulphuric acid was raised above 200 volts. The author believes that we are dealing with a resistance and not with a polarization because he found that the magnitude of the current remained practically unchanged when the direction was reversed. It seems difficult to reconcile this with the rectifying action of the current. When the voltage was reduced to 12 volts, the current strength is no longer independent of the direction.
W. D. B.

A new electric furnace and various other electric heating appliances for laboratory use. *H. N. Morse and J. C. W. Frazer. Am. Chem. Jour.*, 32, *93* (*1904*).—An electric furnace is made with platinum wires arranged vertically to form a cylinder around the crucible to be heated. For temperatures below 400° soapstone slabs are covered with a graphite stove-polish. *W. D. B.*

An electrical method for the combustion of organic compounds. *H. N. Morse and L. S. Taylor. Am. Chem. Jour.*, 33, *591* (*1905*).—A description of an electrically-heated combustion furnace. *W. D. B.*

A new form of Wheatstone's bridge. *A. Coehn. Zeit. Elektrochemie*, 11, *12* (*1905*).—The author describes a cylindrical form of Wheatstone's bridge which is manufactured from his design by Gebr. Ruhstrat in Göttingen.
W. D. B.

A convenient method of mounting carbon resistances. *A. W. Gray. Phys. Rev.*, 18, *57* (*1904*).—The ends of a glass tube are silvered and wrapped with tin foil. Soot is then precipitated on the tube as described by Longden.
W. D. B.

Electrolysis and Electrolytic Dissociation

A study of the silver voltameter. *K. E. Guthe. Phys. Rev.*, 19, *138* (*1904*).—Identical results were obtained with two forms of the Richards voltameter and with a voltameter containing a large silver anode in a porous cup with granulated silver at the bottom of the cup. [Theoretically this last form must give a slightly higher value than the other.] All the silver voltameters, which other people have used, are admitted to be inaccurate. Taking the Clark cell at 15° as 1.434 volts, the electrochemical equivalent of silver is 1.11683 mg. If the Clark is 1.433 volts the value becomes 1.1176 mg. *W. D. B.*

Electrolytic behavior of copper sulphide. *G. Bodländer and K. S. Idaszewski. Zeit. Elektrochemie,* 11, *161* (*1905*).—Cuprous sulphide melts at 1109° and dissolves some metallic copper at that temperature. When a current was passed through the fused salt practically no copper was obtained at the cathode. When solid cuprous sulphide is electrolyzed above 1110° metallic copper is set free, but this does not take place at temperatures below 1100°. In fused mixtures of sodium and cuprous sulphides, copper concentrates at the anode. There seems to exist a compound NaCuS. The decomposition voltage for fused sodium sulphide is about 1.62 volts. *W. D. B.*

Comments on the paper of F. Foerster and A. Piguet. *H. Hofer and M. Moest. Zeit. Elektrochemie,* 10, *833* (*1904*).—Foerster and Piguet (9, 525) believe that there is electrolytic oxidation of acetic acid to carbon dioxide and water. The authors claim that more carbon dioxide is formed than can be accounted for in this way. They believe that the following reaction takes place to a considerable extent

$$CH_3CO'_2 + OH' = CH_3OH + CO_2.$$

No data are given as these are to be published in a later paper. *W. D. B.*

The electrolysis of potassium acetate. *F. Foerster and A. Piguet. Zeit. Elektrochemie,* 10, *924* (*1904*).—It is admitted that Hofer and Moest (preceding review) are right in their criticism of the equation

$$CH_3CO_2H + 4O = CO_2 + 2H_2O$$

and that the equation should be written

$$CH_3CO_2' + OH' = CH_3OH + CO_2.$$

They deny, however, that this correction affects their previous conclusions in any essential point. *W. D. B.*

Theory of metallic precipitation in stirred electrolytes. *R. Amberg. Zeit. Elektrochemie,* 10, *853* (*1904*).—The author considers the application to electrolytic precipitation, of the Nernst and Brunner theory of reaction velocity in heterogeneous solutions. *W. D. B.*

Electrolytic precipitation of metals from stirred electrolytes. *A. Fischer and R. J. Boddaert. Zeit. Elektrochemie,* 10, *945* (*1904*).—Experiments were made on the conditions for the rapid precipitation of nickel, zinc, copper, cadmium, lead, silver, mercury, antimony and tin. With nickel the effective time was forty minutes and with antimony thirty minutes. With the other metals, complete precipitation was obtained in ten to twenty minutes. *W. D. B.*

Anodic dissolving of metals and passivity. *O. Sackur. Zeit. Elektrochemie,* 10, *841* (*1904*).—It is believed "that the tendency of metals to become passive varies inversely as their catalytic action on a mixture of hydrogen and oxygen." In analytical work metallic zinc is used to reduce ferric sulphate to ferrous sulphate. Since metallic iron is not precipitated, the author considers that the zinc becomes passive. As a matter of fact, zinc will precipitate iron from a neutral ferrous sulphate solution. It is the excess of acid which prevents precipitation in the other case. *W. D. B.*

On electrolysis with alternating currents. *A. Brochet and J. Petit. Zeit. Elektrochemie*, 10, *909* (*1904*).—A bibliography is given of electrolysis with alternating currents. At 50°, using a direct current, a platinum cathode loses weight in a cyanide solution while the anode remains practically constant. This effect is more noticeable with barium cyanide than with platinum cyanide. The authors attribute this to a disintegration.

When working with an alternating current in a cyanide solution, no connection could be established between the number of alternations and the current yield, the yield sometimes decreasing with increasing number of alternations and sometimes increasing up to a maximum value and then falling off. With increasing current density the current yield passes through a maximum. The authors divide the metals they studied into three classes. Copper, zinc, nickel and copper dissolve in cyanide solution under the effect, both of direct and of alternating current; silver and cadmium dissolve only with direct current; iron and platinum only with alternating current. The first two classes differ because of the cathode efficiencies. If a metal precipitates at the cathode with direct current as fast as it dissolves at the anode, it will appear insoluble when an alternating current is used. *W. D. B.*

Electrolysis with alternating currents. *M. Le Blanc. Zeit. Elektrochemie*, 11, *8* (*1905*).—A criticism of the work of Brochet and Petit (preceding review). In opposition to Sackur it is explained that the author's statement that the passivity of a metal is due to its low reaction velocity is identical with the author's statement that the metal forms ions very slowly. *W. D. B.*

Electrolytic dissolving of platinum. *R. Ruer. Zeit. Elektrochemie*, 11, *10* (*1905*).—The author protests against the assumption of Brochet and Petit (two reviews back) that the case of the cathodic dissolving of platinum in potassium cyanide with alternating currents is identical with that of the anodic dissolving of platinum in sulphuric acid. The author has found that a direct current will dissolve platinum provided a reducing agent be present at the anode. *W. D. B.*

Preparation of barium platinum cyanide. *A. Brochet and J. Petit. Zeit. Elektrochemie*, 10, *922* (*1904*).—Barium-platinum cyanide can be obtained by the action of an alternating current on a barium cyanide solution when platinum electrodes are used. *W. D. B.*

Note on ion velocities. *H. Danneel. Zeit. Elektrochemie*, 11, *249* (*1905*).—It is believed that the ions of the solvent have a higher migration velocity than any others. The author writes the formula for concentration and molecular conductivity in the form

$$\Lambda - \Lambda' = k\mathrm{N},$$

where Λ is the molecular conductivity, Λ' the product of the molecular conductivity at infinite dilution into the degree of dissociation, and N the concentration. *W. D. B.*

On ion velocities. *S. Tijmstra. Zeit. Elektrochemie,* 11, *249* (*1905*).—In absolute methyl alcohol as solvent, the migration velocity of CH_3O' is greater than that of OH'. This is in line with Danneel's suggestion that the exceptionally high values for $H^\cdot$ and OH' in water are due to these being the electrolytic dissociation products of the solvent. *W. D. B.*

The electrical conductivity of very dilute hydrochloric and nitric acid solutions. *H. M. Goodwin and R. Haskell. Phys. Rev.,* 19, *369* (*1904*).—As a result of very careful measurements the molecular conductivity of *n*/1000 HCl is found to be 375.9 at 18°. For infinite dilution a value of 380.1 is obtained. The value of 395.5 obtained by Noyes and Sammet (7, 323) is believed to be wrong.

W. D. B.

Determination of the relative velocities of the ions of silver nitrate in mixtures of alcohol and water and of the conductivity of such mixtures. *H. C. Jones and H. P. Bassett. Am. Chem. Jour.,* 32, *409* (*1904*).—The curve for the conductivity of silver nitrate in varying mixtures of methyl alcohol and water has a minimum at 25° and at 0°. No minimum is found with mixtures of ethyl alcohol and water but the appearance of the curves suggests the existence of a minimum at some temperature below 0°. The transference number varies with the nature and composition of the solvent, and also with the temperature.

W. D. B.

A study of the conductivities of certain electrolytes in water, methyl and ethyl alcohols, and mixtures of these solvents—relation between conductivity and viscosity. *H. C. Jones and C. G. Carroll. Am. Chem. Jour.,* 32, *521* (*1904*).—Cadmium iodide, sodium iodide and hydrochloric acid show a minimum conductivity in mixtures of methyl alcohol and water. The dissociation of sodium iodide, potassium iodide and potassium bromide in 50 percent aqueous methyl alcohol is greater than in pure water at the corresponding dilution. There is a parallelism between conductivity and viscosity. *W. D. B.*

The electrical conductivity of solutions in methyl alcohol in the neighborhood of their critical point. *C. A. Kraus. Phys. Rev.,* 18, *40, 89* (*1904*).—"Solutions in methyl and ethyl alcohol possess maxima of electrical conductivity, the former in the neighborhood of 150°, the latter in the neighborhood of 100°. Solutions in methyl and ethyl alcohol conduct beyond the critical point, the former conducting much the better. The temperature coefficient of a solution in methyl alcohol undergoes a sudden change at a critical point. This phenomenon is apparent only when the tube is completely filled with liquid at the critical point, or when the solvent passes through the critical point without stirring. An unsaturated vapor solution exhibits no discontinuity at the critical point of the solvent. . . . The vapor of a solvent may become a very good conductor in the neighborhood of the critical point. *W. D. B.*

The significance of the maximum in the conductivity curves of Kraus at high temperatures. *H. C. Jones. Am. Chem. Jour.,* 31, *584* (*1904*).—Since the migration velocities increase with rising temperature while the dissociation decreases, there is a possibility of a maximum conductivity at some temperature. This has been found by Kraus in his work on solutions in methyl alcohol and ethyl alcohol (preceding review). *W. D. B.*

Dissociation relations for ternary electrolytes. *G. Kümmell. Zeit. Elektrochemie*, 11, *94* (*1905*).—The author has determined the dissociation of magnesium chloride, calcium chloride, calcium nitrate, barium chloride, potassium oxalate and lithium sulphate, making use of the transference numbers and the principle of isohydric solutions. It is obvious that the results cannot be any more accurate than the principle on which they rest. *W. D. B.*

On the ionization constant of phenolphthaleine, and the use of this body as an indicator. *H. N. McCoy. Am. Chem. Jour.*, 31, *503* (*1904*).—The ionization constant of phenolphthaleine is found to be 7.5×10^{-11}. For a solution to be just colorless the concentration of hydroxyl as ion should be 10^{-6} or of hydrogen as ion 1.2×10^{-8}. Experiments are cited showing the effect of time on the bleaching of phenolphthaleine by concentrated alkali. *W. D. B.*

Internal metal complexes. I. *H. Ley. Zeit. Elektrochemie*, 10, *954* (*1904*).—A study of the constitution of copper glycocollate. It was found necessary to assume the same color for a solution of the undissociated salt $Cu(OCOCH_2NH_2)_2$ and for the ion $[Cu(NH_3)_n]^{\cdot\cdot}$ because addition of ammonia caused no appreciable change in the color of the solution. *W. D. B.*

The copper and nickel salts of some amino-acids. *G. Bruni. Zeit. Elektrochemie*, 11, *93* (*1905*).—This is a comment on a paper by Ley (preceding review). The author claims that his work was done before that of Ley and that his experiments are the more conclusive. *W. D. B.*

Note on the constitution of certain organic salts of nickel and cobalt as they exist in aqueous solution. *O. F. Tower. Jour. Am. Chem. Soc.*, 27, *386* (*1905*).—Conductivity and freezing-point measurements on the glutarate, hydroxyglutarate and trihydroxyglutarate of nickel, cobalt and magnesium. There is very little evidence of polymerization in any of these cases, though the trihydroxyglutarates yield somewhat higher apparent molecular weights than the other glutarates. *W. D. B.*

A method for the determination of the affinities of acids colorimetrically by means of certain vegetable coloring-matters. *J. H. Kastle. Am. Chem. Jour.*, 33, *46* (*1905*).—When the colored aqueous extracts of certain flowers have been acted on by sulphur dioxide, acids cause a development of color, the intensity of which appears to depend on the strength of the acid. No explanation of this surprising result is offered. *W. D. B.*

Dielectricity and Optics

On the production of ozone in the Siemens generator, and on an improved generator. *A. W. Gray. Phys. Rev.*, 19, *347* (*1904*).—The conditions favorable to the economical production of ozone are :—

1. Good surface insulation of the generator, both internal and external.
2. Dry oxygen.
3. Charging and discharging as soon as possible. For this reason the resistance and self-induction of the circuit should be reduced to a minimum and it is also possible that operation by connection with a Leyden battery might yield better results than the ordinary method of employing an induction coil or an alternating current dynamo, as these machines could not give such a rapid change in the potential difference between the electrodes. Merely placing the

generator in parallel with the spark-gap of an electrical machine, as was done by Shenstone and Priest, is inefficient because the charging takes place so slowly that no illumination, and consequently no ozone is produced.

W. D. B.

Radioactivity as an atomic property. *H. N. McCoy. Jour. Am. Chem. Soc.*, 27, *391* (*1905*).—"These experiments show that the effective (or directly observed) activity of the layers of uranium compounds sufficiently thick to show the maximum α-ray activity depends not only on the uranium content but also on the coefficient of absorption of the rays by the radioactive substance itself." "When [this] absorption is taken into account the total α-ray activity of any uranium compound is strictly proportional to its percentage of uranium. This is a direct confirmation of the theory that radioactivity is an atomic property." *W. D. B.*

On the nature of certain radiations from the sulphate of quinine. *F. C. Gates. Phys. Rev.*, 19, *135* (*1904*).—Quinine sulphate emits light and ionizes the surrounding air while cooling. The phenomenon can be repeated indefinitely and is connected with the temperature change. Although the paper was suggested by the experiments of Le Bon, no effort appears to have been made to determine whether dehydration is a factor. *W. D. B.*

The temperature of the arc. *C. W. Waidner and G. K. Burgess. Phys. Rev.*, 19, *241* (*1904*).—Postulating the accuracy of Wien's law the authors find the absolute temperature of the arc to be 3690° with the Holborn-Kurlbaum pyrometer, 3680° with the Wanner pyrometer, and 3720° with the Le Chatelier pyrometer. When the current was increased from 15 to 30 amperes the temperature as given by the Holborn-Kurlbaum pyrometer increased from 3690° to 3770° ± 10°. *W. D. B.*

Radiation pyrometry. *C. W. Waidner and G. K. Burgess. Phys. Rev.*, 19, *422* (*1904*).—This is a general "study of the sources of error, necessary precautions, and limits of attainable accuracy in the use of some of the best types of radiation pyrometers that are at present available." The authors believe "that the several laws of radiation are in quite satisfactory agreement at the highest attainable temperatures, and thus serve to define the same scale of temperatures." *W. D. B.*

A limitation in the use of the Wanner pyrometer. *L. W. Hartman. Phys. Rev.*, 19, *452* (*1904*).—It was found that the Wanner pyrometer was not accurate when used to measure the temperature of fine wires. The probable cause of the error is a diffraction. "For incandescent bodies presenting considerable surface such as the interior of furnaces or pottery ovens, the instrument seems to satisfy the claims made for it." *W. D. B.*

The luminous efficiency of the carbon filament. *C. E. Mendenhall. Phys. Rev.*, 20, *160* (*1905*).—With 75 watts input the luminous efficiency of an incandescent lamp is about 2.6 percent. This would correspond to a temperature of 2150° abs. if the filament behaved like an ideal black body. *W. D. B.*

The nephelometer, an instrument for detecting and estimating opalescent precipitates. *T. W. Richards and R. C. Wells. Am. Chem. Jour.*, 31, *235*

(*1904*).—In the improved form the images of the two tubes are seen at the same time and a direct comparison thus becomes possible. *W. D. B.*

Infra-red absorption spectra. *W. W. Coblentz. Phys. Rev.*, 20, *273, 338* (*1905*).—The infra-red absorption spectra of a number of organic substances have been studied, the majority as far as 15μ. The structure of the compound has a great influence on the absorption spectra. In many cases it seems as though certain bands are due to certain groups. *W. D. B.*

Water of constitution and water of crystallization. *W. W. Coblentz. Phys. Rev.*, 20, *252* (*1905*).—In the absorption spectrum for $CaSO_4.2H_2O$ the water of crystallization acts like water. This is not the case for the water of constitution in mica and in magnesium hydroxide. From the experiments the author concludes that there is a fundamental difference between water of crystallization and water of constitution. Such a conclusion is absolutely unjustifiable on the basis of this evidence. Everybody knows that the H_2O in magnesium hydroxide shows some chemical reactions which the H_2O in crystallized calcium sulphate does not. The difficulty is that we have no criterion which enables us to tell in every case when we pass from so-called water of constitution to so-called water of crystallization. *W. D. B.*

Studies in luminescence. I. *E. L. Nichols and E. Merritt. Phys. Rev.*, 18, *355* (*1904*).—A qualitative study has been made of the phosphorescence and fluorescence of a number of substances at low temperatures. The results are tabulated under the headings: substances showing neither phosphorescence nor fluorescence at —186° C; substances which show phosphorescence but no fluorescence at —186° C; substances showing fluorescence at low temperatures but no phosphorescence; substances showing both phosphorescence and fluorescence at —186° C. Balmain's paint and the phosphorescent sulphides were the only substances tested which showed diminished phosphorescing power when cooled. *W. D. B.*

Studies in luminescence. II. *E. L. Nichols and E. Merritt. Phys. Rev.*, 18, *403* (*1904*).—Spectrophotometric measurements were made of the fluorescence spectra of fluoresceine, eosine and naphthalene-red when the solutions were excited by light of different wave-lengths. Fluoresceine solutions were studied in detail, the others not so thoroughly. The position of the maximum in the fluorescene spectrum is independent of the nature of the exciting light and fluorescene can be caused by light having a greater wave-length than that corresponding to the maximum of the fluorescence spectrum. The results confirm the conclusions of Lommel and show that Stokes's law is not universally valid. *W. D. B.*

Studies in luminescence. III. *E. L. Nichols and E. Merritt. Phys. Rev.*, 19, *18* (*1904*).—

1. Eosine, naphthalene-red, fluoresceine, rhodamine, resorcine-blue, quinine sulphate, chlorophyll, canary glass, green fluorspar, white fluorspar, and aesculine all exhibit fluorescence of the same type.

2. The fluorescence spectrum in every case consists of a single band situated near the infra edge of the absorption band with which fluorescence is associated.

3. The position of the maximum of the fluoresence band is in all cases independent of the wave-length or composition of the exciting light.

4. The distribution of the intensities in the fluorescence spectrum is independent of the wave-length of the exciting light.

5. Fluorescence occurring at the red end is traceable to a greater distance towards the violet, and fluorescence at the violet to a greater distance towards the red, than is the case with fluorescence bands in the middle of the spectrum because of the increase of luminosity in those directions.

6. Stokes's law holds for none of the numerous fluorescent substances thus far examined by us.

7. Fluorescent substances having absorption bands of shorter wave-length than that with which the fluorescence is associated are capable of excitation by the absorbed light in each band, whatsoever its wave-length.

8. Fluorescent substances may have absorption bands of greater wave-length than that with which fluorescence is associated, as in the case of green fluorspar and chlorophyll. The light absorbed in these bands does not, however, produce fluorescence.

9. Where more than one fluorescence band exists as in the case of chlorophyll, it is probable that each band is due to a distinct fluorescent material contained in the solution. No case is known of double or multiple fluorescence where only one substance capable of fluorescence is present. *W. D. B.*

Studies in luminescence. IV. *E. L. Nichols and E. Merritt. Phys. Rev.*, 19, *396* (*1904*).—Experiments on solutions of fluoresceine in water, eosine in alcohol, and resazurine in alcohol show that there is an increase in absorbing power during fluorescence, the effect being most marked in the case of fluoresceine. It was found that there is also an increase in electrical conductivity during fluorescence, a fact which is looked upon as strong evidence in favor of the view that fluorescence and dissociation are connected. *W. D. B.*

Note on the Budde effect with reference to bromine. *B. P. Caldwell. Am. Chem. Jour.*, 31, *61* (*1904*).—The temporary expansion of bromine when exposed to a flash-light was eighteen times as great as that of chlorine. The author gives no data but he expresses his belief that the temperature change is not sufficient to account for the behavior of the bromine vapor. *W. D. B.*

Crystallography, Capillarity and Viscosity

Fibers resembling fused quartz in their elastic properties. *K. E. Guthe. Phys. Rev.*, 18, *256* (*1904*).—The steatite or soapstone, $Mg_3H_2Si_4O_{12}$, can easily be melted in the oxyhydrogen blowpipe and can be drawn into fibers possessing practically the same elastic properties as quartz fibers. The index of refraction of steatite for sodium light is 1.577. *W. D. B.*

The application of allotropic silver for the preparation of conducting fibers. *N. A. Dubois. Phys. Rev.*, 19, *48* (*1904*).—"The dried films of allotropic silver, although poor conductors, become very good conductors on treatment with gaseous hydrochloric acid.

"The emulsion can be used admirably for the preparation of conducting fibers, and can be applied to the most delicate apparatus in a very few minutes without the danger of injury." *W. D. B.*

ON THE ADSORPTION OF WATER VAPOR AND OF CERTAIN SALTS IN AQUEOUS SOLUTION BY QUARTZ[1]

BY LYMAN J. BRIGGS

Adsorption may be defined as the action by which the concentration or density of a gas, liquid or dissolved substance at a surface is changed with respect to that of the surrounding medium. This term was first applied to this class of phenomena by duBois-Reymond, and seems preferable to "absorption," —a term which is also used to designate the solution of a gas in a liquid.

Gibbs[2] and J. J. Thomson[3] have investigated theoretically the adsorption of a dissolved substance by considering the change in the surface tension of the liquid-solid surface as the concentration of the solution increases. They have shown that if the surface tension of the film increases as the concentration increases, a part of the dissolved salt will pass out of the film, so that there will be less salt in a unit volume of the surface film than in a unit volume of the liquid in bulk; while if the surface tension is diminished by the addition of salt, the salt will move into the film, and the surface film will contain more salt per unit volume than the rest of the liquid. The latter condition is thus essential for positive adsorption of the solute.

Thomson refers, in support of these deductions, to the experiments of Röntgen and Schneider,[4] who found, "that for most solutions, the product of the height to which the solution rises in a capillary tube into the density of the solution is greater for a solution of a salt than for pure water, and that for dilute solutions of most (though not all) substances this product increases with the strength of the solution. It follows from this fact that the tension of the surface of contact of the solution with air in-

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[1] Published by permission of the Secretary of Agriculture.

[2] Trans. Conn. Acad., Vols. 2 and 3.

[3] Applications of Dynamics to Physics and Chemistry, 1888, p. 190.

[4] Wied. Ann., 29, 165 (1886).

creases with the strength of the solution, while the tension of the surface of contact of the solution with glass or any other solid body diminishes as the solution gets stronger."[1]

I am unable to see that Prof. Thomson's conclusion, that "The tension of the surface of contact of the solution with glass, or any other solid body diminishes as the solution gets stronger" necessarily follows from the experiments of Röntgen and Schneider. Their measurements were made by means of a capillary tube, the walls of which were wetted with the solution above the meniscus. The measurements consequently do not involve the tension of the liquid-solid surface, and no conclusion regarding the tension of this interface can therefore be drawn from their results.

These interesting theoretical deductions regarding adsorption cannot therefore be experimentally verified for solid surfaces until we possess a method for measuring the tension of the liquid-solid interface. Zawidski[2] has, however, tested these conclusions for the liquid-gas surfaces of two different systems. Saponine was added to aqueous solutions of hydrochloric and acetic acids, and bubbles of air were then slowly drawn through the solutions. The foam was collected and analyzed, and was *found to be more concentrated than the original solutions*. This is wholly in accord with the theory, since hydrochloric and acetic acids both decrease the surface-tension of water. Similar results have been obtained by Miss Benson,[3] using aqueous amyl alcohol.

This suggests that the decrease in the surface-tension of the liquid-gas interface of a solution which generally occurs when a liquid surface is allowed to stand for a time and which is usually ascribed to the presence of impurities on the surface may be due, in part at least, to changes in the concentration of the surface-layer, which would always take place in such a direction as to lower the surface-tension.

The investigation described in the following pages may be

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[1] Thomson, Dynamics, p. 190.

[2] Zeit. phys. Chem., 35, 77 (1900).

[3] Jour. Phys. Chem., 7, 532 (1903).

divided into two portions: Part I deals with the adsorption of substances in aqueous solution by quartz, under conditions such that changes in the concentration of the liquid-gas interface are eliminated; Part II deals with the adsorption of water-vapor by quartz at different vapor pressures.

Part I. The Adsorption of Dissolved Substances by Quartz

Review of Earlier Work

A general historical account of investigations on the adsorption of dissolved substances up to the year 1890 may be found in Ostwald's *Lehrbuch der allgemeinen Chemie, Vol. I.*[1] These investigations nearly all deal with adsorption by wood or bone charcoal, substances which, while showing marked adsorption effects, are poorly suited for quantitative investigations, owing to the great difficulty in obtaining uniform samples. The foreign substances contained in the charcoal also make chemical reaction possible with the substance under investigation. In fact, Graham,[2] whose experiments are among the most extensive of those employing animal charcoal, satisfied himself that chemical action did take place, and was inclined to consider the effect as being largely due to chemical action when this substance is employed.

Van Bemmelen[3] appears to have been the first to investigate the adsorption of salt and acid solutions in a quantitative way. He worked with sulphuric, nitric and hydrochloric acids, and their three potassium salts. He used amorphous silica as the adsorbing substance, prepared by precipitation from soluble silicates by hydrochloric acid. Ten grams of silica, dried at 100° C, were used in each case. The silica was kept in contact with 100 cc of the solution for twenty-four hours, the mixture being frequently shaken. The results are given in the following table. The first column expresses the number of milligram-equivalents (gram-molecules ÷ 1000) of salt in 100

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[1] For a bibliography of the adsorption of gases, see Mülfarth: Drude's Ann., 3, 328 (1900).

[2] Pogg. Ann., 19, 139 (1830).

[3] Jour. prakt. Chem., 23, 324 (1881).

cc of solution. The remaining columns give the number of milligram-equivalents of the various substances removed from solution by the silica.

Concen.	K_2SO_4	KNO_3	KCl	H_2SO_4	HNO_3	HCl
20	1.0	0.9	0.85	1.1	0.86	0.81
50	2.5	2.14	2.16	2.17	2.17	2.27
100	4.56	—	—	4.0	4.0	4.2

It will be noted from an inspection of the above figures that the quantity of acid or salt removed by the silica is approximately proportional to the concentration of the solution, although in the case of the most concentrated solutions, the amounts removed are somewhat less than would be required by such a relation.

Van Bemmelen, in discussing these results, calls attention to an apparent relation between the amount of salt removed and the amount of water which the silica would give up if dried at 100° C. He found the latter amount to be about 55 percent, which for 10 grams of silica would be 5.5 cc. From an inspection of the table, it will be seen that the amount of salt taken up corresponds to a bodily removal of from 4 to 4.5 cc of the solution. This led Van Bemmelen to suggest that when the silica was put into a solution, the water it contained was replaced by an equal volume of the solution.

Schmidt[1] has investigated quantitatively the amount of adsorption in the following systems: Iodine, from alcohol and benzol solutions, by blood and bone charcoal; acetic, oxalic and succinic acids in aqueous solutions by blood and bone charcoal; picric acid by cellulose; eosine and malachite green by silk. He found in every case that the ratio of the amount of material adsorbed to the concentration decreased as the concentration increased, the adsorption in most cases being relatively much greater for the more dilute solutions.

Schmidt also investigated the adsorption of potassium chloride by precipitated silica, and obtained results agreeing with

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[1] Zeit. phys. Chem., 15, 56 (1894).

those of van Bemmelen; that is, the amount of adsorption was very nearly proportional to the concentration, the ratio increasing slightly as the concentration diminishes. He consequently concludes that dissolved substances are taken up by precipitated silica mainly in the form of a solid solution rather than through adsorption processes.

Van Bemmelen[1] shows that in colloids, there is no way by which we can distinguish between absorption and adsorption. He also states[2] that the phenomenon of physical adhesion must in some cases be considered as a kind of loose chemical combination.

The adsorption of very dilute acid and alkaline solutions by platinum black has been investigated by Kellner,[3] by means of the electrical conductivity method. His results show that the amount of adsorption is relatively greater as the concentration diminishes.

Object of the Investigation

The object of this part of the investigation was to determine the amount of adsorption on quartz surfaces of known area from dilute aqueous solutions of various salts. Quartz is one of the chief constituents of the soil, and a knowledge of its action as an adsorbing agent is of fundamental importance in the study of the retention of soluble substances by soils. Furthermore, quartz is one of the most nearly insoluble substances known, which makes it of special value in adsorption investigations. Finally, it is possible to calculate roughly the surface area exposed in a sample of powdered quartz by separating the particles into groups according to size, and determining the percentage of particles in each group and their mean diameter.

Preparation of the Quartz

The quartz used was obtained from a vein in Lancaster County, Pennsylvania, where the material is crushed to fine powder in large quantities for the purpose of manufacturing

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[1] Zeit. anorg Chem., 23, 321 (1900).

[2] Loc. cit., p. 380.

[3] Wied. Ann., 57, 79 (1896).

porcelain. Upon examination, the material was found to contain a small amount of chlorides, carbonates and bicarbonates, so that a thorough washing was necessary before the material could be used. The washing was carried out in the following manner: About 150 grams of material were placed in a bottle containing distilled water acidulated with hydrochloric acid, and shaken for several hours in a mechanical shaker. These bottles were then placed in a centrifugal apparatus and rotated until practically all the suspended particles were thrown down when the supernatant liquid was decanted. Fresh distilled water was then added and the operation repeated until the specific electrical resistance of the decanted water was from 100,000 to 200,000 ohms. The quartz was then removed from the bottles, dried thoroughly at 110° C, and after thorough mixing was ready for use. A microscopic examination of the quartz showed the grains to be sharp and angular, free from seams and fissures, and practically free from occlusions.

Measurement of the Surface Area of the Powdered Quartz

The calculation of the surface area necessitates the separation of the soil grains into groups according to size, and the subsequent determination of the relative percentages by weight of the various groups, and the mean diameter of the particles constituting each group. The different groups were separated by means of their different rates of subsidence in water, the process being accelerated with the aid of a centrifugal apparatus.[1]

The composition of the material employed in the following experiments as determined by several analyses, is given below:

Diameter mm.	Percentage
0.25–0.1	2
0.1– 0.05	12
0.05–0.005	85
0.005	1

In calculating the surface area, the particles were considered cubical in form, and the mean diameter of any group was assumed to represent the longest diagonals of the cubical particles

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[1] Bull. 24, Bureau of Soils, U. S. Dept. Agr., 1904.

constituting that group. On this basis of calculation, the powdered quartz used was found to have a surface area of about 1000 sq. cm. per gram.

Method Employed in Measuring Adsorption in Aqueous Solutions

The method employed in measuring the adsorption consisted in preparing a series of solutions of each substance under investigation and determining by titration the concentration of each solution before and after adsorption. One hundred and fifty cc of solution were used for each 100 grams of quartz. The solution and powdered quartz were always shaken together for at least thirty hours in a rotating shaker, which insured constant and thorough contact between solution and solid. The glass bottles employed in this work were all treated with sodium hydroxide solutions previous to their use in the adsorption experiments, in order to minimize the action of the alkaline solutions upon the glass. The systems were subject to the fluctuations of the temperature of the room, which averaged about 22° C.

Explanation of Tables

In the following tables, the first column, in the case of each solution, gives the concentration of the solution after adsorption in gram-molecules per liter. In the case of the carbonates the molecular weight was divided by two. The second column gives the total adsorption of salt in gram-molecules by 100 grams of quartz (100,000 sq. cm. of surface) for that particular concentration. Several titrations of each solution were made, hydrochloric acid being used as the titrating reagent. Methyl orange was used as indicator in all titrations of the carbonate and hydroxide solutions. The color change was determined by comparison with an equal amount of indicator diluted to the same volume in beakers of the same size and form.

In addition to the determinations given in the accompanying tables, the adsorption of sodium, ammonium, and magnesium chlorides was investigated. These salts failed to show any meas-

TABLE I

Adsorption of Hydroxides by Quartz

Sodium hydroxide		Potassium hydroxide		Ammonium hydroxide	
Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mols.
0.0007	0.42×10^{-4}	0.0009	0.33×10^{-4}	0.0008	$0.55\times 10_{-4}$
0.0026	0.79	0.0021	0.91	0.0032	0.74
0.0078	1.48	0.0063	1.63	0.0102	1.04
0.028	3.45	0.0235	3.3	0.0344	2.94
0.0866	8.10	—	—	0.1052	7.68

TABLE II.

Adsorption of Carbonates by Quartz

Sodium carbonate		Potassium carbonate		Ammonium carbonate	
Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mols.	Concentration Gm. mols.	Total adsorption Gm. mol.
0.0004	0.06×10^{-4}	0.0029	0.45×10^{-4}	0.0022	0.09×10^{-4}
0.0012	0.18	0.0093	0.76	0.0065	0.45
0.0032	0.97	0.0302	1.65	0.0208	0.45
0.0106	1.13	0.0910	2.4	0.063	1.8
0.0356	1.65	—	—	—	—
0.108	1.95	—	—	—	—

urable adsorption either by titration or conductivity methods.[1] The same result was obtained in the case of sodium nitrate and sodium sulphate, even when an amount of solution was used only sufficient to saturate the quartz, which, for the same amount of adsorption, would produce a relative change in the concentration of the solution about five times as great as in the preceding experiments. These statements must not, of course, be interpreted to mean that there is no adsorption of these neutral salts. The measurements serve simply as a basis for assigning a superior limit to the magnitude of the effect—an effect which may or may not exist. The conductivity method

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[1] An exception occurred in one series of experiments with sodium chloride, when a slight adsorption was observed, but subsequent experiments failed to show any definite effect.

is by no means ideal for such measurements, since there is always the possibility of some substance going into solution, which serves to mask the effect sought. This was avoided as far as possible by washing the powdered quartz thoroughly. The resultant change in the conductivity of the neutral solutions by the addition of the quartz amounted to less than one part in two hundred. This serves to show that there is a radical difference between neutral and alkaline salts in their adsorption by quartz, which is in general agreement with the experiments on the adsorption of these salts by other substances.

Returning now to the adsorption of the carbonates and hydroxides, an examination of Tables I and II shows that while there are many irregularities, the amount of adsorption is dependent upon the acid radical, the adsorption of the hydroxides being more marked than that of the carbonates. On the other hand, the results obtained for potassium, sodium and ammonium hydroxide are quite similar, and the same relation is to be observed in the corresponding carbonate series. In other words, in this series of salts, the influence of the basic element is small compared with that of the acid radical.

These conclusions lead to the idea that possibly the adsorption observed may be largely due to the presence of the hydroxyl ion. Shields[1] has investigated the hydrolysis of a tenth-normal solution of sodium carbonate, and finds it to be about 3 percent at 25° C. On the above supposition, therefore, the adsorption of a tenth-normal sodium carbonate solution and a three-hundredth-normal sodium hydroxide solution should be the same. Reference to the data shows that the adsorption of tenth-normal solution of sodium carbonate is about four times greater than could be explained on this basis. This hypothesis cannot, therefore, explain the marked adsorption of the carbonates, although hydrolysis undoubtedly has some influence on the amount of adsorption.

While precautions were taken to reduce to a minimum the action of the alkaline solutions upon the glass bottles used in

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[1] Zeit. phys. Chem., 12, 167 (1893).

the experiments, the results obtained are liable to some uncertainty in this respect. To investigate this point, experiments were made upon the adsorption of potassium hydroxide by quartz contained in a platinum bottle. Quartz sand was chosen for this purpose in order that the material might be more readily washed. Eighty grams of quartz sand were used, to which 20 cc of approximately tenth-normal potassium hydroxide solutions were added. This amount of the solution was just about sufficient to fill the interstitial space in the amount of quartz sand used. When the system had attained equilibrium, a portion of the solution was removed from the quartz sand by means of a centrifugal machine, care being taken to avoid evaporation during this process. Weighed portions of the solution thus removed were titrated, and the concentration compared with that of the original solution. Three experiments were made with the same sample of quartz, which was washed after each experiment until conductivity measurements showed that no soluble material was being removed. The results are given in the following table, being determined from a mean of at least two titrations of the hydroxide solution in each case. The amount of the salt adsorbed is expressed both in terms of the total adsorption and as a percentage of the total amount of the salt originally present in the 20 cc of solution used:

TABLE III

Adsorption of Potassium Hydroxide by Quartz Sand

Experiment No.	Time Days	Adsorption Percent	Total adsorption Gm. mols.
1	25	1.22	2.44×10^{-5}
2	18	1.24	2.48
3	35	0.98	1.96

The quartz sand used in the experiments in Table III was made up of grains of the following sizes:

Limits mm.	Percent
1–0.5	4.7
0.5 –0.25	36.9
0.25–0.1	57.7
0.1 –0.05	0.7

This gives a calculated surface area, in accordance with the method already described, of about 175 sq. cm. per gram.

The 80 grams of quartz sand employed would then present a surface area of 14000 sq. cm. This surface adsorbed from a tenth-normal potassium hydroxide solution 2.3×10^{-5} gram-equivalents, the mean of the three determinations given in Table III. This corresponds to 1.66×10^{-9} gm. mols. per. sq. cm., or 1.66×10^{-5} gm. mols. per. sq. meter, which is equivalent to about 0.6 mg. of potassium hydroxide per square meter of surface.

There is, however, another point which must be considered in this connection. The alkaline solution thrown out of the quartz sand by the centrifugal machine was found to be very slightly turbid. This turbidity indicates that some chemical action had taken place between the quartz and the hydroxide solution. This could not be detected in the former experiments on account of the fine state of division of the powdered quartz. The carbonate and hydroxide systems investigated cannot then be considered free from chemical action.

The apparent adsorption per square meter is considerably higher for the experiments with powdered quartz in glass bottles than for quartz sand in the platinum bottle, and I consider the latter value more reliable, since the surface could be calculated more accurately, and chemical action between the hydroxide solution and the glass was avoided.

From a consideration of the results given above, we are led to the conclusion, that so far as quartz is concerned, the phenomenon of adsorption is of minor importance in the retention of soluble substances in the soil. The apparent adsorption of potassium hydroxide by fine quartz sand amounted to but little more than one per cent of the salt present in an amount of the solution sufficient to fill the interstitial space of the sand. With the neutral salts, no appreciable adsorption could be observed, even when the powdered quartz was used, which presented as great a superficial area as is found in many soils. The marked retention of dissolved salts which has often been observed in connection with soils appears, therefore, to be due to causes other than direct adsorption on the surfaces of the crystalline quartz particles. In some instances the retention of a dissolved substance by a soil has been shown quite conclusively to be due to chemical fixation or substitution; in other cases, it appears to be associated with colloidal substances in the soil. We have only to refer to van Bemmelen's experiments with colloidal silica to note the marked retention of salts by this class of substances.

Part II. The Adsorption of Water Vapor by Quartz

The adsorption of water vapor by glass surfaces of known area has been investigated by Bunsen,[1] Warburg and Ihmori,[2] Ihmori,[3] and Parks.[4]

Warburg and Ihmori divide the water film condensed on the surface of a solid into two portions, which they call "temporary" and "permanent." The "temporary" portion is that which disappears when the vapor-pressure is reduced to zero. Obviously this is only a relative classification, the temporary portion depending upon the temperature of the system.

Bunsen investigated the "permanent" water film absorbed on a glass surface at a temperature ranging from 20° to 500° C. He passed a stream of dry air slowly over glass fibers, which were kept at constant temperature, and collected the water-vapor which was given off in phosphorus pentoxide tubes, which were weighed before and after each experiment. The temperature was then raised and the process repeated. Bunsen found that water-vapor was given off from glass up to the highest temperature investigated, namely, 500° C. The total amount liberated from 2.11 sq. meters of glass surface, which had previously been thoroughly dried at 20° C. was 22.3 mg.

Warburg and Ihmori suggest two possible causes for the formation of films of water on glass: First, that the vapor pressure of a very thin film of water is lower than the vapor pressure of a thick film; second, that substances of a hygroscopic charac-

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[1] Wied. Ann., 20, 545 (1883); 24, 321 (1885).

[2] Ibid., 27, 481 (1886).

[3] Ibid., 31, 1006 (1887).

[4] Phil. Mag. [6], 5, 517 (1903).

ter, such as free alkalies, are present in the glass in small amounts and exert an attraction for water. They consider that the first assumption is not valid since Sir William Thomson[1] has shown that the surface tension of a very thin film must decrease as the thickness is diminished, and consequently the vapor pressure must increase as the thickness decreases.

Granting that a *free* film can theoretically be made so thin as to decrease the surface tension, and consequently increase the vapor pressure, it does not appear to me that Warburg and Ihmori are justified in applying these conclusions to a film held upon the surface of a solid. As the film on the surface of a solid diminishes in thickness, the tension of the liquid-air interface must *increase* as the surface comes within the radius of attraction of the molecules of the solid. Such a film would therefore have a lower vapor pressure than a free liquid film. Condensation would consequently take place until the vapor pressure of the film is equal to that of the surrounding vapor. The matter may be put more simply by saying that the molecules of the vapor are attracted more strongly by the molecules forming the surface of the solid than by a free liquid surface. Condensation consequently occurs until the surface of the adsorbed film is sufficiently removed from the action of the molecules of the solid to have the same vapor pressure as the free liquid surface. We thus see that contrary to Warburg and Ihmori's conclusions, the condensation of films of water upon solid surfaces may be rationally attributed to an attraction between the solid and the vapor.

Warburg and Ihmori investigated the temporary film on glass surfaces of various kinds at ordinary temperatures by the method of direct weighing. Thin bulbs of glass were suspended from the arm of a delicate balance of great sensibility enclosed in an exhausted receiver, which could be connected at will with a water chamber or with a phosphorus pentoxide drying tube. They found that measurable amounts of water vapor were condensed upon the surface of freshly blown glass bulbs and of

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[1] Nature, March 1870; Natural Philosophy, 1, Part 2, Appendix F., p. 499.

bulbs which had not been thoroughly washed. After washing or boiling these glass surfaces and then thoroughly drying, no adsorption of water vapor could be detected. These results supported their second assumption that the formation of the water films was due to the combination of water with some of the constituents of glass, which were set free when a fresh glass surface was exposed, and which were subsequently removed by washing or long boiling in water.

The adsorption of water vapor by a number of substances, including quartz, was later made by Ihmori, with an improved balance, by the same method. He found no measurable adsorption on washed quartz crystals, although unwashed crystals showed a slight effect.

Dobeneck[1] has made an extensive investigation of the adsorption of water vapor, ammonia and carbon dioxide by various soil constituents including quartz. In his experiments with water vapor, saturated air was passed over the powdered material contained in a U-tube, the whole apparatus being kept at a constant temperature by a thermostat. The results he obtained for the adsorption of water vapor by quartz are much higher than those given in the following experiments, due, I believe, to the capillary condensation which is unavoidable when working at or near the dew-point with a powdered material that is not continually stirred. This phenomenon is entirely distinct from that of adsorption, since it is dependent only upon the form of the liquid surface and should consequently not be confused with adsorption measurements.

An interesting question is raised in this connection, namely, the extent to which adsorption is dependent upon the form of the solid surface. An approximate idea of the magnitude of the effect may be obtained by considering the somewhat analogous case of the capillary surface. A capillary tube 0.001 mm. in diameter would support a capillary column approximately 33 meters in height at ordinary temperatures. The weight of a column of water vapor at this height and 1 sq. cm. in cross section

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[1] Forschungen auf dem Gebiete der Agrikulturphysik, 15, 163 (1892).

at 30° C is about 0.1 gm. The vapor pressure at the top of the column is then about 0.07 mm. or 0.2 percent less than at the bottom. Consequently, we may say that in the case of a thin film on the surface of a spherical solid particle 0.001 mm. in diameter, the vapor pressure would be approximately 0.2 percent greater than for a film of equal thickness, held upon a plane surface of the same solid. The influence of the geometrical form of the solid is therefore so small that it falls well within the limit of error in adsorption investigations.

Object of the Investigation

Warburg and Ihmori, as we have already seen, concluded that the formation of water films on the surface of solids was due to the presence of substances capable of forming solutions with the water vapor. Unquestionably such substances do play an important part in the formation of water films on solid surfaces. However, it is evident that the failure of Warburg and Ihmori to obtain a measurable film in the case of surfaces which had been thoroughly washed, may have been due to lack of sufficient sensibility in their balance rather than to the actual non-existence of the film.

The theory of Gibbs regarding the adsorption of dissolved salts should apply equally well to the formation of films of gases or vapors on the surface of a solid. In the case of any solid which is wetted by water, we know that the surface tension of the solid-gas surface must exceed that of the solid-liquid surface, since the first surface contracts at the expense of the second. Such a solid, if exposed to the vapor of water will, therefore, condense upon its surface a film of the vapor, since by this action the surface energy of the system will be diminished. An aqueous film should thus be found upon the surface of any solid which can be wetted by water, without regard to the presence of soluble substances.

It was determined to test this hypothesis in connection with a carefully washed surface which is wetted by water, and under conditions such as to avoid condensation in capillary spaces. Quartz appeared particularly well suited to an investigation of this kind. Its very slight solubility (if it is at all soluble) in water at ordinary temperatures reduces to a minimum the possibility of the existence of substances on the surface of the quartz grains capable of forming a solution with water. The results of the following investigation show that washed quartz has both a temporary and permanent adsorption film.

Description of Apparatus

The apparatus used in the following investigation consisted of pairs of cylindrical glass bulbs, connected in the manner shown in the accompanying figure (Fig. 1) and supported on the periphery of a rotating drum which was immersed in a thermostat at 30° C. In one of the bulbs of each pair a weighed amount of powdered quartz was placed after having been thoroughly washed and dried, while in the other bulb was placed an aqueous solution of sulphuric acid, the concentration depending upon the vapor pressure at which the adsorption determinations were to be made. The bulb containing the quartz was provided with a smaller auxiliary bulb to catch any of the quartz that might work out of the larger bulb during the course of the experiment. The two bulbs were connected by heavy black rubber tubing, which fitted snugly over the tubulures. The metal drum supporting the cylindrical bulbs was placed with its axis horizontal in a thermostat, and was driven by a helical spring-brass belt from the shaft of the stirrer. The bulbs containing the quartz and the acid solutions thus

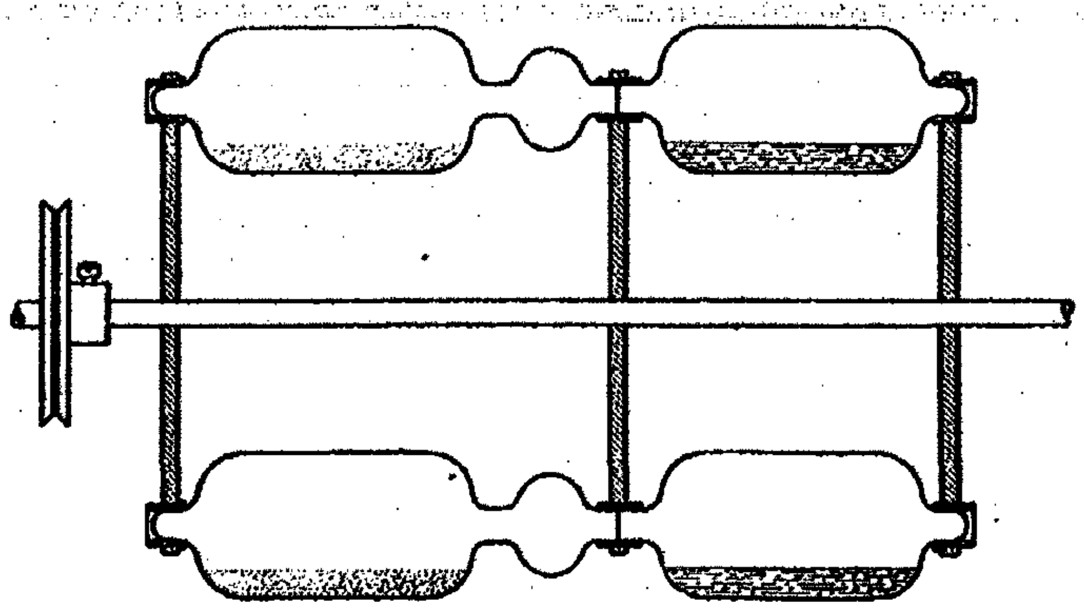

Fig. 1

slowly rotated about a horizontal axis parallel to, but not coincident with, their common axis. As a result of this rotation, the powdered quartz was continuously stirred, while the walls of the bulb containing the acid were kept wetted with the solution. This stirring is of the utmost importance, as otherwise condensation will occur in the minute capillary spaces formed by the contact of the quartz particles.

The concentration of the sulphuric acid solution used in the adsorption experiments, together with the corresponding vapor pressure at 30° C is given in the following table:

TABLE IV

Vapor Pressures of Solutions used in Adsorption Experiments

	Percent H_2SO_4	Sp. gr.[1] 15°/4° C.	Vapor pressure[2] 30° C.
$H_2SO_4 + H_2O$	84.58	1.780	0.235
$H_2SO_4 + 5H_2O$	52.13	1.420	10.684
$H_2SO_4 + 9H_2O$	37.69	1.287	19.594
$H_2SO_4 + 17H_2O$	24.26	1.176	26.117
$H_2SO_4 + 296H_2O$	2.67	1.016[3]	31.35[4]
H_2O	0.		31.510[5]

Experimental Results

In investigating the adsorption of water vapor on quartz, two methods were employed. In the first method, the adsorbed water was removed from the surface of the quartz by exposing the latter to phosphorus pentoxide at room temperature. This removes the "temporary" film. In the second method, the quartz, with its adhering film of water, was weighed, then dried at 110° C, and weighed again. The loss in weight gives the

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[1] Lunge and Isler: Zeit. angew. Chem., 1890, 129; Landolt and Börnstein: "Tabellen," 2 Auf., p. 196.

[2] Regnault: Ann. Chim. Phys. (3), 15, p. 179, 1845. Landolt and Börnstein: "Tabellen," 2 Auf., p. 65.

[3] Determined for the writer by Miss J. R. Pearce.

[4] Interpolated from Regnault's measurements of the vapor pressure of sulphuric acid solutions, and of pure water.

[5] Regnault: see Landolt and Börnstein, "Tabellen," 2 Auf., p. 53.

"temporary" portion plus that part of the "permanent" film which is released by raising the temperature to 110° C.

First Method

The powdered quartz, after having been thoroughly dried, was exposed to water vapor at constant temperature for a time sufficient to bring the system into equilibrium, which was determined by preliminary experiments. The bulbs containing the quartz were then detached from the bulbs containing the sulphuric acid solution, and attached to small glass weighing tubes which contained phosphorus pentoxide supported on glass wool. These systems were rotated as before on a drum, so as to expose all portions of the quartz to the drying reagent. Successive weighings of the pentoxide tubes were made until no further change in weight was observed. The gain in the weight of the pentoxide tube represented the amount of water vapor removed from the bulb containing the quartz. This amount of water vapor was not, however, all obtained from the surface of the quartz particles, a part coming from the water existing in the vapor phase, and from the surface of the glass bulb. To obtain this correction, the quartz was removed from the bulbs, which were once more attached to the corresponding acid bulbs and rotated in the thermostat until equilibrium had been established, when they were again attached to fresh phosphorus pentoxide tubes, and the gain in weight of the latter noted. The total weight recorded in the first experiment less the gain in weight from the empty bulbs gave the weight of water vapor adsorbed upon the surface of the quartz. Care must be observed in such experiments regarding the use of rubber in the form of tubing or stoppers, as it is capable of giving up or absorbing a very appreciable amount of moisture.

The results of duplicate experiments carried on in this manner are given in the following table. The first column gives the vapor pressure at 30° C of the solution employed. The second column gives the total adsorption in milligrams observed in the first experiment. The third column shows the adsorption of the empty bulbs as observed in the second part of the experiment. The fourth column is obtained by subtracting the results in column three from those in column two, and represents the amount of water vapor adsorbed on the surface of quartz particles. Fifty grams of quartz were used in each of these experiments, having a superficial area calculated from mechanical analyses of 400 square centimeters per gram.

TABLE V

Adsorption of Water Vapor by Powdered Quartz

Vapor pressure mm.	Total adsorption mg.	Adsorption by bulb mg.	Adsorption by quartz mg.
26.1	10.4	1.0	9.4
	9.7	1.0	8.7
19.6	6.2	1.8	4.4
	5.3	0.5	4.8
0.2	0.5	0.1	0.4
	0.3	0.1	0.2
	0.9	0.0	0.9

Second Method

In this series of experiments, the quartz was first dried to constant weight at 110° C, and the adsorption was determined from the subsequent gain in weight when exposed to water vapor. The bulbs containing the quartz were closed with well-ground glass stoppers immediately after being taken from the oven, and were cooled in phosphorus pentoxide desiccators. The weighings were made with a counterpoise bulb of the same form, and made of the same glass as those containing the quartz. The bulbs in every case were left upon the balance until successive weighings showed that no further change in weight had occurred. It was not possible to obtain as close weighings as in the former experiments where the smaller phosphorus pentoxide tubes were used on account of the greater amount of surface exposed.

After obtaining the dry weight, the bulbs containing the dry quartz were attached by means of heavy black rubber tubing to the bulbs containing the acid solutions, as before, and placed in the thermostat. The following table shows the gain in weight due to the adsorption of water vapor. The experiments were made in duplicate. The first column gives the number of the bulb; the second, the time in days in which the systems were in the thermostat; the third, the weight of the bulbs containing the quartz; the fourth, the gain in weight; that is, the amount of water vapor adsorbed. Experiments were made with solutions of three concentrations, as indicated in the titles of the tables. Twenty-five grams of quartz were used in each of the experiments, having a calculated surface area of 400 sq. cm. per gram.

TABLE VI

Adsorption of Water Vapor by Powdered Quartz from Sulphuric Acid Solution ($H_2SO_4+5H_2O$) *at 30° C.*

Tube No.	Time Days	Weight gms.	Adsorption mg.
20	0	23.4298	0.0
23	0	23.2442	0.0
20	5	23.4333	3.5
23	5	23.2464	2.2
20	12	23.4331	3.3
23	12	23.2464	2.2
20	19	23.4333	3.5
23	19	23.2465	2.3

It will be noted in Table VI that determinations with tube No. 20 were invariably higher than with tube No. 23. This is probably due to the presence of a film of foreign material left on the surface of the bulb after having been used in an experiment with an adobe clay. This film resisted washing with water and scouring with sand, but was found at the end of the experiment to have been removed by the continuous scouring action of the sharp quartz particles.

It will be seen from the results given in Table VIII that the time necessary to establish equilibrium in this case was much greater than in former experiments. This is probably due in part to the fact that capillary condensation occurred to

TABLE VII

Adsorption of Water Vapor by Powdered Quartz from Sulphuric Acid Solutions ($H_2SO_4+9H_2O$) at 30° C.

Tube No.	Time Days	Weight gms.	Adsorption mg.
17	0	24.9770	0.0
18	0	24.6982	0.0
17	5	24.9812	4.2
18	5	24.7033	5.1
17	12	24.9827	5.7
18	12	24.7042	6.0
17	19	24.9829	5.9
18	19	24.7038	5.6

TABLE VIII

Adsorption of Water Vapor by Powdered Quartz from an Aqueous Sulphuric Acid Solution ($H_2SO_4+196\ H_2O$) at 30° C.

Tube No.	Time Days	Weight gms.	Adsorption mg.
25	0	23.5638	0.0
17	0	24.9771	0.0
25	3	23.5774	13.6
17	3	24.9915	14.4
25	7	23.5844	20.6
17	7	24.9965	19.4
25	12	23.5853	21.5
17	12	24.9993	22.2
25	19	23.5883	24.5
17	19	25.0006	23.5
25	26	23.5910	27.2
17	26	25.0047	27.6
25	33	23.5912	27.4
17	33	25.0030	25.9

some extent. The quartz showed a tendency in the latter part of the experiment to stick to the walls of the tube, which would make capillary condensation possible. This action finally became so pronounced that it was necessary to arrange a mechanical hammer in such a manner as to subject the tube to a continuous series of sharp blows, which dislodged the quartz grains from the inner surface of the tubes. This device prevented the particles from maintaining fixed positions with reference to each other, thus preventing capillary action, and it will be noted that neither tube gained in weight after the hammer was attached; in fact, tube No. 17 diminished somewhat in weight.

Thus we have, in the case of quartz, an adsorption of water vapor which increases as the vapor pressure approaches the dew-point, similar to the observations of Warburg and Ihmori for glass and other substances. Furthermore, quartz possesses also the so-called "permanent" film, as shown by the increased amount of water vapor liberated when the quartz is dried at 110° instead of at 30° C. This quartz had been thoroughly washed with distilled water, and I am, therefore, inclined to the opinion that the formation of the water film in this case is due not to the presence of soluble material on the surface of the quartz particles, but to the attraction of the quartz itself for the water vapor, in accordance with the theory of Gibbs.

The thickness of the "temporary" film in a five-sixths saturated atmosphere, as calculated from the preceding experiments is 4.5×10^{-7} cm, assuming the density of the adsorbed film to be uniform and equal to unity. The maximum thickness calculated from the results obtained by the second method which includes a portion of the "permanent" film is 2.66×10^{-6} cm in an atmosphere within one percent of saturation. This latter value is of the same order as that recently found by Parks, for the thickness of the adsorbed film on glass wool in a saturated atmosphere at 15° C, namely 13.3×10^{-6}.

Summary

An examination of the results given in the preceding pages leads to the following conclusions:

1. Quartz finely divided shows an adsorption action, but the effect is much less than in the case of amorphous silica.

2. The amount of adsorption in the case of solutions of carbonates and hydroxides is not directly proportional to the concentration, but relatively greater in very dilute solutions, the ratio of the amount of salt adsorbed to the concentration of the solution decreasing as the concentration increases.

3. The adsorption of the various salts investigated appears to be a function of the acid radical rather than the basic element. The adsorption of the hydroxide series is more marked than that of the carbonates. On the other hand, the potassium, sodium and ammonium hydroxide curves are similar in form, and the same relation is to be observed in the corresponding carbonate series. The numerical values are somewhat in doubt, owing to the apparent chemical action of the alkaline solutions on the quartz.

4. The apparent adsorption of potassium hydroxide by quartz when in equilibrium with a tenth-normal solution is 1.66×10^{-5} gm. mols. per sq. meter, which is equivalent to about 0.6 mg. of potassium hydroxide per square meter of surface.

5. The adsorption of potassium hydroxide by a fine quartz sand from a tenth-normal solution amounts to only 1 percent of the salt contained in a volume of solution sufficient to saturate the sand. The retention of dissolved salts by soils appears therefore to be mainly due to causes other than direct adsorption on the surfaces of the crystalline quartz particles.

6. No positive evidence of the adsorption of chlorides, nitrates or sulphates could be obtained by the method employed.

7. Quartz, like glass, is capable of condensing a water film upon its surface from an unsaturated atmosphere. A part only of this film is liberated when the vapor pressure is reduced to zero at 30° C.

8. The weight of the water film condensed on the surface of quartz at 30° C. in an atmosphere within one percent of saturation is 26.6 mg. per square meter determined by drying at 110° C. This corresponds to a calculated thickness of the water film of 2.66×10^{-6} cm., assuming the density of the film to be uniform and equal to unity.

9. The results obtained with washed quartz do not support

the conclusion of Warburg and Ihmori, working with glass surfaces, that adsorption is due to the presence of soluble substances on the surface of the solid. The condensation of water vapor on the quartz appears to be due to the attraction of the solid for the molecules of the vapor, in accordance with the theory of Gibbs as applied to the adsorption of dissolved substances.

I take much pleasure in thanking Prof. J. S. Ames and Dr. N. E. Dorsey for valuable suggestions during the course of this work. I am also indebted to various members of the Bureau of Soils, particularly to Mr. A. G. McCall, whose assistance has been of the greatest value in the latter part of this work.

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ON THE RELATION BETWEEN ELECTROLYTIC CONDUCTION, SPECIFIC INDUCTIVE CAPACITY AND CHEMICAL ACTIVITY OF CERTAIN LIQUIDS (WITH A BIBLIOGRAPHY OF DIELECTRIC CONSTANTS)

BY JOSEPH HOWARD MATHEWS

Introduction

For a number of years investigations have been carried on in this laboratory on the relations between electrolytic conduction, specific inductive capacity and chemical activity. The present investigation is a natural outgrowth of that work.

In 1901 Schlundt[1] published an interesting set of exceptions to the Nernst[2]–Thomson[3] rule. He showed conclusively that this rule could not be held in the light of the facts presented. In the case of hydrocyanic acid, for example, we have the exceptionally high dielectric constant of 95. One would expect from the rule above-mentioned that substances dissolved in this solvent would yield exceedingly good conducting solutions, but such is not always the case. While some substances which give conducting solutions with water give better conducting solutions with liquid HCN, on the other hand, many substances which yield excellent conducting solutions with water yield very poorly conducting solutions with HCN. Again, in the case of the amines, whose dielectric constants are low, we get solutions that are fairly good conductors of electricity. A pyridine solution of silver nitrate is a better electrolyte than a butyro-nitrile solution of silver nitrate although the dielectric constant of pyridine (12.4) is very much lower than that of butyro-nitrile (20.3). Other marked exceptions noted by Franklin and Kraus[4] are those of solutions in which liquid ammonia

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[1] Jour. Phys. Chem., 5, 157, 503 (1901).

[2] Götting. Nach., 12 (1893); Zeit. phys. Chem., 13, 53 (1894).

[3] Phil. Mag., 36, 320 (1893).

[4] Am. Chem. Jour., 207, (1900).

plays the part of solvent. Kahlenberg and Lincoln[1] have shown that ferric chloride in chloral does not give a solution having an appreciable conductivity, while ferric chloride in ethyl acetate gives a solution which does conduct. For these solvents, Drude[2] found the values of the dielectric constants to be 6.67 and 5.85 respectively. From a consideration of the facts presented, it is clear that we must recognize the important rôle which the solvent plays. Whether a solution will conduct or not depends as much upon the solvent as upon the dissolved substance. It has been said that the conductivity of a solution depends not only on the number of ions present, but also on their speed. However, solutions are known, which, by freezing- or boiling-point methods, contain few or no ions and still conduct well, and yet their viscosity does not vary enough from that of good conducting aqueous solutions of the same solute to admit of the explanation that the difference in conductivity is due to the difference in the speed of the ions in the respective solutions.

In 1903, Kahlenberg in his work upon the sulphocyanates and mustard oils[3] pointed out that solutions of trichloracetic acid in the mustard oils are extremely poor conductors, notwithstanding the fairly high dielectric constant of some of these solvents, and that this non-conducting solution of trichloracetic acid still acts rapidly upon carbonates and metals. I have personally confirmed the results obtained by Prof. Kahlenberg, and some new examples illustrating the same principle will be given in the present paper. It has been the popular thing for years to believe that such action could only take place in conducting solutions. The researches of Patten[4] upon the action of solutions of hydrochloric acid in various solvents upon the metals show that this belief is untenable. There is also a current belief that the presence of minute quantities of water is sufficient to make a non-conducting solution conduct. When investi-

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[1] Jour. Phys. Chem., 3, 12 (1899).

[2] Zeit. phys. Chem., 23, 309 (1897).

[3] Ibid., 46, 64 (1903).

[4] Trans. Wis. Acad. Sciences Arts and Letters, 14, Part I, 316 (1903); Jour. Phys. Chem., 7, 153 (1903).

gators were at a loss to explain the conductivity of certain non-aqueous solutions they neatly avoided accepting the true explanation by saying that the conductivity could only be due to the presence of minute traces of moisture.[1] This belief, however, has no foundation in fact. A good illustration will be given later.

In the present investigation I have continued the researches begun by Prof. Kahlenberg on the sulphocyanates and mustard oils, and have gone over the work of Eggers[2] and Walden[3] on the dielectric constants of these substances. I have also determined the dielectric constants of a considerable number of liquids which have not been previously measured and have checked others previously determined. The dielectric constants of a number of previously uninvestigated solutions have been determined and their conductivity and chemical activity studied. Two further solvents, methyl and ethyl silicates, have been prepared, their dielectric constants determined, and their specific conductivity and the specific conductivity of solutions of a few substances in them measured. The relation between chemical activity and electrolytic conductivity has been more fully investigated.

In addition it was thought that a complete bibliography of the work done on dielectric constants would be of great benefit to those who have occasion to deal with this interesting subject. I am greatly indebted to the article by L. Graetz,[4] for a considerable number of references which I should not have otherwise secured. I have not had access to all of the literature there referred to, so the titles of some of the original articles could not be obtained. However, the references are included in the bibliography.

Method and Apparatus

All conductivity measurements were made at 25° C. The Kohlrausch method was employed, a glass-stoppered graduated resistance cell being used.

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[1] Trans. Faraday Soc., Vol. 1, Pt. 1, 59 (1905).

[2] Jour. Phys. Chem., 8, 14 (1904).

[3] Zeit. phys. Chem., 46, 103 (1903).

[4] Winkelmann: Handb. d. Phys., 4, 1 Teil 1 (1903).

The dielectric constant apparatus used was that devised by Drude.[1] A Tesla transformer was used. The coil and transformer were made by Drude's mechanician and personally inspected by Prof. Drude before being shipped. The remainder of the apparatus was built at this University. The use of the transformer enabled me to make measurements of greater accuracy and with considerably more ease and certainty than by the method employed by Schlundt and Eggers. A new Zehnder's vacuum tube was procured, which was very much more satisfactory than the one previously used in this laboratory. The apparatus now stands so perfected that it is but a matter of a few minutes time to make a very accurate measurement. The liquids recommended by Drude, *viz.*,—benzene, acetone, water, and mixtures of benzene and acetone, and acetone and water, seventeen in number, were used to calibrate the condensers employed. The benzene and acetone used were pure, and were carefully dried and redistilled. The water used was specially prepared and had a very low conductivity. As a check several substances of known dielectric constant were run. In determining the "zero" of the apparatus it has been the custom to use a copper wire. I found it very much more satisfactory to select about three liquids of the series and by running these determine any change in the "zero". The advantages of this process are these: If there was any error in the original "zero" it would thus be corrected. Other things being equal, the average of three "zeros" so determined would be more nearly correct than the determination of one "zero". Lastly, when a wire is used, the luminosity is so greatly increased that it is more difficult for the eye to judge the maximum resonance than when a liquid is used. The "zero" was checked very frequently. With such precautions it is possible to secure very satisfactory results.

Two condensers were used. One of the ⊥ form[2] for dielectric constants below twenty and one of the bulb form for dielectric constants above twenty. These gave calibration curves of the desired form and accuracy.

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[1] Zeit. phys. Chem., 23, 267 (1897).

[2] Jour. Phys. Chem., 8, 16 (1904).

The kerosene about the spark gap of the vibrator had to be renewed occasionally, though less frequently than when the transformer is not used. Filtering was not as satisfactory as renewing with fresh material. It is essential to the success of the method that the kerosene be kept clean.

Experimental Part

In the light of the facts presented in Prof. Kahlenberg's work upon the conductivity of solutions in the sulphocyanates and mustard oils it seemed desirable to investigate further solutions in which a mustard oil plays the part of solvent. Accordingly an exhaustive list of substances was tested. The results obtained were in the main merely qualitative in character. Where solution took place the conductivity was measured. The materials used were of standard make (Schuchardt or Kahlbaum) and were marked pure. The hydrochloric acid was dried by passing over phosphorus pentoxide. The solution containing the hydrochloric acid was momentarily exposed to the air while being poured into the resistance cell, which was then stoppered. Therefore, the conductivity of this solution probably is too high, due to the moisture taken up from the air. The solvents used were carefully dried and redistilled. For the sake of convenience I have tabulated the results obtained. When the statement is made that the solution does not conduct, it is meant that it does not conduct better than the solvent used.

TABLE I—CONDUCTIVITY OF VARIOUS SUBSTANCES DISSOLVED IN THE MUSTARD OILS

Solvent	Solute	Sp. cond.	Remarks
Allyl mustard oil		2.48×10^{-5}	Dried, b.p. 150°. Pure
“	Hydrochloric acid	1.04×10^{-4}	Saturated with dried gas
“	Sulphuric acid (fuming)		Decomposed the solvent
“	Nitric acid (conc.)		Decomposed oil.[1] Does not conduct
“	Telluric acid		Not soluble. No change
“	Acetic acid	2.8×10^{-5}	1 part acid to 10 parts oil
“	Trichloracetic acid	3.5×10^{-5}	Saturated solution
“	Oxalic acid		Slightly sol. Does not conduct
“	Tartaric acid		“ “ “ “ “
“	Citric acid		Insoluble. No change
“	Salicylic acid		Slightly sol. Does not conduct
“	Succinic acid		Insoluble. No change
“	Quinine sulphate		Slightly soluble. Does not conduct
“	Quinine (pure)		Soluble. Does not conduct
“	Brucine chloride		Insoluble. No change
“	Atropine		Very soluble. Does not conduct
“	Morphine hydrochloride		Sparingly soluble. Does not conduct
“	Saponine		Soluble. Does not conduct
“	Cinchonidine		Sparingly soluble. Does not conduct
“	Monomethyl aniline		Miscible. Does not conduct
“	Dimethyl aniline		“ “ “ “
“	Ortho toluidine		“ “ “ “
“	Benzylamine		“ “ “ “
“	Tripropylamine		“ “ “ “

[1] Conductivity not appreciably greater than that of pure solvent.

TABLE I (*Continued*).—CONDUCTIVITY OF VARIOUS SUBSTANCES DISSOLVED IN THE MUSTARD OILS

Solvent	Solute	Sp. cond.	Remarks
Allyl mustard oil	Phenyl hydrazine	4.2×10^{-5}	Heats up. Miscible
"	Acetyl chloride		Miscible. Very slight increase in conductivity
"	Ethyl chloride		Miscible. Does not conduct
"	Sulphur monochloride	8×10^{-5}	Miscible
"	Tetrachloride of tin		Decomposes solvent
"	Trichloride of antimony	30×10^{-4}	Quite soluble
"	Trichloride of arsenic		Miscible. Heats. Does not conduct
"	Trichloride of iodine		Reacts violently
"	Aluminium chloride		Insoluble. No change.
"	Isobutylene bromide		Miscible. Does not conduct
"	Mercuric bromide	7.8×10^{-5}	Quite soluble. Saturated solution
"	Nickel bromide		Insoluble. No change
"	Cadmium bromide		Insoluble
"	Iodoform	5.3×10^{-5}	Soluble
"	Iodide of lead		Insoluble
"	Mercurous iodide	4.3×10^{-5}	Sparingly soluble. Saturated solution
"	Mercuric iodide	9.8×10^{-5}	Somewhat soluble. Saturated solution
"	Copper iodide		Slightly soluble. Does not conduct
"	Cadmium iodide		Insoluble
"	Arsenic triiodide (com.)		Very soluble. Conducts
"	Arsenic triiodide (pure)	1.4×10^{-4}	Saturated solution. Purified by extraction with mustard oil
"	Iodide of tin	4.08×10^{-4}	Soluble saturated solution
"	Triiodide of iron	2.2×10^{-4}	Extremely soluble. Dilute solution

TABLE I (*Continued*).—CONDUCTIVITY OF VARIOUS SUBSTANCES DISSOLVED IN THE MUSTARD OILS

Solvent	Solute	Sp. cond.	Remarks
Allyl mustard oil	Manganese iodide	9.7×10^{-5}	Slightly soluble
"	Zinc iodide	3.1×10^{-4}	Slightly soluble. Saturated solution
"	Strontium iodide		Insoluble. Does not conduct
"	Lithium iodide		Insoluble
"	Sodium iodide		"
"	Ammonium iodide		"
"	Phosphorus triiodide	3.8×10^{-4}	Fairly soluble
"	Strychnine, mercuric iodide	5.8×10^{-5}	Sparingly soluble. Saturated solution
"	Propyl iodide		Miscible. Does not conduct
"	Bromine (liq.)		Reacts violently
"	Iodine	1.15×10^{-3}	Dissolves readily. Saturated solution
Phenyl mustard oil	"	2.3×10^{-4}	Less soluble than in allyl mustard oil
Ethyl sulphocyanate	"	1.44×10^{-3}	Quite soluble. Saturated solution
Phenyl isocyanate	"		Dissolves. Does not conduct
Allyl mustard oil	Cyanogen iodide	1.36×10^{-3}	41.09 p. c. ICN
"	Pyridine	1.88×10^{-5}	Equal parts by volume
"	Ethyl carbonate		Miscible. Does not conduct
"	Sulphur		Somewhat soluble. Does not conduct

IODINE IN THE MUSTARD OILS.—Iodine dissolves in allyl mustard oil in considerable amount, and gives a conducting solution. During solution heat is evolved, showing that the chemical action is fairly pronounced. An addition product is evidently formed. A series of quantitative measurements upon the specific conductivity of various strengths of solution were undertaken. Small weighed quantities of iodine were added from time to time and the conductivity measured. At first the conductivity did not reach a maximum for nearly half an hour after the addition of iodine, then when once obtained the conductivity gradually diminished again. The maximum was recorded. As the determinations proceeded, this time factor, *i. e.*, the time required for the maximum conductivity to develop became less and less and the tendency for the conductivity to decrease became greater and greater. The readings became approximately constant when a specific conductivity of 6.8×10^{-4} was reached. Further addition of iodine did not materially change the conductivity. The reason for this constancy evidently is that the tendency for the conductivity to decrease became equal to the natural increase in conductivity due to the addition of small quantities of iodine. It will be noted that the maximum conductivity so obtained is considerably less than that obtained when a saturated solution of iodine in the mustard oil is made up directly, *i. e.*, when enough iodine is added *at once* to make a saturated solution. This solution had a specific conductivity of 1.14×10^{-3}. In the case where the saturated solution was made by addition of small quantities of iodine from time to time the addition product was continually forming and thereby reducing the conductivity. In the case where the excess of iodine was added at one dose the proportion of the addition product in the solution was much less and the conductivity higher. Owing to this time factor any attempt to make an accurate measurement of the specific conductivity of a solution of certain strength is futile.

Another fact in favor of the addition product idea is that from a freshly prepared solution of iodine in mustard oil the iodine may be extracted by shaking with an aqueous solution of sodium thiosulphate. But after standing for some time this extraction becomes more difficult, finally reaching a point where it is apparently impossible to free the entire iodine content. However, this might be possible in time.

A solution of iodine in phenyl mustard oil was made which showed a specific conductivity of 1.90×10^{-4}. The specific conductivity of the solvent was 1.4×10^{-6}. Having observed the effect of time upon the conductivity of the iodine-allyl mustard oil solution and sought for its probable explanation, the same question arose in the case of the iodine-phenyl mustard oil solution. In view of the constitution of the latter mustard oil the same behavior would not be expected. Such was found to be the case. The solution having an initial specific conductivity of 1.90×10^{-4} was allowed to stand for ninety-six hours. At the end of that time the specific conductivity had experienced but a very slight change, it having risen only to 2.00×10^{-4}.

In connection with the behavior of iodine in the mustard oils as regards electrical conductivity, it is interesting to note that iodine also dissolves in pyridine and alcohol to give conducting solutions. The specific conductivity of the pyridine used was 1.6×10^{-5}. This value was raised to 1.14×10^{-3} by the addition of iodine. In like manner the specific conductivity of alcohol was changed from 5.8×10^{-6} to 1.61×10^{-4} for a saturated solution of iodine.

It has been observed that iodine dissolves in the phenyl mustard oil to give a conducting solution. According to Brühl[1] those substances which contain oxygen should have a high dielectric constant and high dissociating power. Now iodine is soluble in phenyl isocyanate. Iodine dissolved in phenyl isocyanate does *not* yield a conducting solution. The dielectric constant of phenyl isocyanate is 8.77. Here we have an instance where it is not the substance containing the oxygen which gives a high "dissociating power" and therefore a conducting solution, but a substance containing sulphur which has displaced the oxygen. Numerous exceptions have been found to Brühl's generalization, and it is difficult to see how it can possibly be held.

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[1] Zeit. phys. Chem., 18, 514 (1895).

ARSENIC TRIIODIDE.—Arsenic triiodide as ordinarily obtained contains some free iodine. This can be extracted by repeated decantations of allyl mustard oil. The remaining crystals are red and I found that they analyzed up to the theoretical composition required for the formula AsI_3. The pure salt so obtained is somewhat soluble in the mustard oil at room temperature, and at 60° C it is extremely soluble. Upon cooling a few degrees below this temperature, beautiful crystals of AsI_3 separated out. The conductivity of a saturated solution of AsI_3 in allyl mustard oil was measured, as indicated in the table. The figure found for the specific conductivity was 1.4×10^{-4}.

A short U tube was filled with AsI_3 and the salt fused. Wires were introduced and a pressure of 154 volts impressed, a D'Arsonval galvanometer being in the circuit to detect any current which might pass. The galvanometer showed no deflection. The fusion was then allowed to solidify. The solid salt did not conduct. Therefore, it is perfectly safe to say that AsI_3 does not conduct the current appreciably.

AsI_3 was dissolved in allyl mustard oil and the solution electrolyzed. A gummy deposit was obtained upon the cathode which showed the presence of a considerable amount of arsenic. The electrolytic cell had to be water-jacketed to prevent boiling. Platinum electrodes were used and the anode was corroded considerably.

SULPHOCYANIC ACID.—Following out the work done in this laboratory upon the sulphocyanates and mustard oils by Prof. Kahlenberg[1] it was desired to prepare sulphocyanic acid and investigate its properties as a solvent. Eggers[2] found the following results for the dielectric constants of the mustard oils and sulphocyanates measured by him.

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[1] Zeit. phys. Chem., 46, 64 (1903).

[2] l. c.

TABLE II

Material	Dielectric constant	Temp.
Methylsulphocyanate	33.3	15°.5, C.
Ethylsulphocyanate	31.2	11°.5 C.
Amylsulphocyanate	17.1	19°.5 C.
Ethyl mustard oil	22.0	15°.0 C.
Allyl mustard oil	17.3	17°.6 C.

From these results one would naturally expect to find the dielectric constant of sulphocyanic acid to be higher than that of methyl sulphocyanate which has a value of 33.3. It has been pointed out that the dielectric constant decreases with the increase of molecular weight in a homologous series.[1] Walden[2] even goes so far as to predict the value to be 85.9 or 85.1 for HCNS. He finds that in homologous series in general the first addition of CH_2 produces a decrease in the value of the dielectric constant of approximately 50. Therefore, since the dielectric constant of the methyl compound is 35.9 (the figure obtained by him) the dielectric constant of the sulphocyanic acid should be $35.9 + 50 = 85.9$. Or, comparing methyl alcohol with methyl sulphocyanate whose dielectric constants are 32.5 and 35.9 respectively, the CNS group exceeds the OH group about 3.4. Then since water has a dielectric constant of 81.7 (the value used by him) the dielectric constant of sulphocyanic acid should have a value of $81.7 + 3.4 = 85.1$.

There is considerable question whether Walden's reasoning is justifiable. He quotes[3] the cases of water and methyl alcohol, where the difference is 49.2, formic acid and acetic acid where the difference is 50.54, and hydrocyanic acid and acetonitrile where the difference is 59. Thus it will be seen that in the examples that he himself gives there is considerable deviation from the rule he tries to establish. In the case of liquid ammonia, whose dielectric constant is 16.2[4] and methylamine whose

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[1] Schlundt: l. c.

[2] l. c.

[3] Zeit. phys. Chem., 46, 187 (1903).

[4] Coolidge: Wied. Ann., 69, 130 (1899).

dielectric constant is 10.5,[1] we have no relation such as that suggested by Walden.

After several very unsatisfactory attempts were made to prepare pure HCNS, the method of Klason[2] was tried with somewhat better results. The reagents employed were HCl and KCNS. The two aqueous solutions, one containing 32 grams KCNS and the other 30 cc. of concentrated hydrochloric acid, were cooled to zero. The apparatus consisted of a distilling flask with separatory funnel; a dryer, consisting of four large glass-stoppered U tubes filled with $CaCl_2$ immersed in a constant temperature bath kept at 40° C.; the condensing chamber, consisting of a smaller U tube immersed in a freezing-mixture of snow and salt, a manometer, and a suction-pump.

The cold KCNS solution was poured into the distilling flask, connections were made and a vacuum of 40 mm or less secured. The cold HCl solution was then cautiously run in by means of the separatory funnel. After starting the action by means of a little heat, the reaction went on of its own accord. A pressure of less than 40 mm was maintained throughout the process. The condensed solid obtained was straw-yellow in color. Polymerization started in even at the temperature of the freezing-mixture. It was found impossible to prevent this, even with a freezing-mixture of calcium chloride and snow. The melted substance became darker, heated up considerably and then solidified to a pumiceous structure.

Some of the unpolymerized material was quickly transferred to a condenser, sealed, and an attempt made to measure its dielectric constant. It showed *complete absorption.* Polymerization was allowed to set in and as soon as this process began, the absorptive power decreased. Finally, when the process was complete, a good resonance was obtained, and the dielectric constant found to be 4.9.

Owing to the extreme instability of the compound it was not possible to make any conductivity measurements.

It will be noted that the value 4.9 is for the polymerized

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[1] Schlundt: l. c.

[2] Jour. prakt. Chem., 35, (2) p. 401.

material. It is not pretended that it is the true value, for the product obtained was unsatisfactory. It is very doubtful to my mind whether pure anhydrous sulphocyanic acid has ever been made. The properties as given by the different authorities are very unlike. The experimental difficulties encountered in the preparation and handling of the product are so great that satisfactory results are well nigh impossible. Why this material should show complete absorption I am at loss to state, but such is the fact.

METHYL SILICATE.—This material was prepared, according to the method of Friedel and Crafts,[1] from silicon tetrachloride and absolute methyl alcohol. Considerable care has to be exercised to procure *absolute* methyl alcohol. It was distilled from anhydrous copper sulphate and finally from sodium. The alcohol was added little by little to the silicon tetrachloride contained in an *open* distilling flask. When the violent reaction was over distillation was commenced. The portion passing over between 120° and 122° C was collected separately and several times redistilled.

Measurements of the dielectric constant made upon separate samples of methyl silicate gave the values 5.9 and 6.00. Ferric chloride dissolves in methyl silicate and gives a conducting solution. The specific conductivity of the solvent was measured and found to be 1.6×10^{-6}. The specific conductivity of the saturated solution of ferric chloride was 2.28×10^{-4}. Trichloracetic acid dissolves freely, but does *not* give a conducting solution. The dielectric constant of this solution was found to be 10.3.

ETHYL SILICATE.—A sample of ethyl silicate of Schuchardt's manufacture was redistilled and found to boil at 165°.5 C at 740 mm pressure. The specific conductivity of this solvent was found to be less than 3×10^{-8}. It dissolves iodine in a considerable amount. The dielectric constant of the solvent was found to be 4.10, and the dielectric constant of a saturated solution of iodine was 4.25. Here we have a slight rise in the value of the dielectric constant caused by the dissolved halogen.

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[1] Ann. Chim. Phys., (4) 9, 32 (1856).

Trichloracetic acid dissolves readily in ethyl silicate but does *not* give a conducting solution, its specific conductivity being less than 3×10^{-8}. The dissolved trichloracetic acid, however, raises the dielectric constant from 4.10 to 5.97 for an approximately saturated solution. This solution, though *non-conducting*, attacks metallic magnesium rapidly with the evolution of hydrogen gas.

DIELECTRIC CONSTANTS OF THE MUSTARD OILS AND SULPHOCYANATES.—In view of the discrepancies existing between the measurements made by Walden[1] and Eggers[1] it was deemed advisable to repeat the determinations.

The materials used were of standard make and were dried with fused $CaCl_2$ and redistilled. Conductivity measurements were then made as a check on their purity. It will be observed that only in one case was I able to secure a specific conductivity of the order obtained by Walden. With the utmost care and impartiality, this was impossible. The boiling-point determinations showed the materials to be pure.

The dielectric constant was carefully measured in each case. The values obtained appear in Table III below. For reference I have also included the results obtained by Eggers and by Walden.

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[1] l. c.

TABLE III.—COMPARISON OF RESULTS OBTAINED ON THE MUSTARD OILS AND SULPHOCYANATES

Substance	D. C. Mathews	D. C. Eggers	D. C. Walden	Sp. C. Mathews	Sp. C. Walden	B. P. Mathews	B. P. Eggers	B. P. Walden	Temp.
Ethylsulphocyanate	31.0	31.2	26.5	2.16 10^{-5}	0.26 10^{-5}	143°	142°.5	143°–4	12°
Methylsulphocyanate	35.5	33.3	35.9	3.7 10^{-5}	0.146 10^{-5}	129°	—	130°	12°
Ethyl mustard oil	18.7	22.0	19.4	2.25 10^{-5}	0.6 10^{-6}	130°	131°.2	131°–2.5	18°
Methyl mustard oil	20.3	17.9	19.7	—	—	116°	—	119°.5	38°
Phenyl mustard oil	10.0	8.5	11.0	2.55 10^{-5}	0.18 10^{-6}	218°	219°	222°	20°
Allyl mustard oil	17.2	17.33	—	8.10^{-6}	—	150°	150°	—	18°

[1] Eggers had not redistilled his samples of methyl mustard oil and methyl sulphocyanate, so that the corresponding boiling-points do not appear in the table.

TABLE IV

Eggers took measurements at lower temperatures as follows:

Methyl sulphocyanate,	15°.5 C.
Ethyl sulphocyanate,	11°.5 C.
Ethyl mustard oil,	15°.0 C.
Allyl mustard oil	17°.6 C.
Phenyl mustard oil,	11°.6 C.

Walden's temperatures correspond more closely to mine. Measurements of conductivity were made at 25° C.

A considerable discrepancy was found in the case of phenyl mustard oil. It was thought that the slow decomposition which this substance undergoes might possibly account for this variation. Consequently a sample which had been carefully dried, redistilled and allowed to stand for a month or more was measured. The sample was again dried and redistilled and measurements made on this fresh sample. Precisely the same result was obtained in both instances. The true value has thus been shown to be 10.0 as indicated in the table.

In the case of ethyl sulphocyanate Walden gets the value 26.5 and Eggers 31.2. Working upon a pure sample which had been carefully dried and redistilled the value 31.0 was obtained. This measurement was several times repeated, always with the same result.

In the main the results obtained by Walden were found to be more nearly correct. But this is not at all surprising considering the less perfect apparatus with which Eggers made his measurements.

DIELECTRIC CONSTANTS OF SOME SOLUTIONS.—The dielectric constant of pure, dry, redistilled pyridine was found to be 12.5. A test was made to determine what effect dissolved sugar would have upon the dielectric constant. The pyridine contained 6.47 percent of sugar and the dielectric constant of the solution was found to be 13.5. This result is of interest since Thwing[1] finds the dielectric constant of sugar to be quite low, namely, 4.16.

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[1] Phys. Rev., 2, 51 (1894).

A mixture of aniline and cresol was made and its dielectric constant measured. The value obtained was 6.70 which result falls between the values obtained for the two constituents.

Acetonitrile and alcohol were mixed in approximately equal volumes and the dielectric constant of the resulting mixture was found to be 29.4. Here again we have the dielectric constant of the mixture falling between the values for the constituent substances.

Arsenic trichloride was saturated with dry hydrochloric acid gas and the dielectric constant of the mixture quickly determined.[1] The dielectric constant of arsenic trichloride is 12.35. The dielectric constant of the solution measured was 12.80. In this case we have a slight rise due to the dissolved HCl.

Tin tetrachloride was saturated with HCl gas and the dielectric constant measured. The dielectric constant was not appreciably altered, the slight difference could well be considered as falling within the limit of experimental error. The dielectric constant of the $SnCl_4$ was 3.20 and the dielectric constant of the solution was 3.15.

Carbon tetrachloride was saturated with dry HCl gas and the dielectric constant of the solution thus obtained, measured. The dielectric constant of the solution was found to be the same as that of the carbon tetrachloride.

Nitrobenzene was saturated with dry HCl gas and the dielectric constant of the solution thus obtained was found to be 35.8. The dielectric constant of the pure nitrobenzene is 34.0. Here again we have a rise in dielectric constant due to the dissolved HCl which is known to have a low dielectric constant.

Nitrobenzene dissolves a great amount of trichloracetic acid with considerable absorption of heat. The dielectric constant of a saturated solution was found to be 14.7. The dielectric constant of the solvent being moderately high (34.0), we ought to find a solution of trichloracetic acid a fairly good conductor according to the Nernst-Thomson rule. Accordingly the conductivity of this solution was measured. The specific

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[1] In those cases where HCl was used as solute, it is probable that no great amount was absorbed.

conductivity was found to be 1.46×10^{-5}. Here again we have an interesting exception to the Nernst-Thomson rule. It is perfectly clear that no such relation as this rule maintains actually exists.

In connection with work previously done in this laboratory[1] it was thought advisable to test the action of this solution on the metals. The results obtained appear in Table V, below.

TABLE V

Metal	Remarks
Aluminum	No action
Zinc (cast)	Rapid production of aniline, no gas
Zinc (dust)	Same as for cast zinc. More rapid
Nickel	Solution showed presence of small amounts of aniline at end of twenty-four hours
Chromium	No action
Magnesium (ribbon)	Very rapid formation of aniline with considerable evolution of gas
Magnesium (dust)	Action extremely rapid. Developed heat enough to boil violently. Aniline formed rapidly
Cobalt	Aniline formed. No gas. Action comparatively slow
Cadmium	Action fairly rapid. Aniline formed. No gas
Antimony	No action
Silver	No action
Gold	No action
Copper	Solution turned green. No gas
Palladium	No action
Platinum	No action
Tin	No aniline formed. Metal blackens
Bismuth	Metal and solution darken, stick notched at surface
Iron	Aniline formed. No gas. Action moderate
Mercury	No action
Sodium	Brisk evolution of gas. Aniline formed. (Sodium was placed in the pure nitrobenzene and no evolution of gas took place. This showed that the solvent was dry. No action upon the sodium was apparent after several hours standing)

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[1] Kahlenberg: Zeit. phys. Chem., 46, 64 (1903). Patten: Trans. Wis. Acad., 14, 316 (1903); Jour. Phys. Chem., 7, 153 (1903).

This experiment affords us another interesting indication that chemical action and electrical conductivity do not necessarily go hand in hand. It is clear that in this case cited chemical action is not in any way connected with any electrical phenomena. To further establish this principle, trichloracetic acid was dissolved in benzene in which it is quite soluble. The resulting solution acts upon the metals vigorously. Its specific conductivity was measured and found to be less than 3.0×10^{-8}. This is even a more drastic case than the previous one.

To still further substantiate this point, trichloracetic acid was dissolved in dry kerosene and its action tried upon the metals. The same result was experienced as in the case of benzene.

The dielectric constant of a saturated solution of trichloracetic acid in benzene (containing 74.1 percent of the acid) was measured and found to be 3.65, as against 2.26 for the pure solvent.

The action of various acids in nitrobenzene upon metallic magnesium was tried with the following results:

TABLE VI

Nitrobenzene with	Remarks
Crotonic acid	Gas given off copiously
Trichlor lactic acid	Rapid evolution of gas
Acetic acid (glacial)	Magnesium disappears in time
Dichloracetic acid	Rapid evolution of gas. Solution shows presence of aniline
Oxalic acid	No action apparent
Fumaric acid	Little if any action (twenty-four hours)
Itaconic acid	No action

In all these cases where action occurred we have chemical action of a decided character where electrical conductivity is practically wanting. I say "practically" because no solvent has yet been shown to be an absolute non-conductor. In the light of the facts presented, it is difficult to see how chemical action can be considered as being electrical in character.

CYANOGEN IODIDE.—The iodide of cyanogen was found to dissolve well in allyl mustard oil. It is possible to secure a solution containing over 40 percent of the salt at room temperatures. The specific conductivity of a 41.09 percent solution was found to be 1.36×10^{-3}. The dielectric constant was also determined and the value 19.9 obtained. Metallic magnesium was treated with this solution and bubbles of gas were formed on the surface of the metal and were liberated rapidly. Metallic magnesium remains unacted upon in the pure solvent. When sodium is added to the solution of cyanogen iodide in allyl mustard oil, gas is liberated rapidly and cyanogen iodide is apparently precipitated from the solution. Sodium also reacts somewhat on the pure solvent, but the gas is liberated very much slower. Metallic zinc produces no liberation of gas, but appears corroded. The solution has the characteristic color of a weak solution of iodine in allyl mustard oil.

The fact that the dielectric constant of allyl mustard oil is raised by the addition of the iodide of cyanogen is interesting. The dielectric constant of cyanogen is known to be low (2.52).[1] Schlundt found iodine to have a value of 10.3. In general the addition of more halogen lowers the dielectric constant of a halogen-containing substance. From this fact we should expect the value for cyanogen iodide to be low, at least below the value for iodine. The dielectric constant of allyl mustard oil has been shown to be 17.2. Yet when the iodide of cyanogen is dissolved in this solvent, the dielectric constant is raised from 17.2 to 19.9[1]

A solution of iodine in allyl mustard oil was then made which had the same iodine content as the cyanogen iodide solution just described. The dielectric constant of this solution was found to be 14.8 as compared with the value 19.9 obtained in the case of the cyanogen iodide solution. While cyanogen itself has a low dielectric constant, we find that combined CN has a tendency to raise the dielectric constant, examples of which fact are seen in the following table.

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[1] Schlundt l. c.

TABLE VII

Name	Formula	D. C.	Name	Formula	D. C.
Hydrocyanic acid[1]	HCN	95	Water	HOH	80
Acetonitrile	CH_3CN	36.4	Methyl alcohol[2]	CH_3OH	32.5
Propionitrile	C_2H_5CN	26.5	Ethyl alcohol	C_2H_5OH	21.7
Butyronitrile	C_3H_7CN	20.3	Propyl alcohol	C_3H_7OH	12.3
Benzyl cyanide	$C_6H_5CH_2CN$	14.9	Benzyl alcohol	$C_6H_5CH_2OH$	10.6

Similar differences would be observed in the comparison of the dielectric constants of ethers, acetates, ketones, aldehydes and acids with corresponding cyanides.

Carbon tetrachloride, having a dielectric constant of 2.7 was treated with iodine and the dielectric constant of the resulting solution found to be 2.4. An attempt was made to dissolve cyanogen iodide in this solvent to study further the effect of the cyanogen radical, but it would not dissolve to any extent without the application of heat.

Carbon tetrachloride being a compound well loaded with halogen was treated with more halogen in the form of iodine monochloride. The dielectric constant of this solution was, within the limit of error, the same as for the pure solvent. In this case a further addition of chlorine does not seem to affect the dielectric constant though a change would be expected inasmuch as the dielectric constant of iodine monochloride is in the neighborhood of 30. (Made upon a specimen sample not further purified.)

Iodine monochloride was mixed with benzene with which it reacts violently, and the dielectric constant of the solution determined. The dielectric constant was found to be raised by the presence of the iodine monochloride.

In the case of the HCl in nitrobenzene cited above we have an example similar to that of cyanogen iodide in mustard oil. The dielectric constant of mixture is plainly not additive in character.[3] The grouping of the atoms must be considered. At

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[1] Values taken from work of Schlundt l. c.

[2] Values taken from work of Drude l. c.

[3] See Eggers l. c.

the present state of our knowledge it is impossible to foretell, with any degree of accuracy, the dielectric constant of any unmeasured substance. We know, in a general way, the effect of certain radicals and the effect of the different grouping of the same, but this subject still needs further investigation.

We are continually warned against using solvents that contain the minutest traces of water in our experimental investigations. Some seem to regard it an impossibility to free an organic solvent from water. The conductivity of non-aqueous solutions was by some ascribed to the presence of minute traces of water, which it was impossible to remove. Such an idea has since been shown to be quite erroneous. To make a non-conducting solution conduct by the addition of water it is found that quite an appreciable amount is necessary; an amount, which is greatly in excess of that in a dried sample of the ordinary solvents such as we encounter. In the case of benzene and trichloracetic acid, which solution I have found to be an excellent insulator, I have made successive additions of small known quantities of water and measured the specific conductivity after each addition. I found that it takes an appreciable amount of water to give a measurable increase in the electrical conductivity and that for a relatively considerable addition of water the conductivity does not increase rapidly. I have plotted a curve showing my results. Upon the

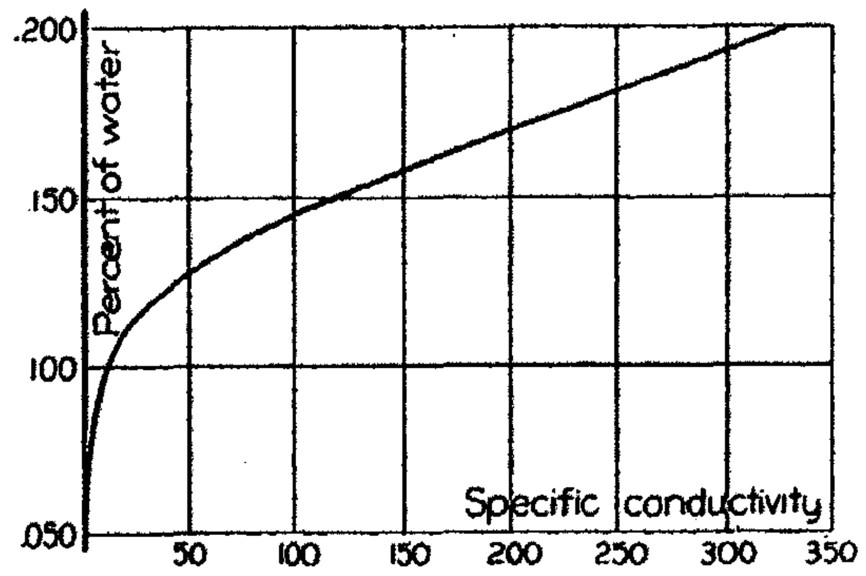

Fig. 1

Curve showing the effect upon the specific conductivity of a non-conducting solution produced by the addition of small quantities of water. The values along the abscissa equal the specific conductivity times 10,000.

basis of actual experimental work the curve was extended much farther than indicated in the figure, but the general direction was found to be the same. The curve shows that the conductivity does not increase rapidly until we have added 0.1 percent of water. At 0.13 percent it reaches a point where further addition of water causes a steady increase in the conductivity.

DIELECTRIC CONSTANTS.—I have measured a considerable number of dielectric constants which have hitherto not been determined, and have checked up a number that have been determined. Practically all of the substances used were dried and redistilled as indicated. For the sake of convenience in reference I have tabulated them alphabetically. It will be seen that in the main those which have been redetermined agree very well with former results.

Summary

The electrical conductivity of a large number of substances dissolved in the mustard oils has been measured. A few of the acids dissolve to form slightly conducting solutions. None of the alkaloids or alkaloid derivatives yield conducting solutions. The same is true of the amines. Some of the chlorides, iodides, and bromides dissolve to give slightly conducting solutions. Iodine, itself a non-conductor, yields a fairly good conducting solution.

Sulphocyanic acid was prepared, though in all probability not in the pure state, and, have found that the product secured gives complete absorption.

I have prepared methyl silicate, measured its dielectric constant and specific conductivity and have employed it as a solvent. Measurements of like character have also been made on ethyl silicate.

The results of Walden and of Eggers have been gone over and checked up. The dielectric constants of some new solutions have been measured as well as their conductivity, and their chemical activity studied. It has been shown that, in many cases at least, chemical action is wholly independent of any electrolytic phenomena, that we may have various chemical

TABLE VIII

Substance	Maker	D. C.	Resonance	Temp.	B. P.	Remarks
Amyl nitrate	Schuchardt	8.95	good	18°	140–45°	
Amylene	"	6.9	"	22		Not redistilled
Aniline	Kahlbaum	7.2		24	180	Schlundt 7.20
Amyl benzoate		4.62		18	238–40	
Anisol	Kahlbaum	3.55	good	18	152	
Benzoic aldehyde	E. de Haen	14.0	"	18	185(?)	
Benzotrichloride	Schuchardt	7.4	"	20		Not redistilled
Cymene	"	2.43	"	18	170–72	Nernst 2.25
Carvol	"	11.0	"	18	224–5	
Benzoylchloride	Kahlbaum	18.6	"	24		Unopened sample
Diamylamine	Schuchardt	2.52	"	18	184	
Diethylamine	"	3.7	"	23		
Dibenzylamine	"	3.6	"	23		Schlundt 3.58
Diphenylmethane	Trommsdorf	2.5		18	243–44	Schlundt 3.55
		2.45	"	18	245	
Dipropylamine	Schuchardt	2.9	"	18	110(?)	New sample
Dimethylaniline	"	5.0	"	18	189.5–90	Schlundt 2.90
Dipentene	"	3.2	"	21	170	Schlundt 5.07
Eugenol	"	6.0	some absor.	18	234	
Ethyl carbonate	"	2.8	good	18	124	
Ethylene diamine	"	15.7	"	18	118–21	
Ethyl benzoate	Kahlbaum	5.6	"	24	207–7.5	
Kresol methyl ether	"	3.47	"	18	165–67	
Kresol (ortho)	Kahlbaum	5.65	"	24	187	

TABLE VIII—(*Continued*)

Substance	Maker	D. C.	Resonance	Temp.	B. P.	Remarks
Kresol (meta)	Kahlbaum	4.95	some absorb.	24°	197.5–8	
Kresol (para)	"	5.48	"	24	197.5	
Methyl benzoate	Schuchardt	6.25	"	24	195.5	
Monomethylanilin	"	5.3		23		Schlundt 5.8
Menthone		8.78	good	18	197–99	
Mercurydiethyl	"	2.45	"	23		Not redistilled
Naphthalenemonobromide	"	4.5	"	18	255–58	Fresh sample
Nitrotoluol		20.3	"	18	206.5–7	Thuering 26.6
Phenyl acetate	Schuchardt	6.40	"	24		Drude 5.29. Not redistilled
Phenetidene	"	7.2	"	21	241–2.5	
Phenyl hydrazine	"	5.7	"	18	225.5	Turner 7.15
Pinacone	"	7.38	poor	24	174–75	
Phenetol	"	4.47	good	21	166.5	
Phenylisocyanate	Kahlbaum	8.77		20	160	
Quinoline		8.7	good	21	231–33	Schlundt 8.8. Turner 8.9
Safrol	Schuchardt	2.52	"	18	200	
Terpinol	"	3.7	"	21	178–80	Drude 2.75
Terpinene	"	2.7	"	21	171–4	
Tin tetrachloride	"	2.0	"	18		Fresh sample
Titanium tetrachloride	"	2.73	"	24		Hermetically sealed
Xylidine (meta)	E. and A	4.9	"	18	210–12	

Cyanogen iodide—Decomposed when an attempt was made to melt it. Dissolved in benzene it did not affect the dielectric constant of the benzene in any degree (2.26). A 41.09 percent solution of cyanogen iodide in allyl mustard oil gives a dielectric constant of 19.9.

actions of a most decided character in solutions which are not conductors of electricity. It has moreover been further emphasized that the Nernst-Thomson rule has no foundation in fact and that the exceptions are as numerous as the confirmations.

The dielectric constants of a number of liquids hitherto undetermined have been measured and presented in ready form for reference.

An exhaustive bibliography of the literature on dielectric constants has been compiled and arranged in the alphabetical order of the authors' names.

In conclusion, it is a pleasure to express my gratitude to Professor Kahlenberg, under whose direction this research was made, for his many suggestions, for his interest in my work, and for the many opportunities he has placed before me.

PREFACE TO THE BIBLIOGRAPHY ON DIELECTRIC CONSTANTS

This bibliography has been compiled in the hope that it may be useful to those who desire to make a study of the subject of specific inductive capacity. By having such a bibliography of the literature upon the subject at hand for ready reference much of the labor of future investigation may be saved and many of the errors of the earlier experimenters avoided. All classes of articles upon the subject have been included without regard to their merits.

This is probably not an absolutely complete bibliography of the literature upon the subject, but it is as nearly complete as time and opportunity have enabled the author to make it. For convenience in reference, the arrangement has been made alphabetically with respect to the name of the author. The abbreviations are such as are in common use and need no further explanation.

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THE CHEMICAL SEPARATION OF THE RADIO-ACTIVE TYPES OF MATTER IN THORIUM COMPOUNDS

BY HERMAN SCHLUNDT AND RICHARD B. MOORE

Our knowledge of the nature of the radio-activity of thorium is largely due to the extensive researches of Rutherford and Soddy.[1] These investigators have shown that the radio-activity of the ordinary thorium compounds on the market consists of four parts, due to four specific types of matter. On the basis of their theory of successive disintegration, the parent thorium is slowly but constantly undergoing change. A very small fraction of the thorium atoms is continuously breaking up, giving off α-particles and leaving a new type of matter, Thorium X, which is also radio-active. Thorium X, in disintegrating, gives rise to a radio-active gas, the Emanation, which breaks up rapidly, sending out particles and depositing a solid on near-by objects. This solid likewise emits radiations and is therefore responsible for the temporary radio-activity exhibited by bodies left in the neighborhood of thorium compounds. The successive changes—Thorium → Thorium X → Emanation → Matter[2] causing imparted or excited activity → The final product—go on simultaneously in thorium compounds, and the radio-activity ordinarily observed represents the combined effect of these different types of matter. According to Rutherford[3] each of the components supplies approximately an equal proportion of the total activity. Thorium X and its disintegration products, however, constitute but an infinitesimal amount of the total quantity of matter, but their rate of transformation is immense in comparison with that of thorium.

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[1] Jour. Chem. Soc., 81, 131, 837 (1902).

[2] This type has been shown to be complex. *Cf.* Rutherford: Phys. Zeit., 254, (1902); Phil. Mag. [6], 5, 95 (1903); von Lerch: Drude's Ann., 12, 745 (1903); Pegram: Phys. Rev., 17, 424 (1903). This product is variously designated by different writers as the induced activity, the excited activity, the imparted activity, and a component of the secondary activity.

[3] Radio-activity, p. 307.

Rutherford and Soddy have succeeded by chemical means in removing from thorium compounds the matter causing the major part of the radio-activity. The thorium, however, still retains some activity, and within a month it recovers its normal equilibrium value. During the same time the separated non-thorium types of matter rapidly lose their radio-activity and at the end of a month are comparatively inactive. (Compare curves A, *a*; Plate I.)

The separation of Th. X from thorium consists in precipitating thorium as hydroxide from an aqueous solution of the nitrate by means of dilute ammonia, added in excess. The filtrate, free from thorium, after evaporation and ignition to remove ammonium salts, yields a minute residue of intense activity compared with that of the original thorium, weight for weight. The precipitate, although containing all the thorium, possesses no emanating power at first, and its activity is less than half of its original value. The matter causing the imparted activity, being insoluble in dilute ammonia solutions, is found in the precipitate. When thorium is precipitated as carbonate, oxalate or phosphate, the residues obtained from the filtrates are inactive and the precipitates show no loss of radio-activity. In fact ammonium hydroxide was the only reagent of those tried by Rutherford and Soddy which separated Th. X from thorium compounds, thus showing that Th. X is insoluble in aqueous solutions of the reagents ordinarily used for precipitating thorium. With the view of arriving at other methods of separation we jointly undertook some experiments with thorium compounds, and, although work is still in progress, a report on some of the methods by means of which a separation is obtained, may be of interest. In connection with this work we found a method of separating, by chemical means, the matter causing imparted activity from the other components, and these experiments are included in this paper.

Separation by means of pyridine

In the course of the preliminary experiments it was found that the separation of Th. X from thorium is readily carried out by means of pyridine. When pyridine is added in excess to a dilute aqueous solution of thorium nitrate, no precipitate forms at room temperatures, but upon heating the solution, the thorium is completely precipitated as hydroxide.[1] The filtrate, after evaporation and ignition in order to expel the pyridine nitrate, yields a very slight residue which was found to be highly radioactive. Its rate of decay is the same as that of Th. X, its activity falling to half value in approximately four days.

Two samples of pyridine from Merck were used in these experiments. One was marked "free from homologues," and the other was the medicinal grade. The samples were redistilled, the former passing over between 114°.5–115°.5, the latter between 114°–118° under a pressure of 748 mm. The two samples exhibited no specific difference in their action with the thorium solutions. Three twenty-gram samples of thorium nitrate, obtained from Eimer & Amend, New York, were used in the course of the experiments. A composite of each sample was prepared by pulverizing it rapidly in an agate mortar. Subsequent hydration was guarded against, so that the small samples used in the separations should contain the same percentage of thorium. The nitrate upon ignition lost 51.3 percent in weight. Assuming that the sample was pure thorium nitrate, the calculated amount of water of hydration present was approximately 3.5 molecules per molecule of nitrate.

Some experiments were carried out for the purpose of ascertaining the conditions favorable for the separation of Th. X by means of pyridine. Within a wide range the dilution of the thorium nitrate solution has little or no effect on the separation. Solutions varying in strength from 0.1 to 10 percent, and containing the same amounts of thorium, yielded filtrates free from thorium, which after evaporation and ignition possessed approximately the same activity. For complete precipitation of the thorium the pyridine must be added in excess. The addition of pure pyridine gave the same results as an aqueous solution of the reagent. Boiling coagulates the gelatinous precipitate and

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[1] Miss Jefferson: Jour. Am. Chem. Soc., 24, 545 (1902).

causes it to settle rapidly. In one case the precipitate was boiled for half an hour, with an excess of pyridine in a flask fitted with a reflux condenser. The residue from the filtrate, however, did not differ materially in activity from the residue of another sample precipitated at the same time from a hot solution without boiling. Not all of the Th. X in the sample is removed by one precipitation with pyridine. In removing Th. X by means of ammonia, Rutherford and Soddy found that three successive precipitations were necessary to free thorium completely from Th. X. The same holds true for the removal of Th. X by means of pyridine. By dissolving the precipitate in hot dilute nitric acid and then reprecipitating the thorium with pyridine, as rapidly as possible, so that the Th. X produced in the precipitate shall not become appreciable, residues were obtained from the successive filtrates with activities, 100, 7.7, and 1.8 respectively. In three successive precipitations with ammonia, Rutherford and Soddy obtained residues whose activities were in the ratio of 100, 8, and 1.6 respectively, and in one of our experiments in which three successive precipitations with ammonia were made the activities of the residues obtained were 100, 9.1, and 1.0 respectively. In several instances, however, the activities of the residues obtained from the second and third filtrates were considerably greater with both pyridine and ammonia, than the values cited, although the conditions under which the precipitations were made were apparently the same.

The amounts of thorium nitrate used in the different experiments, ranged from 0.2 to 1.0 gram, but as a rule a known weight of the nitrate was taken. With amounts greater than 0.2 gram a suitable fraction of the filtrate was evaporated, platinum dishes being used for the most part. The precipitate was dried, together with the filter paper, on a hot iron plate. The greater portion was then removed from the paper and the latter incinerated. Ashless filter paper was always used. The entire precipitate was then transferred to a mortar and ground up under 95 percent alcohol.[1] The contents of the mortar were

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[1] The suggestion for this method was obtained from the work of McCoy on uranium. Jour. Am. Chem. Soc., 27, 4 (1905).

next poured out upon shallow, circular, metal dishes, 12 cm in diameter. Particles of the precipitate adhering to the mortar were washed out with alcohol and the latter was removed by setting fire to it. A thin layer of thorium oxide, of nearly uniform thickness, was obtained in this way, which adhered sufficiently to the dish to prevent shifting of the powder in transferring it to and from the testing apparatus for the subsequent measurements of radio-activity. The amount of thorium oxide spread out on one of the dishes was approximately 0.1 g.

The radio-activity of the precipitates and residues was determined by the electrical method, the Dolezalek type of quadrant electrometer being employed. When the needle was charged to 100 volts, a difference of potential of one volt between the two pairs of quadrants produced a deflection of 280 divisions on a millimeter scale, one meter from the mirror. The directions given by Rutherford in his book on Radio-activity, for the measurement of ionization currents by means of the quadrant electrometer, were found very helpful.

The testing apparatus consisted of a cylindrical vessel of galvanized iron, 15 cm in diameter, and 30 cm high, supplied with an insulated central brass rod, to the lower end of which a circular disc, 8 cm in diameter, was soldered. The vulcanite insulator, carrying the central electrode, was provided with a guard ring to prevent leak across the insulation. The guard ring was kept earthed during the tests and was insulated from the testing vessel by means of sulphur and sealing wax. The lower open end of the testing vessel fitted into a circular groove in a wooden base covered with thin sheet copper, and supported by vulcanite legs. The groove contained about 0.5 cm of mercury which served as a seal. A potential of 150 volts applied to the testing vessel was found sufficient for obtaining saturation values for the ionization currents measured. The electrometer, testing vessel and connections were screened from external electrical disturbances by placing them in a cage of wire netting which was well earthed.

The connections were made in the usual way. One pole of a water battery of 156 cells was earthed, the other was connected to the outside of the testing vessel. From the central electrode of the latter a wire connected with one pair of quadrants of the electrometer, the other being earthed. The central electrode of the testing vessel also had an earth connection which was broken, when readings were made, by means of a special switching device.[1]

In measuring the radio-activity of the precipitates and residues, readings were made at short intervals, usually about an hour, during the first twelve hours after separation. Subsequently, measurements were made at intervals of gradually increasing length, for a period of a month, at the end of which time the activity of the precipitate had acquired a constant maximum value, while the residue from the filtrate had become completely inactive. Between tests the dishes containing the samples were covered loosely with watch-glasses, and care was taken to disturb them as little as possible during the progress of their decay and recovery. On account of the emanation, equilibrium was often not established in the testing vessel for several minutes, after the sample was introduced. The plan followed was to make readings until constant values were obtained. The effect due to the emanation was then determined by covering the sample with two thicknesses of ordinary paper which cuts off nearly all the α-radiation.[2] The difference between the values calculated from the two readings was taken as the activity of the sample. The air leak of the apparatus, about 25 mm divisions per minute, was deducted from the values found. As the measurements for any pair of samples usually extended over a month, and as slight changes in the sensitiveness of the apparatus occurred, it was found necessary to employ the usual standard of uranium oxide in order to ascertain the corrections to be made in connection with the readings, due to such changes.

In carrying out two parallel separations with ammonia and pyridine by three successive precipitations with each reagent and using the same weight of thorium nitrate, it was invariably

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[1] Jour. Phys. Chem., 9, 324 (1905).

[2] Rutherford and Soddy: Jour. Chem. Soc., 81, 837 (1902).

found that the filtrate from the sample precipitated with pyridine, gave a residue of greater activity than the filtrate residue from the sample precipitated with ammonia, while the activity of the precipitate was correspondingly less than that of the precipitate obtained with ammonia. These differences in activity were found to be due to the matter causing imparted activity. When thorium is precipitated with ammonia, Rutherford and Soddy found that the matter causing imparted activity is insoluble in dilute ammonia and hence is found in the precipitate. When the separation is made by means of pyridine the matter causing imparted activity remains in solution, in part, at least, as the following experiment shows: Th. X was removed from thorium by three successive precipitations of a dilute aqueous solution of thorium nitrate with ammonia. The residue obtained by evaporating that portion of the filtrate, given by the third precipitation, was tested for radio-activity and found to contain only about 1 percent of the activity of the residue obtained by evaporating the filtrate from the first precipitation, thus showing that the Th. X had been practically all removed. The thorium hydroxide precipitate, free from Th. X, was at once redissolved in hot, dilute nitric acid, rapidly reprecipitated with pyridine and the precipitate filtered off by means of a suction-pump. The filtrate, after evaporation and ignition, gave a very minute residue which was found to be radio-active. It was identified as the matter causing imparted activity by its rate of decay, its activity falling to half value in eleven hours.

Four successive precipitations then,—three with ammonia and one with pyridine, separate Th. X and a portion of the matter causing imparted activity.

Separation by means of fumaric acid

In the course of our qualitative experiments several of the methods recently worked out for the quantitative separation of thorium from some of the other rare earth metals were tried. In this connection we found the contributions[1] from the quanti-

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[1] Metzger: Jour. Am. Chem. Soc., 24, 901 (1902); Neish: Ibid., 26, 780 (1904).

tative laboratory of Columbia University on the separation of thorium from cerium, lanthanum and didymium, very suggestive and helpful.[1] The separation of thorium from the other metals, named, by means of fumaric acid, as worked out by Metzger, when carried out with thorium compounds alone, effects a separation of some of the radio-active components. This fact was first noticed by Baskerville,[2] who did not, however, identify the products. Metzger found that thorium is precipitated quantitatively from a neutral 40 percent alcoholic solution by means of fumaric acid, while cerium, lanthanum and didymium remain in solution. When thorium was precipitated by means of fumaric acid, from a solution of thorium nitrate, Th. X was found in the filtrate together with some of the matter causing imparted activity. The precipitates and residues obtained were treated in the same manner as the products of the pyridine separation. The Th. X was completely removed by two successive precipitations. The second precipitation was carried out by redissolving the first precipitate in hot dilute nitric acid, evaporating to dryness at 150°, redissolving in hot 40 percent alcohol and reprecipitating with fumaric acid. The activity of the residue obtained from the second filtrate was extremely small when compared with that of the residue obtained from the first filtrate and it was found that one precipitation was sufficient to obtain the results presented below, provided the precipitate was thoroughly washed with hot 40 percent alcohol containing a little fumaric acid. The activity of the residue obtained by evaporating the filtrate and igniting, to decompose the excess of fumaric acid, was found to exceed that obtained from the same amount of thorium nitrate when the separation was carried out by means of pyridine, while the activity of the precipitate was correspondingly less. This difference was found to be due to the presence in the filtrate from

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[1] The contributions from the Harrison Laboratory, University of Pennsylvania, on the use of organic bases in precipitating and separating the rare earth metals, likewise indicated other methods. See Jour. Am. Chem. Soc., 24, 540 (1902); 25, 421, 1128 (1903).

[2] Jour. Am. Chem. Soc., 26, 931 (1904).

the fumaric acid precipitate of a greater amount of the matter causing imparted activity. That a portion of this matter which causes the imparted activity had been separated from the thorium, was shown in the following manner: A sample of thorium nitrate, after undergoing three successive precipitations without lapse of time, with ammonia, when precipitated a fourth time with fumaric acid and the filtrate evaporated and ignited, yielded a minute residue of considerable activity. The residue was much more active than that obtained when the fourth precipitation was made with pyridine instead of with fumaric acid. The same amount of thorium nitrate was used in the two cases and the time required for the experiments was approximately the same. During the first few hours after precipitation the activity of the residue increased in value, reaching a maximum in about four hours, when it decreased according to an exponential law, falling to half value in eleven hours. The curve D, Plate I, which shows the change of activity with the time, has the form characteristic for the radio-active type of matter deposited on a negatively charged plate when exposed for a short time, about fifteen minutes, to the emanation of thorium oxide. The type of matter causing imparted activity, was also separated from thorium compounds by first precipitating the thorium from the solution by means of fumaric acid, filtering and then adding dilute ammonium hydroxide in excess to the filtrate, to which a drop of lead nitrate or ferric chloride solution had been added previous to the addition of ammonia. The small precipitate obtained contained the matter causing imparted activity which decays to half value in eleven hours, after passing through a maximum at approximately four hours from the time of precipitation. (Curve D, Plate I.)

Curves of recovery and decay

The changes in radio-activity, of the types of matter separated from thorium compounds by the foregoing methods are represented graphically in Plates I and II. Curves *a*, *b*, and *c*, Plate I, represent the recovery of activity of the precipitates with the time, when the separations are carried out respectively with ammonia, pyridine and fumaric acid. Curves A, B, and C show the decay of activity of the radio-active products obtained by evaporating the filtrates corresponding to the respective precipitates. In Plate II, the initial portions of the curves of decay and recovery are plotted on a larger scale, but the letters refer to the same products as in Plate I. Curve D, Plate I, shows the decay of activity of the matter causing imparted activity, which was removed by the two methods described above in connection with the fumaric acid separation. The curves represent, in the case of ammonia, three precipitations, with pyridine two, and with fumaric acid one.

In plotting the results, the plan of Rutherford and Soddy[1] was followed. The activities are represented on the axis of ordinates by an arbitrary scale. In Plate I, the final value of the precipitates[2] was taken as 100 in each case. The recovery curves *a*, *b*, and *c* were plotted on this basis. In plotting the curves A, B, C, showing the decay in activity of the residues, the initial value is represented by 100, time being reckoned from the time the precipitation was made. In the case of Curve D, Plate I, the maximum value of the activity was placed at 100 and the time scale represents hours instead of days. Curves A, B, C, *a*, *b*, *c*, Plate II, are plotted on the basis of the initial values of the activities, both the precipitates and residues being taken as 100.

Neglecting for the present the initial irregularities of the curves of decay and recovery in Plate I, a full discussion of which is given further on, it appears from the close parallelism of the curves after the second day that the same radio-active process is taking place in each set of residues and precipitates. After the second day, the three residues have approximately the same activity. The same is true of the precipitates. The activity of the residues decays according to an exponential law, falling to half value in about four days, a rate of decay characteristic of Th. X. In each separation, the initial activities of the precipi-

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[1] Jour. Chem. Soc. London, 81, 839 (1902).

[2] The effect due to the emanation is not included in the values.

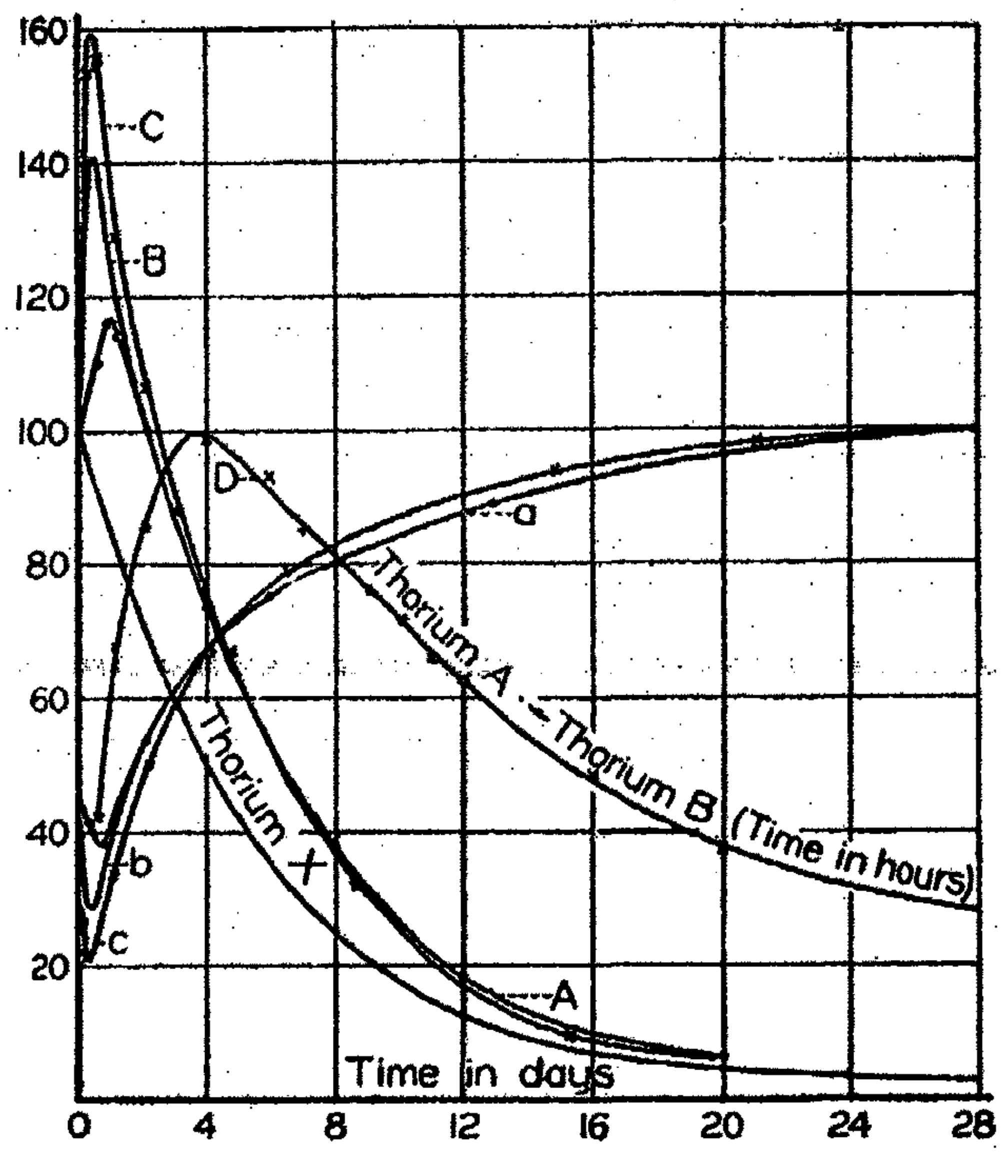

Plate I

Ammonia A,*a*
Pyridine B,*b*
Fumaric acid C,*c*

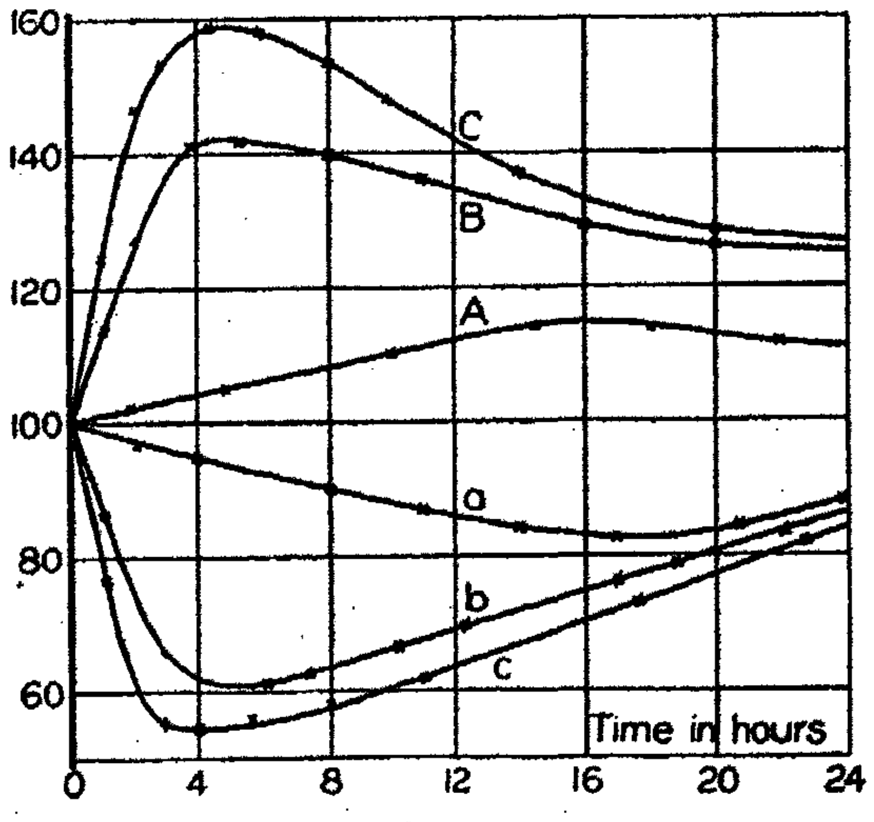

Plate II

tates are about the same, values varying from 41 to 46 having been obtained in different experiments. These precipitates recover their activity in a geometric progression with the time, attaining a maximum value within a month, which is due to the formation of Th. X and its disintegration products. When the recovery curves are extended back, they cut the axis of ordinates at about twenty, which represents the proportion of the final activity due to the "non-separable" activity of thorium, which as Rutherford and Soddy have pointed out may be regarded as a distinct type of matter resulting from the slow disintegration of the inactive thorium itself, and very closely allied to thorium in its properties, or, it may be regarded as the radioactivity due to thorium itself. The value of the non-separable activity found by us is somewhat less than that given by Rutherford and Soddy, *viz.*, 25 percent, but in this connection it must be noted that these investigators record a value of 22 percent for the non-separable portion in one of their experiments. Inactive thorium was not obtained in the course of the separations. Hoffman and Zerban,[1] and Zerban[2] state that inactive thorium was obtained from the mineral gadolinite. On the basis of the non-activity of thorium the activity of thorium compounds must be ascribed to a radio-active type of matter generally associated with thorium and very like it in its behavior towards different reagents. If this view should prove to be the correct one, then, as Rutherford and Soddy have pointed out, the rôle played by the non-separable activity in the theory of radio-active changes would simply have to be assigned to the new radio-active matter so closely resembling thorium in its other properties.

Coming now to the consideration of the initial irregularities in the curves of decay and recovery, it is seen that the residues obtained from the filtrates in the fumaric acid and pyridine separations, increase in activity considerably more than the ammonia residue. Moreover, the fumaric acid and pyridine residues attain their maximum after five hours, while the ammonia

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[1] Ber. chem. Ges. Berlin, 36, 3093 (1903).

[2] Ibid., 36, 3911 (1903). See also Baskerville and Zerban: Jour. Am. Chem. Soc., 26, 1642 (1904).

residue only reaches a maximum after nearly twenty hours. On the other hand, the precipitates obtained with fumaric acid and pyridine drop in activity more rapidly at first than the ammonia precipitate, the curves passing through minimum values at the same time that the curves of decay of the corresponding residues attain maximum values. These differences in the curves are more evident from the plotting in Plate II, which shows simply the initial portions of the curves.

The maximum and minimum in the curves of decay and recovery have been satisfactorily explained by Rutherford and Soddy when the separation is carried out by means of ammonia. Their explanation[1] is briefly as follows: Before any separation is made the activity observed is the sum of the several activities of (1) thorium, (2) Th. X, (3) emanation, (4) matter causing imparted activity, the last named consisting of at least two stages recently designated by Miss Slater[2] as Th. A and Th. B, respectively. The separation with ammonia yields a precipitate free from Th. X and without emanating power at first. In the precipitate is found the thorium, and the matter causing imparted activity (both stages). Immediately after the separation then, neither the residue from the filtrate nor the precipitate is in radio-active equilibrium. Since the precipitate is free from Th. X, which produces the matter causing imparted activity, *via* the emanation, but little imparted activity will be produced during the first day, because comparatively little Th. X is present. In view of the very rapid change of the emanation into the matter causing imparted activity—one-half changing in about one minute—no serious error is introduced by omitting this step in an explanation of the initial irregularities of the curves. The imparted activity present in the precipitate, however, decays, and since its rate of decay is *faster* than the rate at which Th. X is formed, the activity of the precipitate decreases for a time until the activity of the Th. X and its disintegration products compensate the loss of activity due to the decay in the

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[1] Rutherford: "Radio-activity," pp. 295–299. Soddy: "Radio-activity," pp. 117–121.

[2] Phil. Mag. [6], 9, 628, May (1905).

matter causing imparted activity. Rutherford and Soddy established the correctness of this view by separating Th. X from thorium 23 times during a period of nine days, so as to remove the Th. X nearly as fast as it was formed, while at the same time, the matter causing imparted activity decayed. The recovery curve then obtained showed practically no drop, and finally after about a month attained a constant value approximately four times its initial value.

The initial rise in the Th. X curve is explained by considerations similar to those advanced for the decay in activity of the precipitate during the first day. Th. X changes into the matter causing imparted activity, and as the latter disintegrates more rapidly than Th. X, the activity due to the imparted activity more than compensates for the decay in activity of Th. X itself, and the combined effect of these two activities gradually increases during the first day after precipitation, the maximum lying about 18 percent higher than the initial value. The theoretical curve showing the combined effect of two radio-active types of matter, the first producing the second, and having respectively the radio-active constants of Th. X and the imparted activity considered by them, is given by Rutherford on page 299 of his book on "Radio-activity" (see also Curve A, Plate I). The observed and theoretical values show a very good agreement.

The far greater increase in activity exhibited by the residues obtained in the pyridine and fumaric acid separations—the residue from the latter showing an increase of more than 50 percent over the initial value—demands further explanation. Moreover, the fact that the maximum values are reached in about one-fourth the time required for the ammonia residue to come to a maximum, indicates that the distribution of the several types of matter in the separation with fumaric acid and pyridine differs in some respects from the separation by means of ammonia. It will be shown that this difference arises from the matter causing imparted activity—the fumaric acid and pyridine effecting a separation of its components. From his experiments[1] on the matter causing imparted activity of thorium, together with the

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[1] Phil. Mag. [6], 5, 95 (1903).

experiments carried out by Rutherford and Miss Brooks,[1] Rutherford concluded that the imparted activity was complex. On the basis of the results obtained by exposing a negatively charged wire for short intervals to the thorium emanation, Rutherford pointed out that they could be satisfactorily explained by assuming the presence of two products—one not radio-active, that is, emitting no rays, with a rapid rate of change, the other resulting from it, radio-active, but with a slower rate of change. In the first change, one-half of the matter disintegrates in fifty-five minutes, in the second one-half changes in eleven hours. Quite recently, however, Rutherford[2] has stated that the results obtained might be explained equally well by assuming that the matter with the slow rate of change and giving off no rays is the the first product, and that this inactive matter produces a radio-active product with the rapid period of decay. About the same time Miss Slater[3] succeeded in effecting a partial separation of the two types of matter constituting the imparted activity, which had been deposited on a negatively charged wire by a long exposure to the emanation from thorium. She did this by the action of the cathode rays and also by heating to a high temperature. The results of her experiments, Miss Slater states, can be satisfactorily explained on the theory, independently advanced by her, that the first product is inactive and has the slow period of decay, and that it changes into a radio-active product with a rapid period of decay. Miss Slater designated the first product, which emits no rays and has the slow rate of change, Th. A, and the second product which emits radiations and has the rapid rate of decay, Th. B. We shall use this terminology in connection with the further discussion of the initial peculiarities of the curves of recovery and decay. The view advanced by Rutherford and Miss Slater also affords a satisfactory explanation for the initial irregularities in the curves of recovery and decay of the precipitates and residues obtained in the separations with fumaric acid and pyridine.

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[1] "Radio-activity," p. 260.

[2] Phil. Trans. A., 376.

[3] Phil. Mag., May, 1905.

When thorium is precipitated with fumaric acid, the precipitate, instead of containing both Th. A and Th. B, as is the case when the precipitation is made with ammonia, contains only Th. B. The first product of the imparted activity, Th. A, is soluble in excess of this reagent and hence is found in the filtrate with Th. X. As Th. A undergoes change without giving off rays, the initial activity of the filtrate has the same value as that obtained with ammonia. The precipitate, which contains thorium and Th. B, is not in radio-active equilibrium, but before the thorium has formed even a few percent of Th. X, Th. B has changed practically completely into a final inactive product, one half of the change taking place in fifty-five minutes. Hence, as Th. B is responsible for about one-half the ionization produced by the precipitate initially, its rapid decay accounts for the rapid decrease in activity of the precipitate during the first four hours after precipitation. It will be noted that by deducting the effect due to the non-separable activity from the curve representing the combined effect of the non-separable thorium activity and Th. B (Curve *c*, Plate II), the difference curve drops to half value in about one hour which is the characteristic rate of decay of Th. B.

From the above it can readily be seen that if the processes of precipitation and filtration are carried out slowly, so that the first readings are made four or five hours after the first precipitation, the curves will show no initial drop and the result will be the same as that obtained by Rutherford and Soddy with twenty-three precipitations by means of ammonia.

In the residue from the filtrate, Th. X and Th. A are in equilibrium at the outset, but the residue as a whole is not in equilibrium, owing to the absence of the radio-active product Th. B. This product, however, is produced from Th. A at a much faster rate than Th. X decays and since Th. B changes at a still faster rate, the activity of the residue shows a rapid initial rise, reaching a maximum about five hours after separation.

The residue obtained in the ammonia separation being free from both Th. A and Th. B shows a smaller rise initially because the Th. A produced by Th. X is very small in proportion to that present in the fumaric acid residue, and since the increase in activity of the residue depends upon the amount of Th. B produced from Th. A, it follows on this view that the initial increase in activity should be considerably greater when the residue contains the normal amount of Th. A, as is the case in the fumaric acid separation.

The initial peculiarities of the curves representing the decay and recovery of the products obtained in the pyridine separation are not quite as marked as in the fumaric acid separation, probably because the separation of Th. A and Th. B was not quite complete.

The correctness of the view here presented was tested by several experiments. In connection with the fumaric acid separation in the early part of this paper, two methods were given by which Th. A was separated from the other products. In one of these experiments, Th. A was removed from the *precipitated thoria*, obtained with ammonia, by means of fumaric acid, and in the other one, Th. A was removed from the *filtrate* obtained in the fumaric acid precipitation by the addition of ammonia. The curve marked Th. A → Th. B, Plate I, is the theoretical curve of the residue, Th. A, while the plotted points represent the experimental values obtained. It will be observed that this curve closely resembles the initial portion of the curve of the fumaric acid residue (C, Plate II).

In another experiment the thorium was precipitated once with fumaric acid and filtered off; the precipitate was then quickly redissolved in dilute nitric acid, and after the addition of a trace of lead nitrate, the solution was at once subjected to electrolysis for five minutes, a rotating cathode being employed with a current density of about six amperes per 100 sq. cms. of cathode surface. The electrodes were washed and dried quickly and then tested for activity. The slight deposit of lead peroxide on the anode was found to be practically inactive and subsequently showed no change, but the slight deposit on the cathode was highly radio-active, its activity decreasing according to an exponential law, decaying to half value in fifty-five minutes, and finally becoming entirely inactive, and remaining so. This experiment shows that the precipitate of thorium obtained with fumaric acid, contains the product Th. B, and not Th. A, for according to the experiments of Pegram[1] on the electrolysis of thorium nitrate solutions Th. A is deposited on the anode under the conditions of our experiment, but the anode deposit in our experiment was inactive and showed no change with the time, as it should have done if Th. A had been deposited. Our thorium nitrate solutions, when subjected to electrolysis, behaved in the manner described by Pegram—the anode deposit being quite active, the activity decaying to half value in eleven hours after showing the initial rise characteristic of Th. A, while the cathode deposit had a slightly slower rate of decay than the Th. B similarly obtained from the thorium nitrate solution, from which Th. A and Th. X had been removed.

The theoretical curves

The foregoing explanation for the initial peculiarities of the curves of recovery and decay, finds further confirmation in the theoretical curves which are obtained on the basis of the suppositions made. The method of treatment here employed follows, in the main, the exposition given by Rutherford[2] and by Stark.[3] According to the disintegration theory, a constant proportion of the atoms of a radio-active element is continuously undergoing change, and the ionization produced may be used for ascertaining the fraction of the atoms which are changing per second. This constant rate, called the *radio-active constant*, is the fundamental physical characteristic of the different radio-active types of matter. It has a different value for each type of active matter, but is a definite constant for each particular type. The radio-active constant for Th. B is 0.0125, when the time is expressed in minutes, which indicates that Th. B is continuously undergoing change at the rate of 1.25 percent per minute. The ionization produced by a particular type of radio-active matter depending, as it does, upon the number of atoms present and

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[1] Phys. Rev., 17, 424 (1903).

[2] "Radio-activity," pp. 268–272; 297–300 (1904).

[3] Jahrbuch der Radioaktivität., 1, 1, (1904).

their rate of change, is directly proportional to the product of the rate and the number of atoms present. This law of radioactive change is the same as the law followed by a monomolecular chemical reaction, the inversion of cane-sugar for example, and both laws are illustrations of the more general law of nature which Lord Kelvin[1] has happily termed the "Compound Interest Law," which states that the amount of change in a given time is directly proportional to the quantity present in the system.

The rate of change of a radio-active element is expressed by the equation

$$\frac{dn}{dt} = -rn,$$

where n denotes the number of atoms present at the time t, and r the radio-active constant, the minus sign indicating that the change causes a decrease in the quantity of the active element. By integration of the above equation,

$$n = n_0 e^{-rt},$$

where n_0 denotes the number of atoms considered at the outset, when $t = 0$. The activity, I, of the sample at the time t, is given by

$$I = crn = crn_0 e^{-rt},$$

where c is the proportionality constant. The values of the theoretical curve of decay of Th. X (Plate I), were calculated from the above equation. The radio-active constant of Th. X has the value 0.0072 when t is expressed in hours.[2]

When the radio-active substance produces another, which is also radio-active, then the activity at any time, is proportional to the sum of the atoms of each which are undergoing change. The curve showing the progress toward equilibrium will then frequently show irregularities. The residue obtained in the fumaric acid separation contains Th. X and Th. A just after

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[1] Mellor: "Higher Mathematics for Students of Chemistry and Physics," p. 40.

[2] Rutherford: "Radio-activity," p. 298.

separation, but Th. A at once produces Th. B which changes rapidly into a final inactive product. The successive changes occurring simultaneously in the residue are:

Th. X → Emanation → Th. A → Th. B → Final Product.

The activity of the solid residue itself is due to Th. X and Th. B. In the consideration which follows, the second product, the emanation, is not introduced, since its rate of transformation is very rapid in comparison with the other products.

If n, n_1, n_2 denote the number of atoms of Th. X, Th. A and Th. B present at the time t after separation, and r, r_1, and and r_2, the corresponding radio-active constants, then the activity I is expressed by

$$I = rn + kr_2n_2, \qquad (1)$$

where k denotes the ratio of the ionization of Th. B to Th. X. The radio-active constants have the values, $r = 0.0072$; $r_1 = 0.063$; $r_2 = 0.75$, when t is expressed in hours. The value of n is obtained from the formula

$$n = n_0 e^{-rt}.$$

The value of n_2 depends upon the value of n_1 and is determined by the following considerations: Assuming that Th. X and Th. A are in equilibrium immediately after the separation, then the quantities of each present are inversely proportional to their radio-active constants; that is,

$$n : n_1 = r_1 : r.$$

Introducing the values of r and r_1 we have

$$n_1 = \frac{n}{8.75} = \frac{n_0}{8.75} e^{-rt}.$$

Now the number of atoms of Th. B continuously undergoing change is r_2n_2, and the number produced from Th. A, at the same time is r_1n_1. Hence the rate of change in Th. B,

$$\frac{dn_2}{dt} = -r_2n_2 + r_1n_1,$$

whence

$$\frac{dn_2}{dt} + r_2n_2 = \frac{r_1 n_0}{8.75} e^{-rt}.$$

Integration of this equation gives

$$n_2 = \frac{r_1 n_0}{8.75\,(r_2 - r_1)}\left(e^{-rt} - e^{-r_2 t}\right).$$

The theoretical values in the following table were calculated from Formula (1). The value of $k = 0.5$, used, was obtained from the ratio of the ordinates of the activities of Th. B and Th. X at the end of the second day. The experimental values are given in the second and fourth columns of the table while the first column gives the time which had elapsed since the separation. (See also Curves B and C, Plate I.)

Time	Fumaric acid	Theoretical value	Pyridine
0	100	100	100
20 minutes	—	111	—
30 "	116	115	108
60 "	129	127	113
2 hours	147	137	127
4 "	155	144	141
5 "	158	145	142
6 "	158	144	142
8 "	154	142	140
16 "	—	134	—
24 "	128	127	122
2 days	106	107	103
4 "	74	75	73
8 "	37	38	36
12 "	18	19	17
16 "	—	9.5	—
20 "	5.6	4.7	4.5

The times at which the theoretical and experimental values attain a maximum are practically the same, thus confirming the assumptions made. The variations of the experimental from the theoretical values is greater at the outset than the experimental error, but these differences may be accounted for by assuming that the ionization ratio of the two radio-active types of matter varies, gradually assuming a smaller value, which is quite probable in view of the fact that the matter causing imparted activity is formed by the emanation, and the emanating power varies considerably with the nature and physical condition of the substance. Moreover, the presence of the emanation introduces experimental difficulties.

Considering now the ammonia separation, it was shown by Rutherford and Soddy that the filtrate residue simply contains Th. X immediately after the separation, but Th. X at once produces the inactive Th. A, which, in turn, produces Th. B, the last active product. This case differs from the one just considered, inasmuch as no Th. A is present at the outset. Following the same notation as in the previous case, it is seen that n, the number of Th. X atoms present at the time t, is obtained from $n = n_0 e^{-rt}$

The rate of change in Th. A is expressed by $\frac{dn}{dt} = - r_1 n_1 + r\,n$ which, upon integration, gives

$$n_1 = \frac{r\,n_0}{r_1 - r}\left(e^{-rt} - e^{-rt_1}\right).$$

The rate of change in Th. B is expressed by

$$\frac{dn_2}{dt} = - r_2 n_2 + r_1 n_1.$$

This equation, after substituting in it the value of n_1 when integrated, gives

$$n_2 = \frac{r\,r_1\,n_0}{r_1 - r}\left(\frac{e^{-rt}}{r_2 - r} - \frac{e^{-rt}}{r_2 - r_1}\right) + \frac{r_1\,r\,n_0}{(r_2 - r)(r_2 - r_1)}\,e^{-rt}.$$

The activity at the time t is given by

$$\mathrm{I} = rn + \mathrm{K}\,r_2\,n_2,$$

where K again represents the ratio of ionization due to Th. B.

The theoretical values in the table below were calculated from the last equation. In the calculation of the values of n_2, the last term in the equation becomes negligible after the fourth hour. The value of K = 0.44, here employed, is the one given by Rutherford.[1]

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[1] "Radio-activity," p. 298.

Time	Theoretical values	Experimental values
0	100	100
1 hour	100+	101
5 hours	105	106
10 "	111	110
16 "	116	117
20 "	115	117
24 "	114	113
50 "	103	100
3 days	89	88
4 "	75	73
8 "	37.7	38
12 "	18.8	19
20 "	4.7	5

Here again the maxima in the theoretical and experimental values practically coincide, and the theoretical and experimental values show a close agreement throughout.

Removal of Th. X by means of other reagents

Various qualitative tests were made with other reagents which precipitate thorium quantitatively from aqueous solutions of its salts. In many cases the residue obtained by evaporating the filtrate and igniting it, was highly radio-active, showing that a radio-active constituent had been removed. The following additional reagents remove some form of radio-active matter from thorium compounds: aniline, benzoic acid, meta-nitrobenzoic acid, tannic acid, potassium xanthogenate, hydrogen peroxide, piperidine, phenyl hydrazine. In fact the major part of the reagents tried, which precipitate thorium completely, yielded radio-active residues. The precipitates were also radio-active, thus showing that a non-separable portion of the activity is either due to thorium itself or to a new type of matter closely resembling thorium in its behavior towards reagents. The distribution of the radio-active components between the precipitate and residue, when the above reagents are used, is being studied, and in this connection the separations are being conducted with a sample of thorium nitrate which has been specially purified.

Although no very accurate tests on the emanating power of the different thorium precipitates were carried out, still, the values observed show that the different compounds vary considerably in this respect. Rutherford and Soddy[1] first directed attention to this point. They found that when thorium was precipitated apparently under the same conditions, the precipitate often showed marked difference in emanating power. The thorium oxide obtained by us by means of pyridine, generally possessed less emanating power than the oxide obtained by means of ammonia. The thorium fumarate precipitate possessed a high emanating power. Although it varied considerably it was usually more than twice that of the ammonia precipitate. Hence thorium fumarate exceeds in emanating power any of the other thorium compounds thus far examined.

Summary of results

(1) The separation of the radio-active types of matter in thorium compounds by chemical methods, was studied from a qualitative standpoint, and a detailed quantitative study was carried out with two reagents, pyridine and fumaric acid.

(2) The removal of Th. X from thorium compounds by means of ammonia, discovered by Rutherford and Soddy was confirmed. Our experiments constitute an extension of the method of separation employed by these investigators.

(3) Pyridine and fumaric acid remove from thorium nitrate solution Th. X and the inactive product, Th. A of the matter which constitutes the imparted activity of thorium. The precipitate contains the non-separable activity and the radio-active component of the imparted activity, Th. B, which decays to half value in fifty-five minutes.

(4) It was shown both by experimental and theoretical considerations that the presence of Th. A in the filtrate residue, in the separation by means of fumaric acid, and its presence in the precipitate when ammonia is employed, accounts for the initial differences observed in the curves of decay and recovery of the separated products.

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[1] Jour. Eng. Chem. Soc., 81, 851 (1902).

(5) Th. A was isolated from the other radio-active products by chemical methods. Pure Th. B was isolated by electrolysis

(6) Inactive thorium was not obtained in the course of the experiments.

(7) One precipitation of an aqueous solution of thorium nitrate with fumaric acid, yields a thorium precipitate whose activity at the end of five hours is less than one-fourth the final activity of the product.

(8) The emanating power of thorium fumarate was found to be approximately double that of the thorium oxide obtained by precipitation with ammonia, while the emanating power of the oxide obtained in the pyridine precipitation fell below that obtained by the use of ammonia.

Further experiments on the separation of the radio-active products in thorium compounds, by chemical methods, are in progress.

Chemical Laboratory,
University of Missouri, Columbia, Mo.,
June, 1905.

NEW BOOKS

Landolt-Börnstein Physikalisch-Chemische Tabellen. *By Richard Börnstein and Wilhelm Meyerhoffer. Dritte umgearbeitete und vermehrte Auflage. 20 × 27 cm; pp. xvi + 861. Berlin: Julius Springer, 1905. Price: bound, 36 marks.*—This new edition is a monumental work. There are 857 pages of closely printed tables and literature references. The most marked changes are in the sections on pressures, melting-points, thermochemistry, molecular weight determinations, and solubility. Under alloys the freezing-point curves are given graphically for a number of pairs of metals. This is an admirable plan. By the time of the next edition it will be possible to go one step further and give complete concentration-temperature diagrams.

Under vapor-pressures we find the data of Tammann on solutions given in full and also the measurements of Smits. Ramsay and Young's work on the vapor-pressures of different liquids is tabulated in a very thorough manner. Zawidski's measurements on the partial pressures of mixtures of two volatile liquids are given but there is no table of maximum and minimum boiling-points.

Under critical data there is an interesting table giving approximate values for the a and b in the van der Waals formula.

Under the general heading of thermochemistry are grouped the tables for heats of combustion, heats of formation, heats of neutralization, heats of solution, heats of dilution, heats of hydration, heats of inversion, heats of vaporization, heats of fusion, and heats of dissociation.

A most valuable set of tables is that under molecular weight determinations, giving the van't Hoff freezing-point and boiling-point constants for a large number of solvents. For the boiling-point experiments the table shows the boiling-point of the solvent, the molecular rise of boiling-point as determined experimentally, the heat of vaporization as determined experimentally, the boiling-point constant as calculated from the heat of vaporization, and the heat of vaporization as calculated from the boiling-point constant.

In the tables on solubility, care is taken to specify the phase with respect to which the solution is saturated. Electrometric and conductivity determinations of solubility are also included, so that this whole section is thoroughly up-to-date.

Owing to the time necessary to print such a work, the literature references in the first part of the volume do not include all the work of 1902 while the last part of the book comes down to the end of 1904. This is unfortunate of course but probably inevitable in a work of such magnitude. Certainly the way in which the work has been done reflects enormous credit on the editors, R. Börnstein and W. Meyerhoffer and on their collaborators T. Albrecht, F. Auerbach, K. Bädeker, O. Bauer, W. Bein, A. Blaschke, H. Böttger, J. W. Brühl, G. Bruni, A. Denizot, F. Dolezalek, E. Gehrcke, K. Grimm, E. Gumlich. F. Henning, E. Heyn, F. W. Hinrichsen, L. Holborn, W. P. Jorissen, G. Just, P. Kohnstamm, J. Koppel, G. Langbein, O. Lummer, A. Mahlke, F. F. Martens, G. Meyer, J. D. van der Plaats, B. Prager, F. Ritter, W. A. Roth, R. Rothé,

V. Rothmund, H. Rubens, A. Sachs, K. Scheel, R. Schenck, A. Schmidt, O. Schönrock, H. v. Steinwehr, K. Stelzner, K. Stöckl, F. Weigert, H. F. Wiebe and A. Winkelmann. *Wilder D. Bancroft.*

"N" Rays. *By R. Blondlot. Translated by J. Garcin. 13 × 20 cm; pp. xii + 83. New York: Longmans, Green & Co., 1905. Price: $1.20 net; by mail $1.26.*—The French edition of this little book has already been reviewed in these pages (8, 577). M. Garcin's very satisfactory English translation will doubtless find many readers, for the subject is one that has aroused interest even outside of scientific circles. The attractiveness of the book is enhanced by the fact that a phosphorescent screen and table for N-ray experiments accompanies each copy, while an appendix gives directions for using the screen in making observations. The reviewer is compelled to admit, however, that his own efforts to observe the effects described by the use of the screen have proven fruitless.

The present tendency among physicists is to look upon accounts of N-ray experiments with suspicion, and to wait until the remarkable phenomena described at almost every session of the French Academy are confirmed by experimenters free from Gallic influences. In view of the numerous unsuccessful attempts to repeat the experiments of Blondel and his followers such an attitude is no more than natural. Yet its universal adoption outside of France, which seems now not improbable, would lead to a complete deadlock. The condition is somewhat similar to that which arose a few years since in the case of the Rowland effect, when the uniformly negative results obtained by Crémieu cast doubt upon one of the most fundamental assumptions of modern electrical theory. It was the general belief that Crémieu's experiments were in error. Yet they might be correct; and the question was of too great importance to be allowed to remain in doubt. The matter was settled in a very satisfactory way. Pender, whose experiments in this country had uniformly led to results exactly opposite to those of Crémieu, made a trip to Paris, and the two experimenters working together repeated their experiments on the subject in question. It was shown that Pender's position was correct; the Rowland effect does exist as theory requires. But at the same time Crémieu was not wholly wrong; for the investigation of the cause of his negative results led to the discovery of certain peculiarities in the Rowland effect which had not before been suspected, and which will probably prove of considerable theoretical importance.

Can it be doubted that a similar study of the N-rays, in which the enthusiast and the skeptic unite in their efforts to find the true cause of these remarkable phenomena, will prove equally valuable? In the opinion of the reviewer the Carnegie Institution, whose support made possible the joint work of Pender and Crémieu, could not better utilize its funds than by facilitating a similar combination of effort in the case of the N-rays.

Those who doubt the need of further experiments, and feel that the question of the existence of the N-rays is already settled in the negative, will find that this collection of papers, written by a trained physicist in true scientific style, will at least change disbelief into puzzled uncertainty. *Ernest Merritt.*

Le Four électrique, son Origine, ses Transformations, et ses Applications. *By Adolph Minet. Premier Fascicule: Forces naturelles, Électro-métallurgie,* *Chimie par Voie sèche. 19 × 28 cm.; pp. 76. Paris: A. Hermann, 1905. Price: paper, 5 francs.*—This is the first instalment of a large book in which the electric furnace is to be considered from the historical, scientific and technical points of view. This number consists of an introduction, a sketch of laboratory furnaces up to 1904, chapters on units and on sources of electricity, and a section on the fundamental laws of electrochemistry. The author is clear as to the Helmholtz formula for the relation between heat effect and electromotive force; but not so clear as to the Nernst formula for concentration cells. He groups the Nernst formula with that of Thomson, saying that both hold when the temperature coefficient is zero. As a matter of fact the Nernst formula for concentration cells holds only when the heat effect is zero.

Wilder D. Bancroft.

Verflüssigtes Ammoniak als Losungsmittel. *By J. Bronn. 14 × 21 cm. pp. xi + 252. Berlin: Julius Springer, 1905. Price: bound, 6 Marks.*—The author believes that there is a great commercial future for liquefied ammonia as a solvent and he has, therefore, brought together in a monograph all the information he could find as to the properties of liquefied ammonia. The first chapter deals with the physical properties of liquid ammonia, the testing and transport of the same, and the use of it as a refrigerating agent in the laboratory. In the second chapter is discussed the liquefying action of ammonia gas and the absorption of ammonia by different substances. The third chapter is devoted to the older solubility work of Weyl and of Gore. The fourth chapter treats of metal-ammonium and metal-amide compounds while the more recent work on liquid ammonia as a solvent is to be found in the fifth chapter. Reactions in liquid ammonia is the heading of the sixth chapter. The physical chemical investigations are summarized in the seventh chapter and there is a supplementary chapter on the attempts to isolate ammonium.

The author has written an excellent and most comprehensive book. The experiments of Roozeboom appear to have been overlooked but that is all.

Wilder D. Bancroft.

Die Entwickelung der elektrischen Messungen. *By O. Frölich. (Die Wissenschaft. Sammlung naturwissenschaftlicher und Mathematischer Monographien. Heft 5.) 14 × 22 cm; pp. xii + 192. Braunschweig: Friedrich Vieweg und Sohn. 1905. Price: paper, 6; bound, 6.80 marks.*—The book is divided into two parts, the first dealing with the measuring instruments and the second with the methods of measuring. Under instruments we are introduced to the different types of galvanometer and of electrodynamometer, to switchboard instruments, meters and recording instruments; to the various electrometers. Under methods we find the measurement of current, of potential difference, of resistance and of self-induction. The book is written primarily for the electrical engineer as is shown by the very brief notice given to potentiometers and by the statement that the modern ammeter has superseded the voltameter in the hands of chemists. It is quite true that a copper voltameter is an obsolete instrument so far as measuring the strength of the current is concerned, but it is of distinct value as a meter. It gives the total quantity of coulombs which the ammeter does not.

The book is a satisfactory one and the chemist can learn much from it even though it was not written especially for him. *Wilder D. Bancroft.*

Elektromagnetische Schwingungen und Wellen. *By Josef Ritter von Geitler. (Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 6). 14 × 22 cm; pp. viii + 154. Braunschweig: Friedrich Viewig und Sohn, 1905. Price: paper 4.50; bound, 5.20 marks.*—In the first chapter we have Sir Isaac Newton's introduction of the definition of force with the resulting belief in action at a distance, a belief which was not held by Newton. In the second chapter we have the development of action through a medium, the subject being discussed with reference to the three men, Faraday, Maxwell and Hertz. The last chapter deals with the further developments, the main subject being electromagnetic waves and optics, with wireless telegraphy as the final section. From the nature of things this book could hardly be called easy reading for any one save a physicist by profession. This is due entirely to the difficulties of the subject. The book is written in an admirable manner from a definite point of view. The result is that it is fascinating reading in spite of the difficulties involved. *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

The atomic weight of gadolinium. *G. Urbain. Comptes rendus,* 140, *583* (*1905*).—The gadolinium was purified by a fractional crystallization of the double nitrates of gadolinium and nickel in nitric acid, sp. gr. 1.3. From a conversion of the sulphate into the oxide, an atomic weight of 157.23 was obtained with O = 16 and S = 32.06. *W. D. B.*

New method of calculating the exact molecular weights of liquefiable gases, starting from the densities. *P. A. Guye. Comptes rendus,* 140, *1241* (*1905*).—The author uses the formula

$$M = \frac{22.412}{(l + a_0)(l - b_0)}$$

to calculate the molecular weights of liquefiable gases. In the formula a_0 and b_0 are the values for a and b in the van der Waals equation at 0°. They are calculated by means of special formulas from the values for a and b at the critical temperature. The following atomic weights are deduced: H, 1.0077; C, 12.002; N, 14.007; Cl, 35.476; S 32.065; Ar, 39.866. *W. D. B.*

The atomic weights of hydrogen and nitrogen, and the accuracy of the determinations. *A. Leduc. Comptes rendus,* 140, *717* (*1905*).—By the author's method he calculated a value for 1.0076 for the atomic weight of hydrogen while Guye corrects the results of Morley to 1.00765, the last figure not meaning anything. The author's value for nitrogen was 14.005 and attention is called to the fact that the latest determinations make it probable that the atomic weight is less than 14.01. *W. D. B.*

Addition to my papers on the phase rule. *R. Wegscheider. Zeit. phys. Chem.,* 52, *171* (*1905*).—The author has been convinced that many of his previous utterances on the phase rule do not apply to any pair of phases which can become identical, as for instance liquid and vapor, or two liquid layers. *W. D. B.*

The valency of the atom of hydrogen. *R. de Forcrand. Comptes rendus,* 140, *763* (*1905*).—The author believes that we should do away with all such difficulties as changing valence, molecular compounds, etc., if we would double the valence of all the elements. He therefore proposes to look upon hydrogen as a bivalent element. *W. D. B.*

The relative value of the calorimetric methods for determining the heats of combustion of volatile organic compounds. *J. Thomsen. Zeit. phys. Chem.,* 51, *657* (*1905*).—The author discusses the discrepancies between his results and those of Berthelot. He makes the point that combustion in the calorimetric bomb, being explosive, may give different final products from a non-explosive suggestion. This is quite possible but the author makes no attempt to show that it is so. Berthelot's results are also considered to be wrong because they do not show constant differences for constant increments of CH_2. This is hardly a proof because there is no reason to suppose that the heat of combustion is strictly an additive property. No reference is made to Stohmann's work. *W. D. B.*

The numerical results of a systematic investigation of the heats of combustion and formation for volatile organic compounds. *J. Thomsen. Zeit. phys. Chem.*, 52, *343* (*1905*).—Tabulated data for the heats of combustion and formation for nineteen hydrocarbons, twenty-two halogen compounds, forty-seven oxygen compounds, eleven sulphur compounds, and eighteen amines and nitriles. *W. D. B.*

Heat of formation of calcium hydride and nitride. *A. Guntz and H. Bassett, Jr. Comptes rendus*, 140, *863* (*1905*).—The heat of formation of solid calcium hydride CaH_2 is found to be 46.2 Cal; and the heat of formation of solid calcium nitride Ca_3N_2 to be 112.2 Cal. The authors make the heat of formation of quicklime 151.9 Cal. instead of 131.5 Cal. as found by Thomsen. This would change the heat of formation of calcium carbide from −7.3 Cal to +13.1 Cal. *W. D. B.*

Heat of formation of sodium hydride. *R. de Forcrand. Comptes rendus*, 140, *990* (*1905*).—The author finds a heat of formation of 16.6 Cal for sodium hydride. He writes the reaction

$$H_2 + Na = NaH + H$$

and then draws conclusions therefrom. It would seem as though his conclusions could be valid only after he had proved that the reaction was not

$$H_2 + 2Na = 2NaH.$$

W. D. B.

Thermochemical investigations on strychnine and brucine. *M. Berthelot and Gaudechon. Comptes rendus*, 140, *753* (*1905*).—The authors have determined the heats of solution for a number of salts of strychnine and of brucine. *W. D. B.*

Heat of formation of the oximes. *P. Landrieu. Comptes rendus*, 140, *867* (*1905*).—Thermochemical data. *W. D. B.*

Development of the thermometer for determining molecular weights and small temperature differences. *E. Beckmann. Zeit. phys. Chem.*, 51, *329* (*1905*).—A historical sketch of the development of the Beckmann thermometer. *W. D. B.*

Quartz vessels. *M. Berthelot. Comptes rendus*, 140, *817*, *821* (*1905*).—The author has used sealed tubes made of quartz for experiments up to 1400°. The tubes that he used would stand a pressure of a little over two atmospheres at this temperature. The quartz tubes are somewhat permeable to nitrogen and oxygen. *W. D. B.*

One-Component Systems

Physical-chemical studies on so-called explosive antimony. III. *E. Cohen and T. Stengers. Zeit. phys. Chem.*, 52, *129* (*1905*).—Antimony appears to occur in two modifications, α- and β-antimony. Both of these modifications can form solid solutions to a limited extent with the chloride, bromide or iodide of antimony. The α-form is the explosive one and the explosion is due to the change of this modification into the ordinary or β-antimony. *W. D. B.*

Some constants of pure methane and action of solid methane on liquid fluorine. *H. Moissan and H. Chavanne. Comptes rendus*, 140, *407* (*1905*).—Methane melts at —184° and boils at —164° under a pressure of 760 mm. At —187° solid methane reacts explosively with liquid fluorine. *W. D. B.*

Liquefaction of allene and allylene. *R. Lespieau and H. Chavanne. Comptes rendus*, 140, *1035* (*1905*).—Allene melts at 146° and has a vapor pressure of about 10 mm at that temperature. It boils at —32° and its critical temperature is +120.75°. Allylene melts at —110° and has a vapor pressure of about 10 mm at that temperature. It boils at —23.5° and its critical temperature is +129.5°. *W. D. B.*

The heat of vaporization of liquefied gases. *E. Mathias. Comptes rendus*, 140, *1174* (*1905*).—Instead of calculating the true heat of vaporization, the author calculates what he calls the apparent heat of vaporization according to the equation

$$\lambda_0 = Q/\pi,$$

where λ_0 is the apparent heat of vaporization, Q the quantity of heat supplied to the calorimeter to keep its temperature constant, while π grams of the liquid vaporize. The advantage of this is that it eliminates the question of the densities of liquid and vapor. Above 30.59° the apparent heat of vaporization CO_2 drops to about 19 cal or less, thus proving, according to the author, that the classical theory in regard to the critical point is correct. *W. D. B.*

The densities of some gases and the accuracy of the determinations. *A. Leduc. Comptes rendus*, 140, *642* (*1905*).—The author calculated 0.5545 as the density of methane and Moissan and Chavanne find 0.5554 and 0.5540. He calculated 2.491 for chlorine; Moissan and Binet de Jassoneix found 2.488 and 2.492. The calculated values for nitrous oxide and sulphur dioxide agree absolutely with those obtained by Guye and Pintza and by Jaquerod and Pintza. In all cases the author considers the values calculated by his method as more accurate than the experimental data. *W. D. B.*

An empirical relation between the densities of any two liquids. *K. Schaposchnikow.. Zeit. phys. Chem.*, 51, *542* (*1905*).—If δ_T and $\delta_{T'}$ are the densities of any two liquids compared at temperatures equidistant from the respective critical temperatures, the following equation is said to hold:

$$\delta_T = n\delta_{T'} + b.$$

In this equation n and b are constants. The equation is tested for pentane with stannic chloride, fluorbenzene, heptane, alcohol, and carbon dioxide. The pressure is that of the saturated vapors. A similar relation holds for the densities of the saturated vapors. The author points out the connection between his formula and the van der Waals law of corresponding states. *W. D. B.*

Comparative physical properties of pure cobalt and nickel. *H. Copaux. Comptes rendus*, 140, *657* (*1905*).—Cobalt oxide does not dissolve appreciably in fused cobalt while nickelous oxide does dissolve in fused nickel. Both metals take up hydrogen readily. The densities of cobalt and nickel are 8.8, 15°/4°. Cobalt has a hardness of 5.5 on Mohr's scale and nickel of 3.5. Cobalt melts at 1530° and nickel at 1470°. The mean specific heat between 20° and 100° is 0.104 for cobalt and 0.108 for nickel. At 0° the electrical resistance of cobalt is less than that of nickel. The tensile strength of cobalt is given as 50 kg/mm² and that of nickel as 42 kg/mm². *W. D. B.*

Carbon silicide in the meteorite from Canon Diablo. *H. Moissan. Comptes rendus*, 140, *405* (*1905*).—The carborundum found in the meteorite from the Cañon Diablo has a density of 3.2 and appears to be identical with carborundum as made in the electric furnace. *W. D. B.*

Experiments on fire shrinkage. *R. Lucas. Zeit. phys. Chem.*, 52, *327* (*1905*).—When potter's clay or other similar material is baked it shrinks and becomes less porous. This phenomenon is known as fire shrinkage and the volume changes for cobalt oxide, magnesia, kaolin and zirconium oxide have been studied for temperatures varying from 100° to 2000°. The shrinkage depends on the rate of heating, being greater the more rapidly the substance is heated. This difference is less noticeable the higher the temperature of baking. The process is irreversible and consists in a decrease in the volume of the pores rather than in an increase in the density of the material. As the materials studied were amorphous and possessed a large surface, the author believes that the shrinkage is due to capillary forces. *W. D. B.*

Two-Component Systems

Equilibria in the systems $TlNO_3$-KNO_3, $TlNO_3$-$AgNO_3$ and $TlNO_3$-$NaNO_3$. *C. van Eyk. Zeit. phys. Chem.*, 51, *721* (*1905*).—Thallium nitrate solidifies in the regular system at 206°. At 142.5° there is a change to a rhombohedral form and at 72.8° to rhombic form. Potassium nitrate solidifies at 339° and has an inversion-point at 129.5°. Silver nitrate solidifies at 208 5° and has an inversion-point at 159°. The different modifications of potassium nitrate form two series of solid solutions with the different modifications of thallium nitrate. Silver and thallium nitrates do not form solid solutions; but there is a double salt $AgNO_3.TlNO_3$, stable at its melting-point, 81°, but occurring in equilibrium with the melt only over a very narrow range and breaking down at 26°.

W. D. B.

On isodimorphism. *F. Wallerant. Comptes rendus*, 140, *1045* (*1905*).—A concentration-temperature diagram for thallium and ammonium nitrates. The author does not describe his method nor state what precautions were taken to ensure equilibrium. The diagram is a very interesting one and would be more so if one could be certain of its accuracy. Portions of it must be wrong however. *W. D. B.*

The increase in volume of cast iron on solidification. *H. Moissan. Comptes rendus*, 140, *185* (*1905*).—An iron low in carbon becomes denser when passing from liquid to solid while an iron rich in carbon becomes less dense. The contradictory results obtained by previous observers are probably due in part to not taking into account the carbon content of the iron. *W. D. B.*

Cryoscopic studies on hydrocyanic acid. *R. Lespieau. Comptes rendus,* 140, *855* (*1905*).—Cryoscopic measurements with liquid hydrocyanic acid as solvent showed that sulphuric and trichloracetic acids gave the same lowering as chloroform while potassium iodide and nitrate gave double this lowering. This is in accord with Kahlenberg's measurements on the conductivity of these solutions (6, 447) and is a further proof that the action of the solvent is selective. *W. D. B.*

The cryoscopy of the sulphates. *A. Colson. Comptes rendus,* 140, *372* (*1905*).—The author repeats his statement that zinc sulphate and chromium sulphate lower the freezing-point of water only one-half and one-third as much respectively as does sulphuric acid. The formulas are therefore believed to be H_2SO_4, $(ZnSO_4)_2$ and $Cr_2(SO_4)_3$. *W. D. B.*

The effect of temperature on the amount of water of crystallization as a proof of the existence of hydrates in solution. *H. C. Jones and H. P. Bassett. Zeit. phys. Chem.,* 52, *231* (*1905*).—The authors call attention to the fact that hydrates in solution would probably become more complex and more stable as the temperature falls and that salts contain more water of crystallization the lower the temperature. This is looked upon as proof that hydrates occur in solution. Since there is always an evolution of heat when salts take up water of crystallization, they must crystallize with less water as the temperature rises. *W. D. B.*

Compounds of samarium chloride with ammonia. *C. Matignon and R. Trannoy. Comptes rendus,* 140, *141* (*1905*).—Samarium chloride was treated with ammonia at —23°. Measurements were then made of the amounts of ammonia given off at different temperatures. From these results the authors deduce the existence of compounds with 1, 2, 3, 4, 5, 8, 9.5, 11.5 of ammonia. While this may be true, it seems a pity that the observations should not have been checked in some way. The experimental data are certainly inaccurate but one does not know how great the error is. *W. D. B.*

Annealed bronzes. *L. Guillet. Comptes rendus,* 140, *307* (*1905*).—The mechanical properties of bronzes containing more than 92 percent copper are not affected materially by quenching from 400°–600°. The properties of bronzes containing less copper change materially when quenched from above 500°. This is in accord with the diagram of Heycock and Neville, the change in properties above 500° being due to the disappearance of the δ-crystals. *W. D. B.*

Special constituent obtained by quenching an aluminum bronze. *P. Breuil. Comptes rendus,* 140, *587* (*1905*).—The author has examined an aluminum bronze of unknown composition which is put on the market under the name "Portior." It freezes at 1010°–1030° and is said to have an inversion point at 690°–730°. The crystalline structure and mechanical properties depend on whether the metal is quenched from above or below 700°. The author makes no attempt to find out what the phases are and he speaks of the 'martensite structure'. He suggests that people would get ahead faster with the study of steel if they would first study other alloys. While this last is true enough, it would not help if people are to study other alloys in the way the author has studied aluminum bronze. *W. D. B.*

Calcium amalgam and some physical constants of calcium. *H. Moissan and H. Chavanne. Comptes rendus*, 140, *122* (*1905*).—Calcium amalgam is stable in dry air at ordinary temperatures; it absorbs neither oxygen nor nitrogen. Its chemical action is similar to that of sodium amalgam, except that the solution does not become so alkaline. There is said to be a solid form having the composition Hg_8Ca. Metallic calcium has a density of 1.548 and melts at 795°–810°. *W. D. B.*

Multi-Component Systems

Equilibrium measurements with contact sulphuric acid. *M. Bodenstein and W. Pohl. Zeit. Elektrochemie*, 11, *373* (*1905*).—The authors find that the equilibrium relations for sulphur trioxide, sulphur dioxide and oxygen are described satisfactorily by the equation

$$KC^2_{SO_3} = C^2_{SO_2} . C_{O_2}$$

and that the change of the equilibrium constant with the temperature is that required by the van't Hoff formula. *W. D. B.*

The equilibria between iodic and hydriodic acids and between bromic and hydrobromic acids determined electrically and chemically. *R. Luther and G. V. Sammet. Zeit. Elektrochemie*, 11, *293* (*1905*).—The reaction between iodic and hydriodic acids

$$HIO_3 + 5HI \rightleftharpoons 3I_2 + 3H_2O$$

runs practically to an end in acid solutions. In a solution saturated with respect to boric acid and to sodium borate, a measurable quantity of iodide remains unchanged. If one starts with silver iodide instead of hydriodic acid, very little iodine is formed. The equilibrium constant comes out practically the same whether determined electrically or chemically. From the change of the equilibrium constant with the temperature a heat of reaction of 683 Cal is calculated, while the measured value is 642 Cal. The corresponding reaction with bromic and hydrobromic acids was also studied. *W. D. B.*

Action of carbon monoxide on silver oxide. *H. Dejust. Comples rendus*, 140, *1250* (*1905*).—Dry carbon monoxide reduces silver oxide to metallic silver.

$$CO + Ag_2O = 2Ag + CO_2 + 61.2 \text{ Cal.}$$

In presence of water the temperature does not rise so much and the reduction is less complete. This reaction can be used as a rapid method for determining carbon monoxide. *W. D. B.*

A new synthesis of oxalic acid. *H. Moissan. Comples rendus*, 140, *1209* (*1905*).—At temperatures above 80° dry carbon dioxide reacts with dry potassium or sodium hydride forming a mixture of formate and oxalate.

W. D. B.

Studies on solubility changes. *F. Hoffman and K. Langbeck. Zeit. phys. Chem.*, 51, *385* (*1905*).—The authors have determined the solubilities of benzoic acid, salicylic acid, and *o*-nitrobenzoic acid in varying solutions of dextrose, ethyl alcohol, isobutyl alcohol, cane-sugar, laevulose, sodium chloride, potassium chloride, sodium nitrate, and potassium nitrate. In general, the non-electrolytes increase the solubility while the electrolytes cause a slight increase followed by a very marked decrease of solubility. *W. D. B.*

Caustification of potassium sulphate. *T. Herold. Zeit. Elektrochemie*, 11, *417* (*1905*).—The author has determined the solubility of calcium hydroxide at 120°, 150° and 190°. He has also determined isotherms at 0°, 20°, 70°, 150° and 190° for the system CaO_2H_2, K_2SO_4 and H_2O. On the basis of these data he discusses the possibility of converting potassium sulphate into caustic potash.
W. D. B.

Behavior of mixtures of nitric acid and sulphuric acid. II. *A. Saposchnikow. Zeit. phys. Chem.*, 51, *609* (*1905*).—Addition of sulphuric acid to nitric acid, sp. gr. 1.52, lowers the vapor pressure; addition to acid, sp. gr. 1.48, raises the vapor pressure. It is believed that this is due to the sulphuric acid taking water from the nitric acid hydrates. In any case it is obvious that this has a very important bearing on the phenomenon of nitration. *W. D. B.*

The equilibrium between a nitrogen base and organic acids in different solvents. *H. F. Sill. Zeit. phys. Chem.*, 51, *577* (*1905*).—The author has studied the simultaneous dissociation of cinchonine salts into cation and anion, and into free cinchonine and free acid, when dissolved in water, methyl alcohol or ethyl alcohol. The affinity constants for the acids in alcoholic solution proved to be practically proportional to the constants in aqueous solution. The electrolytic equilibrium constant proved to be nearly the same for different salts in the same solvent. *W. D. B.*

Hydration in solution. *G. N. Lewis. Zeit. phys. Chem.*, 52, *229* (*1905*).—Experiments with copper bromide showed that the change of color on adding potassium, ammonium, or lithium bromide was not what it should be if one calculates the dissociation from the conductivity but is what it should be if one calculates it from the change of freezing-point. The author, therefore, concludes that the change of color is not due to a change in concentration of bromine as ion but is due to a dehydration. While the conclusion is very possibly right, the reasoning is peculiar. Similar experiments were tried with the chlorides of copper and of cobalt. No reference is made to the work of Hartley.
W. D. B.

Structure formation in colloids. *H. Bechhold. Zeit. phys. Chem.*, 52, *185* (*1905*).—The author has repeated and modified Liesegang's experiment on the formation of rings in gelatine when silver chromate is precipitated. He finds that silver chromate is practically insoluble in silver nitrate solution while it is distinctly soluble in ammonium chromate or bichromate solution. The character of the rings depends therefore on whether a drop of silver nitrate is added to chromate in gelatine or a drop of ammonium chromate to silver nitrate in gelatine. The effect of the salts on the gelatine is also to be considered as well as the rate of diffusion. *W. D. B.*

Hydration and hardening processes. *E. Jordis. Zeit. Elektrochemie*, 11, *223* (*1905*).—A reply to Rohland (9, 608). The point is made that the hardening of steel is a reversible process while the hardening of cement is not. This would seem to be a question of fact. The reviewer had supposed that cement could be brought back to its initial state by reheating. *W. D. B.*

Synthesis of primary, secondary and tertiary amines. *P. Sabatier and J. B. Senderens. Comptes rendus*, 140, *482* (*1905*).—When a mixture of an aliphatic nitrile and hydrogen is passed over pulverulent nickel, heated to about 200°, the chief product is the secondary amine, but varying amounts of the primary and tertiary amines are also formed. *W. D. B.*

Some new experiments on the preparation of diamonds. *H. Moissan. Comptes rendus*, 140, *277* (*1905*).—Owing to the presence of sulphur and silicon in the meteorite from Cañon Diablo the author has repeated his experiments on diamonds, adding sulphur and silicon to the molten iron. Addition of ferrous sulphide increases the yield of diamonds somewhat though not their size. Addition of silicon increases the size a little but the diamonds are then cubes and never octahedra. *W. D. B.*

Transformation of amylocellulose into starch. *E. Roux. Comptes rendus*, 140, *440* (*1905*).—At 155° water converts amylocellulose into starch. *W. D. B.*

On ferric chloride colloids. *G. Malfitano. Comptes rendus*, 140, *1245* (*1905*).—Dilute solutions of ferric chloride furnish fairly stable colloids by hydrolysis. The author has filtered these solutions through collodion membranes. *W. D. B.*

Brown modification of colloidal ferric oxide. *P. Nicolardot. Comptes rendus*, 140, *310* (*1905*).—If a cold ammonia solution be added to a freshly-prepared concentrated aqueous solution of a ferric salt, the precipitate is white at first. The author considers that there are four ferric oxides, white, brown, yellow and red. *W. D. B.*

Titration of caustic soda in presence of carbonate. *K. Novotry. Zeit. Elektrochemie*, 11, *453* (*1905*).—A mixture of caustic soda and sodium carbonate can be titrated with oxalic acid and phenolphthaleine if one precipitates the carbonate as barium carbonate with barium chloride. The author finds that satisfactory results are obtained only when an excess of barium chloride is added. This decreases the hydrolysis of the barium carbonate. *W. D. B*

Sensitiveness of hydrogen peroxide. *J. Precht and C. Otsuki. Zeit. phys. Chem.*, 52, *236* (*1905*).—A concentration of 3×10^{-9} g H_2O_2 per cubic centimeter reacts perceptibly with a silver bromide gelatine plate at 0°. This is the same order of sensitiveness as that for the catalytic action of platinum on hydrogen peroxide and for the flame reaction for sodium. *W. D. B.*

Osmotic Pressure and Diffusion

The permeability of tubes of fused quartz. *M. Berthelot. Comptes rendus*, 140, *1159* (*1905*).—At 800° there is practically no diffusion of hydrogen, nitrogen, oxygen, hydrochloric acid or carbon dioxide through quartz. At 1300° the diffusion of hydrogen and nitrogen becomes quite noticeable while that of oxygen is even more marked. There is scarcely any diffusion of carbon dioxide at this temperature and hydrochloric acid begins to diffuse only above 1400°. *W. D. B.*

Osmosis through quartz tubes. *G. Belloc. Comptes rendus,* 140, *1253* (*1905*).—After quartz tubes have been used some time, oxygen diffuses through them even at 600°. An examination showed that the tubes had become devitrified. *W. D. B.*

Clays as semipermeable membranes. *P. Rohland. Zeit. Elektrochemie,* 11, *455* (*1905*).—The plastic clays are looked upon as semipermeable membranes because they allow dissolved crystalloids to pass and hold back colloids. This is not the ordinary definition of a semipermeable membrane. *W. D. B.*

Velocities

Decomposition of silver oxide by autocatalysis. *G. N. Lewis. Zeit. phys. Chem.,* 52, *310* (*1905*). A very interesting paper in which it is shown that metallic silver has a catalytic action on the decomposition of silver oxide into silver and oxygen at temperatures above 300°. At each temperature the rate of decomposition is very closely proportional to the masses of silver oxide and of silver. *W. D. B.*

The decomposition of ammonium nitrite in aqueous solution. *W. Biltz and W. Zahl. Zeit. Elektrochemie,* 11, *409* (*1905*).—The authors consider the decomposition of ammonium nitrite as a bimolecular reaction which becomes practically monomolecular, owing to one of the reacting substances being present in overwhelming amount. In no place do they state what they consider the active masses to be. *W. D. B.*

Theoretical considerations on reactions taking place in several stages. *E. Brunner. Zeit. phys. Chem.,* 52, *89* (*1905*).—Another discussion of equilibrium and reaction velocity constants for reactions occurring in several stages. The usual unfamiliarity with the literature is shown. *W. D. B.*

Reaction velocity and chemical equilibrium in homogeneous systems and their application to enzyme action. *A. W. Visser. Zeit. phys. Chem.,* 52, *257* (*1905*).—The author has worked out a formula of his own for the action of enzymes. He claims that it describes the facts better than does the formula of Henri and he claims that there is no justification for the theoretical conclusions deduced by Henri as to the way in which enzymes act. *W. D. B.*

Physico-chemical studies on haemolysis. *V. Henri. Comptes rendus,* 140, *101* (*1905*).—The author has studied the action of a dog serum on chicken blood. The rate of haemolysis is independent of the amount of red corpuscles in contact with the serum; it increases with increasing quantity of serum but much more rapidly; it is very slow in the first ten minutes, then increases rapidly, afterwards dying away. The results can be expressed by the equation for a monomolecular reaction. The serum is able only to change a limited amount of chicken blood. *W. D. B.*

The enzyme of blood which decomposes hydrogen peroxide. II. *G. Senter. Zeit. phys. Chem.,* 51, *673* (*1905*).—Hydrogen as ion has a retarding effect on the catalysis of hydrogen peroxide by haemase. Chlorine, bromine, nitrate, chlorate and perchlorates as ions have a similar effect. Hydrogen sulphide, mercuric chloride, and mercuric bromide are strong poisons, mercuric cyanide a weak poison, while carbon monoxide, arsenic trioxide and formaldehyde have no perceptible toxic action. In many cases it seems as though the toxic effect were due to a chemical action. The toxic action is sometimes the same for the platinum catalysis and for the haemase catalysis, while sometimes it is different. *W. D. B.*

The inversion of some isomeric derivatives of glucose and the mutarotation of the sugars. *C. L. Jungius. Zeit. phys. Chem.*, 52, *97* (*1905*).—The author concludes "that in all probability mutarotation is always due to a reversible change between two stereoisomers that in some cases, glucose and milk-sugar, there is possibly also a hydration or dehydration; but that the stereoisomeric change is always the important factor." *W. D. B.*

Time measurements on the appearance of a precipitate in sodium hyposulphite solutions. *G. Gaillard. Comptes rendus*, 140, *652* (*1905*).—The author has studied the length of time before a precipitation of sulphur occurs in solutions of sodium hyposulphite when different concentrations are used and different substances added. The results were purely qualitative. *W. D. B.*

Theory of the rate of solubility of arsenic. *E. Brunner. Zeit. phys. Chem.*, 51, *494* (*1905*).—"All previous observations on the rate of solution of arsenic can be explained on the hypothesis that the hydration takes place at the surface in a layer which is thinner than that left by the stirring." *W. D. B.*

The effect of diffusion in catalysis by colloidal metals, etc. *H. J. S. Sand. Zeit. phys. Chem.*, 51, *641* (*1905*).—The author considers that catalysis by colloidal metals cannot be classed as a case in which equilibrium is reached instantaneously at the surface of two phases. It seems possible that the Nernst theory of reaction velocity in heterogeneous systems may not apply to chemical reactions because it does not follow that the internal resistance ever becomes infinitely small. *W. D. B.*

A regularity in chemical dynamics. *J. Plotnikow. Zeit. phys. Chem.*, 51, *603* (*1905*).—The author gives thirty-six tables to show that the change of the reaction velocity with the temperature is represented by the equation

$$\frac{dk}{dt} = ak$$

where a is a constant. *W. D. B.*

Oxidation of metals in presence of ammonia. *C. Matignon and G. Desplantes. Comptes rendus*, 140, *853* (*1905*).—The authors have shaken pulverulent metals with oxygen in presence of an ammoniacal solution. They find that the ammonia accelerates the oxidation with mercury, silver, nickel, cobalt, molybdenum and tungsten but not with tin. *W. D. B.*

Different applications of Watts's principle to the dissociation of lead and silver carbonates. *A. Colson. Comptes rendus*, 140, *865* (*1905*).—In presence of water vapor the decomposition of silver and lead carbonates is a reversible reaction. The dry compounds do not dissociate readily and apparently do not recombine at all. The author believes that the water vapor acts by preventing or destroying the polymerization of the oxides at the temperatures involved. In proof of the polymerization he cites the fact that the lead oxide formed at 350° by the decomposition of lead carbonate is colored like litharge and is not white. *W. D. B.*

Effect of water vapor on the reduction of iron oxides by carbon monoxide and dioxide. *O. Boudouard. Comptes rendus,* 140, *40* (*1905*).—At temperatures below 1000° iron oxides are reduced more rapidly by a dry mixture of carbon monoxide and dioxide than by one containing water vapor. Above 1000° the difference between the two series is practically zero. It is believed that this has a bearing on Gayley's experiments with the dry blast. *W. D. B.*

The use of the hot-cold tube in the study of chemical reactions. *M. Berthelot. Comptes rendus,* 140, *905* (*1905*).—The author has attempted to duplicate many of the reactions of the hot-cold tube by heating the reagents to about 1400° in a quartz tube and dropping the tube into cold water. In no case did he obtain the same result as with the hot-cold tube. As he assumes that the cooling is instantaneous in the quartz tube, he decides that all conclusions are faulty which are based on the hot-cold tube. One source of error is believed to be in a possible electrification due to the metal tube. *W. D. B.*

New investigations on chemical compounds. *M. Berthelot. Comptes rendus,* 140, *1153* (*1905*).—The experiments were made in a quartz tube heated to 1300°-1400° and dropped into water (preceding review). Nitrogen and hydrogen did not combine and ammonia decomposed completely. Ammonium chloride is entirely decomposed after being heated one hour at 1300° into nitrogen, hydrogen and hydrochloric acid. Hydrochloric acid does not decompose at 1300°. Hydrogen sulphide is slightly decomposed after an hour at 1300°. *W. D. B.*

Electromotive Forces

Chemical transference of metallic potentials. *F. Fischer. Zeit. phys. Chem.,* 52, *55* (*1905*).—If a copper plate and a platinum one be dipped into a copper sulphate solution, the platinum plate will gradually assume the potential of the copper one owing to the formation of the equilibrium concentration for cupric and cuprous sulphates. Mercury may be substituted for platinum without changing the result. Silver and platinum come to the same potential when dipped in a solution of a silver salt even though the concentration of any argentous salt in the solution must be infinitely small. When zinc and platinum are dipped into the solution of a zinc salt, the platinum comes to the hydrogen potential. In the theoretical discussion the author makes no reference to Luther though this should have been done. It seems probable also that the measurements are not characterized by extreme accuracy. If a platinum and a copper plate be dipped into a copper sulphate solution and short-circuited, it is practically certain that a thin film of copper will be deposited on the platinum. The experiments of Oberbeck prove this. From this it follows that platinum must have a different potential from that of copper. The author refers once to a difference of 0.4 millivolt; but he fails to see that a difference is theoretically necessary in all cases. *W. D. B.*

The cause of the spontaneous depression of cathode potential during the electrolysis of dilute sulphuric acid. *J. Tafel and B. Emmert. Zeit. phys. Chem.,* 52, *349* (*1905*).—It is shown that some platinum dissolves and precipitates at the cathode when sulphuric acid is electrolyzed with a platinum anode. While the lowering of the cathode potential previously observed (9, 347) is connected with this precipitation of platinum, the amount necessary to produce it is so small that the authors believe that the platinum acts catalytically in some way thus changing the surface. *W. D. B.*

The electromotive behavior of copper and zinc in cyanide solutions. *F. Spitzer. Zeit. Elektrochemie, 11, 345, 391 (1905).*—The author has determined the potential differences for zinc and copper in various cyanide solutions. The electrolytic precipitation of brass takes place at a lower potential than the precipitation of copper or of zinc. In line with this is the fact that zinc precipitates copper and copper precipitates zinc from cyanide solution. The author seems to think that this necessitates the existence of a compound between zinc and copper in spite of the fact that a lowering of vapor-pressure occurs with a solid solution just as well as with a compound.

In analytical determinations of zinc or copper in cyanide solutions there is trouble owing to the dissolving of the platinum anode and to the fact that the last traces of zinc are held up by the cyanide. If caustic alkali be added, the cyanide is oxidized about as fast as the zinc is precipitated. It is shown that zinc can be determined electrolytically in a very satisfactory manner if a sodium zincate solution be used. *W. D. B.*

The positions of the metals of the alkalies and the alkaline earths in the voltaic series at high temperatures. *H. Danneel and L. Stockem. Zeit. Elektrochemie, 11, 209 (1905).*—Above 800° sodium does not precipitate calcium from its salts. Below this temperature a sodium-rich alloy is obtained. Potassium precipitates calcium from fused calcium chloride but does not precipitate strontium from its chloride. At high temperatures the order is therefore Sr, K, Ca, Na while at lower temperatures the order is K, Sr, Na, Ca. *W. D. B.*

The variation of potential at the contact sufaces between solutions of electrolytes. *M. Chanoz. Comples rendus, 140, 1024 (1905).*—It is difficult to see what the author has established beyond the facts that a symmetrical concentration cell has no electromotive force and that an unsymmetrical one has an electromotive force reaching 60 millivolts in some cases. *W. D. B.*

The temperature coefficient for the resistance of tantalum. *F. Streintz. Zeit. Elektrochemie, 11, 273 (1905).*—The temperature coefficient for the electrical resistance of tantalum was found by v. Bolton to be 0.3 percent. This is less than that of platinum or bismuth and confirms the rule that the temperature coefficient increases with increasing atomic weight. The author believes that the specific heat of tantalum probably varies a good deal with the temperature. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrolytic refining of lead in fluosilicic acid solutions. *H. Senn. Zeit. Elektrochemie, 11, 229 (1905).*—Addition of gelatine to a lead nitrate or acetate solution improves the quality of the deposit; but the results are never as good as those obtained in fluosilicic acid solutions. Cadmium can also be precipitated satisfactorily from a fluosilicic acid solution. It was possible to obtain pure lead at the cathode with 98 percent current efficiency, starting from an anode containing 1 percent Cu, 12 percent Bi, 10 percent Sb or 10 percent Pt.

The anode loss is greater than one hundred percent owing to the gradual neutralization of the fluosilicic acid. *W. D. B.*

Electrolytic reduction of nitrocinnamic acids. *C. Marie. Comptes rendus,* 140, *1248* (*1905*).—In alkaline solution with a mercury cathode *m*- and *p*-nitrocinnamic acids are easily reduced electrolytically to the corresponding azoxy acids. *W. D. B.*

Relations between electrolytic processes and the temperature of the electrodes. *W. Moldenhauer. Zeit. Elektrochemie,* 11, *307* (*1905*).—The author has measured the temperature changes at the electrodes when solutions of acids, bases or salts are electrolyzed. Cooling the anode increases the yield of persulphates, percarbonates and hypochlorite. *W. D. B.*

Tests on the rusting of galvanized iron and steel wires. *T. Szirmay. Zeit. Elektrochemie,* 11, *333* (*1905*).—Different samples of galvanized wire were placed over water in a bell-jar, the vapor phase containing about 12 percent SO_2 and 15 percent CO_2. The temperature was varied periodically between 6° and 45°. It is claimed that this method of testing is much more satisfactory than the usual one of dipping in copper sulphate solution. The general result of the test was that electrolytically precipitated zinc protected the iron the best and that hot galvanizing was not so effective. *W. D. B.*

Comparative tests on electrolytic and hot galvanizing. *T. Szirmay. Zeit. Elektrochemie,* 11, *335* (*1905*).—Various samples of galvanized iron were exposed to the air and were given mechanical tests. The results were all in favor of electrolytic as against hot galvanizing. *W. D. B.*

Electrolysis of organic acids by means of alternating current. *A. Brochet and J. Petit. Comptes rendus,* 140, *442* (*1905*).—Since the electrolytic oxidation of oxalic and formic acids is not a reversible phenomenon, the same products are obtained whether a direct or an alternating current be used.
W. D. B.

The electrolytic dissolving of platinum in sulphuric acid. *A. Brochet and J. Petit. Comptes rendus,* 140, *655* (*1905*).—A current of varying intensity causes a platinum anode to dissolve in sulphuric acid. The results obtained with an alternating current are due to the varying densities and not to any specific effect of the alternations. The presence of an oxidizing agent is said to prevent the reduction of dissolved platinum. The authors use language in a way that is liable to be misunderstood. They would probably say that a direct current did not cause the copper of a copper voltameter to go into solution. What they would mean by such a statement would be that the loss in the weight of the anode equalled the gain in weight of the cathode.
W. D. B.

Electrolysis with alternating currents. II. *A. Brochet and J. Petit. Zeit. Elektrochemie,* 11, *441* (*1905*).—An intermittent direct current causes a platinum anode to dissolve in sulphuric acid while a continuous current of constant anode density does not. An alternating current has no specific action. The effect of the current density varies with the nature of the electrolytic action.
W. D. B.

Colloidal hydroxide of iron obtained by electrodialysis. *J. Tribot and H. Chrétien. Comptes rendus*, 140, *144* (*1905*).—The removal of the chloride in making 'dialyzed iron' can be accelerated by electrolysis provided a weak current is used. The product is quite as good as that obtained in the ordinary way, and perhaps a little better. *W. D. B.*

The dissociation of cadmium iodide. *J. W. McBain. Zeit. Elektrochemie*, 11, *215* (*1905*).—The author calculates that all the data in regard to cadmium iodide can be brought into line by assuming the existence of $\mathrm{Cd\,CdI_4}$ with a transference number for the anion of 0.42. *W. D. B.*

Theory of amphoteric electrolytes. II. *J. Walker. Zeit. phys. Chem.*, 51, *706* (*1905*).—A recalculation of the data in the first paper (8, 378) gives a better agreement between theory and experiment. The discrepancy found by Winkelblech in the conductivity of asparagine is due to the low conductivity of the substance and the great effect caused by traces of impurity. *W. D. B.*

The dissociation of electrolytes. *C. Liebenow. Zeit. Elektrochemie*, 11, *301* (*1905*).—A modified form of the Kohlrausch formula is shown to represent the conductivity of potassium chloride solutions very well up to a concentration of *n*/5. *W. D. B.*

Action of alkalies on aqueous solutions of acetol. *A. Kling. Comptes rendus*, 140, *1256* (*1905*).—Acetol is apparently a pseudo-acid. *W. D. B.*

Dissociation relations for ternary electrolytes. *K. Drucker. Zeit. Elektrochemie*, 11, *211* (*1905*).—A criticism of Kümmell's results with isohydric solutions (9, 613). *W. D. B.*

Dissociation relations in ternary electrolytes. *G. Kümmell. Zeit. Elektrochemie*, 11, *341* (*1905*).—A reply to Drucker (preceding review). *W. D. B.*

Dielectricity and Optics

The use of the Wehnelt interrupter for measuring dielectric constants by Nernst's method. *F. Krüger. Zeit. phys. Chem.*, 51, *739* (*1905*).—The Wehnelt interrupter can be used satisfactorily in measuring dielectric constants if a suitable self-induction is placed in the primary of the induction coil. *W. D. B.*

Action of radium bromide on the electrical resistance of metals. *B. Sabat. Comptes rendus*, 140, *644* (*1905*).—The rays from radium bromide increase the electrical resistance of wires of bismuth, iron, steel, copper, platinum, brass, etc. The effect is believed to be too large and to be obtained too rapidly for it to be due to a rise of temperature. *W. D. B.*

Emission spectrum of a high tension electric arc. *J. de Kowalski and P. Joye. Comptes rendus*, 140, *1102* (*1905*).—The arc between electrodes of zinc or cadmium gives rise at the cathode to spectra corresponding to those given by the same metals in a non-luminous gas flame. *W. D. B.*

Variation of the banded spectrum of carbon and new banded spectra of carbon. *H. Deslandres and d'Azambuja. Comptes rendus*, 140, *917* (*1905*).—The carbon spectrum from the negative pole varies distinctly with varying pressure. When a capacity and a sufficient induction is included in the circuit, the entire character of the spectrum changes. *W. D. B.*

Some remarks on the rotation of optically active substances. *C. Winther. Zeit. phys. Chem.*, 52, *200* (*1905*).—If the optical rotation of a substance is studied for one kind of light only, there is no way of knowing whether anomalous dispersion occurs. For dispersion experiments the author recommends the use of all the five of Landolt colors. The specific rotation dispersion shows nothing and should be dropped. Experiments should be made at five temperatures and with five concentrations. *W. D. B.*

A new spectrum of gadolinium. *G. Urbain. Comptes rendus*, 140, *1233* (*1905*).—Gadolinium chloride shows four lines in the ultra-violet between 311.6 and 305.0. While it is believed that these lines are due to gadolinium, it is recognized that they may belong to Crookes's victorium if this element exists. *W. D. B.*

Spectroscopy of blood and of oxyhaemoglobine. *M. Piettre and A. Vila. Comptes rendus*, 140, *1060* (*1905*).—The displacement of the band at λ = 634 in solutions of blood or oxyhaemoglobine by fluorides can be used to show the presence of five millionths of sodium fluoride. The authors give details. *W. D. B.*

The ultra-violet absorption of organic dye-stuffs. *P. Krüss. Zeit. phys. Chem.*, 51, *257* (*1905*).—Organic dye-stuffs have adsorption bands in the ultraviolet which depend largely on the nature and number of the chromogenic groups. The apparently colorless bases of the dye-stuffs have marked absorption bands in the ultra-violet. The absorption spectra of many azo dyes change markedly when concentrated sulphuric acid is used as solvent. While the fading of organic dyes by sunlight depends on the ultra-violet absorption bands, other factors enter in. *W. D. B.*

Dissociation of strychnine salts as shown by their optical rotation. *J. Minguin. Comptes rendus*, 140, *243* (*1905*).—Strychnine was dissolved in a mixture of benzyl and ethyl alcohols, and the optical rotation determined. When an organic acid was added, the optical rotation usually changed owing to the more or less complete formation of a strychnine salt. *W. D. B.*

Salt formation in solutions. III. *J. W. Brühl and H. Schröder. Zeit. phys. Chem.*, 51, *513* (*1905*).—Optical measurements show no measurable trace of the enol form in the liquid keto forms of acetacetic ester, camphocarbonic ester and their derivatives. *W. D. B.*

The action of inorganic substances on the rotation of laevulose and glucose. *E. Rimbach and O. Weber. Zeit. phys. Chem.*, 51, *473* (*1905*).—In most cases inorganic substances have relatively slight effect on the optical rotation of laevulose or glucose. Salts forming hydroxyl as ion change the rotation, owing to decomposition. The chlorides of the elements of the second group, and the compounds of cerium and thorium increase the rotation, especially of laevulose. Substances do not necessarily change the optical rotation of

laevulose and glucose in the same sense. The authors believe that the changes in rotation are not usually due to the formation of new compounds.
W. D. B.

Reversible photochemical reactions in a homogeneous system. I. *R. Luther and F. Weigert. Zeit. phys. Chem.*, 51, *297* (*1905*).—The change of anthracene into dianthracene is a reversible reaction taking place under the influence of light. The percentage dianthracene increases proportionally to the brightness of the light and to the surface illuminated. It varies inversely as the volume of the solution. The change of dianthracene is a monomolecular reaction running practically to an end in the dark. *W. D. B.*

On fluorescence. *C. Camichel. Comptes rendus*, 140, *139* (*1905*).—Experiments were made on uranium glass and the conclusion is reached that the coefficient of absorption of uranium glass, for the rays which it emits when fluorescing, is the same whether there is fluorescence or not. Nichols and Merritt have found a different result and the author's conclusion seems improbable *a priori*. *W. D. B.*

The phosphorescence of phosphorus. *E. Jungfleisch. Comptes rendus*, 140, *444* (*1905*).—The author believes that the phosphorescence of phosphorus is not due to an oxidation of phosphorus vapor. When an inert gas is saturated with phosphorus vapor and then mixed with oxygen, there is only a faint luminosity owing to the small amount of phosphorus in the vapor. The author believes that a fairly volatile oxide of phosphorus is formed and that the phosphorescence is due to the combustion of this oxide. *W. D. B.*

Action of very low temperatures on phosphorescent sulphides. *F. P. Le Roux. Comptes rendus*, 140, *239* (*1905*).—The author confirms the experiments of others that a phosphorescent sulphide ceases to phosphoresce if cooled to the temperature of liquid air. If one of these sulphides be cooled to the temperature of liquid air and then exposed to light, it will phosphoresce when warmed. This shows that the change caused by the absorption of light takes place at low temperatures though the emission of light either does not take place at all or takes place so slowly as not to be noticeable under ordinary conditions.
W. D. B.

The chemistry of phosphorescing sulphides of the alkaline earths. *P. Waentig. Zeit. phys. Chem.*, 51, *435* (*1905*).—Pure sulphides of the alkaline earths do not phosphoresce. The phosphorescence is due to traces of bismuth, copper, manganese, chromium, iron or platinum, present as solid solutions. If more of these substances is present than can dissolve, the phosphorescence decreases enormously. The author shows that the phenomena connected with heating and quenching can be accounted for on this hypothesis. The salts of the alkali metals are believed to increase the solubility of the phosphorescing substances. No explanation was found for the fact that friction destroys the phosphorescing power, which returns, however, when the substance is heated above 100°. *W. D. B.*

THE RATE OF THE REACTION BETWEEN ARSENIOUS ACID AND IODINE IN ACID SOLUTION; THE RATE OF THE REVERSE REACTION; AND THE EQUILIBRIUM BETWEEN THEM

(SECOND PAPER)

BY J. R. ROEBUCK

In a former paper,[1] the rate of the reaction between arsenious acid and iodine in a solution containing potassium iodide and sulphuric acid was found to be in close agreement with the formula

$$dx/d\theta = \mathrm{K}\,\frac{(\text{Iodine})\ (\text{Arsenious acid})}{(\text{Sulphuric acid})\ (\text{Pot. iodide})^2} \qquad (1)$$

and the assumption of an hypothetical intermediate product (HIO) in the reaction, served to connect this expression with the equation for the chemical reaction. Except in a single experiment (Table 14, page 379) all of the substances behaved normally; *i. e.*, obeyed the Mass Law without modifying assumptions.

In the reverse reaction, *i. e.*, the reduction of arsenic acid by potassium iodide in the presence of sulphuric acid, the rate was found to be expressed by the formula

$$dx/d\theta = \mathrm{K}\ (\text{Arsenic acid})\ (\text{Pot. iodide})^a\ (\text{Sulphuric acid})^b \qquad (2)$$

where, in the solutions used, the numbers *a* and *b* were greater than unity but as far as could be inferred approaching unity for dilute solutions. Unfortunately this reaction does not take place in strongly diluted solutions,[2] the equilibrium in such solutions lying practically to the right in the equation

$$H_3AsO_4 + HIO = H_3AsO_4 + H + \bar{I}. \qquad (A)$$

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

[2] Zeit. phys. Chem., 47, 121 (1904). The reviewer suggests using only dilute solutions.

The measurements show that the rate to the right is about 100,000 times that to the left.

The equilibrium condition was found to be fairly well expressed by the formula

$$K = \frac{(\text{Pot. iodide})^3\ (\text{Sulphuric acid})^2\ (\text{Arsenic acid})}{(\text{Iodine})\ (\text{Arsenious acid})} \qquad (3)$$

and each constituent, in moderately dilute solution, was proved to have indices close to these. In more concentrated solution the same abnormal action of the acid was demonstrated.

Considering the important bearing of the data upon the Theory of Kinetic Equilibrium, better agreement between the calculated and observed Equilibrium Constants was much to be desired; and it was hoped that further experiments would show the cause of the discrepancy. The abnormal action of the potassium iodide and sulphuric acid required further study. Substitution of hydriodic acid for the sulphuric acid in both rates simplifies the considerations. With these objects in view several series of experiments were carried out.

The methods are, in general, identical with those employed in the previous work. The Units and Symbols are also the same; namely, A = I_3 = tri-iodion = iodine dissolved in a solution of potassium iodide of which latter an excess was always present and was allowed for in calculating C in the reacting mixtures; B = arsenious acid = white oxide of arsenic dissolved in sodium carbonate solution, which was made acid by the sulphuric or the hydriodic acid in the reacting mixture; C = $\overline{I}$ = iodide ion, assuming complete dissociation of both potassium iodide and hydriodic acid but the iodide ions necessary to form tri-iodion with the free iodine are not included in C; D = $\overset{+}{H}$ = the acid (hydrogen) ion and in the experiments the amount necessary to neutralize the carbonate and the arsenite in B is always deducted; E = arsenic acid. The units of mass are 1/100 of the quantities, in grams, in the equation

$$H_3AsO_3 + \overline{I}_3 + H_2O = H_3AsO_4 + (3\overline{I}) + (2\overset{+}{H}). \qquad (B)$$

The unit of time is one minute and the unit of volume is one liter. Except when otherwise stated, the experiments were all carried out at 0° C. For convenience of reference the rate to the right in above equation (B) is spoken of as the "Direct Rate" and the rate to the left as the "Reverse Rate."

PART I. EXPERIMENTS USING SULPHURIC ACID

Series A.—Extended reverse rate measurements

In the reduction of arsenic acid by potassium iodide and sulphuric acid, it was observed in the former paper that the latter constituents seemed to not obey the mass law and to require variable values for *a* and *b* in Equation 2 above. To find the extent of this abnormal action, advantage was taken of the fact that increase of either of these constituents accelerates the rate. Consequently by alternately doubling the one and halving the other, the experiments were made to cover practically the whole possible concentration of the two constituents, still keeping the velocity of the rate within limits allowing of easy measurement. At the same time the concentration of the arsenic acid was always much less than the smaller of the other two concentrations, so that in a first approximation the velocity of the rate was affected only by changes in the concentration of the arsenic acid. That is, in the general formula

$$dx/d\theta = K_5(C - x)\ (D - x)\ (E - x)V^{-3} \qquad (4)$$

C and D are always large compared with E and therefore always still larger compared with x. Thus the expression (4) becomes practically

$$dx/d\theta = K_5CDV^{-3}(E - x) \qquad (5)$$

of which the integrated form is

$$K_1\theta = \text{Log}_{10}(E - x) \qquad (6)$$

where

$$K_1 = K_5CDV^{-3}\ 0.434. \qquad (7)$$

The reactions were carried out in suitable sized flasks kept at 0° C by immersion in a well-stirred bath of snow and water. The solution for the reaction was prepared in two parts which were cooled to 0° C before mixing. In one flask the potassium iodide was mixed with part of the sulphuric acid and part of the water; in the other flask the arsenic acid was mixed with the remaining sulphuric acid and water. By thus dividing the sulphuric acid to about the same concentration in each flask, no rise in temperature took place when the contents of the flasks were mixed and the reaction commenced. To allow for iodine set free during cooling by oxygen dissolved in the acid potassium iodide solution, proportional parts of each cooled mixture were measured out before starting the reaction, added one after the other to several times their volume of cold distilled water, and the free iodine determined. This reading, which was always proportionally very small (averaging about half a cubic centimeter), was subtracted throughout from the total reading and the difference recorded in the Tables.

The progress of the reaction was determined at intervals by measuring out usually 10 cc of the reacting mixture with a cold pipette into a cold beaker, diluting with ice-water to stop the reaction and reduce the concentration of the acid, and then quickly titrating with sodium thiosulphate solution. On account of the oxidation of the sodium thiosulphate by the arsenic acid, care was taken never to add more than a slight excess of the former during titration. In case the reaction had proceeded to any extent or was a very slow one, it was found necessary to add with the cold diluting water, sodium thiosulphate solution in quantity almost sufficient to decolorize the part of the mixture taken for titration, and finishing the addition of sodium thiosulphate solution as quickly as possible. If this precaution was neglected, the reaction of the Direct Rate, accelerated by the dilution, would introduce a serious error into the reading.

At the head of each table is given the initial quantities of each of the reacting substances and the volume in liters of the mixture. Under "Reading" is given the sodium thiosulphate titration obtained as described above. Under θ is given the interval in minutes from the time of mixing the two parts to start the reaction, to the time of diluting the part taken for titration. At the foot of the table is given the reading corresponding to the total possible amount of iodine set free by the arsenic acid in the part taken for titration. The values of x are calculated by the proportionality between this final reading (where $E = x$) and the reading at the time in question. Under K_1 is given the value calculated by Equation (6); throughout the time of the first reading and not the time of mixing is used as zero time in the calculation, thus avoiding the irregular reaction during the time of mixing. This choice of zero time required the use of $(E - x)$ from line one as the initial E; C and D were usually so large that the difference was negligible. In Tables 1, 4, 9, and 10, K_6 is calculated from the integral of Equation (4) assuming only D (or C) constant.

Tables 1–10 were carried out according to the plan outlined above (page 729). The results of these and other experiments are summarized in Table 20. The factor by which K_1 increases for multiplying D by 2 at the concentrations in question is given under "D factor," and the similar number for C under "C factor." Under "D index" and "C index" is given the value required for b and for a in Equation 2 in order to give the corresponding factor. . As will be seen, the numbers increase very rapidly in both cases with increase in concentration. In case of the sulphuric acid (D), where the limits of concentration are wider, the index goes from 1 to 3.7. In Tables 11 and 12 the index has fallen to 1 and from the way in which it falls off this would appear to be the lower limit and to hold for solutions where none of the reacting substances are present in greater concentration than 3 Units per 120 cc. In the case of the iodide (C) the index is approaching 1 in Tables 1 and 2, and probably is 1 in Tables 11 and 12 where, therefore, the general formula (Equation 4) with all indices unity holds. Consequently $K_6 = 3.9$ 10^{-7} calculated from these tables increases in each of the preceding tables with the increase in C and D but parallel also with the increase in $dx/d\theta$.

Dividing the constant 1.2 10^{-2} of Table 2 by the successive D factors 5.4, 3.3, 2.9, 2.6, and calculating the value of K_6 assuming this the value of K_1 where $D = 1.21$ and $C = 1.36$ gives 2.16 10^{-7}.. Taking the constant 0.76 10^{-2} of Table 9 and treating it similarly gives $K_6 = 2.23\ 10^{-7}$. This value is only about half that in Tables 11 and 12. Also the D factors in the pairs of experiments 11–12 and 9–10 are quite different. It will appear later that K_1 is probably a function of $dx/d\theta$ to which these peculiar results may be due. Failing such an explanation, it would appear that the constituents are not independent in their action on the rate but are influenced by the presence of other constituents.

In my former paper it was assumed that under the conditions of measurement the effect of the reaction opposite to the one being measured, could be safely neglected. This assumption was completely justified in the measurements of the Direct Rate as also in the greater part of the Reverse Rate measurements. In a few experiments (for example, Tables 23 and 24*a* of the former paper) the constant shows a falling off at the last reading where the rate is carried to almost complete disappearance of arsenic acid. This may also be observed in some of the tables of the present paper, but where this error extended further than the end measurements, a correction has been made. In taking averages where the last values show a decrease they are omitted.

In Tables 28 and 29 of my former paper, the reverse rate measured was very slow, the direct rate constant is about 10^6 greater, and consequently this error is here not negligible. For the purpose of correction, Tables 28 and 29 of the former paper are produced here as Tables 11 and 12. The suggestion as well as the method of correction I owe to Mr. W. C. Bray.[1] In Tables 11 and 12, K_1' is calculated by Equation (6) but using pairs of consecutive values of $(E - x)$ and the difference between the corresponding values of θ. This method magnifies the experimental errors but is to be preferred as emphasizing also any regular variation in the constant. The actually measured rate R is calculated by supplying the values in

$$R = dx/d\theta = 2.30\ K_1'\ (E - x). \qquad (8)$$

The direct rate is calculated by the equation

$$R_1 = 0.28\, x^2 V/(C - x)^2 (D - x), \qquad (9)$$

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[1] Jour. Phys. Chem., 9, 573 (1905).

and the corrected value of K_1' is given by

$$K_1'' = K_1' \frac{(R + R_1)}{R}. \tag{10}$$

It will be observed that the corrected constant K_1'' shows a regular and pronounced increase.

This increase of the constant might be due to catalysis by a product of the reaction. To test this the experiments of Tables 13, 14, and 15 were carried out. Table 13 serves for comparison with 14 and 15. The experiment of Table 14 was made with an initial charge of tri-iodion and of Table 15 with one of arsenious acid. The value of K_1 and the course of the reaction in all three tables are identical, proving conclusively the absence of any catalysis by these, the only known products of the reaction. Similar experiments at greater concentration of both potassium iodide and sulphuric acid gave the same result.

This increase of the reverse rate constant as the reaction neared equilibrium gave a variation of the kind required for better agreement between the calculated and observed values of K_6. To test the quantitative sufficiency, it was necessary to follow a rate right up to equilibrium. To simplify the considerations C and D should be much greater than A, B, and E, at any time during the reaction. The direct rate should be treated similarly and to this end the equilibrium should be reached with about half the possible amount of tri-iodion. Hence the equilibrium formula

$$K_6 = \frac{(C - x)^3 (D - x)^2 (E - x)}{(A - x)(B - x) V^4} \tag{11}$$

was solved for A using $K_6 = 1.5\ 10^6$ and $10A = 10B = C = D = E = 20x$ and $V = 0.50$. To obtain identical conditions in the reacting mixtures it was necessary to make both direct and reverse rate mixtures from the same reagents, which was accomplished as follows: The reacting mixtures of Tables 16 and 21 were made up from identical quantities of the solutions of tri-iodion (A), arsenious acid (B), potassium iodide (C), and sulphuric acid (D). In Table 21, A with a little water was cooled in one flask and the remaining constituents and water in a second flask. The two parts were mixed to start the reaction which consequently took place with disappearance of tri-iodion and gave a measurement of the direct rate. In Table 16, the two parts were made up differently: C and D were mixed with half the water in one flask and A and B with the remaining water in the other. Consequently in the latter flask the reaction between A and B took place quickly and by the time all were at 0° C, the solution was only slightly colored, almost all A and B having disappeared. On mixing these two parts the reaction took place with the separation of tri-iodion and gave a measurement of the reverse rate.

The reacting mixtures of Tables 17 and 22, were made up from identical quantities of the solutions of potassium iodide (C), sulphuric acid (D), and arsenic acid (E), all being so chosen as to give the same equilibrium mixture as in Tables 16 and 21. In Table 17 the potassium iodide, half the sulphuric acid, and half the water were cooled in one flask, while the arsenic acid with the remaining sulphuric acid and water were cooled in the other. The two parts were mixed to start the reaction which, therefore, took place with the separation of tri-iodion and gave a measurement of the reverse rate. In Table 22, all three constituents were mixed with only sufficient water to keep all in solution while the balance of the water was cooled in a second flask. A quick reaction immediately took place between the three constituents, so that by the time all were at 0° C, almost all the arsenic acid had been reduced to arsenious acid. On mixing with the remaining water, a reaction took place with the disappearance of tri-iodion and gave a measurement of the direct rate. So that these four experiments gave a measurement of each rate with each set of reagents and also a measurement of the equilibrium from each side with each set of reagents. The reactions were very slow, lasting almost a week. To avoid as far as possible the oxidizing action of the air, the solutions were kept in 100 cc glass-stoppered bottles, and 25 cc were taken for each titration. The sodium thiosulphate solution changed slowly during this interval and its strength was regularly checked by a stronger solution of iodine kept away from strong light. This correction on the last day amounted to about 4 percent The readings recorded in the tables are corrected for this change in the thiosulphate solution.

Tables 16 and 17 are the two reverse rate measurements. In both the course of the reaction and the equilibrium readings are practically identical. The solutions used to make up the reacting mixture of Table 17 involved the formation of considerable sodium sulphate which, therefore, has no appreciable effect on the course of the reverse rate; neither is there a small quantity of any other material in one mixture only, affecting the course of the reverse rate. The columns headed K_1, K_1', R, R_1, K_1'', are calculated as shown above from Equations (6), (8), (9), and (10). It will be observed that K_1' shows a more rapid decrease approaching equilibrium than does K_1. K''_1, the corrected value of K'_1, shows a regular increase as was also the case in Tables 11 and 12. K'_6 of Table 11, the slower of the two latter Tables, has the greater final value and this value is somewhat less than the initial values in Tables 16 and 17. It must therefore be concluded that at equilibrium, in dilute solutions at least, $K'_6 = 2.0\ 10^{-6}$.

Under "M" in Table 16 is given the value of the constant calculated from

$$dx/d\theta = M(E - x)^2 = K''_1(E - x) \qquad (12)$$

in which it is assumed that the arsenic acid acts according to the second power. The tabulated values show a much greater variation than K''_1. In these experiments C and D are practically non-variant and it must either be assumed that the arsenic acid $(E - x)$ acts according to a fractional power or that the constant depends on $dx/d\theta$. To make the constant non-variant requires different fractional indices for $(E - x)$ in the different experiments—for example, the experiment of Table 20 (page 385) of former paper has a 10 percent variation of K_1 for a 90 percent variation of $(E - x)$ and the index in this case would be almost unity. It seems simpler to say that K_6 is an inverse function of $dx/d\theta$. This is supported by the fact that the fast rates give K'_1 almost constant but when R_1 is small they show an increase. It offers a satisfactory escape from the conclusion noted on page 732 of the lack of independence of the constituents. It supplies a good reason for the small values of K_6 in Tables 2–13. The increased value in Table 1 may safely be attributed to the divergence of the sulphuric acid from the simple laws when in concentrated solution (4.8 normal). It must also be observed that in the direct rate measurements (Table 14, page 379, of former paper) the sulphuric acid increases its action faster than its concentration when 2.0 normal but its action is still proportional to its concentration when 0.93 normal.

Such a relation may be explained theoretically by the assumption of a reaction in two steps neither of which is instantaneous. This possibility has been discussed[1] theoretically in several papers but I am not aware of any practical application. The equilibrium of the first step is not quite attained while the reaction of the second step is removing one or more of the products of the first, or conversely. In this case some hints may be obtained as to the probable steps. First, no product of the reaction retards the reverse rate so that the first step must be one of addition or at least one that does not produce either of the products of the final reaction. Second, the rôle, normal and abnormal, of the potassium iodide and the sulphuric acid are very similar so that they probably play similar parts in both steps: this is confirmed when hydriodic acid is substituted for potassium iodide and sulphuric acid. Third, arsenic acid must enter the first step. The separation of a very small quantity[2] of a crystalline compound during some of the fast reverse rate measurements, is in line with this hypothesis. Consequently a probable first step is

$$\overset{+}{H} + \overset{-}{I} + H_3AsO_4 = H_3AsO_4HI \qquad (C)$$

where water may be also split off. The second step could then be

$$H_3AsO_4HI = H_3AsO_3 + HIO. \qquad (D)$$

To supply the desired explanation it is only necessary that the

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[1] Bancroft: Jour. Phys. Chem., 4, 705 (1900); Mittasch: Zeit. phys. Chem., 40, 1 (1902); Jungius: Zeit. phys. Chem., 49, 368 (1904).

[2] Quantity too small for analysis.

reaction of equation (C) be of a measurable velocity when the velocity of the second step will be lessened by the decrease in the amount of the first step product and the second rate constant appear to depend on $dx/d\theta$.

Mathematical treatment of the figures on this assumption is involved and does not seem to offer results worth printing. It would require the determination by algebraic means of at least two independent constants, the rate constants of the two steps, and could hardly fail to make a correction satisfactory enough to come within the large experimental error of such work. In case the amount of the intermediate product is small compared with x, the equilibrium function derived from this theory reduces to the form (equation 6) employed in the calculations. Also from the peculiar form of the first step, it is apparently without a point for experimental attack. The temperature coefficients are throughout in excellent agreement as would be predicted from this hypothesis. In fact it offers an excellent qualitative (and probably quantitative) explanation of all the irregularities except the increase of K_5 in Table 1 which is very well accounted for by other means. I have not been able to form any explanation based on electrolytic dissociation which offers at all a satisfactory correlation of these peculiarities.

Temperature Coefficient.—The experiments of Tables 18 and 19 were carried out at 10°C, and the change of K_1 gives 2.37 as coefficient for this temperature interval.

Series B.—Direct rate near equilibrium

In the first paper the agreement between the mathematical expression for the direct rate and the experimental data left nothing to be desired. The experiments, however, did not cover the rate near equilibrium, which became advisable in view of the peculiar form of the reverse rate and of the lack of agreement with the equilibrium formula. The experiments of Tables 21 and 22 were carried out to test the constancy of K_1 near equilibrium. On page 733 is given in detail the method of making the reacting mixtures and of following the course of the reaction. In the Tables K_1 is calculated from the integrated form of

$$R' = dx/d\theta = K_1 (A - x)\, 2.30, \qquad (13)$$

and K_1' from this also, but using pairs of consecutive measurements. R_1 is calculated by supplying the values in Equation (13). R_2 is calculated from

$$R_2 = K_1'\, 2.30\, x \qquad (14)$$

employing the equilibrium value of K_1' namely, 1.49 10^{-4} of Table 16 for Table 21, and 1.55 10^{-4} of Table 17 for Table 22. And K_1'' is given by

$$K_1'' = K_1' \frac{(R' - R_2)}{R'}. \qquad (15)$$

The constant K_1'' shows no regular variation right up to equilibrium. The action of the air is shown in the last two measurements since only near equilibrium is it appreciable. That the increase of K_3 in Tables 16 and 17 is not due to this action of the air, is satisfactorily shown by the constancy of K_1'' which, were the other the case, would decrease. The average values of K_3 in the two experiments are practically identical, namely, 0.260 and 0.262, and these fall within the values found in the first paper where the average was 0.28. The agreement of the two experiments shows as also in the case of the reverse rate, page 735, that the sodium sulphate has no effect on this rate and that there is no other substance present in small quantity in one of the mixtures only and affecting the direct rate. The constancy of K_1'' is also a very satisfactory proof of the accuracy of the method of correction since here the measurements go right to equilibrium.

Temperature Coefficient.—A pair of rates carried out at 10° C gave 0.86 for K_3 at this temperature which agrees satisfactorily with the value of 0.95 of the former paper.

Series C.—Equilibrium experiments

In the former determinations of Equilibria, the field covered was small and there was a possibility that the number found then for K_6 was an accidental value. Unfortunately the field over which equilibrium determinations can be successfully made is not large. Arsenious acid can never be present in large quantity on account of its slight solubility under these conditions. If arsenic acid is increased in the presence of much sulphuric acid and potassium iodide, beautiful spangle-like crystals separate. If potassium iodide and sulphuric acid are increased to any great extent, the equilibrium is reached with practical disappearance of arsenic acid which then has to be determined as the small difference between the total possible and the observed quantity of tri-iodion. Here also the oxidizing action of the air introduces a relatively large error, so that slightly more tri-iodion was occasionally found than could be accounted for by the arsenic acid initially present. It is almost impossible to exclude all the action of the air on hydriodic acid solutions which must stand for days, as in this case to allow the mixture to come to equilibrium.

The previous work having sufficiently demonstrated that false equilibria were not to be feared, the precaution of making the mixtures come to equilibrium from both sides was here given up. The mixtures were made up by measuring out the solutions with pipettes and making up the required volume with water. The mixtures were kept in full, well-stoppered bottles standing in the thermostat till, judging from past experience, ample time had been allowed for them to come to equilibrium. Analyses were made exactly as described for slow reverse rates on page 730.

To test whether any secondary reactions were disturbing the equilibrium, several mixtures were allowed to stand for three weeks at room temperature, and after coming to equilibrium again at zero, a very slight increase in the tri-iodion was observed; this could easily be accounted for by oxidation by the air.

A number of experiments were carried out, using carefully boiled solutions, cooled and handled under carbon dioxide so that the action of the air was reduced to a minimum. The results were practically identical with those where such precautions were neglected.

A large number of experiments were made in the field where they were practicable and a typical set is given in Table

23. K_6 is calculated by Equation (11) and in no case did its value rise to $2.0 \ 10^5$. The true value probably lies between 1.0 and $1.5 \ 10^5$. It is quite probable that the variations in the value of K_6 are due to the experimental difficulty under which the determinations are carried out. The value of K_6 is obtained as the product of twelve experimental numbers, eight of which are determined by the value of the tri-iodion found by titration. This latter may be seriously altered by the action of the air. In concentrated solution of sulphuric acid, however, the value of K_6 will decrease on account of the increase in K_5 and decrease in K_3.

The value of the quotient K_3/K_5, using the equilibrium value of K_5 in Tables 16 and 17, is $1.3 \ 10^5$ while the value of K_6 from these experiments is $1.4 \ 10^5$; better agreement could only be a coincidence. The disagreement in the former paper is to be attributed to the small value of K_5 when $dx/d\theta$ is large.

Temperature Coefficient.—The experiments 10 and 11 of Table 23 were carried out at 10° C and give, by comparison with the other half of the same mixture kept at 0° C, a coefficient for this temperature interval of 1.41. The coefficient calculated from the rate coefficients is 1.43, and from the 20° C coefficient of the first paper is 1.34. So that these are in excellent agreement.

PART 2. EXPERIMENTS USING HYDRIODIC ACID

To complete the study of the reaction, it was necessary to carry out measurements, using hydriodic acid instead of sulphuric. Accordingly, a solution of hydriodic acid, about 6 mols. HI per litre, was made by the action of iodine on red phosphorus in the presence of water. The resulting solution of the acid was purified by several distillations in a current of hydrogen gas. In calculating C and D the hydriodic acid was treated as completely dissociated.

Employing the other solutions used in the previous work, three different series of experiments were carried out; Series D on the oxidation of arsenious acid by iodine in the presence of potassium iodide and hydriodic acid; Series E on the reduction of arsenic acid by hydriodic acid solutions; and Series F, a set of Equilibrium determinations.

Series D.—Direct rate in the presence of hydriodic acid

In making up the reacting mixtures and in carrying out the rates the same methods were employed as are described in the former paper where sulphuric acid was employed. The method used for determining the effect of altering each constituent separately in the presence of one very small constituent, was again employed. The formula found to hold in the case of sulphuric acid was again found true, *i. e.*,

$$dx/d\theta = K_3 \frac{(A - x)(B - x)V}{(C + x)^2(D + x)} \qquad (16)$$

and when B, C, and D are large compared with A (tri-iodion) this becomes

$$dx/d\theta = K_3 \frac{B\,V\,(A - x)}{C^2D} = K_1\, 2.30\, (A - x). \qquad (17)$$

Throughout A (tri-iodion) was the constituent present in small quantity. The integrated form where only D is assumed constant is also used and

$$K_4 = K_3\, V/D. \qquad (18)$$

In Table 24 the constancy of K_1 is sufficient evidence that the first power of A is required in the formula and the same may be observed in each of the succeeding tables. The value of K_1 should fall off slightly on account of the slight decrease in B, C, and D; the larger decrease just at the end is due to the fact that equilibrium is being approached.

In Table 25, while the other constituents are the same as in Table 24, the iodide (C) is multiplied by the square root of 2; K_1 falls to half its value in Table 24, showing that the iodide acts inversely as its square.

In Table 27 the arsenious acid is half its concentration in Table 24, and the value of K_1 falls to half; the arsenious acid (B) acts therefore as its first power.

In Table 26, both C and D are varied but K_4, which is independent of variations in A, B, and C, is double that of Table 24, showing that the sulphuric acid (D) acts inversely as its first power. The relation between the values of K_4 in Tables 28 and 29 confirms this conclusion.

The results of the series are summarized in Table 30, where $K_4 = 0.135$ is constant well within the experimental error. This value is only half that found using sulphuric acid and the difference may be due to the greater dissociation of hydriodic acid.

Temperature Coefficient.—The experiments of Tables 28 and 29 were carried out at 10° C, and the relation of the constants gives 3.2 as the coefficient for this temperature interval; using sulphuric acid, the value was 3.39.

Series E.—Reverse rate in the presence of hydriodic acid

In this series on the reduction of arsenic acid by hydriodic acid it was not possible to duplicate the extended set of rates of Series A, since the $\overset{+}{H}$ ion could never be present in greater number than the $\bar{I}$ ion. The experiments of Tables 31–35 were carried out, using exactly the same procedure as in Series A, and the results are summarized in Table 37 where the headings have the same significance as in Table 20. The C factor and D factor are almost identical in both tables (20 and 37) for the same values of C and D—the divergence from the simple formula (Equation 4) is closely the same for C as for D. The value of K_5 seems to be slightly larger than in the case of sulphuric acid.

Temperature Coefficient.—The experiment of Table 36 was carried out at 10° C and the value of K_1 gives, by comparison with that of Table 32, a coefficient of 2.53 for this temperature interval; the value for sulphuric acid was 2.37.

Series F.—Equilibrium in the presence of hydriodic acid

In this series on equilibrium of mixtures with hydriodic acid, the same methods as are described in Series C were employed. A set of the determinations is given in Table 38. The value of K_6 for dilute solutions seems to lie in the neighborhood of $0.9\ 10^6$. The value of K_4/K_5 from the results of Series D and E, is $2.5\ 10^6$ so that about the same discrepancy is here observed as was found in the former paper in the work with sulphuric acid. From the analogy of the two cases there can be no doubt but that experiments following this reverse rate to equilibrium would show the same excellent agreement as was finally found in Series A.

Temperature Coefficient.—The experiments 11 to 14 were carried out at 10° C and the other half of the same solution at 0° C. The relation between the pairs of constants gives 1.25 as the coefficient for this temperature interval; the ratio of the rate coefficients is 1.27, so that we have here again excellent agreement.

Conclusion

The conclusions of the former paper receive the strongest support from the more extended data recorded here.

The formula for the direct rate (Equation 16) is found to hold with remarkable exactness for both sulphuric and hydriodic acids and K_3 is non-variant right up to equilibrium.

The formula for the reverse rate (Equation 2) is found to hold for very dilute solutions with *a* and *b* unity. With increasing concentration of iodide (C) and acid (D) the values of *a* and *b* increase similarly. The value of K_5 is found to increase as the equilibrium is approached and also when the rate $dx/d\theta$ is lessened by decreasing $(E - x)$. A satisfactory theoretical explanation of these peculiarities is advanced.

The value of the equilibrium constant K_6 is $1.5\ 10^5$—variations being possibly due to experimental errors. This value is in remarkable agreement with the quotient of the two rate constants $K_3/K_5 = 1.4\ 10^5$. The ratio of the rate temperature coefficients also shows the same excellent agreement with the equilibrium temperature coefficient. Finally, the peculiar action of concentrated sulphuric acid, increasing its action faster than its concentration, is shown in each of the rates and in the equilibrium.

In view of the complexity of both rates and equilibrium functions, this application and confirmation of the Theory of Kinetic Equilibrium must be regarded as the most satisfactory known.

My thanks are due to Dr. R. F. Ruttan, in whose laboratory this work was carried out.

Chemical Laboratory of the Medical Faculty,
McGill University, Montreal,
July, 1905.

TABLE OF CONTENTS

TABLE 1

$\bar{I}$ (C), 1.358; H_2SO_4 (D), 28.92; H_3AsO_4 (E), 0.2835; V, 0.12

No.	Reading	θ	x	$E-x$	$K_1.10^4$	$K_5.10^6$
1	0.0	0.0	0.0000	0.2835	—	—
2	5.9	1.0	0.03186	0.2516	—	—
3	15.1	2.75	0.08154	0.2020	5.45	6.54
4	26.4	4.75	0.1425	0.1410	6.72	7.32
5	29.9	6.75	0.1615	0.1220	5.46	6.02
6	35.2	9.50	0.1900	0.0935	5.06	5.66
7	40.2	14.8	0.2171	0.0664	4.20	4.80
8.	47.7	25.0	0.2576	0.0259	4.11	4.84
9	50.2	43.0	0.2711	0.0124	3.12	3.72

Reading 52.5 is proportional to $x = 0.2835$

TABLE 2

$\bar{I}$ (C), 1.358; H_2SO_4 (D), 19.28; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E-x$	$K_1.10^4$	$K_5.10^6$
1	0.00	0.0	0.0000	0.2835	—	—
2	1.95	1.25	0.01053	0.2730	—	—
3	8.1	6.83	0.04374	0.2398	1.02	1.57
4	13.6	11.0	0.07342	0.2101	1.30	1.84
5	19.05	17.0	0.1029	0.1806	1.14	1.82
6	23.5	22.8	0.1269	0.1566	1.12	1.80
7	28.8	31.5	0.1555	0.1280	1.09	1.78
8	33.7	43.2	0.1820	0.1015	1.03	1.74
9	39.3	67.5	0.2122	0.0713	0.86	1.49

Reading 52.5 is proportional to $x = 0.2835$

TABLE 3

$\bar{I}$ (C), 2.716; H_2SO_4 (D), 19.28; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^2$
1	0.0	0.0	0.0000	0.2835	—
2	4.72	0.75	0.02548	0.2580	—
3	15.33	4.82	0.08279	0.2007	2.68
4	23.5	8.75	0.1269	0.1566	2.71
5	29.1	12.25	0.1571	0.1264	2.70
6	34.2	16.25	0.1847	0.0988	2.69
7	39.1	22.0	0.2111	0.0724	2.60
8	45.2	34.8	0.2441	0.0394	2.40

Reading 52.5 is proportional to $x = 0.2835$

TABLE 4

$\bar{I}$ (C), 2.716; H_2SO_4 (D), 9.64; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^3$
1	0.0	0.0	0.0000	0.2835	—
2	1.88	1.5	0.01015	0.2733	—
3	6.73	8.0	0.03625	0.2461	7.02
4	11.5	19.2	0.06210	0.2214	5.17
5	15.5	27.8	0.08370	0.1998	5.17
6	22.05	44.8	0.1191	0.1644	5.11
7	27.55	62.7	0.1487	0.1348	5.02
8	31.2	76.7	0.1685	0.1150	5.00
9	35.9	100.5	0.1938	0.0897	4.89

Reading 52.5 is proportional to $x = 0.2835$

TABLE 5

$\bar{I}$ (C), 5.43; H_2SO_4 (D), 9.64; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^3$
1	0.0	0.0	0.0000	0.2835	—
2	3.15	0.5	0.01701	0.2665	—
3	13.9	6.83	0.07505	0.2084	1.69
4	20.8	12.0	0.1125	0.1710	1.68
5	26.8	17.8	0.1447	0.1388	1.64
6	33.6	26.5	0.1814	0.1021	1.61
7	40.7	36.3	0.2198	0.0637	1.74
8	43.4	50.0	0.2343	0.0492	1.48

Reading 52.5 is proportional to $x = 0.2835$

TABLE 6

$\bar{I}$ (C), 5.432; H_2SO_4 (D), 4.82; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^3$
1	0.0	0.0	0.0000	0.2835	—
2	2.55	4.25	0.01377	0.2697	—
3	6.05	11.0	0.03267	0.2508	4.67
4	11.3	21.5	0.06103	0.2225	4.95
5	20.25	45.0	0.1215	0.1620	4.69
6	28.8	75.0	0.1555	0.1280	4.61
7	34.6	104.0	0.1868	0.0967	4.46
8	40.0	149.2	0.2106	0.0675	4.15

Reading 52.5 is proportional to $x = 0.2835$

TABLE 7

$\bar{I}$ (C), 5.432; H_2SO_4 (D), 2.41; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^3$	$K_1' . 10^3$	$R . 10^3$	$R_1 . 10^3$	$K_1'' . 10^3$	$K_5' . 10^6$
1	0.0	0.0	0.0000	0.2835	—	—	—	—	—	—
2	0.68	1.5	0.00367	0.2798	—	—	—	—	—	—
3	1.9	8.0	0.01026	0.2732	1.85	1.85	—	—	1.85	0.56
4	5.4	26.5	0.02916	0.2543	1.67	1.90	—	—	1.90	0.58
5	11.85	64.2	0.06402	0.2195	1.68	1.65	—	—	1.65	0.51
6	17.25	101.0	0.09316	0.1903	1.69	1.73	7.56	0.41	1.73	0.55
7	24.75	159	0.1336	0.1499	1.72	1.77	6.10	0.85	2.02	0.65
8	29.7	227	0.1604	0.1231	1.59	1.27	3.60	1.21	1.68	0.55
9	32.9	270	0.1776	0.1059	1.58	1.48	3.61	1.50	2.10	0.69
10	37.0	340	0.1998	0.0837	1.55	1.47	2.64	1.89	2.58	0.86

Average 4–8 1.67

Reading 52.5 is proportional to $x = 0.2835$

TABLE 8

$\bar{\text{I}}$ (C), 10.88; H_2SO_4 (D), 4.82; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^2$
1	0.0	0.0	0.0000	0.2835	—
2	5.95	1.67	0.0277	0.2558	—
3	18.0	6.33	0.0837	0.1998	2.30
4	30.9	13.4	0.1372	0.1463	2.08
5	41.5	22.5	0.1930	0.0905	2.17
6	46.6	29.4	0.2162	0.0673	2.10
7	52.0	40.7	0.2418	0.0417	2.02
8	56.2	58.0	0.2613	0.0222	2.06
			Average	4–8	2.09

Reading 60.9 is proportional to $x = 0.2835$

TABLE 9

$\bar{\text{I}}$ (C), 10.88; H_2SO_4 (D), 2.41; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^3$	$K_5 . 10^6$
1	0.0	0.0	0.0000	0.2835	—	—
2	1.1	1.0	0.00512	0.2784	—	—
3	6.05	6.17	0.02815	0.2554	5.73	1.14
4	14.7	16.2	0.07541	0.2081	8.29	1.28
5	22.2	27.5	0.1033	0.1802	7.13	1.10
6	29.8	42.0	0.1387	0.1448	6.91	1.07
7	38.2	64.8	0.1777	0.1058	6.57	1.01
8	42.9	82.0	0.1996	0.0839	6.43	1.02
9	46.6	100.5	0.2169	0.0666	6.27	1.00
				Average 4–6	7.44	

Reading 60.9 is proportional to $x = 0.2835$

Correction for the direct rate is negligible

TABLE 10

$\bar{I}$ (C), 10.88; H_2SO_4 (D), 1.21; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^3$	$K_5 . 10^6$
1	0.0	0.0	0.00000	0.2835	—	—
2	0.7	1.17	0.00325	0.2803	—	—
3	2.35	5.5	0.01092	0.2726	2.82	0.68
4	6.7	17.5	0.03115	0.2524	2.81	0.84
5	17.2	51.5	0.0800	0.2035	2.76	0.84
6	20.5	65.5	0.0953	0.1882	2.64	0.83
7	25.4	88.8	0.1181	0.1654	2.59	0.82
8	29.5	110.0	0.1371	0.1464	2.56	0.82
9	33.3	137.0	0.1548	0.1287	2.45	0.80
10	36.0	160	0.1674	0.1161	2.39	0.78
			Average	4–8	2.67	

Reading 60.9 is proportional to $x = 0.2835$

TABLE 11

Table 28 of First Paper

$\bar{I}$ (C), 2.270; H_2SO_4 (D), 2.293; H_3AsO_4 (E), 0.310; V, 0.155

No.	Reading	θ	x	$E - x$	$K_1 . 10^4$	$K_1' . 10^4$	$R . 10^4$	$R_1 . 10^4$	$K_1'' . 10^4$	$K_5' \times 10^6$
1	0.0	0.0	0.0000	0.310	—	—	—	—	—	—
2	0.35	10.0	0.00161	0.308	—	—	—	—	—	—
3	2.3	66.0	0.0107	0.299	2.30	2.30	1.58	—	2.30	0.38
4	2.65	74.0	0.0122	0.298	2.51	2.53	1.73	—	2.53	0.42
5	9.54	296.0	0.0434	0.267	2.17	2.16	1.33	0.073	2.27	0.39
6	24.6	994.0	0.113	0.197	1.97	1.88	0.851	0.546	3.09	0.56
7	26.6	1177.0	0.122	0.188	1.83	1.11	0.479	0.645	2.60	0.48
8	29.7	1432.0	0.137	0.173	1.77	1.42	0.566	0.830	3.51	0.65
9	35.8	2480.0	0.164	0.137	1.43	1.18	0.371	1.24	5.12	0.98
10	37.3	2880.0	0.171	0.130	1.31	0.57	0.170	1.36	5.12	0.98

Reading 67.5 is proportional to $x = 0.310$

TABLE 12

Table 29 of First Paper

$\bar{I}$ (C), 2.270; H_2SO_4 (D), 1.147; H_3AsO_4 (E), 0.310; V, 0.155

No.	Reading	θ	x	$E - x$	$K_1.10^4$	$K_1'.10^4$	$R.10^6$	$R_1.10^6$	$K_1''.10^4$	$K_5' \times 10^6$
1	0.0	0.0	0.00000	0.310	—	—	—	—	—	—
2	0.2	9.5	0.00092	0.309	—	—	—	—	—	—
3	1.2	70.0	0.00551	0.304	1.17	1.17	8.18	—	1.17	0.38
4	3.7	292.0	0.0170	0.293	0.819	0.817	5.51	0.21	0.848	0.28
5	13.1	991.0	0.0602	0.250	0.938	0.986	5.69	2.96	1.50	0.53
6	14.8	1175.0	0.0680	0.242	0.906	0.770	4.29	3.84	1.63	0.59
7	16.9	1430.0	0.0776	0.232	0.873	0.688	3.67	5.09	1.64	0.60
8	21.6	2470.0	0.0989	0.211	0.675	0.403	1.96	8.60	2.17	0.82
9	22.4	2880.0	0.102	0.208	0.599	0.20	0.957	9.4	2.17	0.82

Reading 67.5 is proportional to $x = 0.310$

TABLE 13

$\bar{I}$ (C), 2.27; H_2SO_4 (D), 2.29; H_3AsO_4 (E), 0.1473; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1.10^4$	$K_1'.10^4$
1	0.0	0.0	0.0000	0.1473	—	—
2	0.3	1.25	0.00032	0.1470	—	—
3	3.25	16.8	0.00349	0.1438	6.06	6.06
4	10.85	65.5	0.01165	0.1357	5.42	5.21
5	14.0	87.5	0.01503	0.1323	5.29	4.98
6	21.3	133.0	0.02287	0.1244	5.48	5.82
7	27.5	182.0	0.02953	0.1178	5.17	4.88
8	33.7	228.5	0.03619	0.1111	5.38	5.46
9	37.8	258.5	0.04059	0.1067	5.39	5.83
				Average	5.46	5.46

Reading 137.2 is proportional to $x = 0.1473$

Correction for direct rate is negligible

TABLE 14

$\bar{I}$ (C), 2.27; H_2SO_4 (D), 2.29; H_3AsO_4 (E), 0.1473; V, 0.120;
$\bar{I}_3$ (A), 0.208

No.	Reading	θ	x	$E - x$	$K_1 . 10_4$	$K_1' . 10^4$
1	0.0	0.0	0.0000	0.1473	—	—
2	0.75	1.5	0.00081	0.1465	—	—
3	3.8	18.5	0.00408	0.1432	5.76	5.76
4	11.75	64.5	0.01262	0.1347	5.80	5.80
5	15.05	87.5	0.01616	0.1311	5.48	5.05
6	21.65	135.0	0.02325	0.1240	5.39	5.07
7	28.5	182.0	0.03061	0.1167	5.46	5.02
8	35.25	228.5	0.03785	0.1095	5.60	5.99
9	38.3	258.0	0.04113	0.1062	5.45	5.64
				Average	5.56	5.47

Reading 137.2 is proportional to $x = 0.1473$
Correction for direct rate is negligible

TABLE 15

$\bar{I}$ (C), 2.27; H_2SO_4 (D), 2.29; H_3AsO_4 (E), 0.1473; V, 0.120;
H_3AsO_3 (B), 0.206

No.	Reading	θ	x	$E - x$	$K_1 . 10^4$	$K_1' . 10^4$
1	0.0	0.0	0.0000	0.1473	—	—
2	0.4	1.75	0.00043	0.1469	—	—
3	3.1	17.0	0.00333	0.1440	5.48	5.48
4	10.6	59.0	0.01138	0.1359	5.91	5.95
5	14.7	87.5	0.01579	0.1315	5.58	5.02
6	20.8	133.5	0.02234	0.1250	5.32	6.07
7	27.4	181.0	0.02943	0.1179	5.30	5.35
8	33.25	227.0	0.03571	0.1116	5.26	5.18
9	36.9	257.0	0.03963	0.1077	5.27	5.20
				Average	5.44	5.46

Reading 137.2 is proportional to $x = 0.1473$
Correction for the direct rate is negligible

TABLE 16

$\bar{I}$ (C), 4.80; H_2SO_4 (D), 4.79; H_3AsO_4 (E), 0.437; V, 0.500

No.	Reading	θ	x	$E - x$	$K_1.10^4$	$K_1'.10^4$	$R.10^4$	$R_1.10^4$	$K_1''.10^4$	$K_5'.10^6$	$\frac{K_3}{K_5'}, 10^{-5}$	$M.10^4$
1	0.0	0.0	0.0000	0.437	—	—	—	—	—	—	—	—
2	1.3	114.5	0.0116	0.4254	—	—	—	—	—	—	—	—
3	3.74	324	0.0332	0.4038	1.08	1.08	2.35	0.014	1.08	1.34	1.96	2.67
4	6.17	548	0.0548	0.3822	1.07	0.62	0.546	0.038	0.66	0.87	3.01	2.54
5	12.45	1256	0.1106	0.3264	1.01	0.968	0.678	0.155	1.19	1.55	1.70	2.74
6	14.42	1555	0.1281	0.3089	0.97	0.800	0.568	0.208	1.09	1.42	1.85	2.83
7	16.7	1950	0.1483	0.2887	0.91	0.744	0.494	0.278	1.16	1.51	1.74	2.49
8	19.9	2707	0.1768	0.2602	0.82	0.596	0.357	0.397	1.26	1.64	1.60	2.06
9	20.86	2951	0.1853	0.2517	0.81	0.590	0.342	0.434	1.34	1.75	1.50	1.88
10	21.69	3242	0.1927	0.2443	0.77	0.447	0.251	0.472	1.29	1.68	1.56	1.88
11	23.43	4190	0.2081	0.2289	0.66	0.299	0.157	0.548	1.50	1.96	1.34	1.53
12	23.9	4804	0.2123	0.2247	0.59	0.130	0.067	0.570	1.23	1.61	1.63	1.83
13	24.47	5622	0.2173	0.2197	0.52	0.119	0.060	0.597	1.30	1.70	1.54	1.69
14	24.55	6121	0.2180	0.2190	0.48	0.028	0.014	0.603	1.23	1.61	1.63	1.78
15	25.34	7060	0.2250	0.2120	0.44	0.150	0.073	0.642	1.47	1.92	1.37	1.44
16	25.66	7568	0.2279	0.2091	0.41	0.118	0.057	0.659	1.49	1.94	1.35	1.40
17	25.85	8502	0.2296	0.2074	0.37	0.038	0.018	0.670	1.44	1.88	1.39	1.44

Reading 49.2 is proportional to $x = 0.437$

Using the equilibrium formula gives

$K_6 = 1.44\ 10^5$ from line 16

$K_6 = 1.40\ 10^5$ from line 17

TABLE 17

$\overline{I}_3$ (A), 0.438; H_3AsO_3 (B), 0.439; $\overline{I}$ (C), 4.39; H_2SO_4 (D), 4.37; V, 0.500

No.	Reading	θ	x	$E - x$	$K_1 . 10^4$	$K_1' . 10^4$	$R . 10^4$	$R_1 . 10^4$	$K_1'' . 10^4$	$K_5'/10^6$	$\frac{K_5}{K_5'} 10^{-5}$
1	—	0.0	—	—	—	—	—	—	—	—	—
2	3.13	1.5	0.0278	0.4092	—	—	—	—	—	—	—
3	4.45	104.0	0.0395	0.3975	1.24	1.24	1.13	0.021	1.26	1.68	1.55
4	6.76	319	0.0600	0.3770	1.12	1.07	0.928	0.049	1.13	1.50	1.73
5	13.3	1027	0.1181	0.3189	1.05	1.03	0.754	0.188	1.29	1.72	1.51
6	15.5	1319	0.1377	0.2993	1.11	0.945	0.651	0.257	1.32	1.76	1.48
7	17.8	1721	0.1581	0.2789	0.96	0.754	0.484	0.337	1.28	1.70	1.53
8	21.1	2478	0.1874	0.2496	0.87	0.642	0.368	0.472	1.47	1.95	1.34
9	21.93	2722	0.1948	0.2422	0.84	0.537	0.299	0.513	1.46	1.94	1.35
10	22.65	3013	0.2011	0.2359	0.79	0.394	0.213	0.545	1.40	1.86	1.40
11	24.45	3963	0.2171	0.2198	0.68	0.323	0.163	0.635	1.58	2.10	1.24
12	25.1	4574	0.2229	0.2141	0.62	0.187	0.092	0.671	1.55	2.00	1.30
13	25.61	5399	0.2275	0.2095	0.54	0.115	0.0553	0.701	1.58	2.10	1.24
14	25.94	5902	0.2304	0.2066	0.50	0.122	0.0461	0.714	2.02	2.69	0.97

Reading 49.2 is proportional to $x = 0.438$

Using the equilibrium formula gives

$K_6 = 1.45\ 10^6$ for line 13

$K_6 = 1.36\ 10^5$ for line 14

TABLE 18

$\bar{I}$ (C), 2.636; H_2SO_4 (D), 4.82; H_3AsO_4 (E), 0.2835; V, 0.120

Temperature 10° C

No.	Reading	θ	x	$E-x$	$K_1.10^3$
1	0.0	0.0	0.0000	0.2835	—
2	0.8	0.83	0.00314	0.2804	—
3	1.9	3.0	0.00746	0.2760	3·10
4	4.8	8.0	0.01885	0.2647	3·49
5	10.85	19.2	0.04260	0.2409	3·58
6	16.8	31.7	0.0660	0.2175	3·57
7	24·3	50·3	0.0954	0.1881	3·51
8	33·7	75·7	0.1323	0.1512	3·57
9	39·3	102.2	0.1543	0.1292	3·32

Average 4–8 3·54

Reading 72.2 is proportional to $x = 0.2835$

TABLE 19

$\bar{I}$ (C), 2.636; H_2SO_4 (D), 9.64; H_3AsO_4 (E), 0.2835; V, 0.120

Temperature 10° C

No.	Reading	θ	x	$E-x$	$K_1.10^3$
1	0.0	0.0	0.00000	0.2835	—
2	2.25	1.0	0.00884	0.2747	—
3	15·6	8.25	0.06126	0.2222	12.7
4	19.8	11.0	0.07775	0.2058	12.5
5	22.85	13.2	0.08973	0.1938	12.4
6	30.15	19.0	0.1184	0.1651	12.3
7	36.7	26.2	0.1441	0.1394	11.7
8	42.1	31.7	0.1653	0.1182	11.9
9	46.2	37·5	0.1814	0.1021	11.8

Average 4 — 6 12.4

Reading 72.2 is proportional to $x = 0.2835$

TABLE 20

Table	C	D	E	V	$K_1.10^3$	C factor	D factor	C index	D index	$K_5.10^6$
1	1.358	28.92	0.2835	0.12	5.4					6.5
							9.0		3.71	
2	1.358	19.28	0.2835	0.12	1.2					1.8
						2.2		1.17		
3	2.716	19.28	0.2835	0.12	2.7					1.6
							5.4		2.41	
4	2.716	9.64	0.2835	0.12	0.51					0.77
						3.1		1.63		
5	5.43	9.64	0.2835	0.12	1.6					1.55
							3.3		1.72	
6	5.43	4.82	0.2835	0.12	0.49					0.70
							2.9		1.54	
7	5.43	2.41	0.2835	0.12	0.17	4.3		2.11		0.51
8	10.88	4.82	0.2835	0.12	2.1	4.4		2.14		1.51
							2.8		1.48	
9	10.88	2.41	0.2835	0.12	0.74					1.13
							2.6		1.38	
10	10.88	1.21	0.2835	0.12	0.27					0.84
11	2.270	2.293	0.310	0.155	0.024					0.39
							2.0		1.0	
12	2.270	1.147	0.310	0.155	0.012					0.38
13	2.27	2.29	0.1473	0.12	0.055					0.42
14	2.27	2.29	0.1473	0.12	0.056	(initial I_2)				
15	2.27	2.29	0.1473	0.12	0.055	(initial H_3AsO_3)				
16	4.80	4.79	0.437	0.500	0.011					1.34
17	4.83	4.82	0.439	0.500	0.013					1.68
18	2.636	4.82	0.2835	0.12	0.354	(Temperature 10°C)				
19	2.636	9.64	0.2835	0.12	1.24	(" ")				

Temperature coefficient (for 10° C)

Nos. 4 and 18 give $0.354 \times 3.3/0.51 = 2.30$

Nos. 4 and 19 give $1.24/0.51 = 2.44$

TABLE 21

$\bar{I}$ (C), 4.80; H_2SO_4 (D), 4.79; H_3AsO_4 (E), 0.437; V, 0.500

No.	Reading	θ	$A - x$	x	$K_1.10^4$	$K_1'.10^4$	$R'.10^4$	$R_2.10^4$	$K_1''.10^3$
1	—	0.0	—	—	—	—	—	—	—
2	38.5	2.0	0.3419	0.0951	—	—	—	—	—
3	37.1	117	0.3295	0.1075	9.56	9.56	1.04	0.368	1.30
4	35.0	321	0.3108	0.1262	9.19	8.97	0.868	0.432	1.35
5	33.5	549	0.2975	0.1395	7.97	6.27	0.564	0.478	1.15
6	29.7	1255	0.2638	0.1632	6.93	6.09	0.534	0.559	1.24
7	28.85	1556	0.2562	0.1808	6.32	3.72	0.238	0.619	1.37
8	27.87	1950	0.2475	0.1895	5.74	3.50	0.215	0.649	1.41
9	26.67	2708	0.2369	0.2001	4.80	2.37	0.153	0.685	1.46
10	26.57	2952	0.2360	0.2010	4.44	0.656	0.0365	0.690	1.30
11	26.38	3243	0.2343	0.2027	4.04	1.10	0.0602	0.695	1.38
12	26.14	4192	0.2320	0.2050	3.32	0.432	0.0233	0.702	1.34
13	25.78	4805	0.2290	0.2080	3.00	0.930	0.0488	0.713	1.45
14	25.61	5633	0.2274	0.2096	2.61	0.362	0.0187	0.718	1.43
15	25.80	6119	0.2291	0.2079	—	—	—	—	—
16	25.82	7057	0.2293	0.2077	—	—	—	—	—
								Average	1.35

Reading 49.2 is proportional to $x = 0.437$

$K_1'' = 1.35\ 10^{-3}$ gives $K_3' = 0.262$

TABLE 22

$\bar{I}_3$ (A), 0.438; H_3AsO_3 (B), 0.439; H_2SO_4 (D), 437; $\bar{I}$ (C) 4.39; V, 0.500

No.	Reading	θ	$A - x$	x	$K_1.10^4$	$K_1'10^4$	$R'10^4$	$R_2.10^4$	$K_1''.10^3$
1	—	0.0	—	—	—	—	—	—	—
2	46.71	2.0	0.4148	0.0222	—	—	—	—	—
3	44.4	105.0	0.3943	0.0427	12.2	12.2	1.89	0.152	1.32
4	40.91	333.0	0.3633	0.0737	10.4	9.52	1.25	0.263	1.15
5	33.8	1040	0.3002	0.1368	8.86	8.17	0.735	0.488	1.36
6	32.06	1332	0.2847	0.1523	7.60	6.19	0.503	0.542	1.30
7	30.2	1735	0.2682	0.1688	7.63	5.36	0.385	0.602	1.38
8	28.27	2491	0.2510	0.1860	6.31	3.39	0.213	0.663	1.39
9	27.83	2736	0.2471	0.1899	5.99	2.57	0.157	0.677	1.37
10	27.54	3026	0.2446	0.1924	5.55	1.41	0.0844	0.686	1.29
11	26.86	3976	0.2386	0.1984	4.47	1.08	0.0615	0.707	1.35
12	26.45	4589	0.2349	0.2021	4.02	1.09	0.0601	0.720	1.42
13	26.28	5413	0.2334	0.2036	3.48	0.328	0.0179	0.726	1.37
14	26.23	5903	0.2329	0.2041	3.19	0.184	0.0100	0.728	1.36
15	26.29	6843	0.2355	0.2035	—	—	—	—	—
16	26.37	7347	0.2342	0.2028	—	—	—	—	—
								Average	1.34

Reading 49.2 is proportional to $x = 0.438$

$K_1'' = 1.34\ 10^{-3}$ gives $K_3' = 0.260$

TABLE 23

No.	$A+x$	$B+x$	$C-x$	$D-x$	$E-x$	x	V	$K_6 \cdot 10^{-5}$
1	0.0062	0.0062	0.310	0.602	0.130	0.0062	0.12	1.76
2	0.0916	0.0916	1.49	0.516	0.248	0.0916	0.12	1.26
3	0.269	0.269	2.895	0.97	0.077	0.296	0.12	1.18
4	0.258	0.258	2.057	2.27	0.0278	0.2577	0.12	0.91
5	0.081	0.079	1.044	0.648	0.334	—0.168	0.12	1.08
6	0.044	0.042	0.606	0.688	0.341	—0.205	0.12	0.94
7	0.084	0.081	0.909	0.522	0.539	—0.539	0.12	0.77
8	0.162	0.159	1.74	0.568	0.223	—0.0875	0.12	0.71
9	0.0134	0.425	1.00	0.86	0.0904	—0.0904	0.12	0.57
10	0.075	0.070	0.918	0.531	0.548	—0.548	0.12	1.08
11	0.072	0.070	1.053	0.657	0.313	—0.177	0.12	1.52

Nos. 10 and 11 Temperature 10° C
Temperature coefficient (for 10° C)
Nos. 7 and 10 give 1.41
Nos. 5 and 11 give 1.41
From rate temperature coefficients, 3.39/2.37 = 1.43
From coefficient for 20° C (of First Paper) 1.34

TABLE 24

$\bar{I}_3$ (A), 0.519; H_3AsO_3 (B), 5.15; $\bar{I}$ (C), 4.54; H (D), 3.88; V, 0.600

No.	Reading	θ	$A-x$	$K_1 \cdot 10^3$	$K_4\ 10^3$
1	28.8	0.0	0.519	—	—
2	27.0	5.83	0.4865	—	—
3	26.2	12.0	0.4721	2.10	1.73
4	21.3	52.5	0.3838	2.20	2.15
5	19.25	76.0	0.3469	2.10	2.07
6	16.2	113.5	0.2919	2.06	2.07
7	13.45	154.5	0.2424	2.03	2.08
8	10.7	212	0.1928	1.95	2.04
9	8.65	271	0.1558	1.87	1.99
10	7.05	330	0.1270	1.80	1.91
				Average 4–8	2.08

TABLE 25

$\bar{I}_3$ (A), 0.519; H_3AsO_3 (B), 5.15; $\bar{I}$ (C), 6.39; $\overset{+}{H}$ (D), 3.88; V, 0.600

No.	Reading	θ	$A - x$	$K_1 \cdot 10^3$	$K_4 \cdot 10^2$
1	28.8	0.0	0.519	—	—
2	28.3	1.08	0.5100	—	—
3	27.9	6.33	0.5027	1.20	2.34
4	26.1	31.3	0.4705	1.16	2.15
5	24.3	56.5	0.4381	1.19	2.22
6	22.8	86.0	0.4108	1.10	2.08
7	20.9	118.0	0.3766	1.13	2.20
8	19.35	154.0	0.3487	1.08	2.07
9	17.25	201.0	0.3108	1.08	2.08
10	15.3	260	0.2757	1.03	2.02
11	14.05	303	0.2531	1.01	2.01
				Average 4–11	2.10

TABLE 26

$\bar{I}_3$ (A), 0.519; H_3AsO_3 (B), 5.15; $\bar{I}$ (C), 3.25; $\overset{+}{H}$ (D), 1.94; V, 0.600

No.	Reading	θ	$A - x$	$K_1 \cdot 10^3$	$K_4 \cdot 10^2$
1	28.8	0.0	0.519	—	—
2	26.9	1.33	0.4847	—	—
3	25.8	3.50	0.4649	8.34	4.21
4	23.0	10.33	0.4145	7.55	3.79
5	19.25	18.8	0.3469	8.29	4.23
6	16.4	30.3	0.2955	7.42	3.92
7	12.3	46.0	0.2216	7.58	4.16
8	8.0	76.0	0.1441	7.20	4.08
9	6.62	92.0	0.1192	6.73	3.90
				Average 3–9	4.04

TABLE 27

$\bar{I}_3$ (A), 0.519; H_3ASO_3 (B), 2.58; $\bar{I}$ (C), 4.55; H (D), 3.84; V, 0.600

No.	Reading	θ	$A - x$	$K_1.10^3$	$K_4.10^3$
1	28.8	0.0	0.519	—	—
2	28.6	1.33	0.5153	—	—
3	28.05	6.75	0.5055	1.55	2.96
4	26.8	22.8	0.4829	1.32	2.47
5	25.4	42.5	0.4577	1.25	2.41
6	23.45	75.5	0.4225	1.16	2.24
7	21.4	115.0	0.3856	1.11	2.16
8	19.05	161	0.3433	1.10	2.22
9	16.65	229	0.3000	1.03	2.10
10	15.24	272	0.2746	1.01	2.07
11	13.6	335	0.2450	0.97	2.04
				Average 5–10	2.20

TABLE 28

$\bar{I}_3$ (A), 0.519; H_3AsO_3 (B), 5.15; $\bar{I}$ (C), 6.34; H (D), 3.88; V, 0.600

Temperature 10° C

No.	Reading	θ	$A - x$	$K_1.10^3$	$K_4.10^3$
1	26.8	0.0	0.519	—	—
2	26.6	1.5	0.5151	—	—
3	26.4	3.0	0.5113	2.27	4.16
4	24.95	9.0	0.4832	3.72	6.70
5	22.75	20.5	0.4406	3.55	6.45
6	19.65	38.2	0.3805	3.57	6.78
7	16.1	64.2	0.3118	3.48	6.61
8	14.15	83.2	0.2740	3.36	6.51
9	10.72	130.0	0.2076	3.08	6.10
				Average 4–8	6.61

TABLE 29

$\bar{I}_3$ (A), 0.519; H_3AsO_3 (B), 5.15: $\bar{I}$ (C), 4.57; H (D), 1.94; V, 0.600
Temperature 10° C

No.	Reading	θ	$A - x$	$K_1 . 10^3$	$K_4 . 10^2$
1	26.4	0.0	0.519	—	—
2	24.55	1.5	0.4826	—	—
3	23.35	3.67	0.4571	10.8	10.4
4	19.5	8.5	0.3834	14.3	14.1
5	16.5	14.3	0.3243	13.5	13.6
6	14.4	19.5	0.2831	13.0	13.2
7	12.5	24.5	0.2457	12.7	13.2
8	10.6	31.0	0.2084	12.4	13.0
9	9.45	35.5	0.1857	12.2	13.1
10	7.78	43.5	0.1530	11.9	12.9
				Average 4–10	13.3

TABLE 30

Table	A	B	C	D	$K_1 . 10^3$	$K_4 . 10^2$	K_3	Temp.
24	0.519	5.15	4.53	3.88	2.11	2.08	0.135	0°
25	0.519	5.15	6.39	3.88	1,13	2.10	0.136	0°
26	0.519	5.15	3.25	1.94	8.3	4.04	0.131	0°
27	0.519	2.58	4.55	3.84	1.11	2.20	0.139	0°
						Average	0.135	
28	0.519	5.15	6.34	3.88	3.5	6.61	0.427	10°
29	0.519	5.15	4.57	1.94	14.0	13.3	0.430	10°
						Average	0.428	

Temperature coefficient (for 10° C.) 0.428/0.135 = 3.17

TABLE 31

$\bar{I}$ (C), 6.54; H (D), 4.91; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 . 10^2$
1	0.0	0.0	0.0000	0.2835	—
2	2.95	1.0	0.01065	0.2728	—
3	8.8	3.75	0.03173	0.2518	1.27
4	19.35	9.25	0.0698	0.2137	1.33
5	29.6	16.0	0.1068	0.1767	1.28
6	39.0	23.5	0.1406	0.1429	1.26
7	43.8	30.0	0.1580	0.1255	1.17
8	52.6	38.8	0.1897	0.0938	1.25
9	57.4	47.0	0.2070	0.0765	1.21
10	62.0	57.0	0.2236	0.0599	1.18

Reading 78.6 is proportional to $x = 0.2835$

TABLE 32

$\bar{I}$ (C), 3.27; H (D), 4.91; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 \cdot 10^3$
1	0.6	0.0	0.0000	0.2835	—
2	1.8	1.0	0.00649	0.2770	—
3	5.45	6.5	0.01965	0.2638	3.85
4	13.3	17.5	0.04797	0.2355	4.27
5	19.2	27.3	0.06925	0.2142	4.26
6	24.95	37.5	0.0900	0.1935	4.28
7	29.4	46.8	0.1060	0.1775	4.19
8	36.0	61.8	0.1298	0.1537	4.19
9	40.2	72.5	0.1450	0.1385	4.19
10	45.0	88.3	0.1623	0.1212	4.10
11	51.6	115.0	0.1861	0.0974	3.99

Reading 78.6 is proportional to $x = 0.2835$

TABLE 33

$\bar{I}$ (C), 3.27; H (D), 2.46; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1 \cdot 10^3$
1	0.0	0.0	0.0000	0.2835	—
2	0.05	1.25	0.00018	0.2833	—
3	1.35	6.25	0.00487	0.2786	1.48
4	5.05	21.3	0.01821	0.2653	1.43
5	9.5	40.8	0.03426	0.2492	1.41
6	15.2	70.3	0.05485	0.2283	1.35
7	19.75	92.8	0.06943	0.2141	1.34
8	23.25	115.5	0.08386	0.1996	1.34
9	26.0	132.5	0.09378	0.1897	1.33
10	29.2	154.0	0.1053	0.1782	1.32

Reading 78.6 is proportional to $x = 0.2835$

TABLE 34

$\bar{I}$ (C), 1.645; H (D), 2.46; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E-x$	$K_1 \cdot 10^4$
1	0.0	0.0	0.00000	0.2835	—
2	0.0	1.0	0.00000	0.2835	—
3	0.4	4.33	0.00216	0.2813	5.73
4	3.2	43.0	0.01728	0.2662	6.28
5	5.55	77.3	0.02997	0.2536	6.23
6	8.7	126.0	0.04697	0.2365	6.23
7	13.5	207.0	0.07830	0.2052	6.75
8	18.25	310.0	0.09856	0.1849	5.96
9	23.0	435.0	0.1242	0.1593	5.76
				Average 4–8	6.29

Reading 52.5 is proportional to $x = 0.2835$

TABLE 35

$\bar{I}$ (C), 3.27; H (D), 1.23; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E-x$	$K_1 \cdot 10^4$	$K_5 \cdot 10^7$
1	0.0	0.0	0.00000	0.2835	—	—
2	0.0	1.25	0.00000	0.2835	—	—
3	1.3	15.0	0.00702	0.2765	7.23	7.12
4	3.65	52.5	0.01971	0.2638	5.90	6.02
5	6.8	113.0	0.03672	0.2468	5.30	5.37
6	10.75	195.0	0.05805	0.2254	5.12	5.19
7	15.35	297.0	0.0829	0.2006	5.10	5.21
				Average	4–7	5.45

Reading 52.5 is proportional to $x = 0.2835$

TABLE 36

$\overline{I}$ (C), 3.27; H (D), 4.91; H_3AsO_4 (E), 0.2835; V, 0.120
Temperature 10° C

No.	Reading	θ	x	$E - x$	$K_1.10^3$
1	0.0	0.0	0.00000	0.2835	—
2	2.05	1.0	0.00805	0.2755	—
3	7.35	4.0	0.02886	0.2546	11.4
4	12.25	7.25	0.04810	0.2354	11.0
5	16.95	10.5	0.06656	0.2169	10.8
6	22.2	14.7	0.08718	0.1963	10.8
7	26.8	18.8	0.1052	0.1783	10.7
8	33.9	25.8	0.1331	0.1504	10.6
9	40.8	34.7	0.1602	0.1233	10.4
10	48.4	47.5	0.1900	0.0935	10.1
				Average 4–8	10.7

Reading 72.2 is proportional to $x = 0.2835$

TABLE 37

Table	C	D	E	V	$K_1.10^3$	C factor	D factor	$K_5.10^6$
31	6.54	4.95	0.2835	0.12	1.33	3.1		1.65
32	3.27	4.95	0.2835	0.12	0.427		3.0	1.06
33	3.27	2.45	0.2835	0.12	0.143	2.3	2.5	0.71
34	1.645	2.46	0.2835	0.12	0.062			0.64
35	3.27	1.23	0.2835	0.12	0.056			0.55
36	3.27	4.96	0.2835	0.12	1.07			

Table 36. Temperature 10° C
Temperature coefficient (for 10° C)
Nos. 32 and 36 give 2.51

TABLE 38

No.	$A+x$	$B+x$	$C-x$	$D-x$	$E-x$	x	V	$K_6.10^{-5}$
1	0.102	0.101	1.372	0.684	0.173	0.101	0.12	0.786
2	0.0062	0.0055	0.364	0.300	0.132	0.00547	0.12	0.822
3	0.667	0.667	3.00	4.83	0.015	0.667	0.12	1.03
4	0.114	0.509	1.74	1.34	0.122	0.0146	0.12	0.96
5	0.038	0.036	0.715	0.475	0.211	—0.211	0.12	0.613
6	0.133	0.131	2.05	0.380	0.253	—0.116	0.12	0.871
7	0.265	0.259	1.26	0.882	0.482	—0.482	0.12	0.527
8	0.050	0.048	0.703	0.463	0.336	—0.199	0.12	0.503
9	0.268	0.518	1.74	1.33	0.118	0.0187	0.12	0.382
10	0.382	0.380	2.73	3.67	0.004	0.133	0.12	0.364
11	0.109	0.503	1.74	1.34	0.128	—0.0093	0.12	1.09
12	0.034	0.032	0.719	0.479	0.215	0.215	0.12	0.812
13	0.248	0.242	1.28	0.899	0.499	0.499	0.12	0.68
14	0.046	0.044	0.707	0.467	0.340	0.203	0.12	0.624

Nos. 11, 12, 13, 14, temperature 10° C

Temperature coefficient (for 10° C)

Nos. 4 and 11 give 1.14

" 5 and 12 give 1.33

" 7 and 13 give 1.29

" 8 and 14 give 1.24

Average 1.25

From the rate temperature coefficients 3.17/2.51 = 1.27

SOLUBILITY AND SPECIFIC ROTATORY POWER OF CARBOHYDRATES AND CERTAIN ORGANIC ACIDS AND BASES IN PYRIDINE AND OTHER SOLVENTS

BY JOSEPH GERARD HOLTY

The term carbohydrate is applied to a large class of organic substances closely related to each other. The majority of these compounds are soluble in water, though those of the class $(C_6H_{10}O_5)_x$, of which starch and inulin are types are, as a rule, insoluble.

The range of solubility of the carbohydrates in solvents other than water is very limited, only bodies like the sugars have been found to dissolve in liquids such as methyl and ethyl alcohols, acetone and pyridine, and then only to a slight extent.

But little work has been done in determining the solubilities of these compounds in various solvents. At the suggestion of Prof. Kahlenberg, I have investigated the solubility and rotatory power of these substances with the hope of ascertaining the effect of the solvent upon the dissolved substance and the influence of the solvent on the specific rotation of the solute.

In some recent investigations carried on in this laboratory by Prof. Kahlenberg, it was found that cane-sugar was soluble in pyridine. Later investigation by G. M. Wilcox[1] has shown the extent of this solubility and also the influence of the pyridine upon the rotatory power of the cane-sugar. The following work represents a further study of the sugars and other carbohydrates with pyridine as a solvent.

Milk-sugar

The first substance used was milk-sugar. This was one of Schuchardt's preparations and labeled chemically pure. The samples used were first carefully dried at about 100° to expel moisture. The substance then corresponds to $C_{12}H_{22}O_{11}.H_2O$.

The pyridine used was purchased from Kahlbaum. It was

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[1] Jour. Phys. Chem., 5, 587 (1901).

first well dried over caustic potash after which it was distilled, and the distillate passing over at 114°–117°, and corresponding to a density of 0.971 at 20° C., was used in determining the rotatory power.

Two different samples of milk-sugar were taken, the one was boiled in pyridine for several hours and then allowed to cool to room temperature. The other, together with the pyridine, was placed in a large test-tube which was then sealed and fixed to a shaking apparatus immersed in a water-bath maintained at a constant temperature of 26°, and operated by means of an electric motor for about 30 hours. By this method a saturated solution was obtained at that temperature.

The densities of the two solutions were then determined and the angle of rotation observed by means of the Landolt-Lippich polariscope. The specific rotation was calculated according to the formula $[\alpha]_D^t = \frac{\alpha_D^t \times 100}{l \times d \times c}$ where α_D^t = the observed angle at temperature t; l, the length of the tube in decimeters; c, the number of grams of the solute in 100 grams of the solution; and d, the density of the solution.

It was found upon evaporation of the two solutions that more sugar had dissolved when it had been shaken with the pyridine, than when the mixture had been boiled. An excess of the sugar was used in each case, and the sample that was boiled caked on the bottom of the flask, forming a hard mass. This, no doubt, accounts for the fact of its lesser solubility, for in coalescing the mass would offer less surface to the pyridine than if it were in finer particles.

The sample that was shaken was found to contain 2.18 grams milk-sugar in 100 grams of the solution, while the other contained only 1.38 grams.

The same strength solutions were now made up with water as the solvent.

It has been observed that the specific rotatory power of certain substances in freshly prepared solutions changes gradually, increasing or decreasing until a constant value is obtained. This peculiar change was first noticed by E. O. Erdmann in milk-sugar and later by Tollens and Fischer in other sugars.

Erdmann[1] and Schmoeger[2] observed, in 1880, that milk-sugar on dehydration changes into a modification, which on re-solution shows a gradual increase in rotation. These were known as the α- and β-modifications, but in 1895, Tanret found a third modification, λ, which in solution could be transformed into the β-variety, the latter then being the stable modification, the rotatory power of which is always constant.

The above phenomenon, which is generally spoken of as multi-rotation, is difficult to explain. Some regard the freshly prepared solution as consisting of molecular aggregations which gradually break down into molecules of lower rotation. Others claim that the decrease in rotation may be due to the taking up or splitting off of water, and again it is claimed that it may be due to the existence of different isomeric modifications which, in solution, are transformed into the stable form. The latter view is the most universally accepted one, but as it too is based more or less upon theory, there still remains more work to be done in this connection before we have the true solution of the problem.

To insure complete transformation into the stable variety, the aqueous solutions made, were first boiled, and then allowed to stand for several days. The values obtained as compared with those of the pyridine solution are given in the following table:

Solvent	Percent milk-sugar	Density	α_D^{26} $l = 2$dcm.	$[\alpha]_D^{26}$
Pyridine	2.18	0.981	1.83	42.57
Water	2.18	1.0075	2.26	51.26
Pyridine	1.38	0.9778.	1.15	41.39
Water	1.38	1.0043	1.44	52.14

It will be noticed that the values for the rotatory power in aqueous solutions are greater than the corresponding ones in the pyridine solutions; also that the rotatory powers in the pyridine solutions increase with increased concentration. These results

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[1] Ber. chem. Ges., Berlin, 13, 1915 (1880).

[2] Ibid., p. 2180.

show just the reverse of what is true of cane-sugar in pyridine. Values for milk-sugar in aqueous solutions have been obtained by several investigators such as Schmoeger,[1] Parcus and Tollens,[2] Tanret,[3] and Hesse.[4] Their results agree fairly well. Schmoeger shows that the specific rotatory power of a 2.372 percent solution of milk-sugar is 52.53 at 20°, and that it is independent of the concentration up to 41.536 percent. Exactly the same value was found by Deniges and Bouvans.[5] The above results agree with those I obtained for about the same percent concentration.

Grape-sugar

The next substance studied was grape-sugar, $C_6H_{12}O_6.H_2O$. This sugar was a pure sample of Merck's preparation. It was found to be very soluble in pyridine, especially so when the mixture was boiled. The solution obtained by boiling was so dark that one was unable to see through it in the polariscope. Consequently, such a solution could only be used which had been obtained by shaking the sugar with pyridine at room temperature till saturated. Four grams of the grape-sugar were placed together with 50 cc pyridine in a large test-tube which was then sealed and the mixture shaken as in the case of the milk-sugar, in a water-bath at 26° for about 30 hours. At the end of that period, it was found that all the sugar had dissolved. The experiment was then repeated, using 6 grams sugar to 50 cc pyridine and after shaking for 30 hours, it was found that only a little more sugar had been dissolved than in the previous case. This shows that 4 grams of grape-sugar in 50 cc pyridine represents practically a saturated solution at 26°, and corresponds to 7.62 percent. An aqueous solution was now made of the same percent strength. A comparison of results is given below:

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[1] Ber. chem. Ges., Berlin, 13, 1918 (1880).

[2] Liebig's Ann., 257, 170 (1890).

[3] Bull. Soc. Chim., Paris (3), 13, 625 (1895).

[4] Liebig's Ann., 176, 98 (1875).

[5] Jour. Pharm. Chim. (5), 17, 363; Chem. Centralbl., 603 (1888).

Solvent	Percent grape-sugar	Density	α_D^{26} l = 2dcm.	$[\alpha]_D^{26}$
Pyridine	7.62	1.0050	11.58	75.62
Water	7.62	1.0292	8.22	52.42

The above results show a decided variation from those obtained with milk-sugar solutions. In the latter, the rotatory power was higher for the aqueous solution, whereas in the case of grape-sugar, the pyridine solution yields much the higher values. Values given in Landolt[1] for aqueous solutions of grape-sugar in the stable modification, are:

$[\alpha]_D^{20}$ = 52.5 and 52.6, which agree very closely with those I obtained.

Laevulose

Grape-sugar is more soluble in water than laevulose, but the reverse is true when pyridine is used as the solvent. The laevulose used was purchased from Kahlbaum, and was supposed to be chemically pure. Separate samples containing 4, 7 and 11 grams, respectively, were each placed with 50 cc pyridine in three test-tubes which were drawn off over a flame and shaken for about 30 hours at 26°, in the apparatus heretofore mentioned.

The sugar in each case was totally dissolved which shows an enormous increase in solubility as compared with the grape-sugar. The above solutions represent 7.61, 12.61, and 18.49 percent strength, respectively, the strongest being almost saturated. The solutions were all dark colored and a short tube of 1 decimeter in length had to be used in the polariscope.

The results obtained are tabulated below:

Solvent	Percent strength	Density	α_D^{26} l = 1dcm.	$[\alpha]_D^{26}$
Pyridine	7.60	1.008	— 5.64	—36.82
Water	7.60	1.0298	— 6.83	—87.3
Pyridine	12.61	1.0267	—10.22	—39.47
Water	12.61	1.0505	—11.63	—87.78
Pyridine	18.49	1.0521	—17.67	—45.44
Water	18.49	1.0755	—17.60	—88.51

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[1] Landolt's "Optical Rotation of Organic Substances" (translation by Long), p. 261.

It is well known that in aqueous solution laevulose rotates the plane of polarization to the left. This is also true in a pyridine solution, but to a less degree—in other words it approaches nearer to a dextro rotation. The values obtained for the pyridine solution increase quite uniformly with increase in concentration. This is also true of the aqueous solutions, but the variation is very small.

Earlier investigations by Herzfeld[1] and Winter[2] give specific rotatory powers for aqueous solutions which vary between 70.59 and 71.47 for a 20 percent solution.

Hoenig and Jesser,[3] on the other hand, have obtained values very much higher, ranging from 89.42 in a 5 percent solution to 98.47 in a 40 percent solution. The latter investigators claim that the low values obtained by Herzfeld and Winter are due to the formation of dextrines in the conversion of inulin into sugar, which could not have been completely removed by their method of purification with ether and alcohol.

Jungfleisch and Grimbert[4] give the following values: For a 9.75 percent solution at 20°, $[\alpha]_D = -89.9$ and for a 48.75 percent solution at 40°, $[\alpha]_D = -82.53$.

In looking over the above values obtained by different observers we see a wide variation in results. Their values do not agree with each other, nor do they agree with those I have obtained, with the exception of those derived by Hoenig and Jesser which check fairly well, considering the differences in temperature at which we worked.

Galactose

The galactose used was prepared by H. Trommsdorff. It did not appear to be very pure, which fact was verified by the results obtained in determining its rotatory power in aqueous solutions. It was found to dissolve quite readily in pyridine, but to a much less extent than the laevulose. After shaking a mixture of the sugar in pyridine for about thirty hours, a saturated

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[1] Liebig's Ann., 244, 287 (1888).
[2] Ibid., 244, 300 (1888).
[3] Zeit. Rübenzucker Ind. (1888), 1028.
[4] Comptes rendus, 107, 390 (1888).

solution of 5.45 percent strength was obtained. This percent was determined by evaporating the solution on a paraffin bath. The substance that remained was a thick, dark, amorphous mass, not unlike a stiff syrup. On this account it is difficult to say whether the above result is correct or not, for if the residue was heated too highly, the sugar would be decomposed, while if not heated enough, some of the pyridine would still remain in the residue. The sugar, as soon as it was dissolved, imparted a dark, brownish red color to the solution, and a short tube of 1 decimeter length had to be used in the polariscope. Great care had to be exercised in obtaining concordant readings on the instrument, and many settings had to be made.

The following are the results obtained:

Solvent	Percent sugar	Density	α_D^{26} l = 1dcm.	$[\alpha]_D^{26}$
Pyridine	5.45	1.0065	3.76	68.49
Water	5.45	1.0196	3.62	65.06

The rotatory power of the two above solutions shows but a slight variation; but, according to results obtained by other investigators, the rotatory power in aqueous solution should be much higher. Rindell[1] gives values for a 10 percent solution as 80.01 at 20° C and as 77.50 at 30° C.

Parcus and Tollens[2] give $[\alpha]_D^{20} = 80.39$ for a 11.081 percent solution. From these values one sees that the specific rotatory power of galactose increases with increased concentration, but decreases very noticeably with increase of temperature.

The low results that I obtained for the aqueous solution are due in part to the weak solutions used and also to the relatively high temperature at which I worked as compared with that at which Parcus and Tollens worked, but the main cause must be attributed to impurities in the sugar.

Mannite

Much work has been done with this substance in aqueous solution and varying results have been obtained. Ordinary

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[1] Scheibler's Neue Zeit. Rübenzucker Ind., 4, 170.

[2] Liebig's Ann., 257, 168 (1890).

mannite dissolved in water was found by Vignon,[1] Muentz and Aubin,[2] and a few others, to possess no activity, but Bouchardat[3] found with a 15 percent solution with a strong sodium light a rotation = —0.25.

In the aqueous solutions with which I worked, I could find no activity, thus verifying the results obtained by Vignon, Muentz and Aubin.

A very interesting phenomenon was observed in trying to dissolve the mannite in pyridine. At room temperature the substance was very slightly soluble but on boiling, a large amount dissolved. It did not, however, remain in solution very long, but on cooling the greater part of it precipitated out in the form of a bulky spongy mass. It was thought possible that the mannite had formed a solid crystalline addition product with the pyridine, but on further investigation it was found that this was not the case. This was shown by taking a small amount of the spongy mass and carefully drying it on filter-papers. All the pyridine could thus be extracted, and the remaining substance was simply pure mannite.

The solution on cooling to room temperature was very dilute. On evaporation it was found that only 0.47 percent remained in solution, which shows the slight affinity between pyridine and mannite.

The results obtained are given in the following table:

Solvent	Percent mannite	Density	$\alpha_D^{26}\ l$ = 2dcm.	$[\alpha]_D^{26}$
Pyridine	0.47	0.9740	—0.20	—21.71
Water	0.47	1.0014	0.00	00.00

The values obtained for an aqueous solution by Bouchardat show laevo rotation. From this one would suppose that a solution of mannite in pyridine would also show laevo rotation which was found to be true.

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[1] Vignon: Comptes rendus, 77, 1191 (1873).

[2] Ann. Chim. Phys. (5), 10, 553 (1877).

[3] Comptes rendus, 80, 120 (1875).

Erythrite

Erythrite is more soluble in pyridine than mannite. On boiling erythrite in pyridine and then allowing the solution to cool, the substance will separate out in form of a large spongy mass like in the case of mannite above described. More of the substance, however, remained in solution than in the former case, but on evaporation the residue remaining was not crystalline, but formed a thick viscous mass of a syrupy consistency. On this account it was very difficult to obtain reliable results representing the percent strength solution that was formed, but by most careful manipulation, a value corresponding to 2.5 percent was obtained. As erythrite is an inactive substance, no further study was made of it.

An attempt was made to determine the solubility and rotatory power of starch and some of the dextrines in pyridine, but it was found that they are all practically insoluble. The same is true of asparagine.

Strychnine, on the other hand, was found to be soluble in pyridine to a slight extent. At high temperatures, the substance was quite soluble, but on cooling to room temperature, it separated out in form of large crystals and the remaining solution on evaporation showed only 1.23 percent strength. The above process is indeed a splendid method to recrystallize the pure base.

An attempt was made to determine the rotatory power at higher temperatures but this was found impossible as the base was continually thrown out of solution, thus blurring the field of vision; hence the results tabulated below are those of a dilute solution obtained at room temperature. Strychnine is insoluble in water and consequently the values obtained for the pyridine solution, can not be compared with those of a corresponding aqueous solution. The results in pyridine solution are as follows:

Solvent	Percent of solute	Density	α_D^{26} l = 2dcm.	$[\alpha]_D^{26}$
Pyridine	1.23	0.9772	—4.72	—195.53

To show the effect of other solvents on strychnine, a few results obtained by other investigators[1] where chloroform, ethyl alcohol and amyl alcohol were used, are here tabulated:

Solvent	Percent of solute	$[\alpha]_D^{20}$
$CHCl_3$	4.00	—130.0
"	2.25	—137.7
"	1.50	—140.7
C_2H_5OH	0.91	—128.0
$C_6H_{11}OH$	0.53	—235.0

The above figures show, in each case, a strong laevo-rotatory power and also a low solubility in the different solvents. The rotation varies widely with each solvent, and in the case of chloroform, with the concentration.

In connection with the above work on the carbohydrates and a few bases, it was thought of interest to see what influence pyridine would have on some of the active organic acids.

Malic acid

Concentrated aqueous solutions of malic acid are dextro-rotatory, which rotation, however, decreases with elevation of temperature; dilute solutions are laevo-rotatory, which property increases with increase of temperature.

In pyridine, malic acid is readily soluble. Two solutions were made at room temperature, corresponding to 7.62 percent and 14.16 percent malic acid, respectively. Aqueous solutions of the same strength were made, and a comparison of results obtained follows:

Solvent	Percent malic acid	Density	α_D^{26} $l = 2$dcm.	$[\alpha]_D^{26}$
Pyridine	7.62	0.9742	—4.00	—26.92
Water	7.62	0.9996	—0.36	— 2.07
Pyridine	14.16	0.9998	—7.15	—50.06
Water	14.16	1.0256	—0.53	— 1.81

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[1] Oudemans: Liebig's Ann., 166, 76 (1873).

One sees from these values that pyridine has a marked influence in lowering the rotatory power of malic acid. It is also of interest to notice that the lowering is almost directly proportional to the concentration of the solution. In aqueous solution, the reverse order is true. Here the highest laevo-rotatory power is obtained in the most dilute solution, which fact is corroborated by results obtained by other investigators.

G. H. Schneider[1] gives for a 8.32 percent aqueous solution of malic acid, $[\alpha]_D^{20} = -2.30$, and for a 14.35 percent solution, $[\alpha]_D^{20} = -1.73$, which results agree quite closely with those I obtained.

Tartaric acid

Tartaric acid is quite soluble in pyridine, but to a lesser extent than malic acid. A fairly concentrated solution can be obtained, but this, on shaking or heating, will precipitate out a white, spongy mass, the whole solution becoming a sort of quasi-solid. This mass is undoubtedly pyridine tartrate.

Pyridine is a fairly strong base and behaves as such toward acids, forming salts. In the work with the above acids then, we are dealing with the pyridine salts of the organic acids used dissolved in an excess of the solvent, and the results obtained must be interpreted accordingly.

The solubility and rotatory power of tartaric acid in pyridine has been determined by Richard Pribram,[2] whose results can be found in the reference given below.

While working with tartaric acid in pyridine it was thought of interest to study one of its esters and the substance selected was di-*n*-propyl tartrate. The latter substance is a thick, oily liquid, boiling-point 303° at 760 mm. The sample used was considered to be of a high degree of purity, which fact was verified by the determination of its specific gravity and also its specific rotatory power. Upon investigation it was found that the propyl tartrate dissolved in pyridine in all proportions and hence no trouble was encountered in studying its rotatory power in pyridine at different concentrations.

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[1] Liebig's Ann., 207, 257 (1881).

[2] Ber. chem. Ges., Berlin, 22, 6 (1889).

The following table gives the values obtained for solutions containing from 100 to 1/8 percent propyl tartrate in pyridine:

Percent propyl tartrate	Density	α	$[\alpha]_D$
100	1.1302	28.78	12.73
95	1.1220	35.94	16.86
90	1.1177	40.75	20.26
75	1.0996	48.09	31.04
50	1.0588	43.06	40.66
25	1.0163	24.27	47.76
20	1.0064	19.20	47.69
15	0.9999	14.39	47.99
10	0.9904	9.67	48.82
5	0.9822	4.81	48.99
2	0.9771	1.96	50.15
0.5	0.9747	0.51	51.81
0.25	0.9743	0.26	50.29
0.125	0.9740	0.12	50.10

The curve obtained by using the specific rotation as ordinates and the proportion of propyl tartrate in the solution as abscissas is represented in Fig. 1.

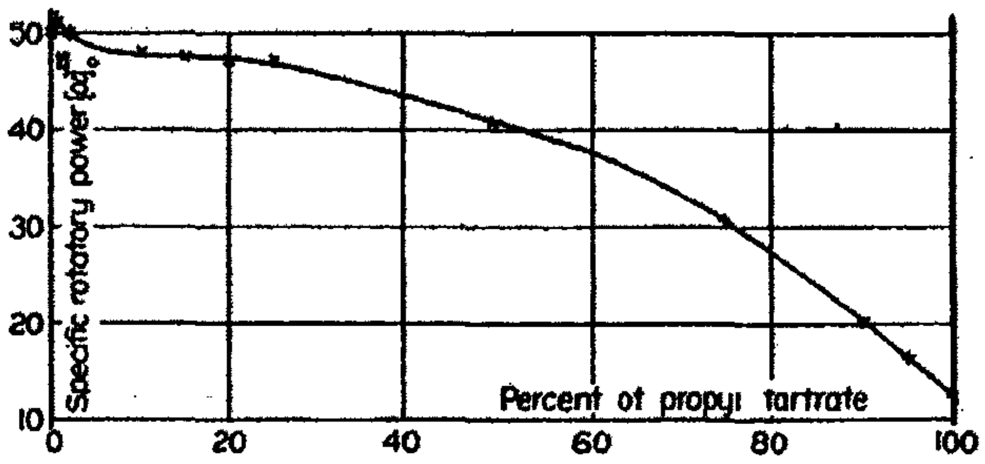

Fig. 1

From this curve we see that the specific rotatory power decreases with increased dilution until a maximum is reached, which point is only obtained when we have a solution containing less than one-half percent propyl tartrate. From this point the drop must be quite sudden, for the pyridine itself is inactive.

The question as to whether the solubility of a substance in a solvent depends upon the size of the solid particles used or not, has received some attention of late. G. A. Hulett,[1] in his work upon the "Relations between Surface Tension and Solubility," has come to the conclusion that the concentration of a solution varies with the size of the solid particles.

It was thought of interest in this connection to see if this was true in the case of cane-sugar in pyridine. A sample of pure rock candy was obtained, ground in a mortar and passed through a series of six sieves representing 6, 12, 40, 80, 100 and 120 meshes per square inch respectively. The different sized samples were then dried for about half an hour at about 100° to expel the moisture and then each placed in a flask containing pyridine and boiled on a paraffine bath for about eight hours. The rotatory power of the different solutions was then determined, but the results obtained were of no special value, for they indicated just the reverse from what we expected. The solutions formed from the coarsest grains were the most concentrated, which undoubtedly was due to the fact that the finest particles on boiling caked more than the coarser ones, thus offering less surface to the action of the solvent. As this method proved impracticable, it was deemed best to proceed, as heretofore explained, by shaking the mixtures of sugar and pyridine at room temperature. The shaking was continued for about forty hours at 26° to insure complete saturation, and the rotatory power was then observed as before. The results obtained showed no difference in the concentration of the solutions, which fact proves that Hulett's theory does not hold good for cane-sugar in pyridine at least.

By the above method I was able to obtain a 6.45 percent solution of sugar in pyridine, a value slightly higher than 6.25 percent, the value obtained by G. M. Wilcox.[2] According to the latter, the rotatory power of cane-sugar in pyridine decreases with increased concentration. This was corroborated by the results I obtained.

Wilcox gives for a 4 percent solution, $[\alpha]_D^{25} = 84.7$, and

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[1] Zeit. phys. Chem., 37, 385 (1901).

[2] Jour. Phys. Chem., 5, 587 (1901).

for a 6.25 percent solution, $[\alpha]^{25}_{D} = 83.6$. For the 6.45 percent solution, I obtained the value $[\alpha]^{26}_{D} = 82.97$, which agrees very closely with the results of Wilcox.

It is a well-known fact that the rotatory power of a substance is dependent upon the nature of the solvent used. If the same amount of an active substance is dissolved in inactive liquids of different nature, the rotatory power assumes different values, depending on the action of the solvent on the dissolved substance. The specific rotation of the substance dissolved may be increased or decreased. Cane-sugar which shows but slight deviations in rotation with reference to concentration and temperature in aqueous solutions shows marked deviation when dissolved in different solvents. Tollens[1] gives the following values for cane-sugar in water, methyl and ethyl alcohols and acetone:

10 parts sugar, 90 parts water, - - - -	$[\alpha]_D = 66.67$
10 parts sugar, 23 parts water, 67 parts ethyl alcohol,	" $= 66.83$
acetone,	" $= 67.40$
methyl alcohol,	" $= 68.63$

By the introduction of various amounts of benzene, carbon bisulphide, acetone, nitro-benzene and chloroform into separate samples of the saturated solution of sugar in pyridine, I obtained the following results:

6.45 grams sugar, 93.55 grams pyridine	$[\alpha]^{26}_{D} = 82.97$
addition of 24.12 grams of benzene	" $= 81.59$
addition of 34.46 grams of carbon bisulphide	" $= 79.59$
addition of 31.42 grams of acetone	" $= 80.92$
addition of 51.10 grams of nitro-benzene	" $= 87.11$
addition of 18.14 grams of chloroform	" $= 88.19$

From these results we see that the addition of each different solvent causes a marked variation in the rotatory power of the solution. The presence of carbon bisulphide, acetone and benzene tend to decrease the rotatory power, whereas nitrobenzene and chloroform increase it to a marked extent. Before a satisfactory explanation of these phenomena can be given,

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[1] Ber. chem. Ges., Berlin, 13, 2303 (1080).

there still remains more work to be done on the nature of solutions.

It seems difficult, however, to explain the observed facts without the assumption of combination of the active substance with these ingredients which so markedly effect the rotatory power.

Summary

The results given in the foregoing pages may be briefly summarized as follows:

The order of solubility of the investigated substances in pyridine, beginning with the most soluble is as follows, the figures indicating parts by weight contained in 100 parts by weight of solution:

Laevulose,	18.49
Malic acid,	14.60
Grape-sugar,	7.62
Cane-sugar,	6.45
Galactose,	5.45
Erythrite,	2.50
Milk-sugar,	2.18
Strychnine,	1.23
Mannite,	0.47

Propyl tartrate not being recorded in the above list stands by itself, it being soluble in all proportions.

It is interesting to note the very great difference in solubility exhibited by malic acid and strychnine. This is hardly surprising, considering the basic and acidic characters of the two substances and the basic nature of the solvent employed.

Saturated solutions in pyridine of cane-sugar, grape-sugar, laevulose and galactose show a greater specific rotatory power than solutions of the same concentration in water. The greatest difference appears in the case of laevulose, while for galactose the difference is very slight. The differences in the case of cane-sugar and grape-sugar are intermediate between the other two mentioned above.

On the other hand, the substances which show a less specific rotatory power in concentrated solutions in pyridine as compared with solutions of same concentration in water are: milk-sugar, mannite, strychnine and malic acid. Of these, the greatest difference appears in the case of malic acid, the difference decreasing with strychnine, mannite and milk-sugar in the order named.

In conclusion, I wish to express my thanks to Prof. Kahlenberg, who has offered so many suggestions and kindly assisted me in the above work.

Laboratory of Physical Chemistry,
University of Wisconsin, Madison, Wis.
June, 1905.

NEW BOOKS

Abhandlungen und Vorträge. *By Wilhelm Ostwald. 15 × 22 cm; pp. x + 468. Leipzig: Veit und Co., 1904. Price: paper, 8 marks.*—"I must confess at the outset that the present collection of my articles and addresses . . . does not, as usual, owe its origin to the persuasion of the author's friends. Rather, now when my part in the development of science is completing a change of direction in its inner and perhaps also in its outer activity, I have felt the need of giving to my colleagues and to myself a sort of justification in this way. And I cannot deny that this is done with some complacency."

Such is Ostwald's frank introduction to this volume of addresses. For addresses they all are; even those that were written to be put into type have unmistakably the quality of spoken appeal. The items of the collection are arranged not chronologically but in groups. There are six on physical chemistry to begin with. The first three of these vividly recall the time when the great protagonist of physical chemistry was fighting for recognition of his subject. This group is followed by a group of five on electrochemistry, and a group of six on energetics and philosophy. The order adopted is the natural one. Ostwald's attempts to make physical chemistry an ordered body of doctrine led of necessity from the more obvious physical chemistry to electrochemistry, with which he concerned himself deeply when the second volume of the second edition of his *Lehrbuch* was writing, and his efforts to give shape to the whole subject naturally led him to reflections on the significance of the energy theory, and to scientific epistemology in general. These three groups are followed by a group of two addresses and one article on technology and economics; and the volume is concluded by commemorative addresses on Ritter, Mitscherlich, Stohmann, Wiedemann, Bunsen, and Wislicenus, with which is included the introduction to the jubilee volume of the *Zeitschrift für physikalische Chemie* that was dedicated to van't Hoff in 1899.

The whole volume is marked by Ostwald's characteristic skill in presenting a subject in the light of its development; and the reader is impressed afresh by the author's marvelous fluency—by the exuberance and connectedness of his style. Presenting, as it does, an interesting phase in the development of physical science, this assemblage of documentary evidence will long remain of extended interest. It is dedicated, "in cordial friendship," to William Ramsay.

J. E. Trevor.

La Statique chimique, basée sur les deux principes fondamentaux de la Thermodynamique. *By E. Ariès. 16 × 25 cm; pp. viii + 251. Paris: A. Hermann, 1904. Price, paper, 10, bound, 13 francs.*—In the moderate compass of two hundred and fifty octavo pages, Lieutenant-Colonel Ariès has supplied an outline of the Gibbsian theory of chemical equilibrium. The subject is treated as a mathematical theory, and accordingly but scant reference is made to experimental results. The treatment is confined to the equilibria of phase-systems under "thermo-elastic" actions, and thus corresponds to the first half of Gibbs's memoir on the equilibrium of heterogeneous substances. The first five of the seventeen chapters develop the general thermodynamic theory of chemical equilibrium, six chapters deal with applications to phase-equilibria, and six are devoted to an exposition of the theory of ideal gases and the theory of dilute solutions.

At the outset the author takes for granted the principles of thermodynamics and their formulation in the equation for the differential of the energy of a body,

$$dU(v, S) = TdS - pdv.$$

The book can thus be read only by students to whom the laws of thermodynamics are familiar. A beginning is made by showing, in considerable detail, that the energy U is a "characteristic function," in the meaning of Massieu, and that the functions

$$U + pv, \qquad U - TS, \qquad U - TS + pv,$$

are characteristic. The statement that these three are the only characteristic functions deducible from $U(v, S)$ is somewhat misleading. It would have been well to have indicated the advantages and disadvantages attaching to the employment of v, S as state-variables. The author next obtains the inequalities deducible from the principle of the dissipation of energy, and announces that the "potential" $U - TS + pv$ is the characteristic function to be exclusively employed in his work. The development of the general theory then proceeds as follows. It is shown that the potential of a homogeneous fluid mixture is a homogeneous function of the first degree in the masses (measured in mols) of the components. The general consequences of this fact are formulated, and the differentials of the four characteristic functions are found. After noting that the number of constituent substances appearing in a system may exceed the number of independently variable components, it is shown that for equilibrium the potential of the system must be a minimum at constant p, T, and the phase rule is obtained and discussed. It is deduced that isothermal increase of pressure decreases the volume of a system, and that isobaric increase of temperature induces absorption of heat, and the Clapeyron-Clausius equation for indifferent states is obtained. Deduction of the conditions that must be satisfied by an indifferent state, discussion of indifference in states of different variance, and determination of the conditions that must be satisfied by critical phases, conclude this part of the work.

The topics treated in Chapters VI to XI, which deal in a general way with applications to phase-equilibria, are the peculiarities of the triple point, the dissociation of $CaCO_3$, H_2Se, and the like, the effect of varying the pressure or the temperature of a two-component system in a two-phase state. equilibrium in systems having but one phase of variable composition, the formation of two or of three liquid layers and the conditions that are satisfied when these layers coalesce in critical phases, and the evaporation of mixtures of volatile liquids.

The four succeeding chapters deal with the theory of perfect gases. The treatment is sketchy. Three pages on the thermodynamics of a single ideal gas are followed by a discussion of the theorem that the entropy of a mixture of perfect gases is additive. The theory of the dissociation of perfect gases is outlined, and is extended to systems in states presenting more than one phase.

Two chapters remain, on dilute solutions and on osmosis. The first of these is a straightforward treatment of the theory of dilute solutions, beginning with Gibbs's formulation of the potential of a solute and proceeding to the generalizations of van 't Hoff and Arrhenius. The second describes osmotic membranes, states that a solvent must have the same molecular potential on each side of an osmotic wall separating solvent and solution, deduces from this the necessity of an osmotic pressure, and comments on the employment of osmotic pressures in the determination of molecular weights.

The book, as a whole, makes a pleasing impression. It treats a definite field, the arrangement of the material is reasonable, and the notation has been intelligently chosen—an important point in a treatise on thermodynamics. As a tolerably clear exposition of an interesting body of theory, the book is well worth reading. *J. E. Trevor*

Leçons sur la théorie des gaz. *L. Boltzmann. Translated by A. Gallotti et H. Bénard. With an Introduction and Notes by M. Brillouin. Seconde Partie. 16 × 25 cm; pp. xii + 280. Paris: Gauthier-Villars, 1905. Price: paper, 10 francs.*—Boltzmann's famous "*Vorlesungen über Gastheorie*" has already become a classic, inasmuch as it sets forth in a most searching manner the claims of the kinetic theory of gases in its older and astonishingly fertile stages of development. Since that time a period of doubt has arisen, beginning perhaps with the researches of Tait, in which even most serious students of the subject, like Burbury, Jeans, Bryan, and others, often fail to understand each other. The present translation of Boltzmann's book will be welcomed by those who have difficulty with German text, particularly so since it has profited by the supervision of M. Brillouin, whose scholarship is acknowledged. He has, moreover, enhanced the value of the book by an introduction and various notes, dealing with the more subtle of the questions at issue.

Boltzmann, as is well-known, insists throughout that the hypotheses of the kinetic theory need not be regarded as realities, but rather as well fitted analogies. Consequences logically drawn from such premises will nevertheless be trustworthy. *C. Barus*

Electrochemie wässeriger Losungen. *By Fritz Foerster. 16 × 25 cm; pp. xvii + 507. Leipzig: Johann Ambrosius Barth, 1905. Price: paper, 20 marks; bound, 21 marks.*—This is the first volume of a series of monographs on applied physical chemistry, edited by Bredig. The object of the series is to present in a clear form what has been done and what remains to be done in the application of physical chemistry to technical chemistry and to the other branches of chemistry. It is clear that this series will be a very interesting one to the physical chemist. Whether it will prove as valuable to specialists in other lines remains to be seen. In the field of applied electrochemistry, for instance, the physical chemist has not yet scored any distinct success. The processes for refining copper, silver, gold, lead and zinc were worked out independently of the physical chemist. The processes for making aluminum, sodium, caustic soda, and potassium chlorate were developed without the physical chemist. The most he can claim is the use of potassium chromate in the electrolysis of chlorides and that was patented by Imhoff before Müller's first paper appeared. It is true that Imhoff had a wrong conception of the way in which potassium chromate acted and that Müller gave the true explanation, but this is of relatively little importance because the technical chemist is more interested in the practical working of a process than in the reason why it works.

This instance illustrates what has been going on in the field of theoretical electrochemistry during the last few years. The technical electrochemists obtained a long start over their academic colleagues and the latter have been kept busy finding out why the former obtained the results they did. The University chemists have had their hands full studying the processes which had been invented by others. Even in the chosen field of the electrolytic reduction of nitrobenzene, they did not really get away from platinum electrodes until the patents obtained by Boehringer and Co. called attention to the interesting results to be obtained with other metals.

All this must be kept in mind when considering the volume by Prof. Foerster. It is really a book telling what physical chemists have learned about applied electrochemistry rather than a book on the application of physical chemistry to electrochemistry. The book is divided into fifteen chapters: electrical energy and direct current; Faraday's law and its practical consequences; theoretical consequences of Faraday's law and the electrolytic dissociation theory; migration of ions; voltage of the bath; resistance of electrolytes; electrical osmose; electrical energy of voltaic cells; general theory of electrolysis; electrolytic precipitation of gaseous hydrogen and oxygen; special electrochemistry of metals; applications of the electrochemistry of metals; electrolytic reduction; special electrochemistry of the halogens; electrolytic oxidation.

The book itself is an admirable one. It is well written, and contains a surprising number of facts. The general point of view is sane, as is the statement in regard to infinitesimal concentrations of ions, p. 107. In spite of the author's remarks, p. 240, most people will continue to believe that the use of the rotating electrode is of great importance in the electrolytic precipitation of metals. *Wilder D. Bancroft.*

Die elektrolytische Chloratindustrie. *By John B. C. Kershaw. 17 × 25 cm.; pp. 123. Halle: Wilhelm Knapp, 1905. Price: paper, 6 marks.*—The author discusses the chemical and electrochemical reactions involved in the electrolytic production of chlorates, his own point of view being substantially that of Foerster. The next chapter is devoted to a description of the various technical processes so far as they can be learned. While some of the statements made here are pretty certainly inaccurate, this is not the fault of the author who has to deduce the process of the National Electrolytic Co., for instance, from an old patent. The next chapter deals with the purification and properties of potassium chlorate, and then comes a chapter on efficiencies and costs. A special chapter is devoted to the preparation of sodium chlorate, of bromates and iodides, and of perchlorates. There is a chapter on the methods of analysis and then comes a list of the patents with extracts from the more important ones.

As the chlorate manufacturers, with the exception of M. Corbin, are personally reticent, the book deals necessarily with the scientific investigations and with the patents. Only one point seems to be fairly certain and that is that every one is using chromate. The author might well have laid stress on the importance of finding a catalytic agent which will accelerate the change of hypochlorite into chlorate. *Wilder D. Bancroft*

Elektrolytische Verzinkung. *By Sherard Cowper-Coles. 17 × 24 cm; pp. 37. Halle: Wilhelm Knapp, 1905. Price: paper 2 marks.*—This little pamphlet gives the methods for coating iron with zinc and discusses the relative merits of hot galvanizing and electro-galvanizing. As the author is the inventor of a process of cold galvanizing, one may rest assured that the case for electrolytic plating with zinc has been put as strongly as possible. *Wilder D. Bancroft*

A Short Introduction to the Theory of Electrolytic Dissociation. *By J. C. Gregory. 12 × 18 cm; pp. 76. New York: Longmans, Green and Co., 1905. Price: $0.50.*—In this little book we find a highly simplified account of the theory of electrolytic dissociation. An introductory chapter discusses the formation of aeriform and liquid solutions, osmotic pressure, electrolysis, electrolytic conductivity, and the freezing and boiling temperatures of solutions. The subsequent chapters consider the ion theory of precipitations, the peculiarities of the behavior of hydrogen and of hydroxyl ions, and, finally, an assemblage of matters—varying the conditions of an electrolysis, step-wise dissociation, the colors of ions, etc. *J. E. Trevor*

Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds. *By Geoffrey Martin. 16 × 24 cm; pp. xii + 287. London: J. and A. Churchill, 1905. Price: cloth, $4.00.*—At the position of each element in the usual arrangement of the periodic table in a plane, suppose erected a perpendicular proportional to the heat of formation of a compound of this element with one given element. A smooth surface passed through the summits of these perpendiculars the author terms the "affinity surface" of the given element. In this construction, the heat of formation of a compound of two elements, when this is large, is taken to be an approximate measure of the mutual affinity of the elements. When the heats of formation are small or negative, the values of the affinities are estimated from the relative stability of the compounds.

In the way indicated, the author has constructed affinity surfaces for a large number of elements. He finds it necessary to draw two surfaces for each element, one with reference to the elements of the odd series, and one with reference to those of the even series. The data used are given, and a number of the surfaces, arranged on the plan of the periodic table, are assembled in a large plate.

It is observed that in each row of surfaces corresponding to a row of the table, the successive surfaces represent successive positions of an advancing wave, that in consequence the surfaces for the elements of a given family have similar forms, and that the surfaces for the alkali metals are fairly symmetrical, with respect to a vertical plane, with those for the halogens. The text includes an extended commentary on these observations. *J. E. Trevor*

Lehrbuch der Physik. *By O. D. Chwolson. Dritter Band. Die Lehre von der Warme. Uebersetzt von E. Berg. 15 × 23 cm; pp. xi + 988. Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, 16, half leather, 18 marks.*—The preparation, from the original Russian, of the German translation of Chwolson's extensive treatise on physics proceeds apace, three of the four volumes having appeared during the past three years. The present volume is on heat. It treats the elements of this subject in the usual order, considering successively thermometry, calorimetry, the conduction of heat, and thermodynamics. Theory, experimental methods, and experimental results are all copiously considered, and extensive references to the original literature are given. In the theoretical work calculus is employed wherever it is called for. The treatise aims to give an account of the present state of knowledge of physics, rather than to envisage this knowledge from certain particular points of view. This is presumably what Ostwald meant when he characterized the work as written "in a more modern sense" than any other known to him. The German text of the translation reads smoothly. The size of the book, the volumes averaging nearly a thousand large octavo pages each, will probably militate against its extensive use by American students. *J. E. Trevor*

A Scheme for the Detection of the More Common Classes of Carbon Compounds. *By Frank E. Weston. 14 × 21 cm; pp. viii + 56. New York: Longmans, Green and Co., 1904. Price: $0.75.*—After eight pages of "preliminary observations"—melting-point, boiling-point, detection of halogens, of nitrogen, of sulphur and phosphorus, inflammability, and behavior with eight reagents—the author divides the substances to be tested for into ten classes according to the elements present. To each of these groups a section of the book is allotted, where they are subdivided, and the reactions of typical members are described in detail.

The explanatory descriptions of what occurs in the experiments are far too full for a students' laboratory text, but for other purposes—notably for the use of physical chemists whose training in organic chemistry is deficient—the book may prove useful.

By some oversight, no doubt, the author's manifest obligations to Noyes and Mulliken's "Class Reactions and Identification of Organic Substances" have not been acknowledged. *W. Lash Miller*

Die Denkmittel der Physik. Eine Studie. *By Kurt Bertels. 15 × 23 cm.; pp. 71. Berlin: Mayer und Müller, 1905. Price: paper, 1.60 marks.*—Half of this book is superscribed "The Form of the Atoms," the other half "Substance and Motion." The writer cannot readily give the upshot of it more fairly than by quoting a few words from the author's conclusion. "Science cannot be sufficiently anthropomorphic, . . . in the sense of the view that all our knowledge is developed from the conditions of our knowing, and that all science is nothing but simplification and control of human experience. . . . There are no valid laws. In the definition of law lie two unprovable assumptions: first, that chronologically distant experiences of the same man can be equal to each other; and second, that different men can have the same experiences. So we know only approximations to supposed laws." *J. E. Trevor*

NAME INDEX

To Papers and Reviews

NAME INDEX

To New Books

SUBJECT INDEX

Exclusive of New Books