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CONTENTS OF VOLUME VI

1. JANUARY

2. FEBRUARY

3. MARCH

4. APRIL

5. MAY

6. JUNE

7. OCTOBER

8. NOVEMBER

9. DECEMBER

INSTANTANEOUS CHEMICAL REACTIONS AND THE THEORY OF ELECTROLYTIC DISSOCIATION

BY LOUIS KAHLENBERG

In a previous article on the theory of electrolytic dissociation,[1] I have briefly discussed the fact that the chemical reactiveness of electrolytes has been urged as a support of that hypothesis. In view of the wide-spread idea that instantaneous chemical action, if not all chemical action, is dependent upon ions, the products of so-called electrolytic dissociation, I concluded to subject this question to further experimental investigation.

The question that I sought to answer primarily was, Can instantaneous chemical reactions causing precipitation by double decomposition (comparable, for instance, with the precipitation of silver chloride in aqueous solutions according to the equation, $AgNO_3 + HCl = AgCl + HNO_3$) take place in solutions that are *excellent insulators?* To investigate this question, hydrocarbons were naturally chosen as the best solvents known for the purpose in hand. Benzene was used as the solvent, though a few preliminary experiments indicated that petroleum ether, or toluene would have served equally well. The benzene used was of the very best crystallizable, thiophene-free variety of Kahlbaum's manufacture. The benzene was allowed to stand for days over phosphorus pentoxide, after which it was redistilled from this dehydrating reagent. It was finally kept standing over metallic sodium. The electrical conductivity of this benzene was then tested. As it is impossible to estimate by means of the Kohlrausch method the electrical conductivity of substances of such enormous resistance, another plan was adopted. It was briefly as follows: What was practically an Arrhenius resistance cell with the plates less than a millimeter apart, was

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[1] Bull. Univ. Wis., Science Series, 2, 297; also Jour. Phys. Chem. 5, 339 (1901).

placed in circuit with a sensitive galvanometer and a direct current dynamo, generating a pressure of 110 volts. The dynamo was a large machine used to furnish light and power; and besides the resistance in the cell above mentioned, there was no resistance in the circuit, except the low resistance of the galvanometer and the necessary connecting copper wires. Before using, the cell was in each case dried by heating, as were all containing vessels used in these experiments. When the cell contained air, only a slight movement of the galvanometer needle could be noted on closing the circuit. On placing the benzene in the cell and closing the circuit, the deflection of the galvanometer needle was somewhat less than when the cell simply contained air. The benzene then conducted less than air. This experiment was repeated at various times with always the same result. In view of the facts found, I did not consider it necessary for my purpose to attempt to measure exactly the specific conductivity of the benzene.[1]

In seeking suitable solutes to be used in benzene some difficulties were experienced; these need not be recounted here, as they were mainly due to the fact that most salts of metals are practically insoluble in hydrocarbons. It was finally found, however, that certain oleates of the heavy metals, namely those of copper, iron, and manganese are soluble in hydrocarbons, a fact discovered by Schön.[2] It might be added at once that the oleates of cobalt and nickel are also soluble in benzene and petroleum ether. I could not find the latter salts described in the literature, and hence concluded that they have probably not been prepared heretofore. In this investigation the oleates of copper, nickel, and cobalt were used. These salts were prepared

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[1] An idea of the sensitiveness of the method employed may be obtained from the following: With twelve large storage batteries (i. e., a pressure of 24 volts) instead of the dynamo, and pyridine of specific conductivity of less than 10^{-7} reciprocal ohms in the cell a deflection of thirty scale divisions was noted. With a pressure of 110 volts and air in the cell, a deflection of about one-half of a scale division was observed; when benzene was placed in the cell, the deflection was scarcely more than a third of a division.

[2] Liebig's Annalen, 244, 266 (1888).

by heating pure oleic acid with the calculated quantity of standard solution of sodium hydroxide (prepared from metallic sodium), and then adding to the sodium oleate solution thus formed, a slight excess of the sulphate of the heavy metal, the oleate of which was desired. The precipitations were made at room temperature. The precipitate was in each case thoroughly washed with water and finally carefully dried in an oven at 110 degrees.

The general characteristics of the oleates of copper, iron, and manganese are given by Schön. The oleate of nickel is a green, amorphous, resinous solid at ordinary temperatures. Cobalt oleate is also an amorphous, resinous solid; it has a dark red color, which turns brown when the salt is heated above 120°, probably because of decomposition. After the oleates of copper, nickel and cobalt were prepared and dried as above described, they were analyzed by careful ignition in a crucible and subsequent reduction with hydrogen. The results obtained were as follows: 3.3315 g copper oleate yielded 0.3337 g Cu, or 10.02 percent Cu; for $Cu(C_{18}H_{33}O_2)_2$ the theory requires 10.16 percent. 5.5671 g nickel oleate yielded 0.5240 g nickel, or 9.41 percent Ni; for $Ni(C_{18}H_{33}O_2)_2$ theory requires 9.46 percent. 3.9200 g cobalt oleate yielded 0.3834 g Co, or 9.77 percent; for $Co(C_{18}H_{33}O_2)_2$ theory requires 9.51 percent.

The oleates of copper, nickel and cobalt are readily soluble in benzene even at room temperatures. The solution of the copper salt is greenish blue: that of the nickel salt is green; and that of the cobalt salt is dark red. The colors of these solutions are then similar to the colors of salts of the corresponding metals in aqueous solutions. On heating the dark red solution of cobalt oleate in toluene, the solution turns blue, and on cooling, it again becomes dark red; this behavior is then exactly like that of cobaltous salts in aqueous solutions. When the electrical conductivity of these solutions was tested by the rigorous method above described, it was found that they do not conduct better than pure benzene. The solutions thus tested were about five percent strong. Metallic sodium does not precipitate the heavy metals from the solutions of these oleates in benzene;[1] indeed the solutions were allowed to stand over metallic sodium so as to insure their thoroughly anhydrous condition. A copper oleate solution was allowed to stand over metallic sodium for weeks, without the least change taking place. This was shown by the fact that no copper appeared on the sodium, and that when the sodium was taken out of the solution, washed carefully with benzene and dissolved in water, not a trace of copper sulphide could be detected on saturating the carefully neutralized solution with hydrogen sulphide. I wish in this connection to call particular attention to the well-known fact that a freshly cut surface of metallic sodium gradually turns pinkish in color even when kept under a thoroughly dehydrated hydrocarbon, — benzene or petroleum ether, for instance. In performing the experiment of placing metallic sodium in a solution of dry copper oleate in dry benzene the slight pinkish hue that the freshly cut surfaces of the metal assume after a time, must not be mistaken for copper. Magnesium, aluminum and zinc have been kept in a copper oleate solution for weeks without in the least changing their appearance and luster. It is abundantly proved then by physical and chemical tests, that these oleates in benzene are not electrolytically dissociated. In the case of the oleate of copper, I made molecular weight determinations in benzene by the cryoscopic method; the results are given in Table I.

TABLE I.

Copper oleate	Benzene	Lowering	Mol. wt.
0.6788	13.54	0.107	2342
1.3805	18.45	0.152	2463

Mr. Walter D. Patton made boiling-point determinations of solutions of copper oleate in benzene. His results are given in Table II.

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[1] If a little water is added to the solution, the sodium is acted upon with evolution of hydrogen and becomes coated with a slimy precipitate, probably consisting of a little sodium oleate (which is practically insoluble in benzene) and hydroxide of the heavy metal.

TABLE II.

Copper oleate	Benzene	Rise	Mol. wt.
0.5551	11.52	0.050	2563
1.0683	11.52	0.090	2750

The theoretical molecular weight of copper oleate is 625.6. The results in Tables I. and II. would, according to the current interpretation of such cases, show that copper oleate is polymerized in benzene solution.

A solution of dry hydrochloric acid gas in the thoroughly dehydrated benzene above described was next prepared. The hydrochloric acid gas was evolved by dropping the concentrated aqueous solution into concentrated sulphuric acid. The gas was further dried by passing it through concentrated sulphuric acid, and finally through a large tower filled with pieces of dry pumice covered with phosphoric anhydride. The electrical conductivity of such a solution of dry hydrochloric acid in dry benzene is no better than that of the benzene itself. The dry carbonates of sodium, calcium (calcite), and barium (witherite), placed in such a solution, are not in the least attacked. Bright magnesium ribbon is not acted upon. Zinc, however, is acted upon,[1] hydrogen being evolved; and this takes place whether the zinc is amalgamated or not; and with about the same rate, judging roughly from the rapidity of the evolution of the hydrogen. The zinc was of the very purest zinc wire of Merck's manufacture. A piece of platinum placed in contact with the zinc under the solution of hydrochloric acid in benzene in no way affected the evolution of hydrogen; the latter always appeared on the zinc, not on the platinum. A dilute aqueous solution of hydrochloric acid appeared to act rather less readily on the amalgamated zinc wire than did the solution of hydrochloric acid gas in benzene on an amalgamated sample of wire of the same piece; but the moment the wire in the aqueous solution was placed in contact with a

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[1] Compare in this connection the interesting observations of M. Gomberg (Amer. Chem. Jour. 25, 324 (1901)) and those of other observers to whom he refers.

scrap of platinum under the solution, hydrogen was very copiously evolved, almost entirely on the platinum.[1] It is well-known that in the last-named experiment the solution of the zinc is accompanied by a current of electricity through the metals and the solution, and that the chemical action is much more vigorous in consequence. On the other hand it is clear that zinc decomposes dry hydrochloric acid in dry benzene, and this apparently goes on without a concomitant electric current; for a piece of platinum in contact with the zinc does not affect the evolution of hydrogen in the benzene solution, as it does in the aqueous solution. Again, contact with platinum or other metals does not cause magnesium to be acted upon by the hydrochloric acid solution in benzene. Iron, nickel, cobalt, copper and cadmium are not attacked by a solution of hydrochloric acid in benzene; tin and aluminum are slightly acted upon; lead very slightly. Mercury, silver and, of course, gold and platinum are not acted upon. These statements hold, whether the metals are in the solution by themselves or in contact with other metals; in fact no visible effect was caused by contact with other metals. Metallic sodium is fairly rapidly acted upon by the benzene solution of hydrochloric acid. The chlorides of the metals acted upon are practically insoluble in benzene; they appear on the metals as a white coating after the action has gone on for a sufficient length of time. The coating around the sodium had a milky gelatinous appearance after the action had gone on for twelve hours. A perfectly bright globule of the metal remained unchanged after being thus coated over.

I wish to state emphatically in this connection, that in obtaining the above results extraordinary precautions were used to guard against the presence of any traces of moisture. A train was used consisting of a hydrogen generator connected with the usual purifying solutions and a final wash-bottle containing concentrated sulphuric acid; the latter was attached to the hydro-

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[1] This is the well-known experiment which, in slightly modified form, Ostwald cites to illustrate what he calls chemical action at a distance.

chloric acid generator consisting of a flask containing concentrated sulphuric acid, into which concentrated hydrochloric solution could be dropped by means of a separating funnel. The hydrochloric acid gas generator was connected with a wash-bottle of concentrated sulphuric acid, and the latter with a tower (40 cm high and 6 cm in diameter) filled with pieces of dry pumice covered with phosphorus pentoxide.[1] This tower was connected by a glass tube with the small flask containing the benzene and substance to be tested. This flask was fitted with an excellent doubly perforated rubber stopper, and was in turn connected by a glass tube to another large tower filled with pumice covered with phosphoric anhydride. Before introducing the benzene and the dry substance to be tested into the flask, the latter, as well as its stopper and connecting tubes, was heated to drive off moisture; and while these parts were still fairly hot, the benzene and substance[2] to be tested were quickly introduced and the whole at once connected with the train. The air was then displaced with dry hydrogen; and finally, the hydrogen generator was cut off by means of a cock and the hydrochloric acid gas was slowly evolved until the train was saturated. In making the precipitations with dry hydrochloric acid by passing the gas into the oleate solutions in benzene, the same train and the same precautions were used. These precipitations will now be described.

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[1] In these towers plugs of dry cotton were used to prevent any of the fine particles of phosphorus pentoxide from being carried away.

[2] The method of drying the benzene has been given above. The metals were cleaned with emery cloth (a new, fresh piece being used for each) and gently heated before introducing them into the benzene, except in the case of sodium and magnesium. The magnesium ribbon was simply thoroughly cleaned with emery cloth; on account of the peculiar behavior of this metal toward hydrochloric acid in benzene, several samples of magnesium ribbon of different makes were used, but always with the same result. A sample of Schuchardt's best zinc was also employed in addition to the sample from Merck; but like the latter sample, it was attacked invariably. The sodium was cut under dry benzene and introduced very quickly into the flask. The carbonates were gently heated; the sodium carbonate was prepared by fusing sodium bicarbonate in a platinum dish. The substances heated were, of course, introduced into the benzene while still hot.

When dry hydrochloric acid gas is passed into a solution of copper oleate in benzene, there is formed *instantly* a heavy brown precipitate which is cupric chloride. The reaction that takes place may be written thus: $Cu(C_{18}H_{33}O_2)_2 + 2HCl = CuCl_2 + 2C_{18}H_{34}O_2$. We have here then, a case of instantaneous precipitation by double decomposition which is perfectly comparable with that of the formation of silver chloride in aqueous solutions, when silver nitrate solution is treated with hydrochloric acid. I wish to emphasize again that these benzene solutions conduct no better than benzene itself. Even at the instant of the formation of the precipitate, there is not the least perceptible increase in the conductivity. I tested this by placing a copper oleate solution in the resistance cell with dynamo and galvanometer in circuit and then quickly pouring into the cell a saturated solution of dry hydrochloric acid in benzene. The precipitate formed instantly, but the galvanometer showed no change. The oleates of nickel and cobalt, when treated in benzene solutions with dry hydrochloric acid, react in a perfectly analogous manner. The precipitate from the nickel oleate solution is brownish yellow; that from the cobalt solution is blue. It is hardly necessary to add again, that in these cases too the solutions are most excellent insulators.

These freshly precipitated chlorides of copper, nickel and cobalt are generally contaminated with oleic acid, which adheres to them, especially if the solutions used are stronger than two or three percent. It is moreover very difficult to wash out this adhering oleic acid with benzene. If the precipitation is made in sufficiently dilute solutions, the amount of adhering oleic acid is slight, and may be washed out with benzene, as the following quantitative experiments show. 4.4510 g copper oleate were dissolved in 200 cc benzene. The solution was saturated with dry hydrochloric acid gas; the precipitate formed was filtered off on a dry weighed filter and washed repeatedly with benzene. The filtrate was shaken up with water and the mixture saturated with sulphuretted hydrogen; there was no precipitate of copper sulphide, showing that precipitation in the benzene solution had been complete. The precipitate and filter were weighed after being dried in the oven and cooled in a desiccator. The weight of the $CuCl_2$ was 0.9625, corresponding to 0.4553g Cu, or 10.22 percent; the previous analysis yielded 10.02 percent; theory requires 10.16 percent. The copper chloride was a brown powder, soluble in water; on evaporating the aqueous solution the characteristic crystals of $CuCl_2 + 2H_2O$ were obtained. 4.9376g nickel oleate were dissolved in 200 cc benzene and treated as just described. The yield was 1.0579g $NiCl_2$, corresponding to 0.4803g Ni, or 9.73 percent Ni; the previous analysis yielded 9.41 percent; theory requires 9.46 percent. The brownish yellow chloride was still a trifle gummy, indicating that the adhering oleic acid had not all been washed out. 4.8793g cobalt oleate were dissolved in 200 cc benzene, and the solution treated as described above. The yield was 1.0275g $CoCl_2$, corresponding to 0.4669 g Co, or 9.57 percent; previous analysis yielded 9.77 percent; theory requires 9.51 percent. The blue powder was quite free from oleic acid, and dissolved in water with characteristic color. The filtrates from the chlorides of nickel and cobalt were shaken up with water; the mixture was made alkaline with ammonia and then saturated with hydrogen sulphide. No precipitate was formed, indicating that in these cases too the precipitation in the corresponding benzene solutions had been complete.

Anhydrous stannic chloride is a most excellent insulator; it was found that its conductivity is no better than that of air. Two samples, one from Kahlbaum, the other from Schuchardt, showed practically the same behavior; these samples were in very securely closed, small glass stoppered bottles, and when it was found that the liquids had such enormous resistance, no further attempts to dehydrate them were made. Stannic chloride mixes with benzene in all proportions, and such mixtures were found to conduct no better than benzene alone. In testing the conductivity, the method above described was used in all cases. When a solution of anhydrous stannic chloride in benzene is poured into a solution of copper oleate in the same solvent, there forms *instantly* a heavy brown precipitate which is principally anhydrous cupric chloride. The reaction then may be written: $2Cu(C_{18}H_{33}O_2)_2 + SnCl_4 = 2CuCl_2 + Sn(C_{18}H_{33}O_2)_4$. The precipitate clings tenaciously to some of the stannic oleate, which it drags down with it; and it is, moreover, extremely difficult to free the precipitate from the adhering oleate by repeated washing with benzene, because of the sticky, gummy nature of the precipitate. A dilute solution (about one percent) of copper oleate in benzene was treated with a slight excess[1] of a dilute solution of stannic chloride in the same solvent. The precipitate was filtered off and washed repeatedly with benzene. However, it always remained gummy. It was dried in the oven to remove adhering benzene. 0.5640 g of this precipitate was treated with water. By far the larger portion dissolved, yielding a blue solution. The latter was finally boiled; and the floating oily pellicle was filtered off and washed with hot water. This oily pellicle was examined further. It proved to consist of oleic acid and tin. A quantitative estimation of the latter was not made, because the sample was hardly large enough to warrant the attempt. The blue aqueous filtrate was precipitated with silver nitrate solution. The silver chloride obtained weighed 0.9064 g, corresponding to 0.2241 g chlorine. The copper, in the filtrate from the silver chloride, was determined as oxide. The yield of the latter substance was 0.2480 g, corresponding to 0.1982 g copper. According to the formula $CuCl_2$, 0.2241 g chlorine correspond to 0.2010 g copper. The filtrate from the first precipitate, formed by adding stannic chloride to copper oleate in benzene, was evaporated and finally carefully heated to 114° to expel stannic chloride; during this process the substance turned darker and possibly suffered slight decomposition. The residue was a dark, thick oily mass at room temperature. 2.5778 g of it was carefully ignited in a crucible, and the residue was evaporated repeatedly with concentrated nitric acid, and finally strongly ignited. The SnO_2 thus obtained was white (showing

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[1] It was found that the calculated quantity did not give complete precipitation of the copper.

that the precipitation of the copper had been complete) and weighed 0.2535 g, corresponding to 0.2004 g Sn, or 7.8 percent Sn; the formula $(C_{18}H_{33}O_2)_4Sn$ requires 9.5 percent Sn. The tin found was then 1.7 percent too low for stannic oleate. The latter salt has to my knowledge not been prepared heretofore. It is clear then that the reaction of stannic chloride on copper oleate in benzene solution is not what is commonly called a "smooth" reaction; but the results are sufficient to show that it takes place in the main according to the equation above given.

Phosphorus trichloride, arsenic trichloride and silicon tetrachloride, obtained anhydrous in well-secured containers from Schuchardt, were found to be miscible with benzene in all proportions. The solutions thus formed were tested and they proved to be insulators like the solution of $SnCl_4$ in benzene. Yet in each case when a solution of copper oleate in benzene is treated with a solution of PCl_3, $AsCl_3$, or $SiCl_4$ in the same solvent, copper is precipitated in form of a dark brown precipitate. The precipitate is essentially cupric chloride; but it is in each case contaminated with some of the oleate, as in the case where $SnCl_4$ is used as precipitant. Oleates of phosphorus, arsenic and silicon have apparently not been prepared heretofore; it will be interesting to see whether such compounds are stable enough to permit them to be isolated. The complete analysis of some of these precipitates and analogous ones from other oleate solutions, notably those of the oleates of nickel, cobalt, manganese and iron, has been undertaken by Mr. A. A. Koch, Assistant in Analytical Chemistry at this University. He will in due time report the results of his investigations.

We see then that HCl, $SnCl_4$, PCl_3, $AsCl_3$ and $SiCl_4$ each precipitate cupric chloride[1] from benzene solutions of copper oleate. This is parallel to the fact that in aqueous solutions soluble chlorides precipitate silver chloride from silver nitrate solutions; and yet none of the above-named benzene solutions

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[1] If a little water is added to such precipitates, they turn greenish in color; in sufficient water the cupric chloride of course dissolves.

are electrolytes. If we were to attempt to apply the terminology of the theory of electrolytic dissociation, we should have to say, — in benzene solutions the reagent for cupric ions is the chlorine ion; but clearly this would be absurd, for these benzene solutions are non-conductors, i. e., they contain no ions.

The solubility of these precipitates is also clearly diminished, as in the case of aqueous solutions of electrolytes, by adding the precipitant in excess. This was noted in particular when a solution of copper oleate was treated with just the calculated quantity of $SnCl_4$, the precipitation was not quite complete; but on adding more of the precipitant the supernatant liquid became clear. We have here then in solutions that are most excellent insulators, all the well-known phenomena of precipitation as they occur in the case of ordinary salts in aqueous solutions.

When hydrogen sulphide, dried over fused calcium chloride and finally over phosphorus pentoxide, is passed into benzene solution of the oleates of copper, nickel and cobalt (these solutions were dried as above described), the sulphides of heavy metals are at once thrown down. If these oleate solutions in benzene are first saturated with hydrochloric acid, so as to precipitate the chlorides, and then saturated with dry hydrogen sulphide, the sulphides of the heavy metals do not form; a slight darkening seemed to take place in the case of the copper. Stannic chloride dissolved in benzene was treated with dry hydrogen sulphide in large excess without any visible formation of sulphide of tin; however, on standing over night a copious precipitate did form. Arsenic trichloride dissolved in dry benzene, showed similar reluctance toward forming a precipitate with dry hydrogen sulphide; when petroleum ether was used as solvent the sulphide of arsenic formed almost instantaneously. The petroleum ether was dried by the same method as the benzene.

In his book on the theory of electrolytic dissociation, H. C. Jones has compiled a list of experiments which show that water is necessary that certain reactions may take place. I wish to state definitely that I have no inclination to call any of the results of these experiments into question;[1] but it is unfortunate that in compiling Hughes' experiments, Jones should have omitted the one[2] that shows definitely that dry hydrochloric acid *does* react with dry manganese dioxide. It has been shown by Hughes[3] that dry hydrochloric acid gas does not decompose the carbonates of calcium and barium; I have stated above that these carbonates are also not decomposed by hydrochloric acid in benzene solution. Hughes has also found that dry hydrochloric acid will not react with dry ammonia; this fact I have fully confirmed, and I wish to add, that this is the only case in which I attempted to confirm the experiments of Hughes, or the others listed by Jones. Yet when anhydrous benzene is treated with hydrochloric acid dried over sulphuric acid and finally over phosphorus pentoxide, and then ammonia (evolved by heating lime mixed with ammonium chloride, and dried by passing through a tower of lime and one of dry pumice covered with phosphorus pentoxide) is passed into the solution, a white bulky precipitate of ammonium chloride at once forms; the benzene vapors, moreover, are sufficient to cause the reaction to take place. In these experiments a train like that described above was used. It was slightly altered, so that the hydrochloric acid gas generator could be cut out after the train had been saturated with the gas, and then the ammonia generator turned on so as to saturate the train with ammonia. Neither the solution of hydrochloric acid gas in benzene, nor the solution of ammonia in benzene, nor the mixture of the two, conduct better than benzene itself; nor is there any change in the conductivity at the instant of mixing the

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[1] A word of explation concerning one of Hughes' experiments must be given here. The latter says (Phil. Mag. 35, 533 (1893)), and I quote in full, "An 'inactive' solvent, such as anhydrous ether in one case and benzene in another, was taken, and silver nitrate dissolved in it by warming. Through the solution a current of dry HCl gas was passed. For some time no change could be observed, and even after an hour only a very slight turbidity was produced." This is readily explained by the fact that dry silver nitrate is practically insoluble in dry benzene as well as in dry ether, even on boiling, a fact of which I have assured myself.

[2] Phil. Mag. 35, 533 (1893).

[3] Ibid. 34, 117 (1892).

solutions. Again when anhydrous pyridine (dried for half a year with fused caustic potash, so that even the sharpest edges of the latter did not suffer the least change) is mixed with benzene, a solution is formed that conducts no better than benzene itself. Yet when such a solution is mixed with a solution of hydrochloric acid in the same solvent, there forms instantly a heavy white precipitate of the hydrochloride of pyridine. Dilute as well as strong solutions will show these phenomena.

That we can have instantaneous chemical reactions in solutions that are most excellent insulators, just as we have them in solutions that are electrolytes, is hereby established; and therefore, whoever claims that the instantaneous chemical changes in aqueous, or other conducting solutions, take place because of the fact that these solutions are electrolytes (or in current phraseology, because they contain ions), must assume the burden of proving his proposition.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
Dec. 1901.

INORGANIC FERMENTS

BY D. MCINTOSH

Colloidal solutions of metals have been known and studied for many years.[1] These solutions, always obtained by chemical means, by the reduction of salts of various metals by sugar, aldehyde, etc., were invariably contaminated by the reducing agent. Bredig,[2] in the last few years, by "sparking" metals underneath the surface of water, succeeded in obtaining pure colloidal solutions.

Solutions of platinum and gold have been studied by Bredig[3] and his pupils, and found to act in many ways, like platinum black and the various organic ferments; that they aided reactions in the same way, and in general had their properties destroyed by the same substances. From these considerations Bredig adopted the name inorganic ferments.

Of the reactions influenced by these colloidal solutions, the principal ones studied have been the decomposition of hydrogen peroxide and the union of hydrogen and oxygen.[4] The results obtained show that the first reaction is hastened by alkalies, while substances, such as hydrocyanic acid and mercuric chloride, retard it, and in two-thirds of the cases investigated, there is a marked analogy between the action of blood and colloidal platinum. The union of hydrogen and oxygen by means of colloidal platinum, was found to be governed by nearly the same conditions as the decomposition of hydrogen peroxide, the only nota-

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[1] Carey Lea. Phil. Mag. (5) 31, 238, 320; Amer. Jour. Sci. (3) 37, 476; 38, 47; 41, 179. Barus u. Schneider. Zeit. phys. Chem. 8, 278 (1891).

[2] Zeit. angew. Chem. 1898, 951; Zeit. Elektrochem. 4, 514, 547 (1898).

[3] Bredig u. Müller von Berneck. Zeit. phys. Chem. 31, 258 (1899). Bredig u. Ikeda. Ibid. 37, 1 (1901). Bredig u. Reinders. Ibid. 37, 323 (1901). Bredig. Anorganische Fermente, Leipzig, 1901.

[4] Loc. cit. and Ernst. Zeit. phys. Chem. 37, 448 (1901).

ble exception being the retardation of the reaction by electrolytes, such as sodium hydroxide and potassium sulphate, while in the other case they hasten the decomposition or have no influence.

Professor Bredig having discovered that colloidal silver in alkaline solution decomposed hydrogen peroxide, at his suggestion I undertook the investigation of the reaction. For the subject as well as for advice, I desire to express my sincere thanks.

Colloidal silver solution

This solution has been described by Bredig.[1] It is prepared by "sparking" pure silver wires underneath the surface of water kept cool by ice. With a current of 10 or 12 amperes and a potential difference of 30 volts, the silver is soon divided into extremely fine particles, which pass readily through filter-paper. These particles are too small to be distinguished by the microscope, and give a deep brown or black color to the liquid, so that when placed in a ten centimeter tube, the light from a powerful sodium lamp is quite cut off. The water used in making this preparation changed its conductivity from $2 \cdot 2 \cdot 10^{-6}$ (Ostwald units) to 40 or 60 times this value.

The silver is slowly precipitated from this solution at ordinary temperatures, more quickly by heat and salts. A solution when new containing 0.084 g per liter, held only 0.053 g after standing five months. Two solutions containing 0.025 g and 0.011 g contained after seven months 0.013 g and 0.005 g respectively.

The amount of silver in solution was determined by taking from 50–200 cc, evaporating it to a few centimeters with nitric acid in a porcelain dish, cooling and titrating with potassium thiocyanide, using ferric alum as indicator. The probable error in these determinations is large, since the silver is present in such small quantities, and in extreme cases might reach 10 percent.

There seems to be a limit to the amount of silver held in solution, and in no case was a solution found with more than 1

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[1] "Anorganische Fermente," Leipzig, 1901.

gram-atom, which is about the limit of solution of colloidal platinum.[1]

The concentrations of some of the solutions used are given in Table I.; weaker solutions were prepared from these by addition of the so-called conductivity water.

TABLE I.

Number of preparation	Liters containing 1 g atom of silver
1	1060
2	1000
3	1300
4	1700

In its colloidal form the metal is only slowly soluble in nitric or sulphuric acid. When permanganate is added the solution is instantaneous and the permanganate is decolorized so that the silver can be sharply titrated. Numbers are given in Table II. for titration with potassium permanganate in presence of sulphuric acid. There seems to be no simple formula to express the reaction.

TABLE II.

Amount used	Silver solution (strength)	Titre. $n/100$ $KMnO_4$
100 cc	1/1060 N	8.0 cc
100 cc	1/1000 N	8.5 cc
100 cc	1/2000 N	4.3 cc

Hydrogen peroxide

The hydrogen peroxide was obtained from the 3 percent commercial by several methods, and the electrical conductivities after decomposition were taken as indicative of its purity. In the first method, due to Bredig, the hydrogen peroxide was distilled under a pressure of 50 mm till only a small part remained. The distillate was made alkaline by barium hydroxide to precipitate sulphuric acid, and the excess of barium hydroxide pre-

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[1] Zeit. phys. Chem. 31, 273 (1899).

cipitated by carbonic acid. After filtration the liquid was distilled under diminished pressure, the first portion being rejected. The product had a conductivity of 20.10^{-6}, while that of the impure solution was 2000.10^{-6}.

Purification by two distillations, the last with a little barium hydroxide, was tried. The hydrogen peroxide had a conductivity of $12-13.10^{-6}$, but the yield was small.

Better results were obtained by fractionating the distillates. By diluting solutions twenty times as strong as necessary with good water, one obtained hydrogen peroxide with a conductivity of 25.10^{-6}. All solutions used in the experiments with silver had conductivities under 30.10^{-6}.

Method of measurement.

The determination of the catalytic power of the silver solutions was with a few exceptions, to be mentioned later, carried out in a bath whose temperature was kept at 25° $\mp$ 0.1 by means of a thermostat. An attempt to measure the rate of decomposition by means of the liberated oxygen, failed on account of the supersaturated solutions of oxygen formed. In general 20 cc of hydrogen peroxide were placed in a small Erlenmeyer flask purified by steam, tightly corked and immersed in the bath. When the liquid had reached the temperature of the bath, portions of silver (or silver and alkali) warmed to 25°, were added. Then at regular time intervals 2–5 cc were pipetted out, run into dilute sulphuric acid containing a little manganese sulphate to hasten the reaction, and titrated with *n*/100 potassium permanganate. Only a little manganese sulphate should be present, since with alkaline solutions manganese dioxide is formed, which rapidly decomposed hydrogen peroxide, causing large errors in titration.

The silver may decompose hydrogen peroxide according to the equation $2H_2O_2 = 2H_2O + O_2$, a bimolecular reaction, or the reaction may be $H_2O_2 = H_2O + O$, a monomolecular one, as with colloidal platinum. The results with silver are given in Table III. Under $A - x$ the number of cubic centimeters used in the titration; under 0.4343 *K* the results calculated as a monomolecular reaction, and under *K* the results as a bimolecular reaction.

(The good constant obtained in III. is probably accidental, as many other experiments gave results no more satisfactory than I. and II.)

TABLE III.

Silver 1/2340. H_2O_2 1/32. One day old

Time (in minutes)	A − *x*	0.4343 K	*x*	K
		1		
0	25.95	—	0	—
3.08	19.6	0.017	6.35	0.0040
5.33	16.0	0.017	9.95	0.0045
9	12.6	0.017	13.35	0.0045
14	9.5	0.014	16.45	0.0047
19	7.7	0.012	18.25	0.0048
29	6.4	0.009	19.55	0.0041
49	4.5	0.007	21.45	0.0037
89	2.7	0.005	23.25	0.0037
160	1.4	0.007	24.55	0.0043
		2		
0	26.85	—	0	—
2	23.0	0.015	3.85	0.0031
5	19.3	0.013	7.55	0.0029
9	15.5	0.012	11.35	0.0030
14	12.3	0.010	14.55	0.0031
24	8.0	0.010	18.85	0.0036
44	3.9	0.008	22.95	0.0040
59	2.1	0.008	24.75	0.0074
		3		
0	25.7	—	0	—
3.5	18.5	0.018	7.2	0.0044
6.75	14.5	0.016	11.2	0.0044
9	12.5	0.015	13.2	0.0046
14	9.6	0.013	16.1	0.0047
20	7.6	0.012	18.1	0.0046
30	5.4	0.010	20.3	0.0049
50	3.0	0.008	22.7	0.0059

TABLE III.—(*Continued*).

Silver 1/2600. H_2O_2 1/32. One day old

1		2	
Time	A – x	Time	A – x
0	27.1	0	28.1
2	23.7	2	24.0
4	21.2	5	21.0
6	19.1	10	18.3
9	17.6	25	15.5
14	15.1	100	15.1
24	12.2	—	—
34	11.2	—	—
70	10.5	—	—
100	10.0	—	—

Silver 1/4600. One day old

0	27.0	0	28.1
10	22.4	10	26.5
20	20.1	20	25.7
60	19.1	35	23.9
—	—	80	22.0
—	—	120	21.8

Silver 1/7800. One day old

0	28.8	0	28.8
10	26.2	10	26.0
25	23.9	25	24.2
60	22.8	60	24.0

Silver 1/40,000

0	33.1	0	32.8
15	32.9	15	32.6
60	32.7	60	32.6

Silver 1/∞

0	30.3
180	30.1
375	29.6
675	29.4

TABLE IV.

Silver 1/12,000

1/16 N. H_2O_2 1/20 N. Na_2CO_3 1/40 N

t	$A-x$	$A-x$	t	$A-x$	$A-x$
0	53.4	52.5	0	35.4	35.4 (calculated)
30	52.5	52.1	5	—	2.1
300	52.1	51.8	10	0.0	—

During the reaction it was noticed that the solution gradually lost its color, as if the silver dissolved in the hydrogen peroxide. When dissolved the catalytic property was destroyed, but color and catalysis both appeared on adding a little alkali. See Table IV. It seems probable that in the solution of the silver, some soluble oxide or hydroxide is formed. This compound, studied by Weltzren,[1] is broken down when alkalies are added, silver being precipitated. In neutral or acid solutions the reactions of colloidal silver on hydrogen peroxide are:

$$1.\ H_2O_2 = H_2O + O,$$

and

$$2.\ Ag_2 + 2H_2O_2 = Ag_2(OH)_4$$

and when alkali is added,

$$Ag_2(OH)_4 = Ag_2 + 2H_2O + O_2$$

When new, the silver solution decomposed hydrogen peroxide, but after a few months lost this property to some extent. In Tables V. and VI. are given the results of a few experiments, in some of which acids or neutral salts are added. No good agreement could be obtained in parallel experiments, as the solution of the silver was influenced by unknown causes.

In alkaline solutions the age did not seem to affect the catalytic properties of the silver greatly. Table VII. gives the results obtained by the use of 1/50,000 normal silver three days old, and seven months old. In the case of silver, which had stood with alkali for some little time, the effect seemed independent of the age.

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[1] Liebig's Annalen, 142, 105 (1867).

TABLE V.

Silver 1/2600. H_2O_2 1/32. Four days old

1/1000 CH_3COOH.

1		2		3		4		1/∞ silver	
t	A − *x*	*t*	A − *x*	*t*	A − *x*	*t*	A − *x*	*t*	A − *x*
0	26.2	0	25.7	0	24.8	0	24.8	0	24.4
1.5	22.8	2	20.3	2	18.6	2	20.3	120	24.3
3	20.3	4	17.8	4	15.2	3	19.4	240	24.1
6	18.8	6	15.7	6	12.6	8	19.2	—	—
10	18.1	9	13.5	10	10.3	240[1]	19.0	—	—
20	17.8	15	10.8	20	7.7	—	—	—	—
40	17.0	25	7.0	—	—	—	—	—	—
—	—	55	6.4	—	—	—	—	—	—

KCl 1/1000.						Na_2CO_3 1/50			
1		2		3		5 cc from 1		5 from 2	
0	25.2	0	25.3	0	25.6	0	20.8	0	21.1
1.5	21.7	1.5	21.6	1.5	20.5	5	17.2	5	15.7
3	19.3	2	19.5	3	17.8	10	14.3	10	13.0
4.5	18.9	4.5	17.9	5	14.8	15	12.5	20	9.5
10	18.8	10	14.2	10	10.3	25	9.5	40	6.2
30	18.7	20	9.6	30	4.0	35	7.8	70	3.6
270	18.2	—	—	—	—	55	5.5	—	—
—	—	—	—	—	—	85	3.1	—	—

TABLE VI.

Silver 1/5400. H_2O_2 1/20. Seven months old

				With H_2SO_4 1/1000			
t	A − *x*	*t*	A − *x*	*t*	A − *x*	*t*	A − *x*
0	36.6	0	33.6	0	36.6	0	34.8
3	29.6	3	29.0	30	36.4	6	34.6
6	26.0	8	19.6	180	36.2	50	33.6
12	23.2	40	7.0	—	—	180	33.0
30	16.0	—	—	—	—	—	—
60	12.0	—	—	—	—	—	—

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[1] When made alkaline the rate of decomposition was too fast to be measured.

TABLE VII.

H_2O_2 1/22. Na(OH) 1/32

Silver 1/50,000. Three days old

t	A − *x*	0.4343 K	*t*	A − *x*	0.4343 K	*t*	A − *x*	0.4343 K
0	27.0	——	0	26.6	——	0	33.8	——
2	13.6	0.065	1	18.4	0.069	5	26.8	0.020
4	8.6	0.054	2	13.8	0.062	10	20.2	0.022
8	2.7	0.054	4	10.0	0.035	15	14.0	0.025
—	—	——	5	7.0	0.050	20	8.8	0.029
—	—	——	—	—	——	25	5.4[1]	0.032

Silver. 1/50,000. Seven months old

0	27.9	——	0	25.4	——	0	33.6	——
1	22.4	0.041	1	21.2	0.034	5	26.0	0.022
2	19.0	0.036	2	18.4	0.030	10	18.6	0.025
3	16.2	0.034	3	16.0	0.029	15	11.2	0.032
5	12.5	0.030	5	12.0	0.028	25	6.6[2]	0.028
7.5	9.3	0.027	7.5	9.1	0.026	—	—	——
10	6.8	0.027	10	7.1	0.024	—	—	——

The reaction of silver in alkaline solution seemed of interest, and many experiments were made to decide the order of the reaction, the influence of alkali concentration, light, temperature, etc.

The alkalies used

The sodium hydroxide used throughout was prepared by the action of water on sodium in an atmosphere of hydrogen. The sodium was contained in a platinum dish, although silver and nickel were at first used. All three were apparently acted on by sodium, but the effect appeared smallest in the case of platinum, due perhaps to the small catalytic effect of platinum salts on hydrogen peroxide. The results with sodium hydroxide made in platinum, silver and nickel dishes are given in Tables VIII, IX, and X respectively.

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[1] Alkali and silver standing 12 hours.

[2] Alkali and silver standing 36 hours.

TABLE VIII.
Sodium hydroxide
H_2O, 1/40

Normal NaOH			1/2 normal NaOH			1/4 normal NaOH		
t	$\overset{1}{A - x}$	$\overset{2}{A - x}$	t	$\overset{1}{A - x}$	$\overset{2}{A - x}$	t	$\overset{1}{A - x}$	$\overset{2}{A - x}$
0	20.6	20.9	0	20.9	20.8	0	21.15	21.2
60	20.5	20.6	60	20.6	20.6	60	20 9	21.1
180	21.0	20.2	180	20.2	20.2	180	20.4	20.7
420	18.8	18.7	420	19.0	19.1	420	19.9	20.0
1260	15.5	14.0	1260	14.7	14.9	1260	18.5	18.7
—	—	—	2700	9.2	8.5	2700	15.5	14.0

1/8 normal NaOH			1/16 normal NOOH			1/32 normal NaOH		
0	21.0	21.15	0	21.1	21.0	0	21.05	21.15
60	20.6	20.8	60	20.9	20.7	60	20.0	20.2
180	19.5	19.7	180	20.5	19.9	180	18.0	18.4
420	18.5	18.7	420	19.9	18.9	420	15.5	16.0
1260	11.0	11.0	1260	17.5	16.7	1260	3.0	3.5

1/64 normal NaOH			1/128 normal NaOH			1/256 normal NaOH		
0	21.1	21.1	0	21.1	21.25	0	21.25	21.2
60	19.4	19.8	60	20.1	20.1	60	20.0	20.5
180	17.0	17.5	180	18.1	18.3	180	19.1	19.4
420	10.8	10.8	420	16.0	16.5	420	18.0	18.3
1260	3.6	3.0	1260	14.0	13.8	1260	15.8	16.4

1/512 normal NaOH			$1/\infty$ normal NaOH		
0	21.2	21.15	0	21.4	21.4
60	21.0	20.8	60	20.4	21.35
180	20.7	20.2	180	21.35	21.35
420	18.5	18.0	420	21.1	21.2
1260	16.8	16.7	1260	21.0	21.1
—	—	—	2700	20.9	20.7

TABLE IX.

Sodium hydroxide

H_2O_2 1/46

Normal NaOH		1/2 normal NaOH		1/4 normal NaOH	
t	A − *x*	*t*	A − *x*		A − *x*
0	17.6	0	17.5	0	17.3
10	17.4	15	17.3	15	17.1
60	16.5	60	16.6	60	16.8
180	15.0	180	15.0	180	15.5
300	13.4	420	13.2	300	14.2
420	12.2	780	9.4	420	13.0
780	8.1	1380	4.8	780	9.8
1140	3.6	—	—	1320	5.6
1/8 normal NaOH		**1/16 normal NaOH**		**1/32 noamal NaOH**	
0	17.6	0	17.4	0	17.0
15	17.2	60	14.4	30	12.8
60	16.2	120	12.5	60	8.8
180	14.4	240	8.4	120	4.8
300	13.3	600	2.5	240	4.0
420	12 0	—	—	—	—
780	8.2	—	—	—	—
1140	4.5	—	—	—	—
1/64 normal NaOH		**1/128 normal NaOH**		**1/∞ normal NaOH**	
0	17.3	0	17.1	0	17.7
60	14.9	60	15.8	120	17.6
120	14.1	120	15.2	1200	17.4
240	12.6	240	14.2	—	—
600	7.5	600	10.0	—	—
1200	2.0	1200	3.5	—	—

TABLE X.

Sodium hydroxide

H_2O_2 1/40

Normal NaOH		1/2 normal NaOH		1/32 normal NaOH	
t	A − *x*	*t*	A − *x*	*t*	A − *x*
0	20.1	0	21.4	0	20.05
10	4.1	10	5.5	10	17.0
—	—	—	—	20	14.8
—	—	—	—	60	6.0

In investigating the action of other alkalies, the potassium hydroxide, sodium carbonate and ammonia were the chemically pure laboratory reagents. These experiments are tabulated in Tables XI., XII., and XIII., and it is of interest in view of the fact that compounds of alkalies and hydrogen peroxide exist[1] that the maximum rate of decomposition takes place at about 1/32 normal alkali concentration.

TABLE XI.

Potassium hydroxide

H_2O_2 1/22

1/4 normal KOH			1/8 normal KOH			1/16 normal KOH		
t	1 A − *x*	2 A − *x*	*t*	1 A − *x*	2 A − *x*	*t*	1 A − *x*	2 A − *x*
0	34.6	34.8	0	34.8	34.7	0	34.4	34.8
30	29.4	28.6	30	27.6	27.4	15	27.7	28.8
60	25.0	24.3	60	21.8	22.1	45	19.0	19.5
120	17.2	17.2	120	13.8	11.7	75	12.4	13.0
180	11.1	10.8	180	7.1	6.8	105	8.1	8.8
1/32 normal KOH			1/64 normal KOH			1/128 normal KOH		
0	32.0	32.0	0	35.0	35.4	0	35.2	36.0
5	28.5	28.4	15	34.0	33.8	30	34.1	34.6
10	26.8	26.8	60	32.3	32.3	60	32.3	32.0
15	25.4	25.3	120	29.8	30.0	240	30.4	29.0
30	22.3	22.3	240	26.5	26.5	360	29.0	27.0
45	20.0	19.6	360	24.0	24.2	480	26.5	24.6
60	18.0	16.1	500	20.2	21.1	—	—	—
90	12.9	11.0	780	12.9	14.4	—	—	—
1/∞ normal KOH								
0	36.2	—						
180	35.8	—						

Ammonia decomposes the hydrogen peroxide rapidly, giving oxygen and water,

$$2H_2O_2 = 2H_2O_2 + O_2.$$

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[1] Calvert. Zeit. Elektrochemie, 7, 622 (1901).

TABLE XII.

Sodium carbonate

H_2O_2 1/22

1/20 normal Na_2CO_3			1/40 normal Na_2CO_3			1/80 normal Na_2CO_3		
t	A − *x*	A − *x*	*t*	A − *x*	A − *x*	*t*	A − *x*	A − *x*
0	34.6	34.8	0	35.0	34.8	0	34.7	35.0
15	31.6	31.6	15	31.0	31.0	30	32.0	32.4
30	27.7	27.7	30	27.7	27.0	60	30.8	31.1
60	22.0	21.9	45	25.2	24.6	120	29.1	29.3
120	13.7	13.8	60	22.7	22.0	270	22.7	25.0
180	8.6	8.8	120	16.6	15.0	570	15.8	17.6
360	2.9	3.0	—	—	—	—	—	—

1/160 normal Na_2Cl_2			1/∞ normal Na_2CO_3		
0	33.7	33.2	0	35.0	—
60	31.6	31.8	240	34.8	—
120	30.6	30.4	1260	33.6	—
240	29.6	29.4	1740	33.2	—
360	28.6	27.5	—	—	—
600	24.6	22.7	—	—	—
1200	17.5	16.8	—	—	—

TABLE XIII.

Ammonium hydroxide

H_2O_2 1/22

1/4 normal NH_4OH				
t	A − *x*	0.4343 K	A − *x*	0.4343 K
0	33.4	——	33.4	——
10	28.5	0.0030	29.9	0.0021
20	26.0	0.0024	26.1	0.0023
30	23.1	0.0023	23.2	0.0023
45	19.5	0.0023	19.8	0.0022
60	16.6	0.0022	16.8	0.0022
90	11.6	0.0022	12.2	0.0021
120	8.2	0.0022	8.6	0.0021

TABLE XIII.—(*Continued*).

1/8 normal NH_4OH				
0	33.6	——	33.6	——
10	29.0	0.0028	29.3	0.0026
20	24.7	0.0029	25.3	0.0027
30	22.3	0.0026	22.7	0.0025
45	17.6	0.0027	18.2	0.0026
60	13.0	0.0030	14.0	0.0028
90	7.0	0.0033	8.1	0.0029
1/16 normal NH_4OH				
0	32.8	——	32.6	——
10	27.5	0.0033	28.0	0.0029
20	23.0	0.0033	22.5	0.0035
30	18.6	0.0036	18.3	0.0036
45	13.3	0.0038	13.2	0.0038
60	9.6	0.0039	9.4	0.0039
1/32 normal NH_4OH				
0	32.8	——	32.4	——
5	28.7	0.0050	28.3	0.0051
10	23.6	0.0062	23.0	0.0065
15	20.0	0.0062	19.6	0.0064
20	16.1	0.0067	15.6	0.0069
30	10.1	0.0074	9.8	0.0075
1/64 normal NH_4OH				
0	30.4	——	30.3	——
10	25.4	0.0034	25.0	0.0036
20	21.1	0.0034	20.9	0.0035
30	17.6	0.0034	18.0	0.0033
40	14.6	0.0034	14.8	0.0034
50	12.2	0.0034	12.6	0.0033
60	10.4	0.0034	11.2	0.0031
80	8.4	0.0030	8.7	0.0029
100	6.1	0.0030	7.1	0.0027

TABLE XIII.—(*Continued*).

1/128 normal NH_4OH

0	30.2	——	29.8	——
10	25.3	0.0033	25.0	0.0033
20	22.4	0.0028	22.0	0.0028
30	20.0	0.0026	19.2	0.0028
40	18.3	0.0024	18.0	0 0024
50	16.4	0.0023	15.7	0.0024
60	15.1	0.0022	14.7	0.0022
80	13.4	0.0019	13.7	0.0019
100	11.2	0.0019	11.0	0.0019

and hydrogen peroxide acts on ammonia according to the equation:[1]

$$2NH_3 + 3H_2O_2 = NH_4NO_2 + 4H_2O.$$

But since potassium permanganate acts on nitrous acid,

$$(5HNO_2 + 2KMnO_4{}^{2} = 5HNO_3 + 2MnO + K_2O),$$

the titrations give but the H_2O_2 decomposed into water and oxygen. The calculations, although the NH_3 is becoming less,

TABLE XIV.

Sodium hydrate, 3/4 normal

H_2O_2 1/22

Silver 1/180,000				Silver 1/90,000			
t	1 $A-x$	2 $A-x$	3 $A-x$	t	1 $A-x$	2 $A-x$	3 $A-x$
0	31.8	31.6	31.2	0	29.9	28.4	28.4
10	30.0	29.2	29.6	5	25.0	24.5	25.0
20	28.0	27.5	27.0	10	21.0	21.2	21.7
30	25.9	25.7	25.0	15	18.2	18.6	19.4
60	22.0	22.1	21.4	20	15.8	16.4	17.2
120	17.5	17.4	16.8	30	12.2	12.6	13.8
180	13.1	13.2	11.6	40	10.3	9.0	11.0
240	10.4	10.9	9.0	—	—	—	—
540	5.0	3.5	2.8	—	—	—	—

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[1] Jahresberichte, 1863, p. 131.

[2] Zeit. anal. Chem. 22, 95 (1883).

TABLE XIV.—(*Continued*).

Silver 1/60,000				Silver 1/50,000			
0	27.6	27.0	26.8	0	24.6	25.4	25.2
2.5	21.1	20.5	20.1	1	19.0	18.6	18.5
5	15.2	14.3	13.8	2	13.3	—	—
10	9.6	8.2	7.3	2.5	—	14.4	14.4
15	5.8	4.4	4.1	3	10.5	11.6	11.6
20	3.0	2.4	2.4	5	6.5	6.9	7.3
—	—	—	—	7.5	3.4	3.9	4.2
—	—	—	—	10	2.0	2.4	2.5

Silver 1/42,000				Silver 1/∞			
0	23.8	23.4	24.0	0	33.8	33.8	—
1	16.5	15.8	18.6	120	31.5	32.2	—
2	10.8	11.2	12.4	420	27.7	30.8	—
3	6.8	6.7	8.4	—	—	—	—
5	4.0	3.7	4.3	—	—	—	—
7.5	2.4	2.1	2.1	—	—	—	—
10	1.4	1.0	1.2	—	—	—	—

point to a monomolecular reaction for the decomposition of H_2O_2 by NH_3.

Strong alkalies cannot be kept in bottles made of glass containing manganese, as enough manganese goes into solution to decompose the hydrogen peroxide quickly. Many experiments with such alkalies were at first made, and the reason for the rapid decomposition only found after a long search.

TABLE XV.

Sodium hydroxide, 1/4 normal

H_2O_2 1/28

Silver 1/360,000				Silver 1/180,000			
t	1 A − *x*	2 A − *x*	3 A − *x*	*t*	1 A − *x*	2 A − *x*	3 A − *x*
0	23.0	22.4	—	0	29.4	28.2	29.2
15	20.4	20.0	—	10	25.1	24.7	25.0
30	19.6	18.0	—	20	22.0	22.0	20.8
45	16.4	15.8	—	30	19.4	19.6	18.3
60	14.6	14.4	—	45	16.7	17.0	15.3
90	12:7	12.2	—	60	14.2	14.4	12.8
120	11.0	10.0	—	90	10.3	10.7	10.6

TABLE XV.—(*Continued.*)

Silver 1/90,000				Silver 1/60,000			
0	25.2	27.0	27.4	0	24.2	25.2	—
1	22.7	24.2	23.2	0.5	20.8	21.8	—
2	21.0	21.0	20.6	1	18.7	19.8	—
3	19.1	18.6	17.4	1.5	16.0	16.4	—
5	16.6	15.6	12.4	2	14.7	14.6	—
10	10.8	8.4	7.2	3	12.4	11.7	—
—	—	—	—	4	10.4	10.2	—
—	—	—	—	5	8.5	8.1	—
—	—	—	—	10	4.2	3.5	—
Silver 1/∞							
0	31.6	—	—				
60	30.0	—	—				
120	29.6	—	—				

TABLE XVI

Sodium hydroxide, 1/8 and 1/32 normal

Silver 1/360,000			Silver 1/180,000			Silver 1/90,000		
t	1 $A-x$	2 $A-x$	*t*	1 $A-x$	2 $A-x$	*t*	1 $A-x$	2 $A-x$
0	30.8	30.4	0	30.0	29.3	0	27.8	27.6
5	30.1	29.5	2.5	24.2	23.4	1	23.0	23.1
15	27.5	26.4	5	18.4	18.1	2	18.6	18.7
30	24.4	20.0	7.5	14.1	13.7	3	14.6	15.0
45	21.0	16.3	10	11.9	10.7	5	9.8	10.8
60	15.2	11.4	15	7.6	6.4	7.5	5.6	7.6
90	8.5	6.5	20	5.2	4.2	10	3.5	4.8
Sodium hydroxide 1/32								
0	30.6	30.4	0	30.0	30.1	0	27.9	25.4
5	27.8	—	2.5	24.2	25.2	1	22.4	21.2
10	26.0	26.8	5	21.2	20.8	2	19.0	18.4
20	23.2	24.1	10	17.1	18.0	3	16.2	16.2
30	21.7	21.8	20	11.6	12.5	5	12.6	12.0
60	18.0	17.4	30	7.1	8.7	10	6.8	7.1
90	13.4	13.0	—	—	—	—	—	—
120	10.2	9.7	—	—	—	—	—	—

Silver in sodium hydroxide solution

The effect of different concentrations of silver in sodium hydroxide solution of from 3/4 to 1/32 normal on the decomposition of hydrogen peroxide is given in Tables XIV., XV., and XVI., where one sees that an increase in silver increases the rate of decomposition, but that the rate is not proportional to the amounts used.

In 3/4 normal sodium hydroxide solution one-half decomposition takes place

with	1/180,000	silver	in	143	minutes
"	1/90,000	"	"	25	"
"	1/60,000	"	"	6.5	"
"	1/50,000	"	"	2.5	"
"	1/42,000	"	"	1.8	"

With 1/180,000 silver the times for 1/2 decomposition are

with	3/4	normal	NaOH	143	minutes
"	1/4	"	"	53	"
"	1/8	"	"	7.4	"
"	1/32	"	"	14.7	"
"	1/64	"	"	69.0	"

As the concentration of alkali increases, we pass through a maximum rate of decomposition, which is also true of platinum, gold and various organic ferments in alkaline solution.

Alkali, when added to colloidal silver, slowly precipitates the metal, which then can take but little part in the catalysis. On calculating the numbers given in the previous tables either as a mono- or a bimolecular reaction, the numbers are not very satisfactory. If the solution be agitated during the reaction so that the silver is brought into better contact with the hydrogen peroxide, the constant shows the reaction to be undoubtedly of the first order. Results obtained in this way are given in Table XVII.

Influence of light and heat

To test the effect of light on the speed of decomposition, a large glass beaker, divided into two parts by a close fitting polished metal plate and filled with water served as a bath. One-half of the bath was illuminated by a 15 ampere lamp, while the

TABLE XVII

Sodium hydroxide, normal

H_2O_2 1/40

Silver 1/60,000

1			2			3		
t	A − *x*	0.4343 K		A − *x*	0.4343 K	*t*	A − *x*	0.4343 K
0	20.8	——	0	20.2	——	0	19.8	——
1.08	18.0	0.025	1	18.1	0.021	1	17.0	0.037
2	16.3	0.023	2	16.2	0.021	2	16.0	0.020
3	14.0	0.025	3.08	14.1	0.022	3	15.1	0.017
5	11.4	0.023	5.2	11.0	0.022	5	12.6	0.017
7.5	8.7	0.022	7.75	8.3	0.022	7.5	10.1	0.017
10	7.0	0.020	10	6.6	0.021	10	8.0	0.017
15	4.5	0.019	15	4.4	0.019	15	6.0	0.015
—	—	——	—	—	——	20	4.4	0.014
4			5			1/∞ silver		
0	20.0	——	0	20.0	——	0	20.8	——
1	17.8	0.022	1	17.9	0.021	60	18.8	——
2	16.1	0.020	2	16.1	0.020	—	—	——
3	14.3	0.021	3	14.3	0.021	—	—	——
5	11.6	0.021	5	11.3	0.021	—	—	——
7.5	9.1	0.020	7.5	8.3	0.022	—	—	——
10.0	7.3	0.019	10.5	6.5	0.021	—	—	——
15	5.1	0.017	15	4.3	0.019	—	—	——
20	3.7	0.016	—	—	——	—	—	——

Silver 1/90,000

1			2			3		
0	20.5	——	0	20.3	——	0	19.9	——
1.92	18.2	0.012	2.5	18.2	0.0082	2.5	17.0	0.012
5	14.7	0.012	3.83	17.0	0.0087	5	14.5	0.012
7.5	13.2	0.011	5	16.1	0.0087	7.5	11.9	0.013
10	11.5	0.011	7.5	14.4	0.0086	10	10.4	0.012
15	9.5	0.0097	10	12.5	0.0091	15	7.6	0.012
20	7.8	0.0091	15	10.0	0.0089	20	6.0	0.011
30	5.9	0.0078	20	7.8	0.0090	30	4.3	0.0096

TABLE XVII.—(*Continued*).

Silver 1/180,000

1			2		
0	19.75	——	0	19.8	——
5	18.05	0.0034	5	18.2	0.0032
10	16.95	0.0029	10	16.8	0.0031
20	15.05	0.0026	20	14.3	0.0031
30	13.2	0.0025	30	12.2	0.0030
45	11.8	0.0022	45	10.15	0.0028
60	9.8	0.0022	60	8.2	0.0028
90	7.4	0.0021	90	6.6	0.0023
120	5.95	0.0019	—	—	——

other was protected from light by means of black cloth. The temperature of experiment was 23°. Table XVIII. shows that light had no effect on the catalysis, since the variations in the two series are smaller than the experimental error.

In Table XIX. the effect of increasing the temperature is shown. The velocity of decomposition increases with rising temperature, but no simple relation seems to exist,[1] due probably to the increasing effect of the alkali and to precipitation of the silver.

TABLE XVIII

Sodium hydroxide, normal

H_2O_2 1/42

Silver 1/150,000. Four days old

In light

t	$A-x$	0.4343 K	$A-x$	0.4343 K
0	17.9	——	—	——
2.5	15.6	0.0104	15.9	0.0096
5	14.2	0.0087	14.2	0.0090
10	11.4	0.0085	11.6	0.0084
15	9.7	0.0077	9.8	0.0077
20	8.2	0.0074	—	——
25	6.6	0.0075	6.8	0.0074
35	4.3	0.0077	4.2	0.0079

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[1] Arrhenius. Zeit. phys. Chem. 4, 226 (1889).

TABLE XVIII.—(*Continued*).

In shadow

0	18.1	——	18.0	——
2.5	16.1	0.0089	15.8	0.0098
5	14.5	0.0084	14.3	0.0087
10	12.0	0.0077	11.6	0.0083
15	9.8	0.0077	9.9	0.0075
20	8.1	0.0076	8.2	0.0074
30	5.5	0.0075	5.6	0.0073

Silver 1/75,000

In light

0	17.2	——	17.2	——
1	13.8	0.042	14.4	0.034
2	11.7	0.036	12.0	0.034
3	9.9	0.035	10.1	0.034
5	7.1	0.033	7.4	0.032
7.5	4.8	0.032	5.2	0.030
10	3.1	0.032	2.1	0.039

In shadow

0	17.2	——	17.2	——
1	14.4	0.034	14.2	0.036
2	12.4	0.031	11.9	0.035
3	10.1	0.033	10.0	0.034
4	8.7	0.032	—	——
5	7.6	0.031	7.3	0.032
7.5	5.3	0.030	5.0	0.031
10	2.5	0.036	3.4	0.031

A few results obtained by the use of ammonia and other alkalies are given in Table XX. It will be noticed that the addition of silver has little influence on the action of hydrogen peroxide on ammonia. The reaction is perhaps more complex than Berthelot[1] thought. When sodium hydroxide is added the rate of decomposition increases. This is explained by the fact that the stronger hydroxide decomposes the compound of ammonia and silver. Potassium hydroxide acts in the same way as sodium hydroxide.[2]

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[1] Ann. Chim. Phys. (7) 11, 223.

[2] Ibid. 11, 217.

There seems to be some uncertainty as to the exact reaction taking place when hydrogen peroxide acts on a nalkaline silver salt.

TABLE XIX

Sodium hydroxide, normal

H_2O_2, 1/40

Silver 1/180,000								
25°			45°			65°		
t	1 A − x	2 A − x		1 A − x	2 A − x		1 A − x	2 A − x
0	21.0	21.0	0	19.85	19.9	0	15.6	15.1
10	19.65	19.5	2.5	15.1	15.6	0.5	10.6	10.9
20	18.5	18.3	5	12.5	13.0	1.0	7.3	7.2
40	16.4	16.0	10	8.0	9.4	1.5	5.3	6.1
60	14.7	14.3	15	6.4	7.6	2	3.8	4.5
80	13.1	12.8	20	4.8	6.0	3	2.6	3.2
—	—	—	—	—	—	4	1.7	2.4
—	—	—	—	—	—	5	1.0	1.6

Silver 1/360,000					
0	20.2	20.2	0	16.7	17.1
5	16.3	16.4	0.5	14.6	13.5
10	14.4	14.6	1.0	11.0	11.2
15	11.5	11.7	2	7.8	8.1
20	9.4	8.5	3	5.3	6.4
25	7.5	7.1	4	3.8	4.3
35	5.8	5.5	5	3.0	3.3
—	—	—	7.5	2.2	1.8

Silver 1/∞			
	25°	45°	65°
0	22.4	22.1	21.1
20	—	21.0	10.0
50	—	—	4.2
80	21.2	17.0	—

TABLE XX.

Ammonium hydroxide, N/4

H_2O_2 1/42

Silver 1/75,000						Silver 1/∞	
				+NaOH			
t	A − *x*	*t*	A − *x*	*t*	A − *x*	*t*	A − *x*
0	17.7	0	16.6	0	15.8	0	19.9
5	16.5	10	15.0	1	13.9	10	17.7
15	14.8	20	13.7	3	11.2	20	16.2
25	13.8	30	12.3	5	8.4	30	14.6
35	12.3	65	9.5	7.5	7.0	40	13.5
65	10.6	—	—	10	5.6	65	10.5
85	8.7	—	—	—	—	—	—

Silver 1/75,000

KOH N/4		Na_2CO_3 N/20			
0	16.4	0	16.1	—	14.4
1	14.5	1	14.1	—	12.3
2	12.9	2	12.6	—	10.9
3	11.7	3	11.8	—	9.8
4	10.6	5	10.7	—	8.6
5	9.6	7.5	8.8	—	7.0
7	7.8	10	7.7	—	5.6
10	5.8	—	—	—	—

Thenard[1] found that the silver salt was completely reduced to finely divided silver. Berthelot[2] makes the reaction much more complicated, dividing it into three stages.

(1) $Ag_2O + H_2O_2 = Ag_2O_2 + H_2O$
(2) $3Ag_2O + 3H_2O_2 = Ag_4O_3 + Ag_2 + O_3 + 3H_2O$
(3) $Ag_4O_3 = 2Ag_2O + O$.

The first reaction takes place very quickly; the third only after three hours. Berthelot, by treating the precipitate with acid and measuring the amount of gas given off, concluded that the oxide Ag_4O_3 was formed. Baeyer and Villiger[3] found

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[1] Ann. Chim. Phys. 9, 96 (1818).

[2] Ann. Chim. Phys. (5) 21, 164 (1880); Comptes rendus, 90, 572 (1880); Ann. Chim. Phys. (7) 11, 217 (1897); Ibid. 23, 52 (1901).

[3] Ber. chem. Ges. Berlin, 34, 749; 34, 2769.

no evidence for the existence of this oxide, and from many experiments concluded that the silver salt was reduced to metallic silver. Results obtained here confirm their conclusions in all respects.

Table XXI. shows experiments in which a silver salt — in this case the sulphate — is substituted for colloidal silver, and these speak against Berthelot's conclusions. With silver sulphate of a concentration of 1/200,000, the mean constant is 0.0025; while with colloidal silver having a concentration of 1/180,000 the constant is 0.0027 (Table XVII.).

TABLE XXI.

Sodium hydroxide, normal

H_2O_2 1/40

Ag_2SO_4 1/60,000			$AgSO_4$ 1/120,000		
t	1 A − x	2 A − x	t	1 A − x	2 A − x
0	17.85	17.85	0	18.35	18.55
5	11.8	11.0	5	13.4	13.3
10	7.4	7.1	10	9.6	9.2
15	5.5	4.9	15	6.7	6.4
20	3.5	2.5	20	5.35	4.4

Ag_2SO_4 1/200,000

	1		2	
t	A − x	0.4343 K	A − x	0.4343 K
0	18.1	——	17.9	——
5	16.9	0.0026	16.6	0.0028
15	14.5	0.0028	14.7	0.0025
25	12.85	0.0026	13.0	0.0023
35	11.8	0.0023	11.9	0.0022
45	9.8	0.0026	10.5	0.0022
60	8.0	0.0026	8.3	0.0023

In the case of colloidal silver no change is noticed when hydrogen peroxide is added with alkali, and the catalytic properties are not destroyed by a large amount of H_2O_2, so that the oxide Ag_4O_3 is probably not here found. Since a silver salt gives almost exactly the same constant as colloidal silver, it seems probable that the silver salt is reduced at once to the metal, which decomposes the H_2O_2. Silver sulphate in neutral or acid solutions does not decompose hydrogen peroxide.

Soluble silver was next investigated in order to compare its action with that of the colloidal form. The "soluble" silver was made according to Carey Lea's directions, and was called by him "Modification C."

107 cc of a 30 percent ferrous sulphate solution and 200 cc of a 20 percent Rochelle salt solution were diluted with 800 cc of water, and to this was added a solution consisting of 200 cc of a 10 percent silver nitrate solution, 200 cc of a 20 percent Rochelle salt solution with 800 cc of water. A dark red or black powder is precipitated, which on the filter appears bronze colored, but when well washed and dried, appears like gold. This dry soluble silver contained a little tartaric acid and iron oxide.

Silver prepared in this way differed from the colloidal only in the size of its particles, which were larger and more easily precipitated on standing, by heat and by salts. One would expect the catalysis to be slower than with colloidal silver. Table XXII. shows that 1/24,000 normal Carey Lea's silver decomposes hydrogen peroxide at about the same rate as 1/60,000 normal colloidal (Table XVII.). The soluble silver in neutral or acid solutions decomposed but a trifling amount of H_2O_2, dissolving as does colloidal silver.

Hydrogen peroxide acts on metallic silver, giving a compound already referred to; when alkali is added this compound is reduced to the metal. From 1/15 normal H_2O_2, which stood over metallic silver for 12 hours, silver of a concentration of 1/10,000 normal was found in solution. The solution was not analyzed, but from the speed of reaction the amount present was determined. The behavior of this silver in presence of alkali and hydrogen peroxide is shown in Table XXIII.

TABLE XXII.

Carey Lea's silver

Sodium hydroxide, normal

H_2O_2 1/40

Silver 1/24,000			Silver 1/48,000		
t	A − *x*	A − *x*	*t*	A − *x*	A − *x*
0	18.8	18.7	0	18.3	19.6
2.5	12.7	12.9	2.5	14.6	15.3
5	9.4	9.4	5	11.2	12.0
7.5	7.5	7.3	7.5	9.8	10.2
10	5.7	5.6	10	8.3	8.5
15	4.1	4.0	15	6.3	6.1
20	3.0	2.8	20	4.6	4.5
25	2.1	2.0	—	—	—

TABLE XXIII.

Sodium hydroxide, normal

H_2O_2 1/40

t	A − *x*	A − *x*
0	20.7	20.7
1	12.2	13.1
2	9.2	9.3
15	2.3	3.1

Influence of poisons

In the papers on inorganic ferments previously referred to, the authors had found that such poisons as potassium cyanide and mercury salts decreased the speed of reaction due to the ferment, and even in some cases "killed" the ferment. With 1/60,000 normal silver the catalytic property was totally destroyed when 1/10,000 potassium cyanide is present, but at 1/120,000 normal had little effect on the reaction. See Table XXIV. The same holds true for silver salts (Table XXV.).

The cause of this is made clear by a simple experiment. When we add hydrogen peroxide to a silver salt in sodium hydroxide solution, silver is at once precipitated, which decom-

TABLE XXIV.

Sodium hydrate, normal

H_2O_2 1/27. Silver 1/60,000.

KCN 1/1000				KCN 1/10,000			
t	1 $A-x$	2 $A-x$	3 $A-x$	*t*	1 $A-x$	2 $A-x$	3 $A-x$
0	24.0	23.7	24.0	0	23.1	23.0	22.9
240	23.5	23.4	23.5	75	22.9	22.8	22.8
1440	21.7	21.7	21.9	1440	21.3	21.3	21.3

KCN 1/120,000				KCN 1/∞			
t	1 $A-x$	2 $A-x$	0.4343 K	*t*	$A-x$	$A-x$	0.4343 K
0	19.1	20.7	—	0	20.6	21.2	—
2	13.4	16.4	0.022	1	16.7	18.4	0.026
4	10.4	11.7	0.027	2	—	16.0	0.026
6	8.6	8.8	0.027	3	12.3	14.3	0.024
8	7.6	6.4	0.028	5	11.6	11.1	0.024
10	7.5	5.0	0.027	7.5	—	8.8	0.022
—	—	—	—	10	8.8	7.1	0.021
—	—	—	—	15	6.0	4.8	0.019

TABLE XXV.

Sodium hydroxide, normal

H_2O_2 1/45. Ag_2SO_4 1/200,000

KCN 1/1150			KCN 1/11,500			KCN 1/115,000		
t	$A-x$	$A-x$	*t*	$A-x$	$A-x$	*t*	$A-x$	$A-x$
0	17.1	17.05	0	16.9	17.1	0	17.3	17.4
5	17.0	17.0	5	16.9	—	5	16.9	16.9
60	17.0	16.7	130	16.9	16.7	30	16.65	16.2
325	16.9	16.6	900	16.15	16.3	240	13.8	13.1
1200	16.6	16.5	—	—	—	—	—	—

poses the remaining hydrogen peroxide catalytically. If potassium cyanide be present in sufficient amounts, potassium silver cyanide is not decomposed, and no black precipitate results. Experimenting in this way, we can predict that bromides, chlorides, sulphides, etc., will stop the catalysis, and these conclusions are in agreement with experiment.

Quite other results were obtained with mercuric chloride. Instead of being delayed, the decomposition was accelerated. In Table XXVI. the effect of mercuric chloride on the catalysis where colloidal silver and silver sulphate are present is shown; and in Table XXVII. the effect when only the mercuric chloride is present.[1] The explanation is the same as for silver salts. Mercuric chloride is reduced to mercury, which decomposed the hydrogen peroxide. Potassium cyanide and hydrogen sulphide acted as with silver. No evidence of a reaction similar to that ascribed by Berthelot to silver was noticed.

Table XXVI.

Sodium hydroxide, normal

H_2O_2 1/45. $HgCl_2$ 1/1150

Colloidal silver 1/180,000			Silver sulphate 1/200,000		
t	A − *x*	A − *x*	*t*	A − *x*	A − *x*
0	17.1	17.15	0	17.1	16.7
2.5	15.4	—	5	15.15	15.5
5	13.15	13.55	10	11.7	12.5
10	9.7	11.8	15	8.9	10.0
15	7.5	9.6	20	6.5	8.0
20	5.6	8.0	25	4.9	5.6

Colloidal mercury was obtained by the same method as the silver by "sparking" a mercury cathode and platinum anode beneath the surface of water. The particles were larger, precipitated to a great extent after standing a month, and in neutral or acid solution had little effect on hydrogen peroxide. The results obtained with this solution are given in Table XXVIII.,

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[1] See Bredig and Reinders. Zeit. phys. Chem. 37, 339 (1901). This work was done before the publication of their paper.

the reaction being calculated as monomolecular. Potassium cyanide and hydrogen sulphide act on colloidal mercury as on silver.

TABLE XXVII.

Sodium hydroxide, normal

H_2O_2 1/40

$HgCl_2$ 1/105			$HgCl_2$ 1/1050		
t	$A-x$	$A-x$	t	$A-x$	$A-x$
0	20.3	20.6	0	21.7	21.4
1	16.5	16.3	5	19.2	19.45
2	15.2	14.55	10	15.35	16.15
3	13.5	12.85	20	9.55	11.1
5	11.05	10.0	30	5.40	7.5
7.5	9.9	8.5	50	4.2	5.8
10	8.7	8.0	—	—	—
15	6.8	6.45	—	—	—
$HgCl_2$ 1,10,500			$HgCl_2$ 1/105,000		
0	21.8	21.7	0	20.85	20.9
30	20.7	20.5	100	18.1	18.2
60	19.6	19.6	185	15.0	15.3
135	15.4	14.4	440	10.1	10.5
210	11.3	10.8	—	—	—
480	4.3	3.5	—	—	—

TABLE XXVIII.

Colloidal mercury

Sodium hydroxide, normal

H_2O_2 1/50

t	$A-x$	0.4343 K	$A-x$	0.4343 K
0	15.1	—	15.2	—
1	12.1	0.042	11.2	0.063
2	9.5	0.044	8.5	0.057
3	7.6	0.043	7.5	0.044
5	5.4	0.039	5.0	0.042
7.5	4.4	0.031	4.0	0.033

From the action of mercury the name ferment seems in some respects an unsuitable one, while in the case of colloidal platinum, both in the catalysis of a mixture of hydrogen and oxygen and of hydrogen peroxide, mercury hinders the reaction; in alkaline solutions it acts as do the other ferments.

Conclusions

The principal points in this article may be summarized in the following statement:

1. Colloidal silver decomposes hydrogen peroxide in acid and neutral solution until it is dissolved.

2. Colloidal silver decomposes hydrogen peroxide rapidly when alkalies are present; the reaction is a monomolecular one.

3. Increase of temperature increases rapidity of decomposition.

4. Light has no influence on the reaction.

5. Silver salts in alkaline solution are reduced totally to silver, which decomposes the hydrogen peroxide, giving a monomolecular reaction.

6. Substances which form compounds with silver not decomposed by hydrogen peroxide exert a retarding influence on the catalysis.

7. Soluble silver acts exactly like colloidal silver or silver reduced from its salts.

8. Colloidal mercury, or mercury reduced from its salts, acts in alkaline solution like colloidal silver.

McGill University,
July, 1901.

NITRILES AS SOLVENTS IN MOLECULAR WEIGHT DETERMINATIONS

BY LOUIS KAHLENBERG

Nitriles have rarely been used as solvents in making molecular weight determinations. In 1897 Werner[1] determined the molecular weight of mercuric chloride, mercuric iodide and silver nitrate in benzonitrile by the ebullioscopic method, and this was the only case that I could find in the literature where a nitrile had been used as solvent. Werner determined the so-called molecular elevation of the boiling-point for this solvent empirically by using diphenylamine as solute and assuming its molecular weight to be that computed from its formula. In this way he obtained 36.5 as the constant for benzonitrile. According to the Trouton-Schiff rule, Werner calculated the constant to be 45.79; he states clearly that he is unable to explain the discrepancy. Recently the latent heat of evaporation of benzonitrile has been carefully measured by Louguinine[2] and also by myself.[3] The results of these investigations are practically identical, the value found being 87.7. From this value the molecular elevation of the boiling-point, when calculated according to the Arrhenius-Beckmann formula, becomes $K = \frac{0.02(189 + 273)^2}{87.7}$ or 48.67, which is the constant that ought to be used in computing the molecular weights. In Table I. are given the results of Werner, recalculated, using this constant. In the table, *s* represents the amount of solute, *l* the quantity of solvent, Δ the observed rise of the boiling-point, and *m* the molecular weight calculated according to the usual formula.

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[1] Zeit. anorg. Chem. 15, 31 (1897).

[2] Archiv. des Sciences Naturelles de Genève, 9, 5-26 (1899).

[3] Jour. Phys. Chem. 5, 230 (1891).

TABLE I.

(Solvent benzonitrile)

Diphenylamine ($(C_6H_5)_2NH$, mol. wt. = 169)

s	*l*	Δ	*m*
0.1298	20.11	0.135	233
0.2357	20.11	0.250	228
0.1104	14.45	0.169	220
Mercuric chloride ($HgCl_2$, mol. wt. = 271)			
0.2123	19.45	0.126	421
0.5446	19.45	0.358	380
0.3738	21.68	0.280	300
0.8710	21.68	0.585	335
Mercuric iodide (HgI_2, mol. wt. = 454)			
0.1737	23.92	0.061	580
0.5135	23.92	0.153	684
Silver nitrate ($AgNO_3$, mol. wt. = 170)			
0.3534	23.74	0.345	220
0.8336	23.74	0.750	239
0.1874	23.50	0.160	243
0.4326	23.50	0.380	236

Table II. gives a series of determinations of my own. The sample of benzonitrile used was the same as that employed in making the measurement of the latent heat of evaporation.

TABLE II.

(Solvent benzonitrile)

Silver nitrate ($AgNO_3$, mol. wt. = 170)

s	*l*	Δ	*m*
0.1098	16.61	0.130	248
0.3352	16.61	0.381	258
0.5208	16.61	0.590	259

In the case of acetonitrile I found the latent heat of evaporation to be 173.6. The value obtained by Louguinine is 170.68. According to the former value the boiling-point constant becomes $\frac{0.02(80.5 + 273)^2}{173.6}$, or 14.39; while according to the latter value it equals 14.63. In making the computations in Table III., the constant 14.39 was used. The sample of acetonitrile employed was the same as that used in making the determination of the latent heat of evaporation. The solutes used were, with the exception of the silver nitrate, of Kahlbaum's manufacture. They were naphthalene, melting-point 80°; diphenyl, melting-point 69–69.5°; and diphenylamine, melting-point 54°. The silver nitrate was obtained from Baker & Adamson, and was thoroughly dried. The symbols in Table III. have the same significance as those in the preceding tables.

TABLE III.

(Solvent acetonitrile)

s	*t*	Δ	*m*
Naphthalene ($C_{10}H_8$, mol. wt. = 128			
0.3103	11.04	0.280	144
0.5153	11.04	0.469	143
0.7910	11.04	0.717	144
0.9952	11.04	0.905	143
Diphenyl ($C_{12}H_{10}$, mol. wt. = 154)			
0.2208	11.25	0.165	171
0.3246	11.25	0.242	172
0.5494	11.25	0.421	167
0.8374	11.25	0.673	159
Diphenylamine ($(C_6H_5)_2NH$, mol. wt. = 169)			
0.1641	11.29	0.168	125
0.5314	11.29	0.549	124
0.6838	11.29	0.679	128
0.8735	11.29	0.833	133
Silver nitrate ($AgNO_3$, mol. wt. = 170)			
0.1856	10.99	0.180	135
0.3050	10.99	0.298	134
0.5397	10.99	0.510	138
0.7977	10.99	0.760	138
1.0350	10.99	0.939	144

If the constant calculated from Louguinine's value for the latent heat of vaporization had been used, the molecular weights in Table III. would have been 1.8 percent higher. As the boiling-point constant of acetonitrile is nearly 2.8 times that of water, the molecular weights in the former solvent are more readily determined with accuracy.

The attempt was made to use propionitrile as a solvent for molecular weight determinations, but it was unsuccessful, inasmuch as in spite of all exertions, it was found impossible to secure a sample of the substance that had a sufficiently constant boiling-point. The same difficulty was met in trying to employ butyronitrile and valeronitrile.

From Tables I. and II. it appears that the molecular weights of the solutes in benzonitrile are all considerably higher than the theoretical values, without, however, reaching a figure corresponding to a double molecule. The mercuric chloride, mercuric iodide and silver nitrate solutions in benzonitrile are fairly good electrolytes; while the solution of diphenylamine in this solvent is a non-electrolyte. From the boiling-point results in the tables one could clearly not have foretold these facts.

Turning now to Table III. we see that naphthalene and diphenyl yield molecular weights higher than the theoretical. The solutions of these substances in acetonitrile are non-electrolytes. Again, diphenylamine, which is also a non-electrolyte when dissolved in acetonitrile, yields an abnormally low molecular weight.[1] In fact the molecular weight of this solute is lower than that of silver nitrate, although the latter substance when dissolved in acetonitrile is an electrolyte par excellence.

A comparison of the results obtained with diphenylamine and silver nitrate is of special interest, because these two substances have practically the same theoretical molecular weight. Though the solutions of diphenylamine in both benzonitrile and acetonitrile are non-electrolytes, and the solutions of silver nitrates in these solvents are good electrolytes, yet in both solvents these solutes behave practically alike. This then is a striking illustration that there is no such simple relation between the

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[1] Reference has been made to this fact on a previous occasion. Compare Jour. Phys. Chem. 5, 344 (1901).

boiling-points of solutions and their electrical conductivity as the theory of Arrhenius claims.[1]

At any given pressure, the boiling-point of a solution is determined by the concentration and by the chemical character of the solvent and solute, which determines the mutual attraction existing between them. This mutual attraction is the essence of the so-called osmotic pressure and is the cause of the process of solution. In applying the gas laws to solutions, we do at times get molecular weights for the solute that are equal to the theoretical within the limit of error of experiment; but more frequently we do not, and this regardless as to whether the solutions are electrolytes or not, as is well shown by the solutions in these nitriles.

It is probable that the high molecular weights in benzonitrile are partly, if not largely, due to the relatively high boiling-point of the solvent (189°). In acetonitrile the molecular weights are much lower. Its boiling-point is 80.5°. Examples of this kind are not uncommon; and I hope to recur to this point ere long in the course of a more general consideration of the subject of solutions.

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Madison, Wis.,
Dec. 5, 1901.

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[1] In the case of silver nitrate when dissolved in acetonitrile, the so-called degree of electrolytic dissociation corresponding to the molecular weight 135 (Compare Table III.) is 26 percent; from the conductivity determinations of Dutoit and Friderich (Bull. Soc. Chim. Paris, (3) 19, 327 (1898)) it is about 34 percent for approximately the same concentration. To be sure, this comparison is not quite fair, as we are not comparing the solutions at the same temperature; but the discrepancy would very likely not disappear even if the comparison were made at the same temperature. Compare Jour. Phys. Chem. 5, 339 (1901).

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SOLUBILITY OF CALCIUM CARBONATE IN AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES IN EQUILIBRIUM WITH ATMOSPHERIC AIR[1]

BY FRANK K. CAMERON AND ATHERTON SEIDELL

The experiments on the solubility of calcium carbonate were made in a similar manner to those described in the preceding papers.[2] Since the solubility of the carbonates is dependent upon the partial pressure of the carbon dioxide in the gas phase in contact with the solution, the effort was made to bring these solutions to equilibrium with ordinary air. Air was therefore drawn through the flasks containing the solutions in contact with the calcium carbonate in the solid phase. The flasks were arranged in series with appropriate rubber and glass tube connections and a continuous stream of air drawn through by an aspirator attached to a hydrant. Before entering the solutions the air was drawn through a dilute solution of sulphuric acid to free it from any traces of ammonia or other impurities in the laboratory atmosphere. Precipitated calcium carbonate was used in order to take advantage of the large surface exposed by the material in this form, and thus bring the solutions to equilibrium as quickly as possible. All the salts used were obtained from Baker & Adamson, were labeled C. P., and were found to be of a satisfactory degree of purity. As small changes of temperature did not produce any marked effect on the solubility of the calcium carbonate, and as the temperature of the laboratory held quite constant during the period when this work was done, it was not deemed worth while to make use of a constant temperature bath.

Since it was found that the major part of the calcium went into solution as the hydrogen carbonate rather than as the normal carbonate, the calcium dissolved is stated in terms of the

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[1] Contribution from the Bureau of Soils, U. S. Department of Agriculture. Published by permission of the Secretary of Agriculture.

[2] Jour. Phys. Chem. 5, 537; 5, 643 (1901).

hydrogen carbonate. Of course the statements and charts in terms of reacting weights would be the same for either the normal or hydrogen carbonate.

In the accompanying figure the calcium salt found to be soluble is plotted in all cases on the axis of ordinates and the amounts of other salt components of the solution on the axis of abscissas.

Solubility of calcium carbonate in sodium chloride solutions at 25° C

Air was passed through the solutions for twenty-seven days, the solutions being tested from time to time to determine when final equilibrium was reached, at which time they gave no reaction with phenolphthaleine; that is to say, the solutions contained no normal carbonate dissolved in them.

At first sight this result appeared very surprising, but it is in line with the observations of Treadwell and Reuter, and with the observations made in this laboratory in the study of the equilibrium between the normal carbonate and hydrogen carbonate of calcium, described in a preceding paper.

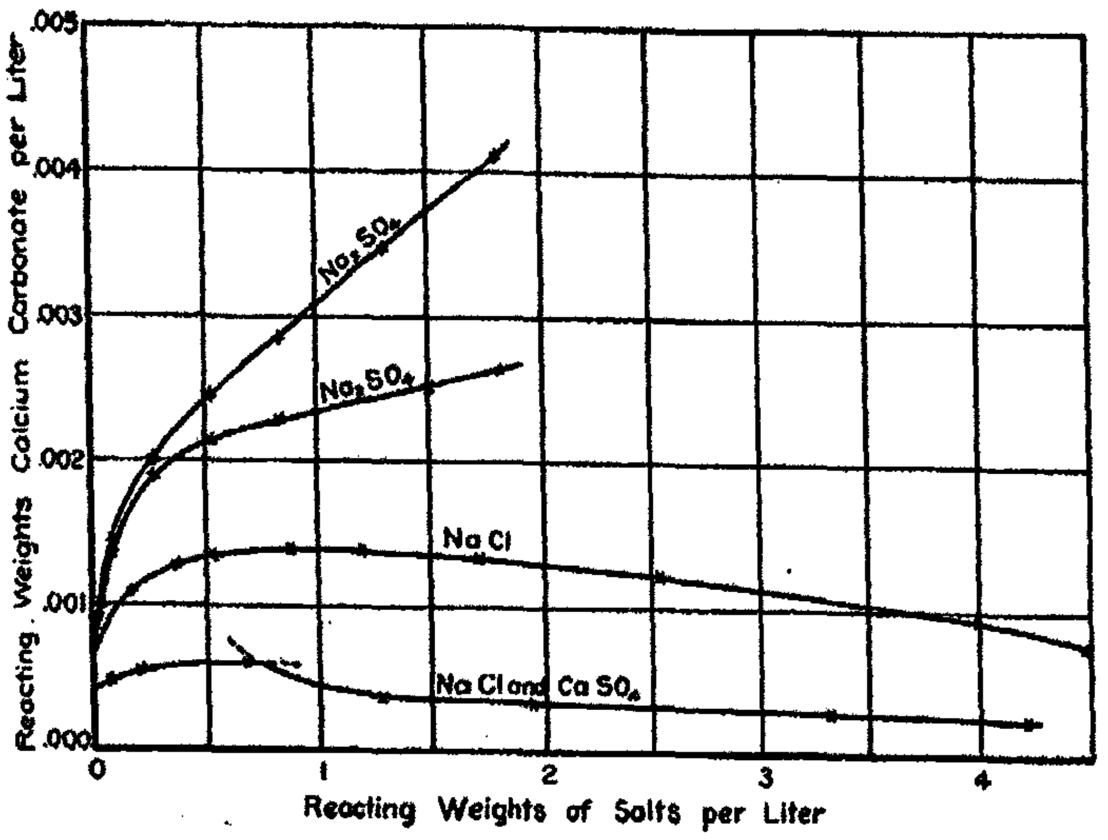
The results obtained in the analyses of the solutions are given in the accompanying table, which is self-explanatory.

TABLE I.

Calcium hydrogen carbonate soluble in aqueous solutions of sodium chloride at 25° C and in equilibrium with air

$Ca(HCO_3)_2$		NaCl	
Grams per liter	Reacting weights per liter	Grams per liter	Reacting weights per liter
0.1046	0.00065	0.000	0.000
0.1770	0.00110	9.720	0.168
0.2051	0.00128	21.010	0.362
0.2152	0.00134	30.301	0.522
0.2252	0.00140	50.620	0.872
0.2212	0.00138	69.370	1.195
0.2172	0.00135	98.400	1.695
0.1971	0.00123	147.400	2.540
0.1569	0.00095	234.500	4.040
0.1227	0.00076	262.300	4.520

These results are presented graphically in the accompanying figure.



The solubility curve presents a well-marked maximum point, corresponding to a solution containing in a liter about 56 grams, or 0.95 reacting weight of calcium hydrogen carbonate; that is to say, at the maximum point the corresponding solution would contain about 0.0561 gram of calcium — equivalent to 0.1402 gram of the normal carbonate. Hence it appears that the solubility of calcium carbonate under these conditions is about 80 times what it would be in pure water free from carbon dioxide.

In the series under consideration it was found that in the solution containing no sodium chloride there was 0.1046 gram per liter of calcium hydrogen carbonate, equivalent to 0.0592 gram per liter of the normal carbonate. Therefore the solubility of the calcium carbonate corresponding to the maximum point of the curve is 2.36 times its solubility in water in equilibrium with the air, but containing no sodium chloride.

Solubility of calcium carbonate in sodium sulphate solutions at 24° C

In this series of experiments normal carbonates were found to be present in the solutions of higher concentrations, although successive examinations at intervals of weeks showed conclusively that the solutions had reached a final state of equilibrium and remained unchanged, even with the prolonged passage of air through them.

In the accompanying table the total amount of calcium in the solutions is given in terms of the equivalent in calcium hydrogen carbonate, although a part of the calcium should more properly be given as the normal carbonate. The actual amounts of the bicarbonate or hydrogen carbonate found in the solution are also given, and in the figure curves are plotted from both series of data. For purposes of comparison this is considered more desirable than giving the amounts of normal carbonate found, which could not well be illustrated in the figures.

TABLE II

Solubility of calcium carbonate in aqueous solutions of sodium sulphate at 24° C, and in equilibrium with air

Total calcium calculated as $Ca(HCO_3)_2$		Calcium actually dissolved as $Ca(HCO_3)_2$		Sodium sulphate	
Grams per liter	R. wts. per liter	Grams per liter	R. wts. per liter	Grams per liter	R. wts. per liter
0.0925	0.00057	0.0925	0.00057	0.000	0.0000
0.1488	0.00092	0.1488	0.00092	2.800	0.0191
0.1729	0.00107	0.1729+	0.00107+	5.235	0.0356
0.2330	0.00145	0.2210	0.00137	11.730	0.0831
0.3240	0.00201	0.3020	0.00188	36.860	0.2612
0.3960	0.00246	0.3440	0.00214	74.010	0.5245
0.4580	0.00285	0.3660	0.00228	116.100	0.8228
0.5630	0.00350	0.3940	0.00245	184.200	1.3054
0.5910	0.00367	0.4060	0.00252	213.700	1.5146
0.6650	0.00413	0.4300	0.00267	255.900	1.8135

It will be observed that the curves do not show maximum points, but that the solubility of the calcium carbonate, both in the form of normal carbonate and of hydrogen carbonate, steadily increases with increasing concentration of sodium sulphate. It is especially worthy of note that the solubility of the calcium carbonate is very much greater in solutions of sodium sulphate than in solutions of sodium chloride, although in the former case the slightly soluble compound, calcium sulphate, is presumably formed, and in the latter the very soluble substance, calcium chloride. Even granting that practically all the calcium sulphate formed again unites with the sodium sulphate to form the soluble double sulphate, and making the further rather improbable assumption that this double sulphate dissociates entirely in such a way as not to yield a calcium ion, the case does not become clear; for, at least in the higher dilutions, it would still be expected that the sodium chloride would have a greater solvent effect than the sodium sulphate. It is true that in the calculation of the data presented in this paper the reacting weight of sodium sulphate is based on the formula Na_2SO_4 instead of on the formula $\frac{1}{2}Na_2SO_4$. An inspection of Fig. 1 will show that even on this latter assumption the sodium sulphate curve would lie well above the sodium chloride curve. Assuming, therefore, that the effect of the sodium ions would be the same in the two cases, it appears that the SO_4 ion has a greater effect than the Cl ion in rendering the calcium carbonate more soluble.

Above a certain concentration (about 50 to 60 grams per liter) with respect to sodium sulphate the curves are practically straight lines; that is to say, the solubility of calcium carbonate in solutions above this concentration is directly proportional to the amount of sodium sulphate present. Assuming the mass law to hold, this indicates that at these higher concentrations the sodium sulphate dissociates as a binary electrolyte according to the scheme

$$NaNaSO_4 \rightleftarrows \overset{+}{Na} + \overset{-}{NaSO_4}.$$

From this point of view it would seem that the relative effects of the $NaSO_4$ ions and the Cl ions on the solubility of the calcium carbonate are to be compared, and that the first-mentioned ion is the more effective.

If it be assumed now that the Ca ion does not unite with the $NaSO_4$ ion to form a more complex ion, but does unite with the Cl ion to form complex ions, the greater solvent effect of the sodium sulphate over that of the sodium chloride becomes intelligible. It is to be frankly admitted, however, that this train of reasoning involves a number of assumptions, and that, while some evidences from other sources may be adduced in support, it can be advanced only tentatively. It further accents the very unsatisfactory state of our knowledge of solutions, especially in other than those of high dilution.

Solubility of calcium carbonate in sodium chloride solutions at 25° C in contact with calcium sulphate in the solid phase

The solutions were found to contain no normal carbonates. The effect of the dissolved calcium hydrogen carbonate on the solubility of the calcium sulphate has been discussed in the preceding paper. By referring to the figure it will be seen that the effect of the dissolved calcium sulphate on the solubility of the carbonate was of the same general nature, but much greater in degree. With increasing concentration of sodium chloride the solubility of calcium carbonate gradually increases up to a maximum point, then drops suddenly, and finally decreases very gradually. The maximum solubility occurs in a solution containing about 40 grams per liter of sodium chloride. It will be remembered that the maximum solubility of the calcium sulphate, when calcium carbonate in the solid phase was also present, was in a solution containing from 80 to 85 grams per liter of sodium chloride.

While the effect of the presence of calcium carbonate on the solubility of calcium sulphate was shown to be slight in solutions containing less than 80 grams per liter of sodium chloride, it will be seen that the effect of the calcium sulphate on the solubility of the calcium carbonate is relatively great in all concentrations with respect to sodium chloride. Furthermore, the normal carbonate appears to be entirely converted to the hydrogen carbonate, in the solutions.

Summary

The solubility curve for calcium carbonate in aqueous solutions of sodium chloride, and in equilibrium with ordinary air, shows a well-marked maximum point. Apparently under such conditions, the solutions contain no normal carbonates.

Sodium sulphate has been shown to have an astonishingly great effect on the solubility of calcium carbonate, the resulting solutions containing not only hydrogen carbonate, but normal carbonate as well. Further, there is no necessary precipitation of the lime carbonate with increasing concentration with respect to sodium sulphate; but the solubility of the lime carbonate steadily increases, with increasing amounts of sodium sulphate in the solution, up to the saturation point of this latter salt.

In the presence of solid calcium sulphate the solubility of calcium carbonate is much decreased. With increased concentration with respect to sodium chloride, the solubility of calcium carbonate increases to a maximum, then suddenly decreases, showing a break in the solubility curve. In equilibrium with ordinary air, the solutions contain no normal carbonates.

NEW BOOKS

The Absolute Atomic Weights of the Chemical Elements. *Established upon the Analyses of the Chemists of the Nineteenth Century, and Demonstrating the Unity of Matter; presented in simple language to the general scientific public. By Gustavus Detlef Hinrichs. 15 × 23 cm; pp. xvi + 303. St. Louis: Carl Gustav Hinrichs, 1901. Price: paper, $1.00, net.* — Down in the bottom of his heart each one of us believes that some modification of Prout's hypothesis is true. The accepted atomic weights are just enough away from multiples of anything or of any combination of several hypothetical elements to deprive any such hypothesis of an experimental basis. On the other hand, they approximate much more nearly the desired values than seems at all probable in case they really are independent values. If the elements as now known are not true elements, we have one of two hypotheses open to us. Either our so-called elements are analogous to solid solutions of the real elements or they are compounds of these elements. If the second hypothesis be true, our accepted atomic weights should be wrong. Mr. Hinrichs undertakes to prove that this is the case. His thesis is that all atomic weights are exact multiples of the twenty-fourth part of the atomic weight of carbon, this latter being taken as exactly twelve.

It will have to be admitted that the tone of the book is inexcusably bad, and that Mr. Hinrichs has gone out of his way to weaken whatever force his argument may have. It is quite possible that our accepted atomic weights are wrong. It is quite possible that chemists have been over-conservative in their attitude. That has happened in other cases and will go on happening to the end of time. It is possible that the men, on whom Mr. Hinrichs pours out his wrath, may be singularly deluded. These are all questions which are open to debate. It is not possible that these men are all deliberately dishonest. This is not a point which we can consider even for a moment. There is, however, another possibility, — that Mr. Hinrichs is singularly deluded. Because one is in a minority, one is not necessarily right.

The tendency on the part of every reader of this book will be to assume that a case that is put so abusively must be very weak. In this particular case, such an assumption would be an injustice, because the substance is very much better than the form. We will therefore outline what seem to be the strong points in the argument and, after that, we will consider the weaknesses.

Mr. Hinrichs points out, quite correctly, that there is no reason to assume that any mean of a series of experiments necessarily gives the value desired. As a case in point he cites the hopelessness of trying to find the weight of a new silver dollar merely by weighing a large number of old ones. Here the true value lies above any single value and can be approximated by extrapolation and definite assumptions with regard to abrasion. Mr. Hinrichs also makes the point that, in the overwhelming majority of cases, the 'probable error' of the chemist is merely an arithmetical farce. All that a probable error shows is the accuracy in reproducing conditions and it does not stand in any relation whatsoever to the real accuracy of the results.

The author claims that all 'dry way' methods are better than 'wet way' methods, and he specifically excludes any silver chloride determinations on the ground of solubility of the salt. This eliminates a large number of determinations which have given results differing from those required by the author's hypothesis and is therefore, tactically, a brilliant move. Whether it is justifiable in a search after truth is not so certain. Errors due to occlusion do occur in 'dry way' processes, though the author makes no reference to them.

In considering the ratio between carbon and oxygen, the author is certainly right in excluding all forms of carbon except diamond. The experiments of Moissan have shown the enormous difficulty in getting pure carbon. Excluding doubtful results the author finds the ratio 12 : 16 exactly. This will not be disputed because Ostwald admits that the variations from the even number fall within the limits of experimental error, though he himself inclines to 12.003 as the most probable value.

Crookes determined the ratio of thallium to thallium nitrate and found 1.303912 for the ten experiments, or 1.303915 if the first experiment be excluded, while Hinrichs calculates a ratio of 1.30392 on the basis of Tl 204, N 14, O 16. [It may be worth mentioning that Ostwald (Lehrbuch 1, 113) gives the total thallium and the total thallium nitrate for the ten experiments from which follows a so-called mean ratio which is smaller than nine out of the ten single ratios obtained by Crookes.] This agreement is very remarkable and seems an extremely improbable one except on the assumption of integral values for thallium and nitrogen. This is not the view taken by the chemical world and it is therefore necessary to consider the ratio of nitrogen to oxygen.

The value assumed by Clarke in 1882 was 14.06, which happened to be very close to that obtained from the density determinations. Consequently Mr. Hinrichs takes the density determinations as accurate. In 1897, however, Lord Rayleigh's measurements gave 14.07 for atmospheric nitrogen (containing argon) and 14.003 for pure nitrogen. This last value is not to be distinguished from 14.00 which our author therefore takes to be the true value. Ostwald takes Stas's value of 14.041 as the correct one; but Mr. Hinrichs excludes Stas's work specifically. If that be done, there seems to be no reason for not taking 14.00 as the true value.

Ramsay and Aston converted borax into sodium chloride. Mr. Hinrichs shows that the results agree admirably on the assumption of Na 23, Cl 35.5, O 16, B 11. The determination of boron carbide by H. Gautier gives a value of 11 for boron. We therefore have the same result for NaCl that we have just considered for Tl and N, that the value is an exact multiple of 0.5. The experiments of Turner and of Svanberg on mercuric chloride make chlorine 35.5 if mercury be taken as 200. This is in harmony with Hardin's electrolytic experiments. The experiments of Erdmann and Marchand on mercuric oxide make mercury 200, so the chain is complete and we may consider sodium as exactly 23.0.

Platinum is made 195 on the basis of Seubert's measurements; sulphur becomes 32 from Marchand's experiments; and Smith's data give 120 for antimony. The value 207 for lead is based on the work of Berzelius, and 56 for iron refers back to Svanberg, while gold is made 197 from Mallet's data.

We have thus oxygen, nitrogen, carbon, boron, mercury, chlorine, thallium, sulphur, lead, sodium, platinum, gold and antimony as confirming the author's views. We miss as yet barium, bromine, calcium, copper, hydrogen, iodine, potassium, silver and strontium, all elements which are popularly supposed to have been determined with considerable accuracy. Of these, calcium is generally accepted as 40 and Ostwald gives bromine as 79.962 with a possible error of 0.038, which thus brings the even 80 within the calculated limit of error. The author takes 137 for barium, rejecting the value of 137.5, which he calculates from the work of Richards. Copper is made 63.5, iodine 127, and silver 108, while the values for potassium and strontium are considered as not known. Hydrogen is made, chiefly from Rayleigh's density determinations, Morley's measurements being rejected on the ground that he found oxygen to weigh more in one flask than in another, and also on the ground of admitted impurities, p. 253, in the gases.

The question may be asked why we should take the synthesis of thallium nitrate as determining the values for thallium and nitrogen and not accept the work of Stas on silver nitrate. Mr. Hinrichs plots the calculated atomic weight of nitrogen against the weight of silver used in the silver nitrate syntheses and shows that for the same weight of silver the values from fused silver nitrate always lie below those from dried silver nitrate. Consequently it is not justifiable to take the mean of both sets of determinations as giving the true value. Further he claims that both sets of observations show fluctuations with the mass taken, the values for nitrogen coming out higher for one hundred and fifty grams of silver than for either higher or lower amounts. As it is, taking the mean of Stas's and Marignac's measurements on fused silver nitrate, nitrogen becomes exactly 14 if silver be taken as exactly 108.

Taking it all in all, the author has developed a very strong argument; but he has had to reject the volumetric determinations of the silver halides and this is the weak point. It is true that the end-points in the titration of silver nitrate by sodium chloride are not the same when approached from the two ends. It is also true that the mean of these two values is not necessarily the correct value. It may also be admitted that silver chloride is soluble in water, between one and two milligrams per liter according to Goodwin. These facts are generally admitted, but that does not prove that methods involving the solubility of silver chlorides are necessarily worthless. This is distinctly not proved and yet it is of fundamental importance. If these methods can be thrown out, the author is probably right in his conclusions. If they cannot be thrown out, the author is still possibly right, but the probability of it is very much decreased.

The reviewer is not as yet prepared to say that Mr. Hinrichs is right in his conclusions; but it does seem as though the question of the atomic ratios was distinctly an open one. It seems also as though it would be profitable to science if some of the data accepted by Mr. Hinrichs should be verified and that work of this sort is of far more immediate importance than to determine the atomic weights of a large number of elements.

There is another way of looking at this matter which may be profitable. What does the fact that the views of Mr. Hinrichs have not been accepted prove in regard to their accuracy or inaccuracy? Absolutely nothing at all. The natural conservatism of scientific men is so great that a revolutionary truth has to fight its way and to fight hard. Mr. Hinrichs has never made any atomic weight determinations himself, nor has he ever had students who have done so. This has been fatal to the acceptance of his views, but it has proved nothing in regard to their merit. The question at issue is not one of manipulation, but of the critical interpretation of results. The man with great manipulative skill may also have a highly developed critical sense, but it is not necessarily the case and the two faculties are quite as likely to be found separately as together. Consequently two of the arguments against Mr. Hinrichs fall to the ground, namely that his views must be wrong because they have not met with favor and that he is not qualified to judge because he has never shown his ability to make atomic weight determinations.

The whole question is therefore open and can be broadly stated as follows; Do the methods approved by Hinrichs give the results that he thinks they do?

Wilder D. Bancroft

Die Normalelemente *und ihre Anwendung in der elektrischen Messtechnik. By W. Jaeger. 16 × 24 cm; pp. 131. Halle: Wilhelm Knapp, 1902. Price: paper, 6 marks.*—The book opens with a chapter on the definition and classification of normal cells, the definition being as follows: "A normal cell is a chemical system with phases of constant composition in reversible equilibrium." The second chapter deals with the general theory of normal cells, the sub-heads being: relation between the energy of the system and the electromotive force; calculation of the energy of a cell; variation of the electromotive force of a cell with the concentration of a solution; temperature coefficient; osmotic theory. The third section is devoted to special forms of normal cells with the Clark and Weston cells as the important features. Chapter four takes up the standardization and use of normal cells. The whole makes a very valuable and serviceable monograph, presenting the main facts in a clear and concise manner. As the author does not consider the effect of pressure, his incorrect application of the phase rule does no harm.

The official German value for the Clark cell is now 1.4328 int. volts at 15°, and for the Weston cell is 1.0186 int. volts at 20°. It seems rather a pity that no reference should have been made to the work of Richards on the silver voltameter.

Wilder D. Bancroft

Ueber radioaktive Substanzen und deren Strahlen. *By F. Giesel. (Sammlung chemischer und chemisch-technischer Vorträge, VII. Band, 1 Heft.) 16 × 24 cm; pp. 28. Stuttgart: Ferdinand Enke, 1902. Price: paper, 1.20 marks.* — The only one of the new radio-active metals which seems to be at all certain is radium, with an atomic weight higher than 174 and a characteristic spectrum. Polonium loses its radio-activity on standing and its spectrum is not yet known to differ from that of bismuth. Actinium shows only the thorium lines and the monograph was written before anything had been published about carolinium. The radio-active lead of Hofmann and Straus is believed to be 'induced' lead. This is the more probable since the experiments of the Curies, of Rutherford and others show that many metals can be made temporarily active. All that we know about this at present is that this charge or whatever it is is transmitted by or through the air and is not a direct result of the light rays. *Wilder D. Bancroft*

Ueber feste Lösungen. *By Giuseppe Bruni. Deutsch von E. E. Basch. (Sammlung chemischer und chemisch-technischer Vorträge, VI. Band, 12 Heft.) 16 × 24 cm; pp. 415-468. Stuttgart: Ferdinand Enke. Price: paper, 1.20 marks.*—This is a carefully written and readable review of the subject of solid solutions. In general the ground has been thoroughly covered, though there is no reference to Cady's work on naphthalene and chloracetic acid; to Walker and Appleyard's work on picric acid, water and silk; to Küster's work on ether, rubber and water, and on iodine, starch and water.

Wilder D. Bancroft

Physikalisch-chemische Propaedeutik, *unter besonderer Berücksichtigung der medicinischen Wissenschaften, und mit historischen und biographischen Angaben. By H. Griesbach. Erste Hälfte, pp. 1-272 (1895). Price: 6 marks. Zweite Hälfte: erste Lieferung, pp. 273-592 (1896); zweite Lieferung, pp. 593-944 (1897). 16 × 24 cm. Leipzig: W. Engelmann.*—This unique work purports to deal with "the fundamental theories of physico-chemical science, with special reference to medicine." The "First half" appeared in 1895, and contained eighteen chapters on physico-chemical science and logic; methods, objects and origin of the science; space and time; causation; measurement, graphic representation; matter, energy, work, force; momentum, motion, rest, velocity, resistance to motion; divisibility, constitution of matter, ether hypotheses, historical sketch of atomism; living and lifeless matter.

The "second half" was advertised to appear in the same year, and the headings of its twenty-one chapters were given. It appears, however, that the author has found the task of condensing a text-book of physics, chemistry, and biology into the space of 500 pages to be more difficult than he had anticipated; the "first section of the second half" was not ready until 1896, and although larger than the whole "second half" as originally contemplated, it contains but five chapters, viz., fermentation and pathogenic phenomena; porosity; air-pressure, barometer, manometer; changes of state of aggregation; and generalities on the state of aggregation. The "second section" brings three more,—molecular mixtures; classification of the forms of energy; and generalities on the various kinds of energy. There is still a "third section of the second half" and then the second volume begins.

Judging by the length of the individual chapters, this growth of the work under the hands of its author has been confined to certain sections. The chapter on fermentation has become a treatise on bacteriology of 220 pages; the generalities on the states of aggregation occupy 136 pages; and the 231 devoted to "molecular mixtures" contain, with much else, a full account of the "dissociation theory."

The chapter on "porosity" on the other hand, is restricted to 20 pages; a short résumé of its contents may afford some idea of what is to be found in this remarkable book. To begin with, the existence of "intermolecular spaces" is argued from the phenomena of compressibility, the turgescence of gelatine in water, and the contraction observed when alcohol and water are mixed. Pores of another order of magnitude are observable in the sponge, while the porosity of wood may be evidenced by squeezing mercury through it, with which phenomenon the author groups the passage of carbonic oxide through hot iron, of carbon through hot porcelain, and of air through the shells of eggs. The pores of the skin are next described, and their importance in respiration (especially to the amphibiae) explained; and the conditions under which medicaments may be administered through the skin are deduced. Porosity of building materials comes next; and then the porosity of the soil, with methods of measurement, and illustrations of the importance of this factor in hygiene and in agriculture. The remainder of the chapter is devoted to adsorption. After a paragraph on experimental methods and a table giving the amounts of eleven different gases absorbed by charcoal, the author refers the difficulty of removing the last traces of air from barometers, and the necessity of using exsiccators in gravimetric analysis, to adsorption; describes Moser's breath-pictures, Davy's glow-lamp and Doebereiner's hydrogen igniter; and closes the chapter with a reference to the value of turf as an antiseptic bandage, and to the use of charcoal in filtering water, in preserving meat, and in refining sugar.

When it is added that this short chapter is illustrated by four figures; that of its twenty pages, two (in fine type,) are devoted to a description of the structure of the hen's egg, two more to the anatomy and physiology of the human skin, and one to an historical "excursus on the air-pump"; that there is a quotation of half a page (in English) from Boyle, and four lines from Hippocrates; that references to the literature occupy two pages; and finally that space is found for short biographical notices of Papin, Babinet, Kyan, and Doebereiner, and for an historical sketch of the Accademia del Cimento, some idea may be conveyed of the variety and comprehensiveness of this unique production.

In the originality of its plan Griesbach's *Propaedeutik* reminds one of Lehmann's *Molekularphysik*, although it far exceeds the latter work in scope; the treatment is simple, though of necessity much condensed; the text is accompanied by full marginal notes; and the statements of fact are accurate and up to date. Although no previous knowledge of science on the part of the reader is presumed, both chemists and students of medicine will find in this book information on all sorts of interesting and important subjects that are usually not included in the "courses" on science in the universities. *W. Lash Miller*

Justus von Liebig und Christian Friedrich Schönbein. *Briefwechsel, 1853-1868. Mit Anmerkungen, Hinweisen, und Erläuterungen versehen, und herausgegeben von Georg W. A. Kahlbaum und Eduard Thou. 14 × 22 cm; pp. xxi + 278. Leipzig: Johann Ambrosius Barth, 1899. Price: paper, 6 marks.* — By far the greater number of the letters are from Schönbein, with brief but sympathetic replies from Liebig, whose high opinion of his correspondent "tireless in creating, always producing something unexpected and out of the ordinary" is everywhere visible.

Throughout the whole period of the correspondence Schönbein was devoted to the study of his "chemical hero" oxygen; but his numerous and important discoveries attracted comparatively little attention at the time, the majority of the chemists of that day being "so busy with the preparation of new compounds, and so much occupied in forcing the varied materials of their science into three Spanish boots, hydrogen, water, ammonia, that they could pay but little heed to researches owning any other object". Schönbein's rather contemptuous opinion of the "Typists" was fully shared by his correspondents, Liebig, Graham, and Faraday; Faraday's *dictum* is the shortest: "I am too stupid to understand the organic chemistry of the present day!!"

Times have changed, however; and the "Schönbein Feier" (in connection with which these letters are published) is celebrated when the phenomena of catalysis, slow oxidation, nitrification, and the like are attracting universal attention; and when our author's contention that fermentation is conditioned by the catalytic action of unorganized matter has just received striking confirmation.

The letters are most interesting; and many of the experiments described in them would make capital lecture demonstrations. *W. Lash Miller*

Leçons sur les Moteurs à Gaz et à Pétrole. *By L. Marchis.* (*Actualités scientifiques.*) *11 × 18 cm; pp. l + 175. Paris: Gauthier-Villars, 1901.*—This neat little volume is the outcome of a course of lectures given by Marchis at Bordeaux, in 1899-1900, before an audience of engineers. It begins with an account of the successive designs of gas motors, and petroleum motors, and then enters in detail into a theoretical study of the action of the various types of these prime movers. Establishment of the best conditions for working and determination of the thermal efficiency to be approximated in each case, are the primary aims of the book. The theoretical treatment is prefaced by an exposition of the principle of the equivalence of heat and work, and is followed by a chapter on the calorimetric study of indicator diagrams, and by another on entropy-temperature diagrams. The work has been done with extreme care, and with a proper use of the principles of thermodynamics. *J. E. Trevor*

A Manual of Volumetric Analysis. *Treating on the subjects of indicators, test-papers, alkalimetry, acidimetry, analysis by oxidation and reduction, iodometry, assay processes for drugs with the titrimetric estimation of alkaloids, estimation of phenol, sugar, tables of atomic and molecular weights. By Virgil Coblentz. 15 × 23 cm; pp. viii + 181. Philadelphia: P. Blakiston's Son and Co., 1901. Price: bound, $1.25, net.*—This book gives an excellent presentation of all the ordinary methods of volumetric analysis, and of some that are not commonly included in text-books. The treatment of indicators is unusually complete, although it is doubtful whether the beginning student would derive much benefit from the paragraph on the theory of indicators. On the whole the work will answer very well the purpose of a handbook for the student and a small reference book for any worker in this field.

The occurrence of errors in spelling and in the use of words is unfortunate in books anywhere, and must be protested against in those intended for instruction. They may not be unusually frequent in this volume, yet when the eye lights by chance on "comprehensive" for "comprehensible," and the persistent transformation of the name Poirrier into Porrier, one must infer that other errors of the same kind would be found if the text were closely examined.

A. P. Saunders

An Introduction to Chemical Analysis. *For students of medicine, pharmacy, and dentistry. By Elbert W. Rockwood. 13 × 19 cm; pp. vi + 255. Philadelphia: P. Blakiston's Son and Co., 1901. Price: bound, $1.50, net.* — This is one of those books upon which the reviewer need use few words. It is intended for a special class of students; and though not free from minor errors, its material is wisely selected to meet the needs of those for whom the book was made.

A. P. Saunders

Analyse des Matières grasses. *By Georges Halpen. (Encyclopédie scientifique des Aide-Memoire). 11 × 18 cm; pp. 176. Paris: Gauthier-Villars. Price: paper, 2.5, boards, 3 francs.* — This interesting little volume arose out of a course of lectures given by the author on the analysis of fats and oils, at the Institut Pasteur. It is provided with numerous tables, and gives what appears to be a fairly complete survey of this somewhat special field.

A. P. Saunders

Les Plantes tinctoriales et leurs Principes colorants. *By V. Thomas. (Encyclopédie scientifique des Aide-Mémoire). 11 × 19 cm; pp. 196. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs.* — This volume of the handy and well-printed *Aide-Mémoire* series continues the treatment of the author's earlier volume, in the same series, on *Les Matières colorantes naturelles.* It gives a systematic account of the natural vegetable dyes; and closes with a rapid review, accompanied by a bibliography, of the subject of the glucoside colors.

J. E. Trevor

3500 Questions on Medical Subjects. *Third edition, enlarged. Philadelphia: P. Blakiston's Son and Co., 1901.* — This is a quiz-book for medical students. Seventeen of its pages are devoted to chemistry. It seems well adapted to its purpose.

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

On the existence of a new element associated with thorium. *C. Baskerville. Jour. Am. Chem. Soc.* 23, *761* (*1901*). — On boiling neutral thorium chloride with sulphur dioxide part of the thorium precipitates as basic sulphate. From the filtrate, the balance of the thorium is precipitated by ammonia. A similar separation can be effected by fractional crystallization of a citrate solution. The thorium oxide from the more insoluble portion has a density of about 9.2, while the other oxide runs above 10.5. The first is thorium; the second is believed to be a new element, to which the author assigns the name carolinium. Carolinium is markedly radio-active, thorium probably not at all. The atomic weight of thorium is about 223, while that of carolinium is over 260. Carolinium tetrachloride is more volatile than the thorium compound, and this fact had previously been noticed by Chydenius who did not investigate the matter further. The paper is a preliminary one. *W. D. B.*

The atomic weight of antimony. *G. C. Friend and E. F. Smith. Jour. Am. Chem. Soc.* 23, *502* (*1901*). — Hydrochloric acid was passed over potassium antimonyl tartrate, converting this salt into potassium chloride. The resulting atomic weight of antimony is 120.353. *W. D. B.*

On the tendency of the atomic weights to approximate to whole numbers. *R. J. Strutt. Phil. Mag.* (*6*) 1, *311* (*1901*). — From the theory of probabilities it is shown that the atomic weights should follow some modification of Prout's law, and that the chance of an accidental coincidence in the approximation to whole numbers is not more than *1* in 1000. *H. T. B.*

Remarks to a paper by T. Middel. *W. Felgentraeger. Drude's Ann.* 5, *234* (*1901*). — In a paper by Middel (5, 406) the cause was given for the change in sensitiveness with temperature of the balance used by Richarz and Krigar-Menzel in their work on the mean density of the earth. In the present note the author states that the change is better attributed to the unequal expansion of the steel knife edges and brass beam. *H. T. B.*

The air barometer. *H. A. Naber. Drude's Ann.* 4, *815* (*1901*). — This is an exceedingly interesting and valuable historical sketch of the development of the air barometer. The advantages of such a barometer are set forth at some length. In conclusion the author requests that historical or other references be sent to him. *H. T. B.*

One-Component Systems

On the melting-point of gold. *L. Holborn and A. Day. Drude's Ann.* 4, 99 (*1901*). — In the authors' previous paper on the measurements of high temteratures (5, 613), the melting-points for a number of metals were given, by what the authors call the wire method and crucible method. For gold, only the former method was given, and it is therefore considered of interest to determine the melting-point, using a greater quantity of the material, 450 grams of the pure gold being used. It is shown that the influence of air is very small and produces no error. By the crucible method the melting-point is 1063.5°, whereas by the wire method it is 1063.9°. For the calibration of a thermojunction the latter method is considered to be in every way satisfactory, and requires the use of only 0.03 gram of gold. *H. T. B.*

The liquefaction of hydrogen. *M. W. Travers. Phil. Mag.* (*6*) *1*, *411* (*1901*). — The author describes very completely his apparatus for liquefying hydrogen, on the same principle as the method used by Dewar. The advantages shown are cheapness and expediency. It is shown that hydrogen remains a perfect gas down to very low temperatures, but that the point at which the Joule-Thomson effect changes sign has not yet been determined. *H. T. B.*

On atomic and molecular volumes. *J. Traube. Drude's Ann.* 5, *548* (*1901*). — The author considers as a continuation of his earlier work, the molecular and atomic volume at the boiling-point, at 0° C, at the critical temperature, and at the absolute zero. He finds it convenient for liquids, as with gases, to introduce three different volume conditions. 1. A "Kernvolume;" 2. The constant b (van der Waals) which is as the "Kernvolume" variable; 3. The molecular covolume. A section of the paper is devoted to the work of de Heen, Battelli and Galitzine on the critical condition. It is shown that the value of b for gases is in the proportion of $\sqrt{2}:1$ greater than b for liquids, in which case the work of these investigators may be accepted as being in accord with other work. In regard to the volume of the solid material on solidification it is shown that the diminution in volume stands in an inverse ratio to the degree of association of the liquid at the temperature of solidification.

H. T. B.

On the expansion of metals at high temperatures. *L. Holborn and A. Day. Drude's Ann.* 4, *104* (*1901*). — Reviewed (5, 613) from Sitzungsber. Akad. Wiss. Berlin, 1900, 1009.

Studies with the air thermometer. *A. W. Kapp. Drude's Ann.* 5, *905* (*1901*). — The author describes a change which he introduced in the Jolly air thermometer to facilitate more accurate readings at high temperatures up to 400° C. The manometer, as first suggested by Neumann, is connected to the thermometer bulb by a long metal capillary tube, thus placing it beyond the reach of the heated region. Various mechanical devices are included and described to aid in securing accurate readings. Some observations are given at the end to show the accuracy of the instrument. *H. T. B.*

Measurements of the expansibility of a hard Jena glass. *J. T. Bottomley* *and W. T. Evans. Phil. Mag.* (*6*) 1, *125* (*1901*). — The glass adopted by the authors for high temperature, air-thermometer work is a hard Jena glass, called by Messrs. Schott and Genossen, Verbrennungsrohrenglas. Measurements by the weight-thermometer method are made of the cubical expansion of this glass. The results obtained are 0.00177, 0.00182, 0.00183, 0.00181. *H. T. B.*

Thermal absorption of carbonic dioxide. *S. Arrhenius. Drude's Ann.* 4, *690* (*1901*). — The paper is the outcome of the author's earlier work on the influence of carbonic dioxide in the air on the temperature of the earth. Tyndall's work on the absorption of heat by carbonic dioxide is studied in connection with later work, and the conclusions are applied at considerable length to the question of the temperature of the atmosphere and earth being influenced by the presence of CO_2 and water vapor. *H. T. B.*

On the influence of temperature on the thermal conductivity of glass. *J. Krüger. Drude's Ann.* 5, *919* (*1901*). — The work described in the present paper was undertaken to reconcile the discrepancy between the results of Paalhorn and those of Focke for the temperature coefficient of the same kind of glass. The cause of the error is pointed out as one inherent in the method employed, and a modification is suggested which appears to obviate it. A very slight decrease in thermal conductivity with rise of temperature is shown.

H. T. B.

Two-Component Systems

The boiling-point curve for mixtures of ethyl alcohol and water. *W. A. Noyes and R. R. Warfel. Jour. Am. Chem. Soc.* 23, *463* (*1901*). — The authors find the minimum boiling-point, about 0.13° below the boiling-point of pure alcohol, for a solution of aqueous alcohol containing 96 parts of alcohol by weight. It is a real pleasure to have this matter settled conclusively.

W. D. B.

Multi-Component Systems

Contributions to the knowledge of reversible reactions. *W. N. Stull. Jour. Am. Chem. Soc.* 23, *508* (*1901*). — The action of hydrogen sulphide on zinc or cadmium sulphate in sulphuric acid solution or on zinc or cadmium chloride in hydrochloric acid solution is slow. With saturated hydrogen sulphide the range of concentration of free acid within which it would be possible to separate cadmium completely from zinc is only about seven percent in hydrochloric acid solutions, while it is seventeen percent in sulphuric acid solutions.

W. D. B.

On the decomposition of sodium nitrate by sulphuric acid, II. *C. W. Volney. Jour. Am. Chem. Soc.* 23, *489* (*1901*). — The first stage is represented by the equation

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3.$$

This takes place below 100°. The next stage, occurring between 100° and 122°, is to be written

$$NaH_3(SO_4)_2 + NaNO_3 = 2NaHSO_4 + HNO_3.$$

W. D. B.

On the decomposition of the chlorides of alkali metals, I. *C. W. Volney.*

Jour. Am. Chem. Soc. 23, *820* (*1901*). — The reaction between sodium chloride and sulphuric acid takes place in two stages:

$$2NaCl + 2H_2SO_4 = NaH_3(SO_4)_2 + HCl + NaCl,$$
$$NaH_3(SO_4)_2 + NaCl = 2NaHSO_4 + HCl.$$

The first reaction takes place spontaneously and involves practically no heat effect. The mass must be heated in order to bring about the second reaction. When potassium chloride is substituted for sodium chloride, the first reaction evolves heat, while with ammonium chloride there is absorption of heat.

W. D. B.

The sulphohalides of lead. *V. Lenher. Jour. Am. Chem. Soc.* 23, *680* (*1901*). — The author has prepared the sulphohalides of lead by dissolving lead sulphide in a strong solution of the halogen acid and adding water. No attempt is made to determine any limiting conditions, and this may be taken as a typical instance of the kind of work done by people who are not familiar with the phase rule. *W. D. B.*

The reaction between chlorine and ammonia. *W. A. Noyes and A. C. Lyon. Jour. Am. Chem. Soc.* 23, *460* (*1901*). — The normal relation between chlorine and ammonia is represented by the equation

$$12NH_3 + 6Cl_2 = N_2 + NCl_3 + 9NH_4Cl,$$

but this result is obtained only when the two gases are taken approximately in the proportions called for by the equation. *W. D. B.*

The indirect weighing of quantitative precipitates. *R. W. Thatcher. Jour. Am. Chem. Soc.* 23, *544* (*1901*). — If we know the sum of the volumes of a liquid and a precipitate, the sum of the weights and the specific gravities of liquid and of precipitate, we can write four equations connecting the four unknown quantities, the single weights and the single volumes, and can therefore solve for all four or for any one. The author shows that this method gives satisfactory results in a number of cases. In considering the ease and accuracy of the method, one point seems to have been overlooked. If we are to determine densities to the fifth decimal place we must hold our temperature constant at least to 0.05°, and there is no reference in the paper to any such point. *W. D. B.*

Velocities

Studies on solutions of stannous salts, III. *S. W. Young. Jour. Am. Chem. Soc.* 23, *450* (*1901*). — The reaction for the oxidation of stannous chloride in aqueous hydrochloric acid solution may be written

$$SnCl_2 + 2HCl + O = SNCl_4 + H_2O,$$

or

$$SnCl_2 + 3H_2O + O = Sn(OH)_4 + 2HCl.$$

In the first case the stannic chloride would be hydrolyzed by the water with formation of $Sn(OH)_4$ and hydrochloric acid, a change which could be detected by measuring the conductivity at intervals. Experiments showed a change corresponding to the first reaction irrespective of whether the oxidizing agent were oxygen, potassium bichromate, ferric chloride, hydrogen peroxide, or sodium hypochlorite. It was not possible to calculate a satisfactory reaction velocity constant, but the author shows that Ostwald is wrong in assuming that maximum reaction velocities at any moment can occur only when catalytic agents are present. *W. D. B.*

Theory of cloud formation on mountains. *F. Pockels. Drude's Ann.* 4, *459* (*1901*). — This is an interesting attempt to work out quantitatively some of the causes governing the condensation of moisture from air rising from the sides of mountains under the increased wind pressure at the base. A number of diagrams are given, showing the relation between the mountain profile and the rate of formation of cloud under certain specified conditions. A zone of maximum cloud formation exists, depending more on the contour than on the height of the mountain. *H. T. B.*

Electromotive Forces

Researches with standard cells, in particular the Weston cadmium cell. *W. Jaeger and S. Lindeck. Drude's Ann.* 5, *1* (*1901*). — This paper contains a complete summary of the recent series of experiments made at the Reichsanstalt to test the efficiency of the Weston cadmium cell. A great mass of numerical data forms several pages of the Annalen, representing an immense amount of labor and contributing a valuable addition to the large quantity of literature on this subject. As has been pointed out in a review of a previous paper (5, 619) the irregularities shown by this cell are ascribed to the strength of the amalgam, and the adoption of an amalgam of 13 percent instead of 14 percent, as previously used, causes the irregularities to disappear. A redetermination of the temperature coefficient vindicates the original formula proposed by one of the authors for his type of cell, although for a 13 percent amalgam a new formula has been obtained which agrees more nearly with the observed value. *H. T. B.*

On the irregularity of the Weston cadmium cell with a 14.3 percent amalgam in the neighborhood of 0°. *W. Jaeger. Drude's Ann.* 4, *123* (*1901*). — A reply to the criticisms offered by Barnes and independently by Cohen of the author's work on the Weston cells. It is claimed that only in a 14.3 percent amalgam will the irregularity in the Weston cell occur, and that there is complete agreement with the author's temperature formula between $-16°$ and $+40°$ for a cell of 13 percent amalgam. A large number of cells are tested with a more or less complete vindication of the author's results. It is of interest to have a more thorough investigation of the Reichsanstalt form of cell taken up in this way, and more particularly to have the somewhat widely scattered notes on this work summarized. *H. T. B.*

On the thermoelectric properties of oxides and metallic sulphides. *E. van Aubel. Drude's Ann.* 4, *416* (*1901*). — The author shows that the conclusions reached by Anton Abt (5, 620), that the additive, thermoelectric properties of some of the metallic sulphides and oxides, are by no means general, as shown by his own work. The author's somewhat harsh criticism by no means detracts from the interest and possible significance of Abt's work. *H. T. B.*

On the characteristic curves for the electric discharge through rarefied gas. *E. Riecke. Drude's Ann.* 4, *592* (*1901*). — By the characteristic curve the author refers to the relation between electromotive force and current strength for any particular tube. In the present paper the dependence of the characteristic on the pressure of the gas and on the influence of a magnetic field is studied very completely. *H. T. B.*

Magnetic properties of nearly pure iron and aluminium. *S. W. Richardson and S. C. Laws. Phil. Mag.* (*6*) 1, *296* (*1901*). — A preliminary note in which it is shown that the magnetic behavior of impure alloys of iron and aluminium is very different to iron itself. A later paper by Richardson and Lownds gives a more complete exposition. (Next review.) *H. T. B.*

The magnetic properties of the alloys of cast-iron and aluminium. *S. W. Richardson and L. Lownds. Phil. Mag* 1, *601* (*1901*). — The majority of the experiments described were made by the ballistic method on a specimen of iron containing 3.64 percent of aluminium. Among the most important conclusions cited by the author are the following: "The hysteresis loss at first diminishes as the temperature rises. It then increases and reaches a maximum value at about 550° C, which temperature is about 80° higher than the temperature of maximum induction. On further heating, it falls off rapidly and becomes negligible at about 700° C. An abrupt increase in the permeability takes place at 652° C (during heating), followed by an equally abrupt diminution on further heating. The curve connecting the temperature of minimum permeability and the percentage of aluminium for the specimens investigated, is a straight line. The microscopic examination of the specimens shows the presence of crystals." *H. T. B.*

Electrolysis and Electrolytic Dissociation

The electrolytic separation of mercury from copper. *C. R. Spare and E. F. Smith. Jour. Am. Chem. Soc.* 23, *579* (*1901*). — It is shown again that mercury can be completely separated from copper by electrolyzing a cyanide solution at 65° with a current density of not over 0.0003 amp/cm^2. The authors believe that the traces of carbon, often found in metals deposited from cyanide solutions, are due to incomplete washing. *W. D. B.*

The precipitation and separation of silver in the electrolytic way. *W. H. Fulweiler and E. F. Smith. Jour. Am. Chem. Soc.* 23, *582* (*1901*). — Silver can be separated completely from copper in a cyanide solution with a current density of 0.0002 amp/cm^2 even when the atomic ratio of copper to silver is five to one. When zinc and cadmium salts are present in the solution, cadmium tends to precipitate with the silver, bnt this can be prevented by heating the solution to 75°-80°. *W. D. B.*

The electrolytic method applied to uranium. *L. G. Kollock and E. F. Smith. Jour. Am. Chem. Soc.* 23, *607* (*1901*). — Uranium hydroxide can be deposited quantitatively from acetate, nitrate, or sulphate solutions. No separation from iron can be effected in acetic acid solutions, but uranium can be separated in these solutions from barium, calcium, magnesium or zinc. *W. D. B.*

The electrolytic determination of molybdenum. *L. G. Kollock and E. F. Smith. Jour. Am. Chem. Soc.* 23, *669* (*1901*). — Molybdenum can be precipi-

tated quantitatively as the hydrated sesquioxide by electrolyzing a solution of sodium molybdate acidified with sulphuric acid. The current density is 0.0003-4 amp/cm². The precipitate is evaporated with nitric acid before weighing.
W. D. B.

On the change in conductivity of salt solutions in liquid sulphurous acid, etc. *A. Hagenbach. Drude's Ann.* 5, *276* (*1901*).—Salt solutions in pure liquid SO_2 are shown to behave as electrolytes up to and over the critical point. The compressed gas solutions show the conductivity of electricity by ions. The solutions used were those of KI, NaI, KBr and KCl. The temperature coefficient was found to be negative up to the superior limit (160° C), with the exception of KI, which shows a maximum at 90° C. The conductivity of saturated vapors shows a maximum at the critical point. Determinations with water solutions could not be made accurately on account of the solution of the glass, but the maximum conductivity of a water-glass solution was found to be under 310° C. Considering the temperature expression of the conductivity deduced by Arrhenius, it is shown that it is not applicable for temperatures near the critical point. The absorption spectra of a number of iodide solutions are examined and it is found that in general these show a correspondence either to the undissociated salt molecules or to the ions. *H. T. B.*

On the internal resistance of the Weston cell. *I. Klemencic. Drude's Ann.* 2, *848* (*1900*).—The author shows that the internal resistance of the cell made by the European Weston Instrument Co. remains constant with lapse of time, and otherwise indicates the suitableness of the cell as a standard. The Reichsanstalt type of cell is tested also, and shows similar readings. There is a little too much tendency to condemn the Clark cell, the arguments being far too insufficient. *H. T. B.*

On the application of the calorimeter to measurements with rapid oscillating currents. *F. Harms. Drude's Ann.* 5, *565* (*1901*).—In order to show the anomalous absorption in alcohol the heating effect produced by the absorption is compared with that which should be obtained by calculation from Ohm's law. Calorimetric determinations are made for a number of substances from the results of which the anomalous absorption is shown as an increase in conductivity of the material.

Liebenow's theory of electric resistance in metallic alloys is studied for rapid oscillations with waves from 14 to 5 meters. *H. T. B.*

On the relation of the conductivity of metals for heat and electricity. *E. Riecke. Drude's Ann.* 2, *835* (*1900*).—The object of the present paper is to show the relation between Drude's equation representing the ratio of the heat to the electrical conductivity deduced from the electron theory (5, 420) and one obtained by the author in 1898, from a slightly different standpoint.
H. T. B.

The precipitation of colloids by electrolytes. *W. R. Whitney and J. E. Ober. Jour. Am. Chem. Soc.* 23, *842* (*1901*).—The authors give a brief sketch of the previous work on the subject and describe their own work on the coagulation of arsenic sulphide by the chloride of barium, strontium, calcium, and potassium. Equivalent quantities of the hydroxides of the four elements are carried down. The paper closes with a bibliography of the subject.

W. D. B.

On positive and negative ions. *J. Stieglitz. Jour. Am. Chem. Soc.* 23, *796* (*1901*). — The author takes Jakowkin's equation

$$HClO + HCl \rightleftarrows H_2O + Cl_2$$

and postulates that the ions of hypochlorous acid are the active masses. Granting this, we have $\overset{-}{HO}$ and $\overset{+}{Cl}$ as the dissociation products. This is interesting and may be true; but the author practically assumes what he is going to prove.

W. D. B.

Improved electric furnace for laboratory use. *S. A. Tucker and H. R. Moody. Jour. Am. Chem. Soc.* 23, *473* (*1901*). — The improvement consists in making the furnace of carbon bricks luted together with Dixon's stove paste.

W. D. B.

Conductivity produced in hydrogen and carbonic acid by the motion of negatively charged ions. *J. S. Townsend and P. J. Kirkby. Phil. Mag.* (*6*) 1, *630* (*1901*). — In continuance of the previous work of one of the authors on the conductivity produced in air by the motion of negatively charged ions (5, 421), the experiments described in the present paper have been made. The experimental arrangements being the same, the two gases, H and CO_2, are substituted in place of air. The results are worked out on the collision theory described in the previous paper. It is found that a negative ion makes 11½ collisions per second per cm in hydrogen and 29 collisions in CO_2, from which it is possible to compare the mean, free path of the negative ion with the mean, free path of the molecule. In comparison to a molecule, the mean, free paths in the three gases are as follows:

4.8 : 1 in H,   4.6 : 1 in CO_2,   4.3 : 1 in air.

If the ratio had been 4 : 1 it is computed that the molecules could actually touch on collision.

Considering the energy necessary to ionize a gas, the authors conclude that it could not be more than $\frac{5 \times e}{300}$, where e is the charge in electrostatic units, while from the measurements of Rutherford and McClung the value comes $\frac{175 \times e}{300}$.

It appears from the author's general results that it requires less energy to ionize hydrogen than air or carbonic acid gas.

H. T. B.

Research on the electrical discharge in rarefied gases. *W. Wien. Drude's Ann.* 5, *421* (*1901*). — The work described in the present paper was undertaken to study, and if possible to determine the nature of the Canal rays. The supposition advanced by Riecke that they consist of positive metal ions from the cathode does not seem probable in so far as they journey towards the cathode and actually pass through it when perforated. Bose considered that they were metal particles from the anode, but this seems impossible, since it would require a transport of positive particles. From a study of the magnetic deflection of the rays, in a similar manner to the method adopted in the author's previous work, it is shown that they are probably developed from the gas itself. Rays of different angular deflection are found, giving widely different values of the ratio of the charge to the mass. No definite conclusions are arrived at, but some ideas are advanced in the light of the modern theory of gas conduction which may lead to a more complete explanation. *H. T. B.*

Determination of the conductivity of a gas in the positive glow. *J. Stark. Drude's Ann.* 4, *215* (*1901.*) -- This is a continuation of the author's previous paper (5, 621). The question of the conductivity of a gas is taken up from the point of view of that of an electrolyte.

It is shown that for small current densities the conductivity increases in proportion to the current strength, but for large current densities it increases faster. The relation of the conductivity to the sectional area is studied, as well as the dependence on the pressure. It is shown that the conductivity is a function of the current density, pressure and sectional area. *H. T. B.*

On gaseous ionization and unipolar discharge from glowing bodies. *J. Stark. Drude's Ann.* 4, *402* (*1901*). — The author discusses various kinds of ionization at some length, including J. J. Thomson's theory of the generation of ions by collision. The influence of field strength and temperature form a considerable part of the paper. The complicated subject of unipolar discharge from glowing bodies is briefly discussed. *H. T. B.*

On the specific velocity of ions in the discharge from points. *A. P. Chattock, W. E. Walker and E. H. Dixon. Phil. Mag.* (*6*) 1, *79* (*1901*). — In a previous paper (5, 88) Chattock described certain experiments by which he was enabled to measure the specific velocity of the positive and negative ions in a point discharge in air. In the present paper further experiments are given for hydrogen, carbon dioxide, air, oxygen and a non-conducting liquid, such as turpentine. The agreement of the results with the velocities measured for the same gases, ionized by X-rays, is shown. For turpentine the value of the velocity is of the same order as that in ordinary electrolytes. In conclusion a sensitive pressure gauge is described, which it is claimed must have been sufficient to indicate pressures of a few ten-thousandths of a millimeter of water.

H. T. B.

On the relation of fluid dielectrics to the passage of an electric current. *E. Schweidler. Drude's Ann.* 4, *307* (*1901*). — For a fluid dielectric, such as toluene, the author studies the effect of the passage of a current from the analogy of the passage through an ionized gas. The phenomena of "fatigue" and "recovery" of the material are studied, and the presence of free electricity at the two electrodes is shown. *H. T. B.*

Remark to the paper of E. V. Schweidler: on the relation of fluid dielectrics to the passage of an electric current. *E. Warburg. Drude's Ann.* 4, *648* (*1901*). — The author claims that the work of Schweidler (preceding review) is of the same purport as his own in 1895. *H. T. B.*

On the relation of fluid dielectrics to the passage of an electric current. *E.*

Schweidler. Drude's Ann. 5, *483* (*1901*).—The author's first paper on the behavior of toluene to the passage of an electric current (see two reviews back) is followed by the present paper, which is a continuation of the work for benzene, petroleum and hexane. The influence of impurities on the conductivity of these poorly conducting substances is studied in order to see whether these have any effect in causing the variation from Ohm's law. Negative results were, however, obtained. *H. T. B.*

Glowing discharge in gas mixtures. *W. Heuse. Drude's Ann.* 5, *670* (*1901*).—Mercury vapor exerts a great influence on the spectrum of a gas as shown by E. Wiedemann and again by P. Lewis. At high temperatures mercury vapor is alone visible. In order to investigate this point the author determines the potential gradient in a discharge tube at both the positive and negative ends. Experiments were tried first on nitrogen alone at different temperatures, then on mercury vapor alone, and then on a mixture of nitrogen and mercury vapor. It was shown that the presence of a small quantity of nitrogen lowers the gradient in the positive glow, while the effect of mercury vapor on the cathode fall only commences between 70° and 100° C, and from that point onward causes it to rise. *H. T. B.*

Glowing discharge in helium. *W. Heuse. Drude's Ann.* 5, *678* (*1901*).—The potential gradient in the positive glow, the cathode fall, the potential gradient throughout the tube and the spectrum of helium, form the subjects of the present paper. The helium was prepared from clèveite. *H. T. B.*

On the effect of a magnetic field on the discharge through a gas. *R. S. Willows. Phil. Mag.* (*6*) 1, *250* (*1901*).—The object of the present paper is to explain the phenomenon noted in discharge tubes when the pressure is from a 1/10 to 1 mm, that a transverse, magnetic field causes a large increase in the current passing and a corresponding drop in the potential. This is an apparent contradiction of the usual effect of a transverse, magnetic field on a rarefied gas.

It is shown, however, that the two curves, showing relation between pressure and potential for magnetic field on and off, cut each other at a certain pressure, and when in the region above or below this critical pressure, one or the other phenomenon will be noted.

Curves are also given to show how the potential gradient in the tube varies under the influence of the magnetic field. *H. T. B.*

Contribution to the knowledge of the coherer action. *K. E. Guthe. Drude's Ann.* 4, *762* (*1901*).—In continuance in the line of work commenced by the author previously, the coherer is the subject of further investigation. The negative coherer action whereby the resistance between the metal surfaces increases instead of diminishes, is found to be due to insufficient contact previous to the coherer action. It is found possible for different metals to reproduce the negative action at will, and at the same time to avoid it. Metal powder coherers are liable to the negative action for this reason. A critical potential between the metal surfaces is found above a certain value of the current strength, and is independent of any increase of current or electromotive force. An electromotive force below the critical potential produces no coherer action.

An interesting relation is found between the critical potentials and atomic weights for different metals. The product of the two is found to be equal for Ag, Cu, Zn and Al, while the products for Cd, Sn, Fe and Ni are just double the value of the last. Bi is found to be six times and Pb four times.

The influence of an alternating current on the resistance of the coherer contact is found to be analogous to a metal resistance. The influence of temperature, which is studied carefully, is to lower the contact resistance.

H. T. B.

Motion of the electric particles in an electrostatic field and electromagnetic force. *E. Riecke. Drude's Ann.* 4, *378* (*1901*). — This is a continuation of the author's previous study of the motion of electric particles in a homogeneous, magnetic field. The case of a uniform, electric field combined with a uniform, magnetic field is studied. *H. T. B.*

On the striæ in a stream of electric particles. *E. Riecke. Drude's Ann.* 4, *388* (*1901*). — The author develops a theory somewhat different from Thomson's theory to account for the striæ in a discharge tube, from the ionic standpoint. It embraces more assumptions, and is hence less simple and straightforward. *H. T. B.*

On the behavior of liquids in capillary tubes under the influence of an electric current. *S. Lemström. Drude's Ann.* 5, *729* (*1901*). — The present paper was undertaken by the author from a consideration of a paper by Quincke "On the transportation of material particles by the electric current," and consists essentially of a more complete study of the electric current on capillary phenomena. A capillary tube partially immersed in a liquid is placed under the pole of an influence machine, such that when the other pole of the machine is connected to earth and the liquid is connected to earth a current passes through the capillary tube, and through the intervening air space. By having the liquid connected either to the negative or positive pole, a current of liquid is made to pass either up or down the tube. A number of experiments were tried in various ways and among the most interesting it was shown that with water as well as with dilute solutions of salts, when the liquid is connected to the negative pole a current of liquid flows upward with the electric current, the quantity being proportional to the time, within certain limits, and to the intensity of the current. When the liquid was connected to the positive pole the reverse effect was noted. The botanical aspect of the question is presented by the author in relation to the various experiments tried on the influence of electricity on plants, and some light is thrown on the conflicting results so far obtained. *H. T. B.*

Dielectricity and Optics

On the dependence of the dielectric constant, etc., on pressure and temperature. *J. Koenigsberger. Drude's Ann.* 5, *113* (*1901*). — A theoretical discussion of the laws governing the dependence of the dielectric constant, the magnetization number and the refractive index on the pressure and temperature. The author's deductions differ somewhat from the equations given by other observers. *H T. B.*

Indices of refraction for electric waves, measured by a modified radiomicrometer. *G. Pierce. Phil. Mag.* (6) 1, *179* (*1901*). — The modified radiomicrometer consists of a thermo-junction of constantan and magnanin, combined with the electric resonator devised by Klemencic, the whole attached directly to the suspension of a galvanometer and thus forming one piece of apparatus. An ingenious device for providing the liquid dielectric in the oscillator, in place of the usual bath of oil, is to allow the oil to flow down the upper terminal and cover the spark with an adhering drop. By this means it is possible to bring the reflecting surface very near to the spark. The length of wave used was 4.4 cm. The substances examined were paraffin, hard rubber, and various kinds of wood. In the case of the latter double refraction was shown, thus substantiating previous work by other observers. To show that the absorption in the two directions in the wood could not account for the different displacements of the waves, a brief, mathematical discussion of the theory of stationary waves is given. *H. T. B.*

Becquerel and Röntgen rays. *F. Himstedt. Drude's Ann.* 4, *531* (*1901*). — Contrary to the results of Elster and Geitel, it is shown that Röntgen rays have the same influence in stopping the sparking from an electric machine as radium when brought in the neighborhood of the spark gap.

The effect of a low temperature is tried on the radio-activity of radium, but with apparently, nearly negative results. Various experiments are described on the effect of the phosphorescence of radium on the eye (more completely described in the next paper), and the effect in lowering the resistance of the selenium cell by the radiation emitted from radium, as well as by the X-rays.

H. T. B.

On the action of Becquerel and Röntgen rays on the eye. *F. Himstedt and W. A. Nagel. Drude's Ann.* 4, *537* (*1901*). — As the optic nerve is not sensitive directly to Becquerel or Röntgen rays, the feeble light noticed from radium must be ascribed to fluorescence set upon the material of the eye itself. The author studies the question from this point of view very thoroughly, and finds that all parts of the eye fluoresce with equal intensity. *H. T. B.*

On radium radiation. *P. Villard. Comptes rendus*, 130, *1178* (*1900*). — By means of two, specially arranged, superposed photographic plates, the author shows that the penetration is less for the radium rays that can be deflected by a magnetic field than for the rays that cannot be so deflected. *W. D. B.*

On the induced radio-activity caused by salts of radium. *P. Curie and A. Debierne. Comptes rendus*, 132, *548* (*1901*). — The phenomenon of induced radiation becomes more intense when one works with closed vessels. The authors show that there is transmission of something through the air. While the hypothesis of Rutherford accounts for all the facts, the authors do not yet feel certain that it is the only one that will do so. *W. D. B.*

On induced radio-activity and the gases made active by radium. *P. Curie and A. Debierne. Comptes rendus*, 132, *768* (*1901*). — When the active mass and a piece of copper are placed in a sealed tube, the copper becomes active and the degree of activity appears to be independent of the nature of the atmosphere in the tube and of its pressure,—at any rate so long as the pressure exceeds one centimeter of mercury. If the tube be opened and the pressure kept below 0.001 mm Hg, the copper ceases to be active, and the gas that is withdrawn by the pump is intensely radio-active. This gas when examined shows no new spectrum rays. *W. D. B.*

On secondary radio-activity. *H. Becquerel. Comples rendus*, 132, *734* (*1901*).—The author decides that the emission from radio-active substances consists of a gaseous emanation and a radiation. The gaseous emanation is stopped by glass and by mica. The author distinguishes at least three kinds of radiation : rays which are not deflected by a magnetic field and which are readily absorbed; rays which are not deflected and which have great penetrating power; rays which are deflected. *W. D. B.*

Action of radium rays on selenium. *E. Bloch. Comples rendus*, 132, *914* (*1901*).—The resistance of a selenium cell was reduced when the selenium was exposed to radium radiation. *W. D. B.*

On the deflection of a magnetic needle by cathode rays. *J. von Geitler. Drude's Ann.* 5, *924* (*1901*).—The author finds that the cathode rays have a magnetic effect. *H. T. B.*

On the influence of rays on the spark discharge. *E. Warburg. Drude's Ann.* 5, *811* (*1901*).—A reply to a paper by R. Swyngedauw. The author shows that the effect of ultra-violet rays on the spark discharge results entirely in a diminution of the retardation and not in a lowering of the spark potential, and this whether the potential is applied slowly or quickly. This stands in contradiction to the assertions of Swyngedauw. *H. T. B.*

Optical rotations of certain tartrates in glycerol. *J. H. Long. Jour. Am. Chem. Soc.* 23, *813* (*1901*).—The simple metallic tartrates show a larger specific rotation in glycerol than in water; the antimonyl tartrates show nearly the same rotation in the two solvents, while potassium boryl tartrate shows a much lower rotation in glycerol than in water. *W. D. B.*

On the molecular refraction of chloral hydrate dissolved in different solvents. *M. Rudolphi. Zeit. phys. Chem.* 37, *426* (*1901*).—The author finds that the apparent molecular refraction of chloral hydrate varies markedly with the solvent used. No other results are obtained and the author considers the possibility of the dissociation of chloral hydrate into chloral and water as barely worth mentioning, in spite of the fact that he gives the melting-point as 46°-47°. *W. D. B.*

Refractive indices of calcium chloride solutions. *G. J. W. Bremer. Arch. néerl.* (*2*) 5, *202* (*1900*).—The refractive power of the calcium chloride solutions, when expressed by the Lorentz formula, does not depend on the concentration and differs but little from that for water.

The differences between the index of refraction of a given calcium chloride solution and that of water, both referred to the same rays, has about the same value irrespective of the wave length of the light used. These differences are proportional to the amount of anhydrous salt dissolved in one hundred grams of water. *W. D. B.*

On the phosphorescent glow in gases. *J. B. B. Burke. Phil. Mag.* (*6*) 1, *342, 455* (*1901*). — These two papers form an extensive and careful study of the brilliant phosphorescence which, under certain pressures, follows the ring discharge in different gases. Among other things the author shows that the glow is a volume effect and consists of unelectrified particles. It appears to be due to impurities, but the glowing particles resemble, to a certain extent, the emanation from thorium. An electromotive force has no effect, and the conductivity shown to exist in the glow is electrolytic in nature. *H. T. B.*

On the band spectrum of clay and nitrogen. *G. Berndt. Drude's Ann.* 4, *788* (*1901*). — On account of the uncertainty in the measurements of Hasselberg of the band spectrum of aluminium, whether it belonged to aluminium or to aluminium oxide, the author studies the spectrum of aluminium in atmospheres of nitrogen, hydrogen and oxygen. It was found that oxygen was necessary for the production of the spectrum, and that in the other two gases only the N and H lines were visible with the metal lines of aluminium. *H. T. B.*

Spectroscopic notes concerning the gases of the atmosphere. *Lord Rayleigh. Phil. Mag.* (*6*) 1, *100* (*1901*). — The first note is in regard to the results of Gautier, who showed by chemical means that normal air contains about 2 parts in 10,000 of hydrogen and varying amounts of hydrocarbons. The author examines air spectroscopically, but finds it is more probable that the faint C-line, which he distinctly observes in air, is due to hydrogen cooled from the glass of the sparking chamber or from the platinum electrodes.

The second note is a simple and convenient method of demonstrating at atmospheric pressure the presence of argon from small quantities of air, 5 cc only being necessary.

The third note is a diffusion method for concentrating helium from the atmosphere. *H. T. B.*

Photographs of the ultra-red spectrum of the alkali metals. *H. Lehmann. Drude's Ann.* 5, *633* (*1901*). — Sensitive plates prepared from Burbank's receipt were found to be the most satisfactory for all rays from the ultra-violet into the ultra-red. Emission spectra of the metals obtained by volatilizing in the arc, were photographed. The metals studied were lithium, sodium, potassium, rubidium and caesium. *H. T. B.*

Normals from the arc spectrum of iron. *H. Kayser. Drude's Ann.* 3, *195* (*1900*). — The author publishes another table of the arc spectrum of iron, based on Rowland's normals and obtained by means of a Rowland grating. An accuracy of 0.003 Ångstrom units is claimed. *H. T. B.*

On the influence of small impurities on the spectrum of a gas. *P. Lewis. Drude's Ann.* 2, *447* (*1900*). — In a previous paper the author describes experiments to determine the spectral effect of small admixtures of mercury vapor to pure hydrogen gas. In the present paper the experiments are continued for nitrogen, and in addition the influence of traces of oxygen and hydrogen on the nitrogen spectrum is studied. The result of the work shows that very small quantities of the added gas have a large influence on the spectrum. The intensity of the nitrogen spectrum reaches a maximum at about 3.5 mm pressure, and decreases with increase of pressure. The presence of the mercury vapor diminishes the intensity, but at the same time prevents the intensity of the nitrogen lines from falling off so rapidly with increasing pressure. The effect, however, is not so simple and regular as in the case of hydrogen. This seems to be the general effect of impurities on the spectrum of a gas. *H. T. B.*

On the sensitiveness to light of fluoresceine, its substitution products and the leuko bases of the same. *O. Gros. Zeit. phys. Chem.* 37, *157* (*1901*). — The following conclusions are drawn :

The leuko bases of the triphenyl methane dye-stuffs are very sensitive to light.

Introduction of a nitro group into a leuko base of the fluoresceine dye-stuffs increases very much the rate at which the leuko base oxidizes to the dye-stuff in the dark.

The bleaching of the triphenyl methane dye-stuffs is due to oxidation.

It is probable that the reaction taking place in the light is chiefly an ion reaction.

The oxidation of the leuko base is accelerated by the presence of the resulting dye-stuff so long as the latter's concentration does not exceed a certain limit.

The sensitiveness to light of the leuko bases and the dye-stuffs is much increased by the presence of other dye-stuffs.

The effect of light on the reaction between mercuric chloride and ammonium oxalate is also increased by the presence of dye-stuffs.

The catalytic action of the dye-stuffs is perceptible while the concentration is very low and passes through a maximum with increasing concentration.

It is probable that the catalytic action of the dye-stuffs is due to their absorption of light. *W. D. B.*

On the transparency of hydrogen for light. *V. Schumann. Drude's Ann.* 4, *642* (*1901*). — Spectrum photographs of hydrogen are taken with the light passing through a tube, which may be either exhausted or held at atmospheric pressure. The extraordinary transparency of hydrogen is shown, and the author concludes that within the limits of his experiments, the gas does not absorb light at all. A tube filled with hydrogen is found to be more transparent than the same tube exhausted, which is considered to be due to the evolution of mercury vapor and fatty vapors under the diminished pressure.

It was found that the transparency was very seriously diminished by passing the gas through a rubber tube, the contamination from the rubber being most marked. *H. T. B.*

On the dependence of the absorption of light in solid bodies on the temperature. *J. Koenigsberger. Drude's Ann.* 4, *796* (*1901*). — Two classes of bodies are treated, metallic and non-metallic. Of the former it is shown that the influence of temperature has no effect on the absorption or reflection of light from their surfaces, over a range from 10° to 360°, and in the case of platinum as high as 800°. For the latter substance the author gives the following rule : "In solid, selective, absorbing bodies an increase in temperature causes a displacement of the absorption curve towards greater wave lengths, at the same time in single cases a small extension of the absorbing boundary. The size of the maximum absorption does not apparently change." *H. T. B.*

Absorption of light in colored glasses. *R. Zsigmondy. Drude's Ann.* 4, *60* (*1901*). — From the point of view of the wide use of colored glass, the investigation of the absorption for transmitted light is of considerable practical interest. Calling the intensity of the light before transmission I., then the extinction coefficient $E = \frac{-\log J}{d}$, where J is the intensity of the transmitted light, and d is the thickness of the glass. The absorption constant $A = \frac{E}{gS}$, where S is the specific gravity of the glass and g is the number of milligrams of coloring oxide in one gram of glass. The constant A is plotted with wave length, and a number of beautiful tables are given, showing the relation for different coloring oxides. Cobalt oxide has the greatest absorbing power, and the oxide of iron the least. *H. T. B.*

An electrically heated "Black" body. *O. Lummer and F. Kurlbaum. Drude's Ann.* 5, *829* (*1901*). — A platinum tube electrically heated by a heavy current and enclosed in suitable thermal shields is used, and a temperature of 1500° C obtained. The interior of the tube is blackened with a chromium, nickel and cobalt oxide, which is found to stand high temperatures. The apparatus gives good results. *H. T. B.*

On the pressure of light waves. *D. A. Goldhammer. Drude's Ann.* 4, *834* (*1901*). — This is an elaborated, mathematical discussion. *H. T. B.*

On the electric analogy of the Zeemann effect. *W. Voigt. Drude's Ann.* 4, *197* (*1901*). — The object of the paper is to show that the Lorentz theory (electro-optical) of the Zeemann effect leads to the same results as the author's application of Kirchoff's law to the inverse phenomenon. *H. T. B.*

On the change of wave form of light passing into a dispersing and absorbing medium. *W. Voigt. Drude's Ann.* 4, *209* (*1901*). — A continuation of an earlier paper on the same subject, the object being to correct a slight error in an important assumption upon which the equations were based. *H. T. B.*

Contribution to the knowledge of the physical properties of silver reflecting surfaces. *C. Grimm. Drude's Ann.* 5, *448* (*1901*). — The present paper is a study of silver reflecting surfaces from various preparations by reason of the extensive use of silver mirrors for optical work. Changes take place in the mirrors which affect their utility and constancy for various kinds of work. Determinations of the electrical resistance show a gradual change in the character of the layers corresponding to a change from the molecular, which has been called colloidal silver, to normal silver. A decrease in resistance is a result of this inversion. The molecular silver behaves less as a metal than the normal, so that fresh surfaces from all preparations show a large initial resistance, and a phase difference on the reflection of light that corresponds more with a non-metallic body. While the inversion from the molecular to the normal silver takes place, a gradual lowering of the resistance follows. *H. T. B.*

On the spectral equation of polished platinum. *D. A. Goldhammer. Drude's Ann.* 4, *828* (*1901*). —The author points out that the formula deduced by Thiesen and the new formula obtained by Planck are incorrect when compared with the observations of Lummer and Pringsheim. *H. T. B.*

Temperatures in Geissler tubes. *K. Kerkhof. Drude's Ann.* 4, *327* (*1901*). — From the work of G. Wiedemann on the temperature of a gas under discharge, the law was formulated that the temperature of the gas is inversely proportional to the cross section of the tube. Taking the temperature of Geissler tubes of large section and calculating, according to the law, for capillary tubes enormously high values would be obtained. To test this point the present work has been undertaken for CO_2, O and H. It is shown, theoretically and practically, that the temperature is more nearly proportional to the reciprocal of the radius and not the cross section. *H. T. B.*

On the absorption of gas in a Crookes tube. *R. S. Willows. Phil. Mag.* (*6*) 1, *503* (*1901*).—The well-known phenomenon of the exhaustion of a Crookes tube at certain pressures by the simple passage of the discharge, forms the subject of the present paper. The reason the author gives, as the result of a large number of experiments with various tubes and electrodes, is that the gases form a chemical combination with the glass. To reduce the effect to a minimum, Jena-glass should be used in preference to lead-glass, and the latter in preference to ordinary soda-glass in the construction of the bulb. *H. T. B.*

On the stresses in solid bodies due to unequal heating, and on the double refraction resulting therefrom. *Lord Rayleigh. Phil. Mag.* (*6*) 1, *169* (*1901*).— A mathematical discussion of the stresses shown optically in glass, when unequally heated. The subject is of special treatment of Hopkinson's work, with reference to the optical method of examination.

In the case of so-called, toughened glass, the author considers that the cause of the toughening, which has hitherto been supposed due to a crystalline structure, can be explained by reference to the known conditions of stress.
H. T. B.

Determination of the frequency of an alternating current. *R. Wachsmuth. Drude's Ann.* 4, *323* (*1901*). —A watch spring, clamped at one end and free to vibrate when plucked, has attached a small square of paper. When illuminated by an alternating current, such that the period of vibration of the spring is the same as the alternating current, the paper appears to stand still. The time of vibration of the watch spring may be calculated from its dimensions.
H. T. B.

On the radiation law of black bodies. *F. Paschen. Drude's Ann.* 4, *277* (*1901*). —This is a very complete discussion of the subject, taking into consideration the laws proposed by different observers. From the author's own measurements, carried out with great care, the law of Planck from $\frac{1}{\lambda T} = 0.002$ to 0.0001 is found to be correct. *H. T. B.*

Sur la double réfraction accidentelle dans les liquides. *L. Natanson. Bull. Acad. Sci. Cracovie*, , *161* (*1901*). —This is a hydrodynamical study of the "accidental double refraction," which is observable in liquids subjected to states of strain. In the examination of the case in which the states of strain are produced in a viscous liquid contained in the space between a rotating cylinder and a concentric cylindrical envelope, a relation is found between the angular velocity of the cylinder and the double refraction per unit length. This relation agrees well with available observations of Umlauf and of de Metz.

J. E. T.

Crystallography, Capillarity and Viscosity

Structure, system and magnetic properties of fluid crystals and their mixture with solid. *O. Lehmann. Drude's Ann.* 2, *649* (*1900*). — A very complete and exhaustive discussion of physical crystallography, more in particular with reference to the evidence to support the idea, advanced by the author in 1890, of the existence of fluid crystals. A crystal is defined as an anisotropic body, of which the condition of aggregation can be liquid or solid, but not gaseous.

H. T. B.

On the relation of both elasticity constants of isotropic media to the molecular theory. *W. Voigt. Drude's Ann.* 4, *187* (*1901*). — The author endeavors to show that the application of the old molecular theory of elasticity, which has hitherto led to contradictory results, is in complete accord for crystalline bodies, when the reciprocal action between two molecules is in a direction corresponding with the symmetry of the crystal. For isotropic bodies the particles are supposed to be composed of minute fragments of crystals in all possible arrangement (quasi-isotropic). *H. T. B.*

Rapid measurement of surface tensions. *P. A. Guye and L. Perrot. Comptes rendus,* 132, *1043* (*1901*). — It is claimed that measurements accurate to one or two percent can easily be made by the method of weighing the drops, provided corrections are introduced for the number of drops and for the rate of formation. *W. D. B.*

On the thickness of films and the sphere of action of molecular force. *G. Quincke. Drude's Ann.* 2, *414* (*1900*). — A reply to G. Vincent to refute the charges of inaccuracy in the author's early work on the subject. *H. T. B.*

On the relation between the viscosity parameter and some other physical constants. *A. Batschinski. Zeit. phys. Chem.* 37, *214* (*1901*). — The author deduces the relation

$$\frac{M^{1/2}\theta^{1/2}}{E(MR)^{2/3}} = \text{const.},$$

where M is the molecular weight, MR the molecular refraction, θ the critical temperature, and $E = \eta T^3$ the viscosity parameter. When E is expressed in c. g. s. units, the mean value of the constant is 39,500 as deduced from fifteen substances. Starting from this value as given it is of course possible to solve approximately for the critical temperature. *W. D. B.*

Experimental determinations of the capillary constants of condensed gases. *L. Grunmach. Drude's Ann.* 4, *367* (*1901*). — Similar to the author's previous measurements of the capillary constants of a long series of fluids and molten metals, a number of experiments are tried for liquid gases, such as sulphurous acid, ammonia and chlorine.

The method of capillary waves is used, due to Kelvin, with the use of a tuning fork of high frequency to produce the waves, as proposed by Matthiessen.
H. T. B.

Deductions from capillary phenomena. *A. Einstein. Drude's Ann.* 4, *513* (*1901*). — Allowing a liquid of surface O_1 and temperature T_1 to change its surface isothermally to O_2 then increases its temperature to T_2, keeping the surface constant, and then return to its original surface O_1 and temperature T_1 by first isothermally diminishing the surface and then lowering the temperature, the quantity of heat that enters the liquid should equal the quantity that is removed, and the sum of the mechanical work should equal O. As the data show, this is not the case. The author investigates the question mathematically on the ground that with the change in surface is connected an exchange of heat, and that a peculiar specific heat pertains to the surface. The relative potential of the two molecules is put in the form involving what the author calls characteristic constants for the molecules (c). Then the characteristic constant for the atom of the element is an integral part of the molecule, or

$$c = \Sigma c_a.$$

An expression for Σc_a is found in terms of the mechanical work, absolute temperature and the molecular volume. *H. T. B.*

On the surface tension of oil-covered water surfaces, and the sphere of action of molecular force. *R. H. Weber. Drude's Ann.* 4, *706* (*1901*). — Olive oil carefully shaken with alcohol is used, and is found not to spread out over the surface of water when the shaking has been done several times. Two methods of measuring the surface tension of the oil and water surface are used, one, the surface drop method of Quincke, whereby the contour of the oil drop is measured, and by the cohesion balance.

It is found that the edge of the oil drop in water changes with an increase or diminution of the water surface. The boundary tension of oil against water is also found to be dependent on the size of the boundary surface. The results of the work point to the action of the water on the oil, and the author makes the suggestion that it may be due to hydrolysis of the oil. *H. T. B.*

On surface tension. *H. Hulshof. Drude's Ann.* 4, *165* (*1901*). — A theoretical discussion of surface tension on the assumption of a density in the capillary layer that changes continuously from that of the liquid to that of saturated vapor. It is shown that the surface tension must necessarily exist, and that it leads to a value of the capillary energy identical with the molecular constant in the thermodynamic theory of van der Waals. *H. T. B.*

Investigation into the influence of capillary on the velocity of efflux of fluids. *C. Christiansen. Drude's Ann.* 5, *436* (*1901*). — Two types of outflow are studied experimentally, where the liquid flows in drops and where it flows in a stream. In the relation between outflow and height of head it is shown that the increase in the quantity of liquid that drops out decreases and passes through a minimum as the head increases, which is the point where the drops first form into a stream. A sudden increase in the quantity then takes place to be followed by nearly equal increments in quantity with further increase in head. In studying the effect of surface tension on the outflowing liquid (water) the time of discharge was taken with the stream in air and in water or salt solution. It was found that the time of discharge in air was greater than in water for high heads, and the reverse for low heads. Various other experiments were tried mainly showing the influence on the time of discharge by altering the form and character of the stream. Vapors of alcohol and ether were found to have an effect in altering the surface tension. The effect of altering the direction of efflux was tried with negative results. The capillary effect due to electrical potential was found in the case of mercury. Polarization with the anode stream causes a lengthening of the stream and an increase in efflux, the reverse being the case with cathodic polarization. *H. T. B.*

On the viscosity of mixtures of liquids and of solutions. *C. H. Lees. Phil. Mag.* (*6*) 1, *128* (*1901*). — A theoretical study of the formula first proposed by Arrhenius for the calculation of the viscosity of a mixture which contains 90 percent of one constituent. Three cases are considered which lead to three formulæ, called by the author the "mobility", the "viscosity" and the "logarithmic." From a comparison of the experiments of Thorpe and Rodgers, Linebarger, and Wijkanders, it is shown that the observed viscosity is less than that given by the mobility formula. An empirical formula is proposed, which gives what the author calls "a first approximation towards a representation of the viscosity of a physical mixture in terms of the viscosities and natures of its constituents". The author goes on to say "Like other empirical formulæ, it will in time be replaced by a formula founded on theory and capable of including cases in which the liquids, owing to some chemical action on each other, give rise to mixtures having viscosities outside the limits of those of their constituents". The formula is also applicable in the case of the variation of viscosity with temperature. *H. T. B.*

On the viscosity of gases and the variation with temperature. *P. Breitenbach. Drude's Ann.* 5, *166* (*1901*). — The author's earlier communicated results are compared with the formula proposed by Sutherland. For hydrogen the smallest trace of another gas causes a large increase in the viscosity coefficient. *H. T. B.*

On the viscosity of argon and its change with temperature. *H. Schultze. Drude's Ann.* 5, *140* (*1901*). — On account of the fact that Lord Rayleigh did not enclose his apparatus in a suitable temperature jacket, the author makes a redetermination of the viscosity, taking greater precautions, and thereby extending the range of temperature. The method used is the transpiration one. The value obtained from a series of experiments on carefully prepared argon is 2104×10^7 at 0° C. For the effect of temperature as high as 183.7° C. the formula proposed by Sutherland is amply substantiated. *H. T. B.*

THERMOSTATS AND THERMOREGULATORS

BY WILLIAM C. GEER

As ordinarily applied in chemical or physical work, the term constant temperature may mean almost anything, varying with the observer and his work and ranging from variations of several degrees to a few ten-thousandths of a degree. The error permissible in the results should, of course, determine the maximum variation of temperature, which is allowable in each particular instance. Since investigations may be made much more valuable by the refinement of methods, the attempt to attain greater constancy of temperature has led to the production of many ingenious forms of thermostats.

The object of the present paper is, primarily, to present a form of thermostat which seems to have some desirable features. Several points which were at first thought to be original were found, on looking over the literature, to have been used by others. It has, therefore, been thought best first to summarize the most important work which has been done in this field, and then to describe a simple effective regulator and working thermostat.

In order to keep a body at constant temperature, it is necessary, if it be colder than its surroundings, to supply heat to it in quantities just sufficient to compensate for loss by radiation, or, if the converse be the case, to take heat from it in quantities just sufficient to balance the absorption. In either case the desired constancy may be more readily obtained by surrounding the body with some medium (a bath) which is held at the desired temperature. The two general methods of obtaining this condition are radically different.

In the first, the bath consists of phases in equilibrium — such as liquid or vapor in equilibrium with solid or liquid.

Since this equilibrium is dependent on pressure and concentration as well as temperature, in order that the latter be defined accurately, the two former variables must be fixed. Under this section must be treated all thermostats depending on fixed points:—(1) melting- or freezing-points; (2) boiling-points; (3) inversion points; (4) cryohydric points.

The second method comprises all the liquid and air-baths to which heat is supplied under mechanical regulation. There may be considered here the cases where

(1) The regulation is not automatic,

(2) The regulation is automatic and is accomplished by means of a thermoregulator which

(*a*) Controls a gas supply,
(*b*) Controls an electric current,
(*c*) Controls some other heating agent.

I. Thermostats dependent on the equilibrium of phases

The conditions which determine equilibrium between phases being known, the methods of obtaining constancy of temperature under these conditions should be, apparently, ideal for thermostat work. Practical difficulties arise, however, which limit their usefulness. These are mainly due to the difficulty of maintaining the different phases of the system used as the bath, in perfect equilibrium with each other. The chief advantage of the method should be that a regulator is not required.

The melting- or freezing-points of a few solids are much used. The melting-point of pure water is employed for zero degrees, while De Visser[1] used pure acetic acid for 16.7° C.

Thermal equilibrium between solid and liquid can be obtained only by taking very careful precautions, while the labor and expense involved limit the application of this method, in practice, to the substance water.

The boiling temperature of liquids is fixed if the concentration and pressure are defined. By making use of different liquids and varying pressures, it is possible to obtain a very wide range of temperatures. This at present may be carried from liquid hydrogen —257° C (55 mm) (Dewar) to zinc at 930° C (760 mm) (Holborn and Wien), but these are by no means the limits.

Using mixtures of sulphuric acid and water, L. Hämmerle,[4] Sprengel,[5] and Laspeyres[6] obtained ranges of boiling temperature from 100° to 317° which, by means of specially constructed apparatus, they applied to thermostat work. Different mixtures were used by Alluard[3] and Reynolds.[2] In these cases where pressure regulation was not attempted, the degree of constancy of the boiling temperature leaves much to be desired.

Lothar Meyer[7] constructed an apparatus for fractional distillation at constant pressures below that of one atmosphere. This was modified by Stadel[8] and others, and later by Brown[9] with whom the pressure variations did not exceed 0.25 mm. Making use of carbon bisulphide, water and paraffin oil, he was able by changing the pressure to keep a bath at any temperature from 25° to 300°, maintaining it "absolutely constant" without, however, giving more definite results. The vapor-pressure measurements of Ramsay and Young[10] gave a series of values between 0° and 360°, while the accurate work of others has determined many more fixed boiling temperatures. Since this is the case, the method may be employed in the comparison and standardization of thermometers. Wiebe and Böttcher[11] and Pomplum[12] have described the results of such work. Traube and Pincussohn,[13] making use of a small mercury pump, regulate by hand every five or ten minutes. For pressures below 0.5 atmosphere, they claimed to be able to maintain the temperature constant within ± 0.01° as long as desired.

The apparent advantage of this method of liquid-vapor equilibrium is that no heat regulation should be required. Superheating must be avoided, however, and the liquid kept in ebullition. The great difficulty arises in the attempt to maintain constant pressure — a problem as difficult as that of constant temperature. The effect of gravity on the boiling-point of liquid layers of different depths is always present and at low pressure is very marked indeed, although even at ordinary pressures it may not be ignored in careful work.

A series of well-defined temperatures is given by the inversion points of elements or compounds. For use in thermometer calibration, Richards and Churchill[14] have employed a series of salts having a total range of sixty degrees. From their work the following table is taken:

Salt	Inversion temp. Hg thermometer.
Sodium chromate	19.71°
Sodium sulphate	32.484
Sodium carbonate	35.3
Sodium thiosulphate	48.0
Sodium bromide	50.8
Manganese chloride	57.8
Trisodium phosphate	73.4
Barium hydroxide	78.0

The range of inversion points is presumably extensive, but has not been worked over to any extent.

Cryohydric methods have been very rarely used in constant temperature work, except in the case of freezing-point determinations. The actual cryohydric temperature is rarely reached with any degree of accuracy because of the lack of thermal equilibrium between its solid and solution phases.

All the methods dependent on phase equilibrium have definite limited spheres of usefulness which are not lessened by the simplicity of method which in many cases they allow.

II. Thermostats dependent on mechanical regulation

The thermostat which is most useful in the laboratory is one into which objects may be placed, or from which they may be removed, without disturbing the essential parts of the apparatus. The only forms which meet this condition are the open liquid baths and air-baths. To keep these at constant temperatures the heat supply must just balance the radiation loss; this requires careful regulation.

Non-automatic regulation

Thermostats without automatic heat regulation are few in number. Pulfrich[15] described a method of maintaining a refractometer cylinder at constant temperature by means of a water current. The water at constant pressure was passed through a gas-heated copper spiral into the chamber surrounding the cylinder. If the water pressure changed, it was necessary to use a gas regulator. Rothe[16] described a thermostat which was adapted for thermometer calibration. It was a well insulated bath heated by means of an electric current passing through a central coil of wire.

In the use of all thermostats of this kind, the assumption is made that the conditions during operation will remain the same as at the time of adjustment. This, however, is rarely the case — a change of gas or water pressure, of dynamo power, of laboratory temperature would cause a very noticeable change in the temperature of the bath. Satisfactory results may often be be obtained if the operator is at hand to control the conditions; nevertheless even this careful attention may not prevent sudden changes. For general laboratory work, therefore, the most desirable thermostat contains some form of thermoregulator through whose action the slightest change of thermal condition will be exactly compensated.

Automatic regulators

Automatic thermoregulators, one and all, depend upon the principle that a change of heat conditions in the bath causes, in some substances, a volume change which directly or indirectly regulates the heat supply. Since the regulation is consequent upon this volume change, an absolutely constant temperature is never attained. The most efficient regulator is therefore the one which reduces to a minimum this oscillation about the mean value.

Regulators controlling gas supply

Since gas is the most common source of heat in the laboratories, the majority of regulators are adapted to control the gas supply. Kemp[17] made what was in all probability the first gas regulator. It consisted of a U-shaped glass tube of which one end was an elongated bulb which served as an air thermometer. The expansion of the air within this bulb forced mercury into the other arm against an inner gas-inlet tube, thus cutting off the gas supply. In order to prevent the flame from being extinguished, a small opening was made in the side of the gas delivery tube. The gas was, of course, approximately adjusted at the outset. By this means, its supply was controlled and the compensating change occurred. The action was not very sensitive and the lag was marked so that the apparatus never gave good results. All regulators which thus directly control a glass supply are modifications of the Kemp type. Bunsen[18] changed the form of the instrument and used mercury in place of air. Reichert[19] added a side arm and a screw for adjusting the instrument. Ostwald[21] used a calcium chloride solution in place of air and added an adjustment device. This is the form which is quite generally used by physical chemists. By the replacement of the air by ether, Andreae[24] obtained a more sensitive action. Several other vapor regulators have been described, but while these are very sensitive, they also, like Kemp's original form, are easily influenced by changes in atmospheric pressure which renders them unsatisfactory.

In all these regulators where mercury and gas are in contact, the surface of the mercury becomes contaminated in the course of time, and this interferes with the regulation. To overcome this difficulty Kreusler[20] and James,[22] who modified Kreusler's apparatus, used a float upon the surface of the mercury which opened and closed a valve. Schlösing[25] and D'Arsonval[26] employed a membrane between the expanding substance and the gas supply. Thus the mercury or other liquid expanded against a diaphragm which served as a valve to control the gas supply. This valve was greatly improved by Pensky.[27] The main difficulty with membrane regulation lies in the selection of a suitable diaphragm (rubber being excluded, if long service is desired).

The regulators which thus directly control a gas supply have been used widely and with satisfactory results. The chief defect is that they require too much time to adjust (especially when students are using them) and that for some work they are not sufficiently sensitive.

The earliest regulators were made of metal. Bonnemain[28] (1824) and Ure[29] (1831) appear to be the first who made use of these. Lothar Meyer[30] employed a rod which communicated its expansion or contraction by means of a lever to a gas valve. The apparatus was quite complicated but, like all metallic regulators, was useful for high temperatures. By far the most sensitive form of metallic regulator may be made by brazing or riveting together two long thin bars of metal with different coefficients of expansion. One end of the combination being fastened, a slight change in temperature gives an exaggerated motion to the free end, which may move a device for changing the heat supply. Gumlich[31] and Knipp[33] have described apparatus of this kind. Bodenstein[32] has recently made use of the difference in expansion of porcelain and iron to control high temperatures. There seems to be no good reason why such regulators should not give efficient service in the laboratory as well as in technical practice.

The electro-magnetic gas regulator consists of a contact thermometer and an electro-magnet which is arranged so as to move a valve controlling the gas supply. These are connected in series with a battery. The typical contact thermometer consists of a capillary joined to a long bulb filled with mercury, into which is sealed a platinum wire. Into the capillary extends another platinum wire. Expansion of the mercury will bring about contact between the wire and the mercury thread in the capillary, closing the circuit, moving the valve, and thus regulating the gas supply. The usual arrangements are made for a small constant flow of gas which cannot be extinguished.

The invention of the contact thermometer evidently should be accredited to Maistre,[34] although Du Moncel[35] used one but a short time later. These electromagnetic regulators have never been used so extensively as those based on the Kemp model, since the sources of the electric current have been less accessible than gas. While designed primarily for the control of a gas supply, the Maistre contact thermometers have been employed to regulate other heating agents.

The use of a hot liquid circulated either in a closed or open circuit by means of a centrifugal pump, is one which is capable of very extended use in the most accurate kinds of work, for example, the recent work of Barnes[†] on the specific heat of water. It is necessarily used, however, in conjunction with a thermostat whose temperature is controlled. Barnes employed a circulating system comprising a thermostat, a pump driven by a water motor, and the observation bath. The thermostat was after the model of Gouy.[36] Schalkwijk[23] heated a bath by means of a circulating water current, which was in turn heated by gas, controlled by a regulator containing xylene.

The above-mentioned regulators, designed primarily for use in connection with gas as the heating agent, have been more extensively used than any others. It is well to point out here, however, that when a temperature differing but few degrees from that of the room is to be maintained for a considerable time, special precautions are necessary to prevent the gas flame from being extinguished.

On p. 106 there are collected a few references under the heading "Miscellaneous Regulators," thermostats where oil lamps were employed, combinations of gas heating with water currents and others.

Current regulators

Within the last few years, several thermostats have been described in which an electric current has been used as the source of heat. Two methods were employed — one in which the current was passed through a heating resistance of wire or electric lamps, the other making use of an electrolyte which was itself the resistance. Duane and Lory[37] made use of the latter method. They passed an alternating current through a solution of salt held in a wooden thermostat having zinc electrodes. They claimed a temperature constant to 0.001°. The thermoregulator, in the form of a contact thermometer, was made of

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[†] Proc. Roy. Soc. London, 67, 238 (1900).

brass tubes which were filled with alcohol. The expansion of the alcohol was communicated to the mercury through which a relay circuit was made, which interrupted the heating current.

Electrolytic baths, however, have very distinct disadvantages. The heat will be the greatest where the lines of flow are the most concentrated. If the bath is made of a non-conductor, the electrodes of equal size, the bath large, and the bodies placed therein comparatively small and non-conductors, then there will be equal heating throughout and the bath will possess many advantages. If a metallic body be placed in the bath, the lines of flow will concentrate toward it and thus the greatest heat will be at or near the surface of this body. The tendency would be, therefore, for the bath to be unequally heated. This difficulty may be overcome to a large extent by stirring as vigorously as did Duane and Lory. But under these circumstances this form of thermostat possesses no superiority due to this mode of heating.

Gouy[36] described a thermostat which was heated by incandescent electric lamps within brass tubes. The regulator was an alcohol-mercury contact thermometer. To counteract the striction in the capillary, he used a mechanism which gave to the upper platinum wire a vertical movement of 15 mm through a definite period. By this means he secured a temperature constant to 0.0002°. Young[38] used lamps beneath a bath. The regulator was a crude form of contact thermometer, and the variation observed was a few hundredths of a degree.

From the results of the last four observers, it would appear that when the electric current is used as the heating agent, it is possible to reduce the temperature oscillations to so great an extent that this method of heating thermostats is superior to all others over the range of temperature to which it has been applied.

Thermostat requirements

From a study of the above-described forms of apparatus and a consideration of the requirements of a constant temperature bath, it is to be concluded that a good thermostat should satisfy the following conditions:

(1) It should be well insulated, and have a low radiation constant.

(2) The heat supply should be capable of quick and delicate control.

(3) The fluid of the bath should be thoroughly stirred.

(4) There should be used a thermoregulator which is simple in construction and adjustment, and sensitive in action.

Insulation is necessary to conserve the heat and to protect the bath from sudden temperature changes. If the heat supply is properly controlled, the extent of the temperature variation is also controlled. To have every layer of the bath liquid at *exactly* the same temperature, is quite impossible, but by thorough stirring, the difference in temperature between layers may be reduced very appreciably. Simplicity in the apparatus is a prime requisite; many regulators have so many parts to be kept in order that their usefulness is thereby limited. The best regulator is the one which is the most sensitive, most easily made and kept in adjustment, and which will work with the least attention.

The bibliography, on pp. 101–5, shows the main types of thermoregulators and thermostats. It is perhaps not complete, but contains references to the most prominent types which have been employed in thermostat work. Many patented devices have been omitted. Combinations of different types are frequently and successfully used, e. g., the thermostat described by Rothe[39] for low temperatures. One may with confidence predict that the most important development in constant temperature work in the future will be along the lines of combinations of the various types described.

III. Description of an electrically operated thermostat

In the Laboratory of Physical Chemistry of Cornell University, experiments were performed last year which gave rise to the apparatus to be described. Since the experience of several years with many forms of gas regulators had been so unsatisfactory, and since an ample supply of electric power was available, heating by electricity was resorted to, in the hope that much better results could be obtained. These results are given in the following paragraphs.

For the preliminary experiments a seven-liter water-bath was well insulated with cotton wool and 3.5 ohms of No. 10 German silver wire were coiled in the bottom upon a board. Above the coil was a large brass fan of a diameter nearly equal to that of the bath, driven by a small water motor. Upon a tray suspended above the fan, was placed the thermoregulator.

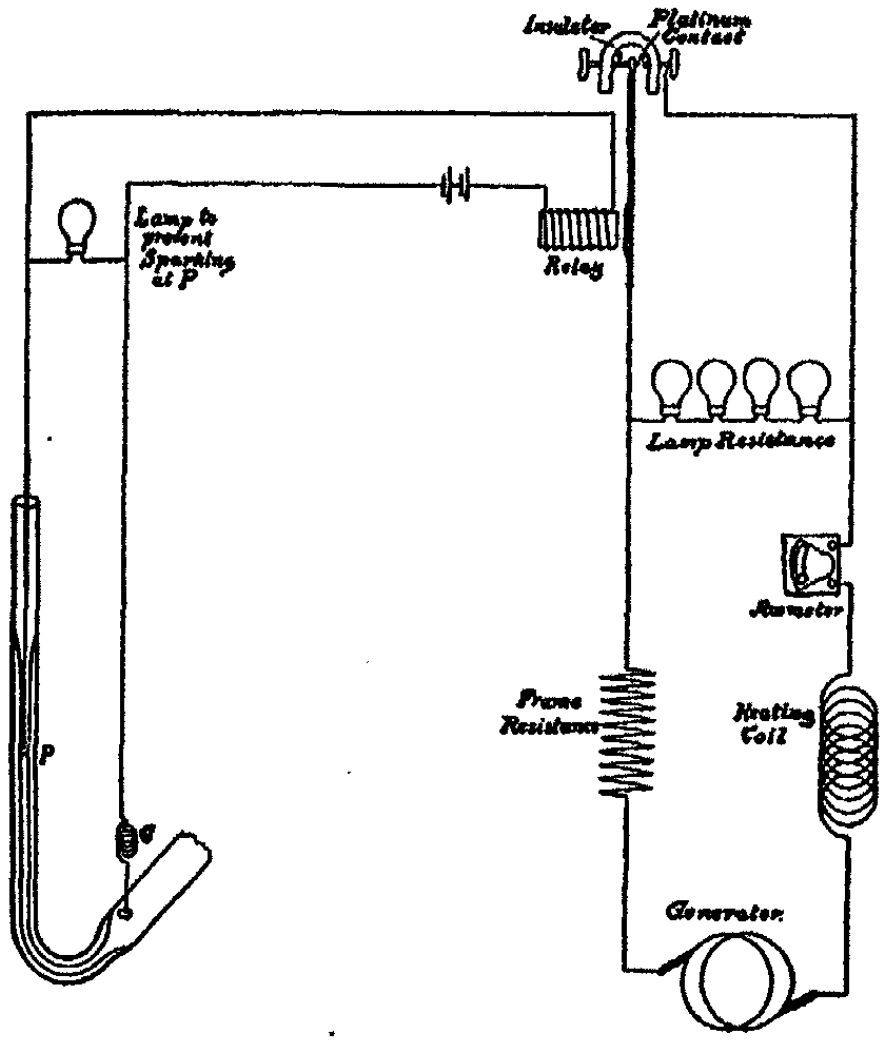

Fig. 1

The radiation constant of the apparatus was determined for several temperatures from that of the room to 75° C. From the data so obtained, the current necessary to compensate this loss was computed from Joule's law. A curve was plotted with degrees above the room temperature as ordinates and current in amperes as abscissas. Thus, for any desired temperature, within the useful limits of the apparatus, the required current could be found with ease. This current was taken from the 110 volt alternating incandescent lamp circuit of the laboratory.

The electrical connections are shown in Figure 1. The "frame-resistance" consists of a large wire resistance frame by means of which the maximum current flowing through the heating coil is regulated. The "lamp-resistance," which is in multiple with the relay contact, allows a constant current to flow through the heating coil, thus allowing the bath to be continually heated. The relay is controlled by the thermoregulator to be described. The two resistances are so adjusted that the constant current through the heating coil and the lamp-resistance is slightly less than that required to compensate for the loss by radiation. When the platinum contact of the relay is made the lamps are short circuited and a current, somewhat larger than necessary, flows through the coils. The constant current is made so small and the additional current so large that irregularities of the power in the main will produce no ill effects in the bath. The adjustment of the frame- and lamp-resistances is made with considerable care in order to avoid breaking excessive currents, since the consequent arc slightly fuses the platinum points, causing them to adhere to each other. No trouble arises from this source if the resistances are properly adjusted and a strong battery is used on the relay circuit.

The details of the thermoregulator which was employed to control the circuit just described, are shown in Fig. 2. The regulator was made to lie flat upon the wire tray in the lower part of the bath.

The principal parts of the apparatus are of glass. The main tube BMGFNR is 0.75 cm internal, 1.05 cm external, diameter and before bending was 60 cm long. The capillary BA is 0.046 cm internal diameter[1] and 16 cm in length, with a tube 6.5 cm long and 0.8 cm external diameter (the same size as the capillary tube) sealed above it. The stop-cock tube is 24 cm long. The whole was bent into the shape shown in the figure and was filled with 30 cc of mercury. By experiment mercury[2] proved to be much

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[1] It was found that the diameter should not be much less than that described, since striction becomes excessive and the apparatus less sensitive.

[2] By a change in the form of the capillary, alcohol, toluene or other liquid with large coefficient of expansion may be used.

more serviceable than alcohol, because of its high thermal conductivity, and the fact that neither leakage nor evaporation occurs through the stop-cock. The length FG and the width MN are each 15 cm. The platinum wire K is carried by the small brass apparatus D. By means of this, the wire may be easily raised and lowered, thus allowing of very accurate adjustment. The threaded rod H, to which the wire is soldered is, when adjusted, held in position by the jam-nut J. The band L clamps the brass part to the glass tube. C is a second platinum wire sealed through the glass. The tube is filled with mercury through the stop-cock E, which is closed when in use. As is seen, the regulator is so constructed that if, even after long use, it has become dirty, it may be cleaned very readily.

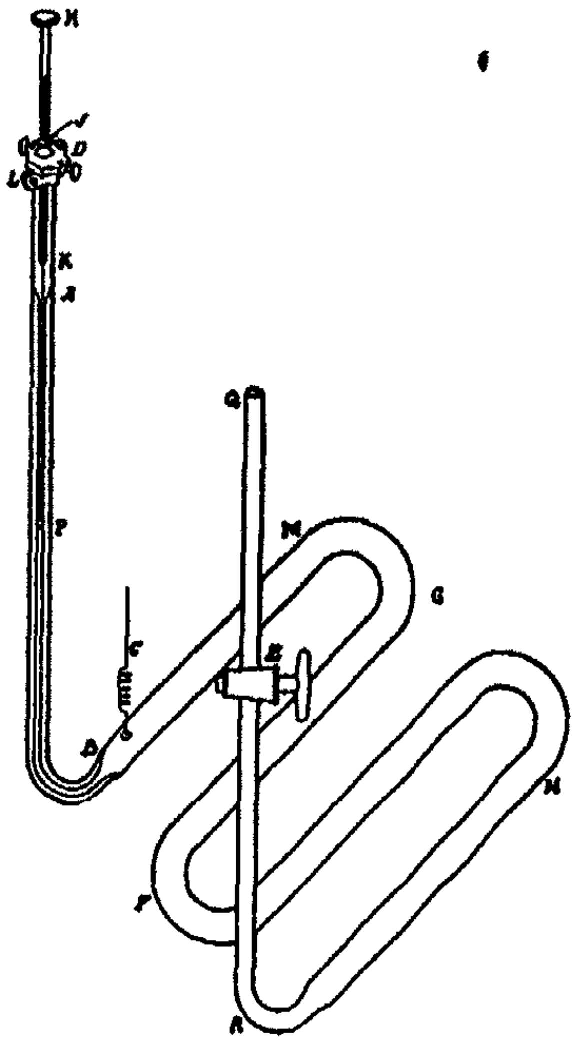

Fig. 2

The relation of the regulator to the electrical heating circuit is shown in Fig. 1. The relay used was a 150-ohm instrument actuated by two storage cells. In order to prevent inductive sparking with its attendant difficulties at the contact point P, a non-inductive resistance is connected in multiple with the regulator. For this purpose, one incandescent electric lamp was used, the resistance of which was just enough to prevent the relay from operating when the connection was broken at P. As the mercury thread separates from the platinum wire the electromotive force induced in the relay coils passes through the lamp without producing a spark at the surface of the mercury.

The action of the apparatus, when adjusted, is as follows: with a slight rise in the temperature of the bath, the mercury thread touches the wire at P, the relay acts, the platinum contact is broken, the lamp resistance is thrown into the circuit and the heating current reduced. A slight fall of temperature produces the opposite effect, the lamp-resistance is short circuited and larger current flows through the coils.

The capillary of the regulator is so small, the amount of mercury so large and has so great a surface exposed, that the regulator is extremely sensitive.

In using the apparatus, when connections are made, the temperature of the bath is brought to about one-tenth of a degree below that desired, by means of hot water. The current is then turned on, and when a thermometer indicates that the temperature desired is attained, the rod H is quickly screwed down until the platinum wire just makes contact at P, indicated by the click of the relay. The rod is clamped in this position by means of the jam-nut. The frame-resistance is then carefully adjusted. The apparatus now operates automatically as long as desired. The bath may be set at any desired temperature, as is evident from a consideration of Fig. 2, with as great accuracy as the skill of the operator will allow.

Throughout many runs of from three to five hours each, with the above-described seven-liter bath, at temperatures from 20° to 50° C, variations of not over 0.002° were to be observed on a Beckmann thermometer. During the great majority of runs no change at all could be read, although the readings were taken with great care and every effort made to avoid striction of the thermometer thread. On reheating, after the bath had cooled, it was found that the apparatus returned to within a few hundredths of a degree of the temperature of the previous run.

It became necessary to use a larger water-bath than that described, and so one similar to the above, of thirty liters' capacity, was constructed. This bath was heated by means of two coils in multiple, which had an equivalent resistance of four ohms. With thirty liters of water, the radiation constant was determined and from this were calculated the current, in amperes, and power in watts necessary to compensate the loss. These results are given in the following table:

Bath temperature	Radiation constant	Amperes	Watts required
22° + 5°	13.5	1.8	12.9
22° + 10°	26.5	2.1	17.5
22° + 15°	39.5	3.2	40.1
22° + 20°	52.4	4.3	69.4
22° + 25°	65.6	5.4	115.0
22° + 30°	78.8	6.5	167.0

The constant current was about one-half of that given in the table, the auxiliary current from one to three amperes more.

In all baths the position of the thermometer has much to do with the temperature observed, unless the stirring is extraordinarily vigorous. Measurements made with the thermometer bulb at the surface of the bath, and at the tray showed a maximum temperature difference of 0.005°, which decreased very appreciably when the efficiency of the stirring was greater. No care was necessary to keep the oscillation of temperature within ±0.005°, while in actual use it was easy to hold the temperature so constant that a Beckmann thermometer failed to show any change.

The thirty-liter bath has been used considerably in this laboratory on various kinds of constant temperature work. During many runs of from five to nine hours each no change over 0.002° could be observed. The apparatus was found to operate perfectly, no attention being necessary.

It is well to state that the apparatus and method of maintaining a water-bath at constant temperature, present certain advantages. The regulator is simple in form, is easily made, easily filled and, when necessary, easily cleaned; it is very sensitive, due to the large surface of the regulator and the expanding material used; it is capable of quick and accurate adjustments; so far as our experience has gone, the mercury in the capillary does not become oxidized at the point of contact with the platinum. In the thermostat itself it is of advantage to have a heating current pass continually while the auxiliary current is sent only as required. Of the four requirements of a thermostat mentioned on p. 94, all seem to be present, except possibly a low radiation constant.

Although others may present themselves, the main disadvantage seems to arise from the large current used and the expense of relay and resistances. The former may be obviated by the use of two or more incandescent lamps in multiple in the bath as the source of heat, according to the method of Gouy. This may be as serviceable as the use of the coils of wire, although it is not employed in this laboratory. Many devices may be employed to replace the relay. They are, as a rule, not so reliable as a good telegraph relay of about 150 ohms resistance.

The apparatus described above, therefore, is a serviceable form of electrically controlled and heated thermostat operating over a moderate range of temperatures with considerable accuracy.

In conclusion, this paper presents first a review of those thermostats employing the principle of chemical equilibrium to obtain a constant temperature, secondly, a brief sketch of the main types of thermoregulators which have been employed in scientific research, and thirdly, a description of an efficient thermoregulator designed to control the temperature of an electrically heated thermostat.

For suggesting the line of work and for valuable assistance in prosecuting the same, the writer expresses with pleasure most sincere thanks to Dr. H. R. Carveth.

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ANALYTICAL CHEMISTRY AND THE PHASE RULE CLASSIFICATION[1]

BY WILDER D. BANCROFT

We define physical chemistry as the study of the formation, separation and identification of phases and the examination of the various relations between the factors governing change and equilibrium. This is practically equivalent to saying that physical chemistry aims to present the science of chemistry as a complete and systematic whole. It has been found that the best method of presenting the subject as a whole is to classify our material first according to the number of components, distinguishing one-component, two-component, three-component systems and so on, while, for the sake of brevity, we often call all systems containing more than two components multi-component systems. Having made our first great separation into groups, we subdivide each group according to the number of phases. This classification according to components and phases is known as the phase rule classification. It is unquestionably the best classification for presenting what is ordinarily included under physical chemistry, and some of us hold the belief that it will one day be possible to treat such a subject as organic chemistry profitably along these same lines. That, however, is a dream of the future and only the first steps in this direction have as yet been taken.

If the aim of physical chemistry is to present the science of chemistry as a complete and systematic whole, it is obviously impossible to omit so important a branch of chemistry as analytical chemistry, and it is therefore necessary to consider this subject with reference to the phase rule classification. It is my object to show that the scientific significance of analytical

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chemistry can be brought out clearly and naturally in a course of lectures on elementary physical chemistry. This does not mean that analytical chemistry should be taught as laboratory work in connection with such a course. The actual drill in a series of specific methods is one thing and can best be acquired in a distinct course arranged for that end. The relation of these methods to the science of chemistry is another matter and one which I think is not very generally appreciated.

In the elementary course to which I have referred we begin with the simplest case, that of a one-component system and study the physical states of the substance, the thermal and optical relations, density, viscosity, surface-tension, conductivity, etc., and the way in which all these vary with varying conditions of pressure, temperature, wave-length, intensity of magnetic field, electromotive force, etc. This is also our first introduction to analysis. Any property or combination of properties can be used as a means of identification. In organic chemistry, for instance, the melting-point or boiling-point, is one of the most frequently used standards, while in inorganic chemistry we rely more on other tests. In gas analysis, we make use of the pressure-volume-temperature relations in order to tell us the mass of the gas, after we have determined its nature in other ways. It was a density determination, however, that led to the discovery of argon and the other inert gases. In microchemistry we depend largely on the crystalline form as a means of identification, while the spectroscope gives us a very sensitive method of recognizing certain substances by means of the rays emitted or absorbed at various temperatures.

Our knowledge of these properties and consequently our identification by means of them presupposes that we have pure substances to study, a condition which can be approximated very closely in a number of instances, but which very possibly can not be realized actually in any one. We must therefore have some criterion as to the purity of any given substance, and since a pure substance is one in which the presence of the other component or components cannot be detected by any analytical means at our disposal, it will obviously be in order to take up next the characteristics of two-component systems, including — so far as may be — all special properties. These properties will be the same that we studied in the case of the one-component systems with the added complication of the variation of these properties with the relative masses of the two components. A pure substance is then to be considered as the limiting case of a two-component system, the case in which the mass of the second component approaches zero. The delicacy of our tests will depend on the amount of variation of some property with the concentration when the concentration is very small.

Having determined that a given substance is not pure, it is often of interest to know what the impurity is. In some cases this can be done directly by volatilizing or precipitating one component more or less completely and identifying it. Instances of this are the separation of two liquids by fractional distillation, the sublimation of ammonium chloride from a mixture of ammonium and potassium chlorides, the driving off of occluded gases, the evaporation to dryness of a solution, or the freezing-out of either solvent or solute. These particular types are but a relatively small proportion of those to be considered. In the remaining cases, we either start with two or more impurities, in other words with a multi-component system, or we add one or more components in order to get a phase or a characteristic which we can identify. A general system of qualitative analysis is not possible until we have studied the properties of multi-component systems.

In the study of multi-component systems, special stress is laid on the variation of solubility with the nature and concentration of the other components, and also on the formation of compounds by metathetical reactions, both points of utmost importance in qualitative and quantitative analysis. It is not too much to say that the bulk of what is included in a qualitative test for bases and acids is based on a study of relative solubilities and is therefore physical chemistry pure and simple. In the qualitative analysis of the laboratory course we are dealing, so far as possible, with a carefully selected number of facts in regard to the solubilities of a limited number of substances, the basis of selection being the desire to obtain a limited number of substances successively as solid phase of approximate purity.

To illustrate this point, let me run over the regular scheme for the detection of the bases as given by Dennis and Whittlesey in their little manual. Silver, mercury as mercurous salt, and lead are distinguished by the insolubility of the chlorides. The chloride of silver is soluble in ammonia, while the mercurous chloride blackens. Lead is recognized here by the solubility of the chloride in hot water and the sparing solubility of the chromate or iodide. Mercury as mercuric salt, lead, copper, cadmium, bismuth, antimony, tin and arsenic are distinguished by the formation of sparingly soluble sulphides in hydrochloric acid solution and the last three, antimony, tin and arsenic, are grouped together owing to the solubility of their sulphides in ammonium sulphide. Mercury is identified by the insolubility of the sulphate in nitric acid, lead by the insolubility of the sulphate in sulphuric acid, cadmium by the relative solubility of the sulphide in sulphuric acid as compared with the sulphide of copper. Bismuth is recognized by the insolubility of the basic chloride and copper by the color in ammoniacal solution or the insolubility of the ferrocyanide. Arsenic and antimony are distinguished from tin by the volatility of the hydride and from each other by the insolubility of the antimony-silver compound, by the orange color of the insoluble antimony sulphide and by the insoluble ammonium arsenomolybdate. The final test for tin is the reduction of mercuric chloride by stannous chloride.

In the next group, nickel and cobalt are recognized by the fact that the sulphides, when formed, are insoluble in dilute hydrochloric acid. They are distinguished by the insolubility of cobaltic hydroxide in boiling ammonium hydroxide solution, while the solubility of nickel sulphide in solutions containing ammonium salts is worth referring to. Iron gives a black sulphide soluble in hydrochloric acid; but the color reaction of the sulphocyanate is the real test. Chromium is recognized by conversion into insoluble lead chromate, aluminum by the precipitation of the hydroxide from boiling aluminate solutions on addition of ammonium chloride. Manganese is identified by the color of the permanganate solution and zinc by the insolubility of the sulphide in acetic acid.

The test for barium is the insoluble chromate or sulphate; for strontium the precipitation of the insoluble sulphate by calcium sulphate; for calcium the insoluble oxalate, and for magnesium the insoluble phosphate.

Out of this whole list, the only bases not finally identified by the production of an insoluble substance are mercury as mercurous salt, copper, iron and manganese, and the test for copper with ferrocyanide is much more sensitive than the color test, while with mercury we have the change of one insoluble precipitate into another.

One great advantage of looking at the matter from the standpoint of relative solubility is that neither teacher nor student can fail to recognize that the test will succeed only in case the amount of substance formed is more than is necessary to make a saturated solution. Looking at the matter in this way we see that the text-books on qualitative analysis should lay emphasis on the approximate limits of sensitiveness in each particular precipitation. Though this point has been urged for years by Ostwald, it is still ignored very completely in most laboratories.

Where a graded scale of solubilities is impracticable, other methods of identification must be resorted to, and these are just as much to be classified under qualitative analysis as those methods which ordinarily pass under that name. Thus a separation by fractional distillation, if carried out for the purposes of identification, is qualitative analysis quite as much as the orthodox precipitations of the inorganic chemist or the more recent "group reactions" of the organic chemist, and it would give the student a clearer idea of the interrelation of the different branches of chemistry if this point were insisted upon more often. Some of these methods are so recognized. In the qualitative tests for sulphur and iodine, we sublime these substances without change. In blowpipe work on charcoal we leave behind the substance we are to identify. In the case of the borax bead we depend on color changes. The absorption spectrum is of great importance as a qualitative test in many rare earth separations.

After we have determined what the constituents are in a given mixture, it is only natural to ask how much of each constituent is present. From a scientific point of view quantitative gravimetric analysis is a matter of separation and estimation of a phase, and a course in quantitative gravimetric analysis is very largely a course to develop manipulative skill. I quote Fresenius on this point. "The most extensive and solid theoretical acquirements will not enable us, for instance, to determine the amount of common salt present in the solution, if we are without the requisite dexterity to transfer a fluid from one vessel to another without the smallest loss by spurting, running down the sides, etc. The various operations of quantitative analysis require great aptitude and manual skill which can be acquired only by practice." The choice of phase for determination in gravimetric analysis depends primarily on the solubility relations as in qualitative analysis, but is subject to the further condition that the new phase must be one which can be weighed accurately, or which can be converted into one which can be so weighed. In electrolytic work the precipitation is effected by the current instead of by an addition of a reagent.

While quantitative gravimetric analysis is a matter of phase separation and estimation, other methods of quantitative analysis are based on relations between some property of a phase and the relative masses of the constituents. If we tabulate the way in which any given property varies with the relative mass of any one of the components, we can then use the data thus obtained as a means of determining the relative mass of that constituent — provided the property in question varies only with the relative mass of that constituent. The density, color, boiling-point, freezing-point, conductivity, index of refraction, temperature of clouding, electromotive force, rotation of the plane of polarized light are a few of the properties that have thus been used.

Since many of these properties, such as the density, boiling-point; etc., vary with the relative masses of all the constituents, these properties can be used only for analysis in the case of two-component systems. Thus we can determine the amount of alcohol in aqueous alcohol from the density, but the test fails completely if the alcohol contains acetone, fusel oil, or any other impurity. We can determine the strength of acetic acid by its freezing-point, but the test fails if ammonia has been absorbed from the air. We can determine the amount of phenol in a hot aqueous solution by observing the temperature at which the solution clouds, but the presence of anything else changes the temperature of clouding and makes the method worthless. Conductivity determinations are of no value when two or more salts are present in relatively varying amounts. In the cases where these methods are serviceable, it is to be noticed that the property in question usually varies with the temperature and pressure as well as with the relative masses and that each measurement must therefore be made at a definite temperature and pressure to be of any value. The flash test for kerosene is one in which so many factors enter that the conditions have to be and are specified in great detail.

While many of the properties of systems are useful for analytical purposes practically only in two-component systems, this is by no means necessarily the case. Within certain limits the rotation of the plane of polarized light by an aqueous sugar solution is independent of the nature and relative masses of the other components and consequently this property can be and is used, within these same limits, as a means of quantitative analysis. Similarly the difference of electrical potential between a metal and an electrolyte is assumed to be a function of the concentration of the same metal as ion in the solution and not to be primarily a question of the concentration of any other substance as ion. So long as this condition is satisfied, the measurement of an electromotive force gives us the means of analyzing for that metal as ion, a method which has been used very much in physical chemistry.

When studying the various properties of multi-component systems, we should naturally include color phenomena in presence of so-called indicators. After we have settled, once for all, that a given color change takes place when the ratio of the masses of an acid and a base exceeds a certain value, we can then use this knowledge to enable us to determine the amount of an acid in a solution by finding the amount of the base necessary to produce the color change. This is the general principle underlying all quantitative volumetric analysis. It is to be noticed that this is entirely independent of any hypothesis that we may make to account for the color change occurring at all or occurring at that definite ratio. Indicators had been used for years before the present explanation of their action was advanced and methyl orange is one of the standard indicators, though we are by no means certain what the significance of the color change actually is.

A theory as to the cause of the particular ratio is equally superfluous, though possibly very desirable. We find experimentally that the color change occurs for instance when the ratio of sodium hydroxide to hydrochloric acid exceeds 40:36.5 in round numbers, and that is all that is necessary for the volumetric determination of sodium hydroxide by means of hydrochloric acid or vice-versa. If we choose to account for this particular ratio in terms of combining weights and compounds, we may do so; but our analytical methods rest on the experimental data and not on the hypothesis. This will be seen if we reflect that the facts on which we base the atomic hypothesis were obtained by quantitative analysis. As a matter of fact, we do not always get exact ratios in volumetric analysis. In titrating silver nitrate with sodium chloride we have two distinct end-points, one where further addition of sodium chloride produces no precipitation and one where further addition of silver nitrate produces no precipitation. These two end-points do not coincide and neither corresponds to the atomic ratio between silver and chlorine. Yet we can take either one and get results which are as accurate as the determination of the end-point. When we titrate a ferrous solution with permanganate, it is not necessary that we know the reaction. We standardize against a known solution of ferrous iron. As a matter of fact, we don't use the atomic ratio, because we apply a correction for the amount of permanganate necessary to produce a standard tint. When the iron solution contains hydrochloric acid, other precautions are necessary. I quote from Fresenius: "Make the iron solution to be tested up to 1/4 liter, add 50 cc to a large quantity of water acidified with sulphuric acid (about one liter), titrate with permanganate, then again add 50 cc of the iron solution, and titrate again, etc., etc. The numbers obtained at the third or fourth time are taken. These are constant, while the number obtained at the first time, and sometimes also the second time, differs. The result multiplied by 5 gives exactly the quantity of permanganate proportional to the amount of ferrous iron present."

We shall also see that the analytical results come first and the theory afterwards if we consider the neutralization of phosphoric acid in presence of methyl orange or phenolphthalein. The ratios are different with the two indicators, while the nature of the indicator does not affect the ratio when we neutralize sulphuric acid. We re-state the result in terms of the electrolytic dissociation theory, but this is not essential for analytical purposes and our analyses will remain accurate even if the electrolytic dissociation theory be superseded. When it comes to titrating weak acids in presence of methyl orange, for instance, we find either that the end reaction is not sharp or that it occurs at a slightly different ratio from that predicted by our theory. In the first case we discard the indicator; in the second case, we actually adopt the experimental ratio, though we usually disguise this by taking the so-called theoretical ratio[1] and applying a "correction." Titrating chlorides in slightly acid solutions with silver nitrate when using sulphocyanate as an indicator would be a case in point.

I have taken up this question of volumetric analysis at

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[1] Cf. Ridenour. Jour. Franklin Inst. 152, 119 (1901).

some length because I wished to bring out that there is no really fundamental difference between analysis by means of density determinations and analysis by titrations. In both cases we construct a table empirically and refer back to that. In many cases of titration we can predict our table with a somewhat greater degree of accuracy than we can predict the densities of mixtures from a knowledge of the percentage composition; but that is all. Our methods of titration or of precipitation are better adapted to multi-component systems than many of the so-called physical methods because they are, as a rule, methods for one component or constituent. This, however, is subject to limitations. Precipitation with silver nitrate and weighing as silver chloride is not accurate when bromides or iodides are present. Precipitation with sulphuric acid and weighing as barium sulphate is inaccurate when lead salts are present. Of course no one would make this latter mistake; but I doubt whether most analysts appreciate the close analogy between removing lead salts before making quantitative determinations for barium and removing all except two components before making a quantitative analysis by density determinations. In the first case the process is a simple one and they have done it often. In the second case the process is not always feasible and it is a problem which rarely occurs. Consequently it seems to involve entirely new principles. As a matter of fact, there are special advantages and special limitations in each analytical method; but it is a complete mistake to try to draw a sharp line between analysis by comparison of so-called physical properties and analysis by comparison of so-called chemical properties. The two pass one into the other and it is utterly impossible for us to say, for instance, whether the density of a given solution is due to the partial formation of a compound or not.

I have tried to show the theoretical aspect of analytical chemistry when considered from the standpoint of physical chemistry and this brings us face to face with the problem of how far the teaching of analytical chemistry and of physical chemistry should be modified in consequence of such a point of view. I can see no reason at present for making any very radical changes, and yet a general broadening would be profitable in both cases. The physical chemist should know more analytical chemistry than he usually does. Our mathematical relations are based on results obtained by quantitative determinations and are to be confirmed by other results obtained by quantitative determinations. The more accurate our mathematical relations become, the more accurately we must make our determinations if we are to reach any definite conclusion as to the accuracy of our hypotheses. Of course if we are dealing with approximation theory and regard a difference of ten percent as a pretty good agreement, we can afford to be slovenly and inaccurate in our analytical work. In the theory of solutions we have been going through a period of that sort with its attendant results; but I hope that a new era is dawning when we shall develop exact theory, and when we shall study all solutions and not merely infinitely dilute ones.

The advantages to the analytical chemist from the point of view which I have outlined are that he will perceive that there is much more to analytical chemistry than he had perhaps realized, that there are many cases where other methods besides those of gravimetric and volumetric analysis are important, and that he should be familiar with those methods. This has already been recognized by Krüss in his little book, "Spezielle Methoden der Analyse," published in 1892. I am not suggesting anything really new, but I can carry it further now than Krüss could do nine years ago. It is essential to know the analytical methods of the physical chemist. It is quite as important to know them and the subject from the phase rule point of view.

One illustration will suffice. An analysis of a piece of steel will show the percentage composition. It may show a little more, the amount of "free" and "combined" carbon; but the result of the analysis tells relatively little about the physical properties, which however are the essential things from a technical point of view. A microscopical analysis will give a great deal of information and is rapidly coming more and more into use. It is quite as important therefore for an analytical chemist in a steel works to understand microchemical analysis as to be familiar with the more usual methods of analysis. Having got the facts, it is necessary to interpret them, and this cannot be done satisfactorily without a knowledge of the phase rule. The microscope may show the existence of a number of compounds; but it tells nothing as to the relative stability or as to the conditions of formation. Of course these can be worked out empirically and have been so done to a certain extent, but this means an immense waste of time. The recent work of Roozeboom in applying the phase rule to iron and steel shows clearly the difference between having a theory to guide one and groping more or less blindly. This has been fully recognized in England at any rate. The way in which the properties of a metal or alloy vary with the thermal history is quite as important as the way in which these properties vary with the percentage composition, and the two should be studied together. Is the analytical chemist going to qualify himself for such work or not?

Cornell University

A THERMOSTAT, SENSITIVE TO A THOUSANDTH OF A DEGREE

BY W. P. BRADLEY AND A. W. BROWNE

For the prosecution of certain inquiries relative to critical phenomena it was desirable to maintain constancy of temperature for several hours within a thousandth of a degree. This requirement was met by the use of the thermostat whose construction is illustrated in Fig. 1.

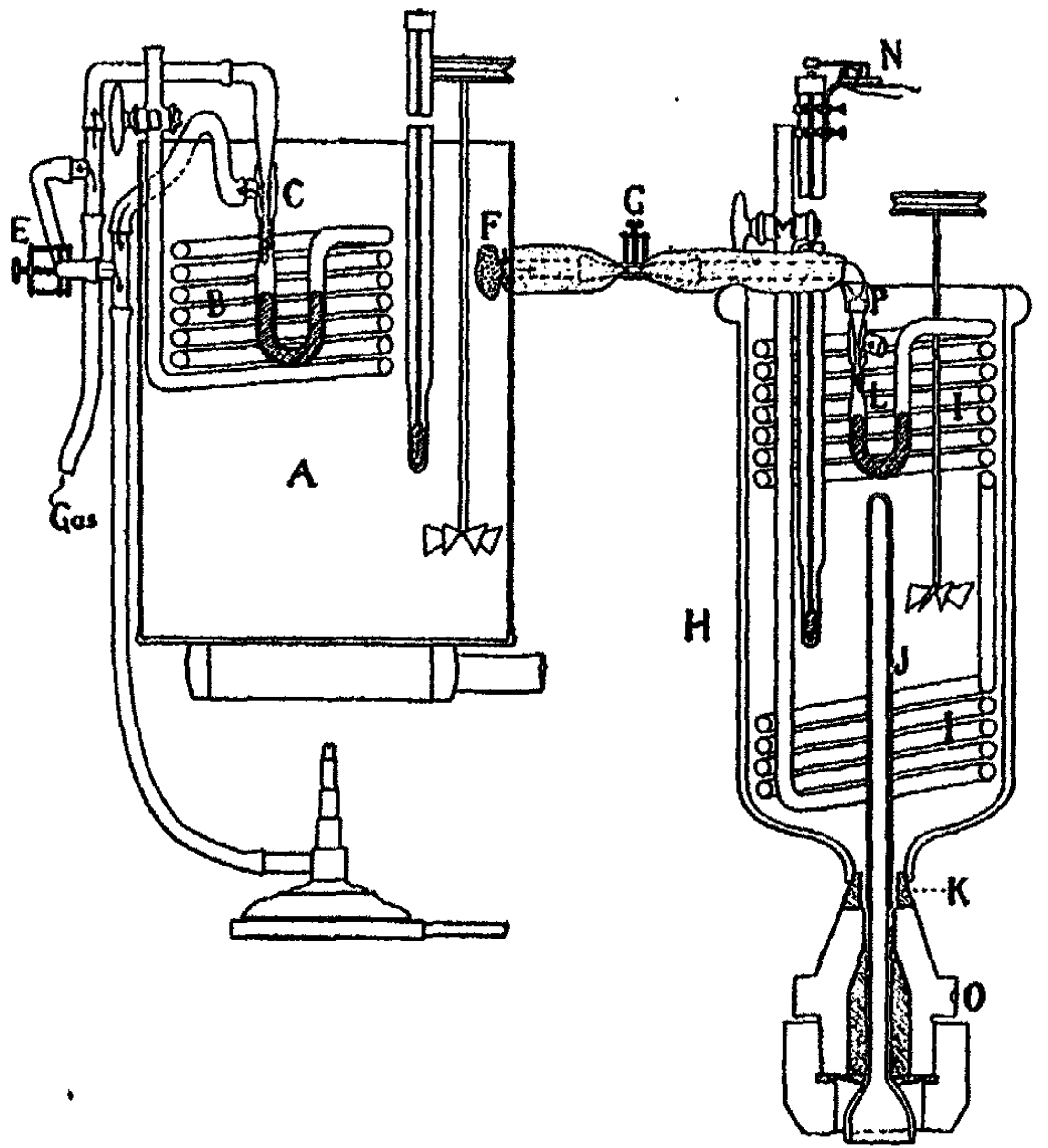

Fig. 1

O is the cap of a Cailletet apparatus, and J is the upper end of a glass compression tube which contains the glass to be examined. Mounted upon the former by means of a flexible rubber joint K, is a glass bell H, which, with its contents, is the thermostat.

The regulating medium is contained in a continuous glass spiral I, which is so disposed as to give an unobstructed view of the top of the compression tube. The spiral is closed at one end by a very accurately ground glass cock M, and terminates at the other in an upright U-shaped portion L containing mercury. The constriction in the outer limb of the U is the point at which the inflow of heat is regulated — or, as it may be called, the cut-off.

A is a reservoir of warm water which feeds the thermostat. The water flows through a short, narrow, and well insulated tube FGP to the cut-off, is throttled at that point, and then escapes into the bell H. A cloth filter F serves to retain any sediment.

The reservoir is provided with an ordinary attachment for maintaining constant level of water, and the bell H has an overflow. These are not shown in the cut.

The temperature of the thermostat is read upon the stem of a Beckmann thermometer which carries the usual electric hammer N.

The factors which contribute to the efficiency of this thermostat may be classified as follows:

1. Those which induce, on the part of the regulating medium, a prompt response to changes of temperature in the thermostat. These are: (*a*) effective circulation; (*b*) a large ratio between the surface of the regulating medium and its volume.

These factors taken together produce a promptness of response in the regulator which greatly exceeds even that of the Beckmann thermometer.

2. Factors which produce a large linear movement of the mercury at the cut-off. These are: (*a*) the constriction in the walls of the regulator at the cut-off; (*b*) the large quantity of expansive medium used; (*c*) its high coefficient of expansion.

Factors (*a*) and (*b*) are nearly always well provided for, even in thermostats which are intended for rough work only. In the present apparatus, the combined effect of the three factors is a vertical motion of the mercury at the cut-off greater than that produced in the Beckmann thermometer by the same change of temperature.

3. The factor which tends to prevent irregularities in the amount of heat lost from the thermostat by radiation, viz., insulation of the bell.

4. Factors which tend to prevent irregularities in the amount of heat introduced into the thermostat. These are: (*a*) the nature of the thermal vehicle employed; (*b*) the relation between the temperature of this vehicle and that of the thermostat; (*c*) steadiness of temperature in the reservoir; (*d*) the pressure or "head" under which the feed-water flows; (*e*) the narrow orifice of the conduit through which it flows.

These factors will be considered in detail.

I

Promptness of response to changes of temperature is the *sine qua non* of efficiency in a thermal regulator. In comparison with this, mere amplitude of response is of small moment. It is obvious, in fact, that very small amplitude indeed will suffice, if the response is immediate. On the other hand, sluggishness of reaction tends directly to create and perpetuate thermal oscillation; and great amplitude, if coupled with sluggishness, may even accentuate this tendency. These are considerations which have not received as yet the practical attention which they deserve.

(*a*) *Circulation.*—In order that every change of temperature may be followed as quickly and faithfully as possible by the regulator, and in order also that the temperature in every part of the thermostat may be the same, the best possible circulation is indispensable in the bath. The device employed to secure this result, as shown in the figure, is a simple propeller wheel, soldered upon a piece of brass wire which serves as a shaft. This wheel was easily cut from a bit of sheet copper and was trimmed into symmetry after mounting. Its diameter, limited by the amount of space available in the bath, is 3½ cm. It is driven by a small water motor at a speed of 800–1000 revolutions per minute.

The results are eminently satisfactory. In an actual test, during which the nature of the circulation was revealed by the presence of suspended matter in the water of the bath, it was found that on the average a given small portion of water returned to the wheel after a complete circuit about once a second. Moreover, the current was so effectually broken up by the disposition of the regulator coils that it penetrated every part of the bath in reasonable degree with the same rapid motion. As the dimensions of the bell are 25 x 12 cm, the mass of water thus circulated is about 2500 cc.

The best results are obtained when the wheel has such a direction of rotation that the water is drawn upward through it. If the blades are immersed to a sufficient depth, the surface of the water, though distorted, does not break.[1]

(*b*) *Surface.* — Provision is thus made for bringing every change of temperature anywhere in the bath into immediate reaction with the whole surface of the regulator. The rapidity with which the regulating medium can now respond obviously depends in large degree on the extent of surface which it presents. The greater the surface, the sooner will the full effect of the change be felt.[2]

From this point of view the spherical form of regulator, which presents the minimum of surface, is clearly the worst

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[1] We tried at first various stirrers of the centrifugal type. The motion which they produce in the bath is largely a rotary one. For the present purpose they are much inferior in point of efficiency to the simple propeller.

[2] In the Journal of the American Chemical Society, 1901, page 330, S. W. Young calls special attention to this point in a brief discussion of thermostatic sensitiveness. He distinctly states, however, that he made no experiments in this direction.

We deem it not improper in this connection to mention that we had already been testing the tubular form of regulator for several weeks before the appearance of the article mentioned.

which could be chosen. The usual short cylinder is little better. In each of these, the great bulk of the medium is withdrawn from the direct action of the bath, and, except in the case of mercury, which is a good conductor, must be heated by the slow process of convection. In the present apparatus the regulator is tubular and is wound for convenience into spiral form. The glass tubing employed happens to have an internal diameter of 5½ mm and a total length of four meters. Its internal capacity is therefore about 90 cc, and the area of the surface which the inclosed liquid presents is not far from 700 sq cm. The same amount of liquid in spherical form would have a surface less than one-seventh as great. Still smaller internal diameter, with or without increase of length would be entirely practicable and proportionally advantageous.

A glass regulator is open to objection on the ground of its low thermal conductivity. In this respect metal tubing would give better results. On the other hand, the transparency of glass is a factor which more than offsets any advantages which metal might offer. It permits a ready inspection of its contents. For one thing, the regulator must be entirely free from bubbles of gas, however minute. Their compressibility makes accuracy of regulation impossible. Their presence could not be detected in a metal except perhaps indirectly by their effects. In glass they can be located at once.

The bubbles are noticed, if at all, within a few hours after the regulator has been filled. They seem to be due to the film of air which adheres to the surface of the glass. To avoid them, the newly filled regulator should be allowed to stand some hours before use. It is then to be emptied, thoroughly rinsed, and carefully refilled. If the liquid employed in the regulator is capable of dissolving air at all, it is well to have it freshly distilled before use.

Whatever the material of the regulator may be, the walls ought to be as thin as is consistent with strength and rigidity. Thick walls only serve to hinder free interchange of heat between the bath and the interior. In this respect the present regulator is capable of considerable improvement. Its walls measure 1 mm in thickness.

2

When those conditions have been secured which provide in high degree for promptness of response on the part of the regulator, the next factors to be considered are those which produce a large linear motion at the cut-off.

(*a*) *The constriction.* — The outer limb of the U is greatly constricted to form part of the cut-off. Its internal diameter at that point does not exceed 1.5 mm.

(*b*) *Volume.* — The large volume of the spiral, already stated as approximately 90 cc, also contributes greatly to the end in view.

(*c*) *The medium.* — Mercury, though an excellent conductor of heat, seemed to us undesirable as a regulating medium for two reasons. Its coefficient of expansion is low; and its high specific gravity appeared likely to endanger the safety of the spiral.

Organic liquids possess in general a coefficient of expansion several times as great as that of mercury. Unfortunately, those whose coefficients are the highest, such as ether, methyl and ethyl bromide, methyl formate, etc., are unavailable because of their low boiling-point. Ethyl alcohol was finally chosen as promising on the whole the best results.

3

Insulation. — Perfect insulation alone would secure constancy of temperature in a closed system. In practice, insulation is able to do no more than to reduce the speed with which change of temperature occurs. Fortunately this is sufficient for thermostatic purposes. If the changes occur slowly enough, the regulator has time to feel them and to react before the allowable limit of variation is reached. To secure this result with the present thermostat is a simple matter. We simply wind the sides of the bell with bands of cotton batting about an inch in width and thickness. With this arrangement one can secure at will a view of any portion of the interior by simply pushing apart the bands at the proper places.

The top of the bath has never been shielded at all from radiation, although it exposes a surface of more than 1000 sq cm. In fact, it is only for the finest work that insulation on the sides is required. Without any insulation whatever, the thermostat will functionate within one-hundredth of a degree, as has been proved by actual trial; and this too in a room where the temperature sometimes varies 10–12 degrees in the course of the day. (Compare also 4(*c*).)

4

While it is desirable to shield a thermostat from sudden and irregular losses of heat, it is much more important to avoid sudden and excessive inflow. Sluggishness on the part of the regulator and excessive supply of heat are the two radical defects of thermostats in general. It is obvious that both of these defects work in the same direction. Both tend to produce oscillation of temperature. Whenever the inflow is excessive, the cut-off closes entirely. Once closed, it remains so until the temperature of the bath, in its downward course, has sunk again below the normal. When it does open, it opens wide. Another excessive inflow follows, with the same result as before.

It is unnecessary to say that the oscillation of temperature thus established, whatever its amplitude may be, is fatal to fineness of regulation. It will be noticed, moreover, that the very points of construction which are usually well provided for, namely those which produce large linear motion at the cut-off, are precisely those which tend to perpetuate such an oscillation when once established.

What is required for accurate results is a "throttling" of the inflow, not an alternate opening and closing of the conduit. Almost as much heat ought to be flowing at all times as will suffice to counteract the loss by radiation. All that should be required of the regulator is a quick control of the slight additional amount needed from time to time. Attention to this point would doubtless increase the efficiency of almost any thermoregulator. Several factors make such a throttling possible.

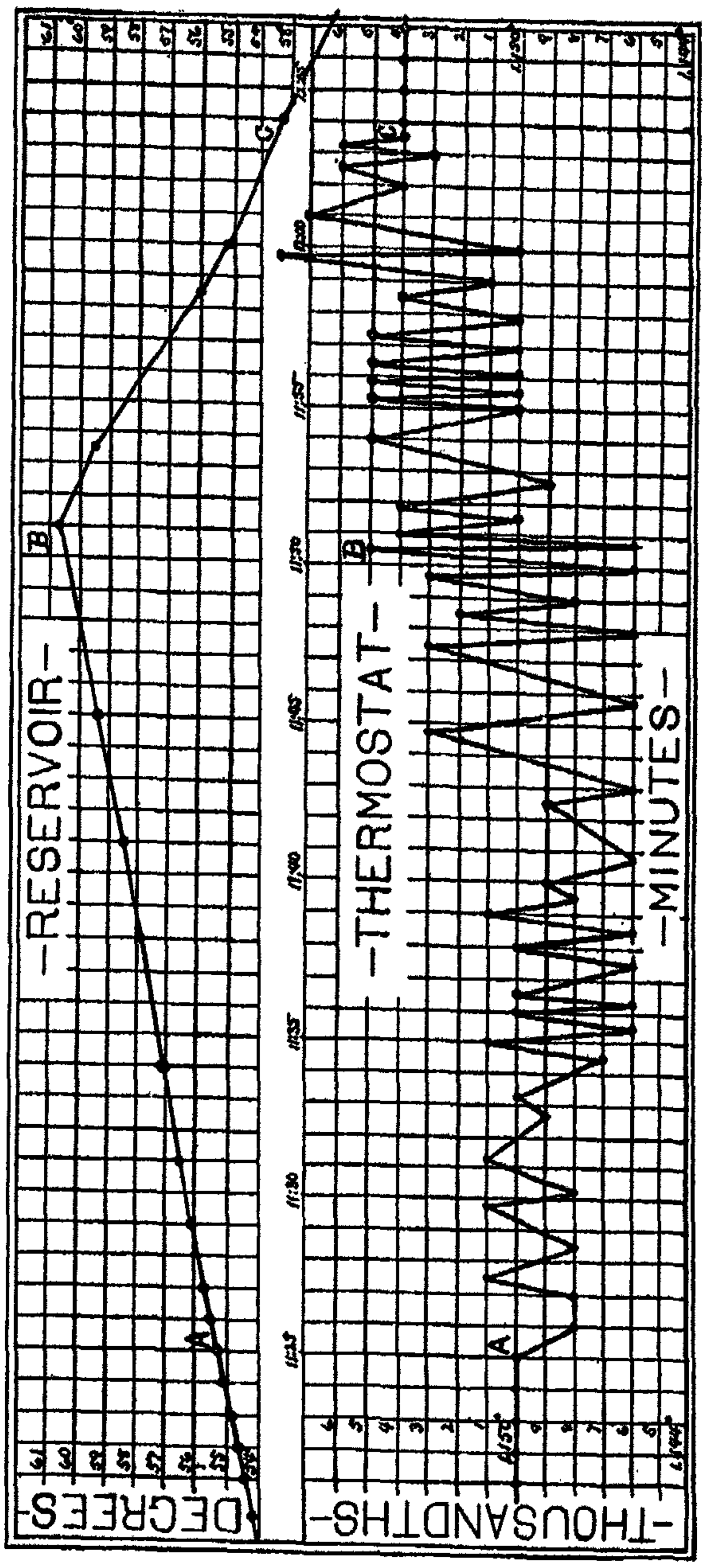
(*a*) *The thermal vehicle.*—As a source of heat for fine thermostatic work, the gas flame seems quite unsuited. The rapidity with which gas flows through an aperture makes fineness of adjustment difficult. Very slight increase in the aperture makes a relatively large change in the amount of gas which passes. The difficulty may be avoided by the use of electricity or warm water as the source of heat. For reasons of convenience, we chose the latter.

(*b*) *Temperature of the vehicle.*— A study of the proper relation between the temperature of the vehicle and that of the thermostat led to interesting results.

It hardly needs mention that the water of the reservoir must always possess a temperature somewhat higher than that of the bath, in order to counteract radiation from the latter. The difference amounts to a few degrees only, and depends upon a number of factors, but more especially upon the effectiveness of the insulation of the bath, the size of the water conduit FPL, and the pressure under which the water flows.

Now we find that above this minimum working temperature, whatever it may be, there is a considerable range within which the precise temperature of the feed-water is a matter of indifference. Within this range, the temperature of the thermostat remains exactly the same, no matter what that of the reservoir may be. Within this range, the regulator throttles. Just as soon as this range is overstepped, in other words, when the accession of heat which follows a slight increase in the size of the opening at the cut-off notably exceeds the real requirement, the throttling suddenly ceases. The action of the regulator becomes at once oscillatory, and the readings of the thermometer swing rapidly up and down in sympathy.

Fig. 2 shows quite clearly the effect of this sudden transition from throttling to alternate opening and closing. In the experiment there illustrated, the temperature of the reservoir,—shown in the upper portion of the diagram,—was allowed to rise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steadily. That of the thermostat, which lay in the neighborhood of 26°, remained for a time perfectly constant upon the same thousandth of a degree. This section of the curve ends at the point A. Only the last five minutes of it are shown.

On the other hand, when the temperature of the reservoir passed 55°–56°, constancy in the thermostat ceased and the curve became broken. Not only so, but the oscillations, which now occurred continuously, became constantly greater in amplitude as the inflowing water became hotter.

At 60°–61° (B) the gas flame under the reservoir was extinguished and the temperature of the feed-water fell. This was the signal for a reversal in the curve of the thermostat. In general, the oscillations decreased in amplitude, though not as regularly as they had previously increased, and they finally ceased altogether as suddenly as they began. (C). The temperature of the reservoir at this point was about two degrees lower than at A where the oscillations began. From this time on, the temperature of the thermostat remained constant again until that of the reservoir fell below the working range. Only the first few minutes of this period are shown.

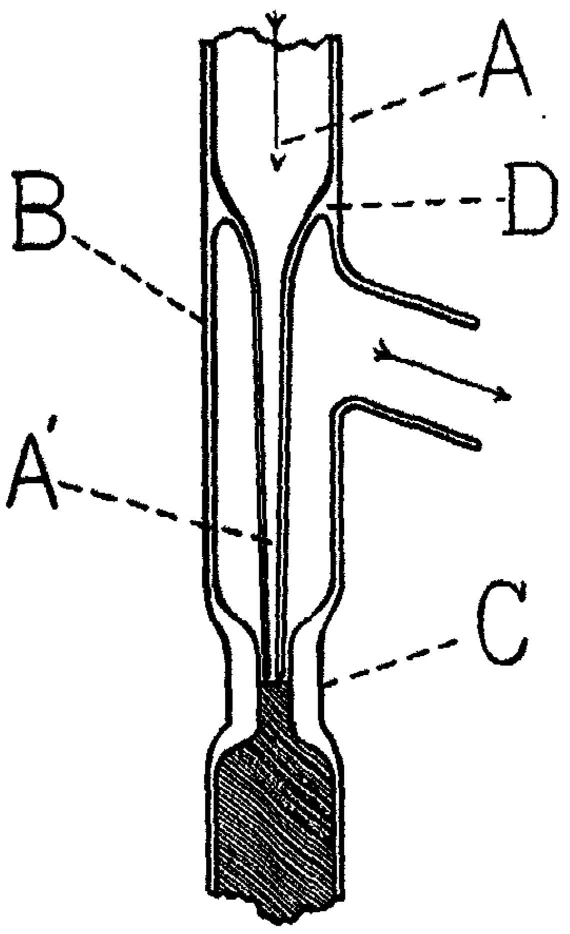
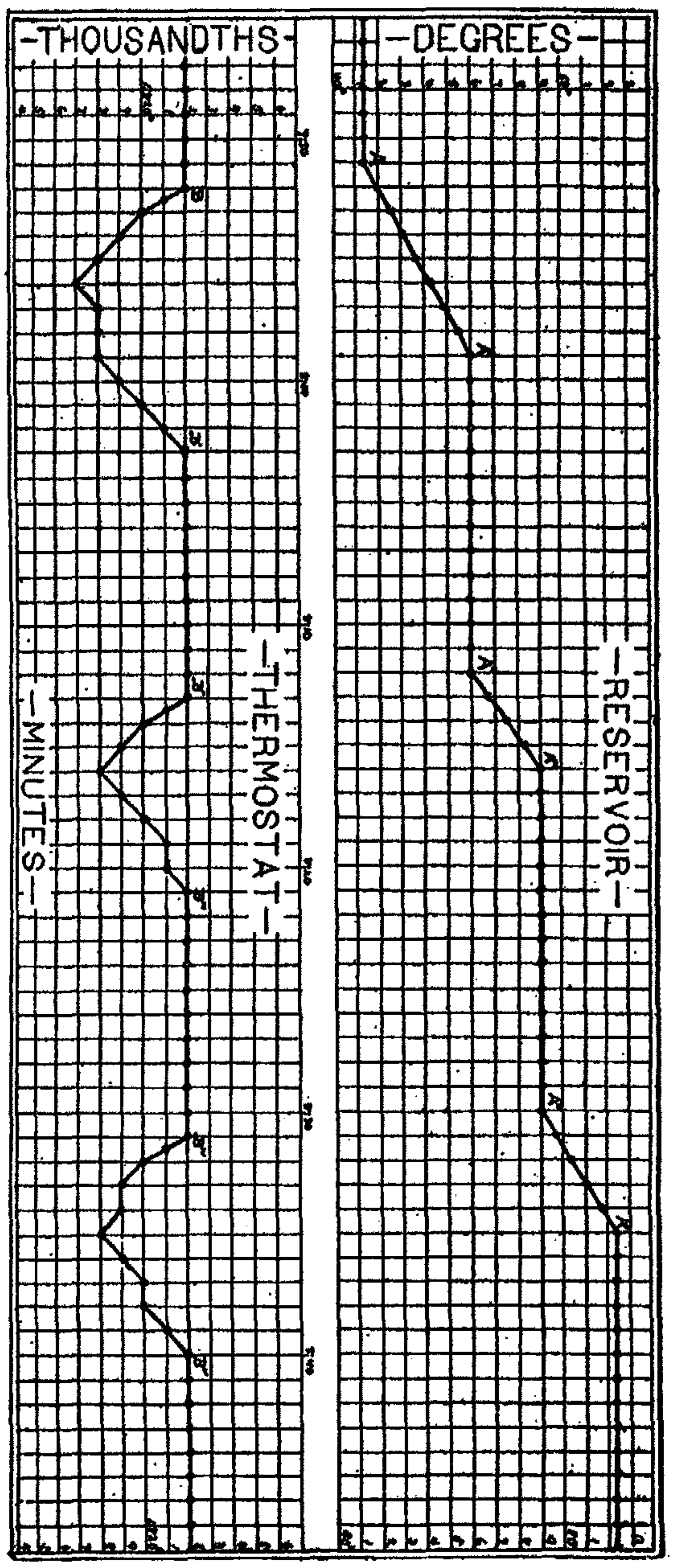


Fig. 3

One cannot fail to notice however that the temperature of the first period of constancy in the thermostat is not the same as that of the second. It is lower in fact by four thousandths of a degree. The explanation of this difference is simple, though not at once apparent. It lies in the fact that any considerable change in the temperature of the feed-water is felt more quickly in the conduit than in the walls of the U which envelops it. The walls of that portion of the conduit (A′, Fig. 3) which lies below the joint D expand or contract earlier than the walls of the envelope B. When the temperature of the feed-water begins to rise, for example, a differential expansion takes place, which results practically in thrusting the cut-off slightly lower into the constriction C. This means of course that the temperature of the thermostat must fall somewhat. On the other hand, if the temperature of the feed-water falls, the end of the conduit is slightly drawn up with reference to the constriction. Its position being higher, the temperature of the thermostat must rise before normal flow can be reestablished.

These changes of level are exceedingly slight, to be sure, but they are unmistakable. One striking manifestation of their results is to be observed in the sudden elevation of the entire field of oscillation in the curve of the thermostat at the point B, where the heating of the feed-water ends and the cooling begins. To the left of B, the entire lower curve in fact is to be thought of as lying slightly lower than it would if the reservoir temperature were stationary; to the right, as slightly higher. The true position of *normal constancy* is accordingly neither that of the first period nor that of the second, in the diagram. It undoubtedly lies *between* A and C in a vertical sense, not far from 1.152° as read from the Beckmann.

The effect of change in the temperature in the reservoir is shown in another way in Fig. 4. In this experiment, a stationary period is followed at A (upper half of the diagram) by a rise of nearly five degrees which ends at A′. Then after thirteen minutes of stationary temperature, there is an elevation of three degrees. Later still three degrees more are added. For a minute after the beginning of each rise, no effect is noticeable in the thermostat. A certain amount of time is required for the newly heated water to reach the cut-off. Then there begins in each case a rather steep fall of some thousandths, followed at once by a somewhat slower recovery. In every case the restoration of stationary temperature in the reservoir means the recovery of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constancy in the thermostat. This recovery moreover is exact. Whether the stationary temperature of the feed-water in the experiment lay at 41.4°, 46°, or 52.3°, the thermostat returned faithfully to the same thousandth, because all three of these temperatures lie within the working range already mentioned.

When the temperature of the reservoir alternates between falling and stationary, just the opposite effect is produced. Instead of the depressions shown in Fig. 4, corresponding elevations are obtained in the curve of the thermostat. There is no other difference so long as the temperature of the reservoir keeps within the working range.

(C). *Regulation in the reservoir.* — It follows that all coarse fluctuations in the temperature of the reservoir should be avoided if one wishes to eliminate the last readable variation in the thermostat. This means, in the first place, that the reservoir also must be provided with a regulator. As a matter of fact, we employ for this purpose a portion of a regulator originally intended for the thermostat, which was accidentally broken. Its capacity is only 50 cc.

The efficiency of the tubular type of regulator is illustrated here also, in an unexpected degree, under very adverse circumstances. Although the reservoir is of metal, painted black and entirely destitute of insulation, although the source of heat in this case is an unprotected gas flame, whose fluctuations in size are very noticeable, and although the nature of the regulation, as might have been expected under the circumstances, is strictly oscillatory, nevertheless the maximum variation, at a temperature of 50°, does not exceed one-twentieth of a degree.

It is not at all necessary to the end in view that the regulation in the reservoir should be as fine as this. We have reason to believe that a variation of half a degree would be entirely admissible. As the allowable limit of variation however depends on the amount of differential expansion of the conduit and its envelope between the points D and C (Fig. 3), it follows that the shorter the tongue A′ can be made, the better. This is a point which did not occur to us till the present regulator was completed. It is after all of secondary importance.

The regulator in the reservoir having secured a reasonably stationary temperature in the feed-water as it enters the conduit, fluctuations in the conduit itself are avoided by suitable insulation throughout its entire length, and also by using in its construction tubing of narrow bore. The more rapidly the feed-water passes through to the thermostat the better.

But the temperature of the feed-water is not the only circumstance which affects the amount of heat admitted to the thermostat. The volume of the inflow is also a factor. Precisely the same disadvantages which follow the introduction of water which is too hot can be produced by too copious an amount. Attention must be paid therefore to the conditions which affect the amount of flow. One of these is the "head" of the flow, and another, the size of the aperture by which the water leaves the conduit.

(D) *Difference of water level.* — After a number of trials, we found that a difference of level of 10 cm between the water in the reservoir and that in the thermostat was ample for the maintenance of a temperature of 30° in the latter. If the temperature to be maintained were considerably higher, this difference would have to be increased. The precise amount of head in any given case is easily determined by trial.

The constant level attachment to the reservoir and the overflow from the thermostat have already been mentioned.

(E) *The orifice.* — The conduit at its lower end is capillary. Its size at the orifice may best be indicated by the fact that it allows the passage of water, under a head of 10 cm, at the rate of 80–100 drops a minute.

It chanced that the annular space between the end of the capillary and its envelope (C, Fig. 3) was very slightly smaller than the bore of the capillary itself. This circumstance affords a decided advantage; for when the mercury rises too rapidly in the constriction, — as it will usually do at the beginning of a run, before the regulator has settled down to normal working, — it rises into the interior of the capillary itself instead of around it. The advantage lies in the fact that the subsequent fall of the mercury is in the direction of the water-pressure and not against it. There is accordingly less danger that small globules of mercury shall become detached, and lodge in the constriction or above it, away from the main body.

It may not be uninteresting to note the manner in which the thermostat takes up its normal functions at the beginning of a run. This is represented in Fig. 5. When the temperature is still below that of final constancy, the feed-water flows unchecked except by the narrowness of the conduit. The temperature, measured in thousandths, goes bounding upward, passes the normal point A by a few thousandths, falls again by radiation to a point very little below the same, and finally rises to the normal at B where it remains. The experiment whose readings are represented in the diagram is fairly typical. It is a rare occurrence when the temperature crosses the normal line more than twice before becoming constant.

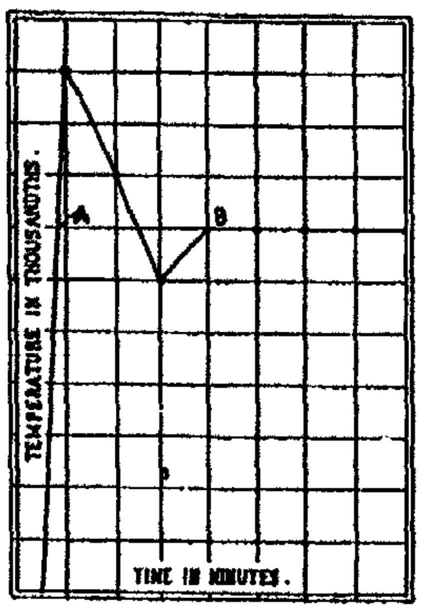

Fig. 5

As to the length of time during which this thermostat is capable of maintaining constancy of temperature, we are able to hazard no conjecture. As was stated at the outset, the instrument was not constructed for the study of thermostatic conditions, nor to test thermostatic efficiency. It was needed for actual use, and such tests as have been made are for the most part incidental. The longest run so far made lasted four hours. During the first two hours, readings were taken every minute; during the last two, every three or four minutes, at convenience. *Every one of these readings was the same thousandth of a degree.* It may be that another hour or two might have brought a change, as the mercury showed signs of a tendency downwards toward the close of the run. This was due, however, in our opinion, not to any irregularity of function in the thermostat itself, but to the lodgment of a minute quantity of sediment in the cut-off, attributable to imperfect filtration of the city water. Partial stoppage of the cut-off between the tip of the capillary and the surface of the mercury would force the mercury to a slightly lower level in order to maintain the same amount of flow as before. This lower level would of course correspond to an equivalent fall of temperature in the thermostat. Unless changes of temperature are to be read upon some thermometer more sensitive than the Beckmann, it seems hardly worth while to search for the cause of a fall which amounts to less than a thousandth of a degree.

The manner of regulation which this thermostat exhibits is oscillatory after all. But it is needless to say that the oscillations are not of the coarse type discussed above. Under normal conditions, the thread of the Beckmann can be seen to move alternately up and down, but not by an amount sufficient to warrant a difference of reading in the third place of decimals. The amplitude of the oscillations, in other words, is less than one thousandth of a degree.

Besides great constancy of temperature, one other serious demand was made upon this thermostat by the inquiries to which reference has been made. It was very desirable that its regulator should be capable of rapid and accurate adjustment, so as to correspond to any temperature within a considerable range. These two requirements seem at first thought antagonistic. A change in the temperature of the thermostat involves a change either in the volume of the regulator or in the mass of alcohol which it contains. In either case a joint is necessary at some point in the regulator, and a joint involves a possibility of leakage.

At first we sought to utilize some sort of plunger or screw, which could be made to penetrate more or less into the regulator and so change its volume. But it soon became apparent that any joint tight enough to retain alcohol was subject to a slow process of readjustment, lasting for a considerable time after each movement of the plunger or screw. This involved vexatious delays.

On the other hand, we hardly expected to find any simple glass cock by means of which the alcohol in the regulator could be increased or decreased at will, without danger of leakage. In this, however, we were agreeably disappointed. Such a cock is shown at M in Fig. 1. There is absolutely nothing peculiar about it. It is just such a one as every laboratory affords, only it appears to have been ground very perfectly indeed, whether by accident or otherwise we cannot say. It certainly required no grinding at our hands. With the aid of the least bit of vaseline as lubricant, it turns smoothly and does *not* leak.

Above this cock, the tube of the regulator is continued to a length of about 10 cm. This prolongation contains at all times a certain amount of alcohol. The addition of a bulb at this point would be advantageous as an alcohol reservoir.

To set the regulator at any given temperature below the boiling-point of alcohol, the cock is first opened, and water, either hot or cold, as the case may be, is added by hand to the bath until the desired temperature is reached. Effective stirring is maintained meanwhile as a matter of course. By the aid of a rubber tube, one end of which is slipped over the open end of the regulator above the cock, while the other is held in the mouth, sufficient air pressure is exerted upon the alcohol to raise the mercury in the U up to the orifice of the feed-water conduit. The cock is then carefully and snugly closed.

As the feed-water is cut off for a moment by this procedure, the temperature of the thermostat must fall slightly before the flow is reestablished. But one easily learns to make due allowance for this during the addition of the hot or cold water, and is thus able to adjust the regulator within one or two hundredths of a degree.

* * *

It only remains to add that whenever the thermostat is allowed to cool off at the end of a day's work, the cock M should be left open. Otherwise the contraction of the alcohol might be sufficient to draw water or even air past the mercury seal into the spiral. In the latter case, which is much the more serious, it is necessary to disconnect the reservoir at P, raise the regulator bodily out of the bell, and by giving it a peculiar spiral or wobbling motion, work the air bubble downward till it enters the vertical portion of the regulator and escapes by the cock.[1]

One other bit of manipulation is sometimes necessary. Occasionally through carelessness or inattention, especially at the beginning of a run, a little mercury will become separated from the main body and lodge in the wedge-shaped annular space just above the end of the capillary. When this occurs, one shuts off the warm water at G, and disconnects the joint P. Then, by means of the rubber tube, as already described, one imparts to the water around the capillary a sudden backward motion. This usually dislodges the mercury. If instead of joining the parent mass below, the mercury is drawn up within the capillary, it is sure to descend again as soon as connections are made and the flow of the feed-water is reestablished This operation, though simple, involves a resetting of the regulator at the temperature desired, and unfortunately this cannot be done with absolute accuracy.

Wesleyan University,
Jan. 17, 1902.

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[1] Throughout this article we describe the thermostat *as it is.* By providing each limb of the U with a bulb of suitable size, one might easily avoid all danger of drawing water or air into the spiral, thereby securing absolute permanency of adjustment.

THE NOMENCLATURE OF VARIANCE

BY J. E. TREVOR

The well-known phase rule of Gibbs asserts that an n-component system having r coexistent phases in a state of equilibrium has

$$n + 2 - r$$

degrees of thermodynamic freedom. When, for example, a two-component system has four coexistent phases, the equilibrium values of the pressure, the temperature, and the relative masses of the components are constants; when three phases coexist one of these quantities is independently variable, the others being functions of it; when two phases coexist two of the quantities are independent; while, when only one phase remains, the values of three of the variables must be assigned in order that the state of the system may be determinate.

For convenience in discussing phase equilibria, I proposed a few years ago to term the number

$$n + 2 - r$$

the "variance" of the system; and so to distinguish between "nonvariant states", "monovariant states", etc. when the variance in zero, unity, etc. Now that this nomenclature is becoming somewhat widely used, as by Bancroft, Duhem, Roozeboom, Saurel, and other authors, although not always in exactly the same form, it will be well if a set of suitable terms can be generally agreed upon. I would therefore suggest that the number

$$n + 2 - r$$

be still termed the "variance" of the system to which the letters relate; and that when the variance is successively zero, one, two, three, and more than two, the system be said to be in an

Invariant,
Univariant,
Bivariant,
Trivariant,
Multivariant,

state. One would thus speak of one-component, two-component, etc. systems in invariant, univariant, etc. states; and, incidentally, avoid the use of the very undesirable term, a "q-variant system."

The nomenclature here suggested is so convenient, and so decidedly an improvement on its original form in which awkward or hybrid words like "nonvariant" and "monovariant" were used, that it would seem to be worthy of general adoption.

Cornell University

NEW BOOKS

Die Theorie des Bleiaccumulators. *By Friedrich Dolezalek. 17 × 25 cm; pp. 112. Halle: Wilhelm Knapp, 1901. Price: paper, 6 marks.* — This is an attempt, and a very instructive one, to treat the lead accumulator from the viewpoint of the electrolytic dissociation theory. The headings of the chapters are: chemical theory of the cell; thermodynamic theory of the cell; osmotic theory of the cell; change of the electromotive force with the strength of acid; change of the electrode potentials with the strength of acid; temperature coefficient; effect of external pressure; behavior on charging and discharging; reversibility; reactions on open circuit; internal resistance; capacity; current and energy efficiency; reactions in the cell during formation; methods of measurements.

The author has done his work well, almost too well. Everything is explained with such ease that one has a lurking suspicion that perhaps we have not been told everything. The book is rather too much like a trip through a chemical works.

As a matter of fact, this criticism is not unjust. Many of the difficulties cited by Schoop are ignored absolutely. One reason for this is that the reversibility of the cell practically throws out most of the other explanations. In the last resort, however, the question of reversibility rests on the application of the Helmholtz formula, and no proof is given that the Helmholtz formula applies only to reversible cells Until this proof is given, the conclusions can not be accepted as final. Two reversed calomel cells give very satisfactory results according to the Helmholtz formula, but it is very doubtful whether they are strictly reversible except for zero current. *Wilder D. Bancroft*

Outlines of Electrochemistry. *By Harry C. Jones. 17 × 25 cm; pp. 106. New York: D. Van Nostrand Company, 1901. Price: bound, $1.50.* — This is a reprint of a series of articles published in the *Electrical Review.* The following are the headings of the chapters: introduction; osmotic pressure; theory of electrolytic dissociation; some applications of the theory of electrolytic dissociation; electrolysis and theories of electrolysis (two chapters); velocity of the ions; conductivity of solutions (two chapters); calculation of the electromotive force of elements (three chapters). The price seems high.

Wilder D. Bancroft

Jahrbuch der Elektrochemie. *Berichte über die Fortschritte des Jahre 1900. By W. Nernst and W. Borchers. VII. Jahrgang. 16 × 24 cm; viii + 596 pp. Halle a/S: Wilhelm Knapp, 1901. Price: paper, 24 marks.* — This is distinctly the best volume of the series. The reviews are longer than heretofore and more carefully written. The only criticism to be made is that the pure and applied parts have been worked out without sufficient reference, one to the other. Thus Kahlenberg's experiments on the precipitation of lithium from pyridine solutions appear twice; and the same is true for the cut of Lob's stirrer. These things increase the size of the volume unnecessarily.

The most interesting points in the volume are perhaps Richards's study of the silver voltameter, Gouy's investigation on the maximum surface tension, Foerster's work on the chlorate formation and the experiments of Haber and others on the reduction of nitro-compounds. It is worth noting that Kahlenberg's view in regard to the sour taste of acid sodium salts is sustained.

Wilder D. Bancroft

Modern Chemistry. *By William Ramsay. Part I., Theoretical; Part II., Systematic. (The Temple Primers) 9 × 14 cm; pp, 124 and 197. New York: The Macmillan Company. Price: limp cloth, 40 cents each.* — The first volume gives a sketch of theoretical chemistry. Chapter I. deals with elements, phlogiston, discovery of oxygen, combining proportions, Dalton's law, Gay-Lussac's law of volumes, Avogadro's hypothesis, atomic weights, molecular weights, Dulong and Petit's law, equivalents, isomorphism. The second chapter is devoted to gaseous and osmotic pressure, the laws of Boyle, Gay-Lussac, Pfeffer and Raoult. In the third chapter we learn about dissociation and about electrolytic dissociation or ionization. The preparation, classification and valency of the elements, and the structural formulas, classification and nomenclature of compounds are discussed in the fourth chapter. In the fifth chapter the subheads are methods of determining the equivalent and molecular weights of the elements, allotropy. Isomerism, polymerism, optical and crystallographic isomerism, stereoisomerism, tautomerism constitute the sixth chapter, while the seventh, and last chapter, deals with energy.

The second volume is devoted to systematic chemistry. A preliminary chapter on methods of preparing elements and on their physical properties and constants is followed by chapters on the hydrides; halides; oxides and sulphides; nitrides and phosphides; borides, carbides, and silicides; anhydrides, acids, and salts; alloys.

The preparation of hydrocyanic acid by distillation of ferrocyanide with sulphuric acid depends on the relative volatility of the two acids, not on the relative strengths as the author seems to imply. It is a pity to confuse the question of what constitutes a compound with the question as to what compounds exist in solution.

Wilder D. Bancroft

Les Carbures d'Hydrogène, 1851-1901. *Recherches expérimentales. By M. Berthelot. 16 × 24 cm. Paris: Gauthier-Villars, 1901. Vol. I., l'Acetylène. Synthène totale des carbures d'hydrogène. pp. x + 413. Vol. II., Les carbures pyrogène. Séries diverses. pp. 558. Vol. III., Combinaison des carbures d'hydrogène avec l'hydrogène, l'oxygène, les éléments d l'eau. pp. 456. Price: paper, 45 francs.* — This is a collection of the papers on this subject published by the author during the last fifty years. The first volume is devoted to the synthesis of acetylene and the polymers of acetylene; to the explosive properties of acetylene; to the synthesis of methane, ethane, ethylene, etc.; to the synthesis of formic acid from carbon monoxide; to the combination of acetylene and nitrogen, oxygen, the halogens, and with metallic compounds.

The second volume begins with a study of the action of high temperatures on hydrocarbons and closes with the investigations on propylene, trimethylene, the terpenes, camphor, etc. The third volume deals with the general formation of the derivatives of hydrocarbons, subdivided into hydrogenization, oxidation, and synthesis of alcohols.

The whole constitutes a monumental work, the importance of which is not fully appreciated even yet. These investigations of Berthelot's are bound to form one of the bases for the scientific organic chemistry of the future. The work will have to be repeated with more careful observation of conditions and limits, but that is true of all organic chemistry. This work of Berthelot's is essentially qualitative, but it is along the right lines, a line from which organic chemistry has disgressed. *Wilder D. Bancroft*

Ricerche sperimentali. *Edited by Raffaello Nasini. 15 × 21 cm. Padua: R. Stab Prosperini, 1901.* — This is a collection of the investigations published during the years 1898-1900 from the chemical department of the University of Padua. Under the guidance of Professor Nasini, thirty papers were published dealing with all sorts of subjects, in physical chemistry, inorganic and organic chemistry, analytical chemistry. It is all interesting reading and is an evidence of the scientific activity in Italian universities. *Wilder D. Bancroft*

The Electromotive Force of Metals in Cyanide Solutions. *By S. B. Christy. 15 × 23 cm; 83 pp. Berkeley, 1900.* — This pamphlet is a bulletin of the Department of Mining and Metallurgy of the University of California and is reprinted from the Transactions of the American Institute of Mining Engineers. The author has made a number of measurements on the potential difference between metals and potassium cyanide solutions of different strengths. In 6.5 pct KCN solutions, gold gives a greater potential difference than silver, lead, mercury or iron, but a lesser one than zinc or copper. In solutions containing 0.0065 pct KCN gold stands in the series below everything except mercury. Special experiments showed that even in the presence of air, solutions containing less than 0.001 pct KCN do not act upon gold strips. In concentrated solutions of potassium cyanide saturated with oxygen, gold dissolves less readily than in more dilute solutions and the author shows that this is due to the decreased solubility of oxygen in concentrated cyanide solutions. Taken altogether, this is a most interesting and instructive investigation.

Wilder D. Bancroft

Briefwechsel zwischen J. Berzelius und F. Wöhler, *im Auftrage der Königl. Gesellschaft der Wissenschaften zu Göttingen. Mit einem Kommentar von J. von Braun. Herausgegeben von O. Wallach. 16 × 23 cm; Erster Band, pp. xxii + 716; zweiter Band, pp. 743. Leipzig: Wilhelm Engelmann, 1901. Price: paper, 40, bound, 46 marks.* — These volumes fill out the gap in the publication of the letters which passed between Berzelius, Liebig, and Wöhler. Those of Liebig and Wöhler have long been familiar; those of Berzelius and Liebig appeared in 1893. These three books should be on every chemist's shelves, and what is more, every chemist should read them. The three men who wrote them are not only among the greatest of chemists, but they afford three types of scientific mind, as different from one another as can be imagined. Historically, Berzelius is the most impressive figure of the three, as he is one of the most impressive in the history of science; but if he is impressive when viewed in his relation to the development of chemistry, he is none the less so when seen from a more intimate side. Wöhler's attitude towards him was ever that of pupil to master, and rightly so; he was, as Wöhler often calls him, his "fatherly friend." There was, it is true, 21 years difference in their ages, but the relation must have been the same had they been of like age; for the mind of Berzelius was on a plane of sureness and individuality to which his gifted pupil never attained. As one turns over the many pages of these volumes, it is to the letters of Berzelius that one comes back again and again with ever increasing interest.

Much space in the correspondence is of course given to the investigations in hand at the time. It is astonishing to consider the rapidity with which Berzelius worked, and the extent of ground which he covered. His wonderfully complete and general knowledge of chemistry he attributes mainly to the preparation of the Jahresberichte. Wöhler complains of having much writing to do. "Yes, that is tedious, to be sure," replies Berzelius, "but we must admit that without this very writing we should not after all grow to what we might. If Davy, for example, had had to write when he was young, as you have to do now, I am convinced he would have advanced chemistry by a hundred years; but now, he has given us nothing but brilliant fragments; just because he was not obliged from the first, to work himself into all parts of the science as a whole. * * * Write on, therefore; there will come an end to it; but the knowledge that you acquire by it will remain. I curse the Jahresberichte when I begin them; but I praise them when they are done, and I see how the work has increased my store of facts." The letters of Berzelius are full of such wisdom. When Wöhler asks about fitting up a laboratory, Berzelius replies that he has no advice to give. "You know yourself, that if I have any gift in that direction it consists in knowing how to get along with what there is, and not in arranging things well and comfortably, to which I have neither had nor could find means or way."

The warm friendship with Liebig and the gradual estrangement between them, which one seems to live through in reading the Berzelius-Liebig letters, is here seen only in side-lights; but in the references to him, we can see how the old ties break, one by one.

"I am heartily sorry when I find Liebig at fault, but he loves haste too much," writes Berzelius in 1834. In 1838—"I think better, almost, of Liebig, now that we have begun to quarrel a little, than I did before; for he is a child, but a child of truth and honor." In 1839—"I have the idea regarding him, that he stands much lower as a philosophic than as an experimental chemist, in which last respect he takes one of the highest places. Our relations seem now to be growing somewhat difficult; I suspect that he is much displeased with me because I cannot accept his theories. I am sorry for that; but in such case I cannot remove the cause. * * * What a happy folk we men of science should be, if we could wash ourselves clean of the vanity that gives us so many dark hours." And later,—"I cannot possibly understand how he can, against the spirit of chemical theory, regard chlorine as part of an organic radical. * * * There must be something in scientific matters like what we call Tact in social,—a feeling that tells one what is right and proper, although the reasons may not for the moment be clear; and this feeling some possess in a high degree, while others, who may be gifted with greater genius, entirely lack it. When I see a wrong theoretical idea, I feel it, even though the correct one may be unknown to me, and without being able to make clear to myself that it is false; just as the ear hears a false tone". This sureness of himself was the source of Berzelius' strength, as it often was of his weakness. In 1842 he writes:—"As a result of too much thinking and burrowing over theoretical matters, for which he has no natural aptitude, * * * he seems to have got into a state of nervous excitement in which he is no longer himself, and by which he will be ruined if he does not take a holiday of some length, say a year." The idea that Liebig was actually going mad became stronger and stronger in the mind of Berzelius; but the coolness that came between them had of course its cause in their divergent theoretical views.

His "feeling" for the correctness of theories did not, as we have seen, always stand him in very good stead. It failed him again when he wrote of Faraday's work on the law which bears his name,—"This work, which is in its intention only theoretical, is of such a narrowness of view that it has very much lessened the opinion I formerly had of Faraday." Indeed throughout his career it may be doubted whether the feeling for correct theory was not rather conspicuous by its absence.

The progressive spirits of the French school he both hated and despised. Towards Dumas he was ever bitterly hostile. "I must confess that I have long watched my opportunity to set the dogs on that chemical robber, Dumas." And of Laurent, Gerhardt, and most of the others he thought little better. Towards the end he felt that the tide of progress in chemistry had turned away from his ideas, and this no doubt embittered his feeling against the younger school. "It is," he cries out in 1846, "just as if no one had read what I have preached in the Jahresberichte ever since 1839. Cassandra's fate has fallen upon me."

Perhaps the chief interest of such letters as these lies in the revelation of those personal feelings that may often lead to the best work,—the interest and encouragement of friends, the criticism and hostility of enemies. There is a living background to such a career as that of Berzelius of which one gets only a glimpse now and again through published articles in the journals. And he is no less wonderful in his old age fighting for his outworn theories against the newer views of Liebig, and Laurent, and Gerhardt, than when he himself was in the vanguard of progress thirty years earlier.

With Mitscherlich it was the story of Liebig over again; with the difference that the former really lost all his friends in the end, and was left a pathetic figure, alone. "He is unsatisfied with himself and all the world," writes Berzelius in 1831, "and sees danger and betrayal in every word. Nature did not allow him to be simple, and by his perpetual and discontented striving after influence and position and a sort of despotism over others, he has made a host of enemies, and sees himself now, in the midst of annoying, complicated surroundings which allow no moment of rest and contentment to his spirit, because in it all he has not the strength to raise himself above the judgment of others, or to declare open war against them." And again,—"He is a strange creature, who would rather ruin everything with his best friends than carry out what he has undertaken to do." And later, — "Now that Mitscherlich has deceived me in two matters, I have for him only the respect,— the great respect, I would say — which I pay to the man of science; the personal interest has gone, without quite being replaced by dislike. I do not scorn him, but what is more and worse, he is indifferent to me."

Warm-hearted and kind as Berzelius was to those he liked, he was probably no very agreeable companion to such as in any way annoyed him. "I do not like being in the laboratory," he writes, "with Hünefeld and Maus, because they are both of them so little at home in chemistry that they keep asking questions continually; this incessant questioning makes me cross and short in my replies, with the result that they do not ask any more, but do their work wrong, and then I get angry again."

As he advanced in life he suffered severely from gout; sometimes he was bed-ridden for weeks at a time. This illness and the years of incessant and vigorous labor brought Berzelius to old age before his time. On August 20, 1839, he writes, — "I am sixty years old to-day, and feel it too in my capacity for work, especially in regard to chemical researches. The quiet and agreeable waiting for results, which formerly made the pleasure in work, is gone; it disturbs me not to reach them at once, and if they do not appear soon, the work becomes a bore to me. I forget what I have done unless I jot it down at once; and if I do, I forget to consult my notes, from the old habit of remembering everything so well. If the work branches out and I have to notice many things, I confuse them and my memory plays me false, so that I take one for the other. Furthermore, the summer heat has destroyed a good deal for me, and the cursed flies, which neither paper nor glass will keep out, have drowned themselves by dozens in my solutions, or completely devoured little quantities of animal matters which I had placed out on watch-glasses for spontaneous evaporation." In 1841, when he was only 62 years old, he complains, — "I am now in the time of life when only the remembrance of things of long ago remains, while that which happened yesterday or the day before, is completely forgotten. For this reason I am no longer equal to any investigations but those simple ones which can be completed within a few days, and in which I need remember no complicated details." He was at that time busy with his investigation of the gall, which he had begun a few years before, and was slow in finishing. Later he says, — "I have lost the desire for experimenting; keep on pottering, however, with the gall, but without pleasure; I should like very much to finish with it before the years make me quite useless." Six years later he writes, — "One is no longer fit for exact investigations with 68 years on one's back; the eye is not so sure, and the hands do not obey as they did; one has not the same patience, not the same composure, with which when some least thing goes wrong with an experiment one makes it again and yet again." He did not indeed do much after this; and it was in the following year, 1847, that his last long illness came. His scientific interests and his activity in writing, however, he kept up almost to the very end.

In his own country Berzelius was a prominent and public-spirited man; so that we come to hear a good deal incidentally, of affairs in Sweden through these years,—of the cholera outbreak in 1834, of public events of different kinds, and of the honors which were from time to time bestowed upon himself.

On the whole, the impression of Berzelius' character left by these letters, is that of a man of perfect sincerity in every act, of untiring energy in his work, of kindly sympathy with those he loved, of broad-minded public spirit, and of that mixture of modesty with the consciousness of worth which is so characteristically the gift of very great men.

Much space is taken up in the letters with the discussions regarding the publication in German, under Wöhler's care, of Berzelius' Lehrbuch and of the dealings with the publisher Arnold in this connection.

In all of this I have said very little of Wöhler. His letters are full of interest to him who reads for a picture of the growth of chemistry through those years; but the intense personal quality, the picturesqueness, the lofty independent spirit, are not there. Wöhler's was a quiet, affectionate temperament; his aim was to avoid the centers of conflict and keep the peace between his friends too if he could. His letters are not dull; far from it; only one reads those of Berzelius first.

The understanding and enjoyment of the letters, which cover the period between 1824 and 1848, is very much facilitated by a synoptical index at the beginning, and by many good foot-notes throughout, the work of J. von Braun.

On the whole two "stately" volumes, and most welcome ones.

A. P. Saunders

Die Principien der Mechanik. *Mathematische Untersuchungen. By Leo Königsberger. 14 × 21 cm; pp. xii + 228. Leipzig: B. G. Teubner, 1901.*—The Lagrangian function, or specifically the Lagrangian equations of motion, is a means, primarily, of expressing what may be called the Newtonian dynamics of matter with greater breadth by generalizing the coordinates. The equations were, however, soon found available by Maxwell, among others, for treating the motion of other agencies than ponderable matter. Helmholtz in his theory of cyclic systems gave to the equations even greater comprehensiveness, by systematically generalizing the forces, the momenta, the accelerations, velocities, etc. Thus forces and energies and works are allied to the usual conceptions only in mathematical form. The forces may be ordinary forces, or they may be torques, or electromotive intensities; the momenta may be electrokinetic; while electric currents occur like velocities, self-inductions like moments of inertia, etc.

Königsberger, following Helmholtz and Hertz in his development of the doctrine of concealed motions, proceeds to investigate in like manner, systematically, all the usual principles of dynamics. Beginning with D'Alembert, he treats in turn Lagrange's equations, Hamilton's principle, the doctrine of energy, Gauss's principle of least constraint, Maupertuis's principle of least action, the principle of areas, of the motion of the centre of mass, Helmholtz's principle of concealed motions, the general doctrine of potential, and the equations of Laplace and Poisson, not to mention other relevant matter.

To enter into a non-technical discussion of these subjects seems out of the question. Königsberger expressly disclaims all intention of deducing propositions with a direct bearing on the physical universe. It is purely the broader mathematical development which fascinates him. To the reviewer, this disclaimer seems overdrawn. Any system of dynamics which contains the Newtonian world as a special case is likely sooner or later to lead to new points of view when the specialization is made. Witness, for instance, the interpretation reached of Weber's electrodynamic law of attraction. This is found deducible from the law of gravitation, provided a third *concealed* point is so attached to the system as to act upon it only through inertia. Indeed Königsberger is pursuing the subject with a trenchant enthusiasm rare in the veteran. A recent paper communicated to the Berlin Academy treats the Lagrangian equations from the point of view of two dimentional time.

The book is dedicated to the memory of Helmholtz, and is in a measure inspired by famous Heidelberg associations. *C. Barus*

Catalase. *By Oscar Loew. 15 × 23 cm; 47 pp. Washington: Government Printing Office, 1901.*—This is Report No. 68 of the Department of Agriculture. The author decides that the power of decomposing hydrogen is not the property of any hitherto described enzyme, and he therefore calls the enzyme which has this power, catalase. It exists in an insoluble and a soluble form to be known as α-catalase and β-catalase. The author has studied these two forms of catalase with reference to their behavior towards various salts, mercuric chloride, acids and bases, alcohol, chloroform, phenol, formaldehyde, nitrous acid, prussic acid, hydrogen sulphide, hydroxylamine, phenylhydrazine, and alkaline silver solutions. *Wilder D. Bancroft*

Geometric Exercises in Paper Folding. *By T. Sundara Row. Edited and revised by W. W. Beman and D. E. Smith. 12 × 19 cm; pp. xiv + 148. Chicago: Open Court Publishing Company, 1901. Price: bound, $1.00, net.*—This little book is a systematic development of the geometry of plane figures bounded by straight lines, based upon the idea of superposition. Take any irregular piece of paper and fold it upon itself; a crease is formed—a straight line. Spread the paper out and again fold it, so that the former crease is folded on to itself; a new crease is formed, at right angles to the first. Using this idea, and that of comparison of equal distances (using length of a crease for unit of measure), most of the exercises in Euclid's first four books are proven; and a method is given for constructing any number of points on nearly all of the classic curves, and some problems connected with them. A chapter is devoted to the progressions and the summation of a few infinite series, including an approximation construction for π.

For teachers of elementary geometry the book is really of considerable value, as it shows in a forcible and tangible way how properties vaguely known to us by experience are logical and necessary consequences of a few definitions. A set of colored squares of paper is provided with the book.

Virgil Snyder

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 new investigation concerning the atomic weight of uranium. *T. W. Richards and B. S. Merigold. Proc. Am. Acad. 37, 365 (1902).* — The authors oxidized uranous bromide UBr_4 to uranyl bromide UO_2Br_2 by means of hydrogen peroxide. An atomic weight of 238.53 was obtained. Further work is planned. *W. D. B.*

On praseodymium. *C. v. Scheele. Zeit. anorg. Chem. 27, 53 (1901).* — The author discusses the belief of Bettendorf and of Muthmann that praseodymium is a complex substance and gives his reasons for not sharing this view. The sample of praseodymium oxide has now been tested spectroscopically for lanthanum and found to contain none. Taking oxygen as 16.00 and sulphur as 32.06, the atomic weight of praseodymium becomes 140.52 ± 0.02 *W. D. B.*

The periodic system of the elements. *H. Staigmüller. Zeit. phys. Chem. 39, 245 (1901).* — The author arranges the elements in lines of seventeen with gaps of ten between carbon and nitrogen and between silicon and phosphorus, while hydrogen is completely isolated. *W. D. B.*

The significance of changing atomic volume, I. *T. W. Richards. Proc. Am. Acad. 37, 3 (1901).* — Since the molecular volumes of compounds are not, as a rule, the sum of the atomic volumes of the components, the components must have variable atomic volumes. This is then formulated: "The atomic volume is not constant, but a function of pressure and temperature, and probably of electrical stress." The author next writes the energy equation

$$de = dQ - pdv$$

in the form

$$Pdv = dQ - pdv,$$

where P is the internal pressure. The value of P can be calculated approximately from the specific heat at constant pressure C_p,

$$C_p = (P + p)\frac{dv}{dt}.$$

While this value of P "can hardly represent anything very definite, it must nevertheless be supposed in a general way to increase when the self-affinity increases. Hence, while giving no certain knowledge, its study may give an indication of affinity." From data in regard to zinc mercury and their oxides, the author concludes: "Thus there appears to be in this case a connection between the compression of substances and their tendency to combine one with another." *W. D. B.*

The significance of changing atomic volume, II. *T. W. Richards. Proc. Am. Acad.* 37, *399* (*1902*). — The author shows that there is a distinct parallelism between the heat of formation of the chlorides and the contraction which takes place. A jump is then made from volume change to work and the author formulates the following law: "The work needed for the compression involved in the formation of one solid or liquid by the combination of two others *is approximately* proportional to the heat evolved."

As a way of rendering plausible the repulsion of one atom for another, which is partially overcome by the potential energy of affinity, the author puts forward the hypothesis of an elastic atom and states his belief that he will be able to show: —

1. That the conception is not inconsistent with the two laws of energy.
2. That it conflicts with none of the quantitative conclusions of the atomic hypothesis, nor the kinetic theory of gases, if heat be assumed to be due to mechanical energy operating upon atomic inertia.
3. That it is able to interpret the actual derivations of gases from the gas law better than any other theory, retaining the essential import of the equation of van der Waals, and modifying the equation only as regards the changeability of a and b.
4. That it is consistent with the varying specific heats of substances in the solid, liquid, and gaseous states.
5. That with the help of this theory, such physical properties as tenacity, ductility, malleability, and coefficient of expansion assume for the first time a conceivable consistency.
6. That upon it may be based a definition of the essential influence of chemical change and equilibrium.
7. That the variable compressibility of atoms furnishes a plausible explanation for many of the phenomena of quantivalence, including even the feeble affinities holding water of crystallization and other so-called molecular combinations.
8. That it explains all the tridimensional relations of material, such as stereochemistry and crystal form, at least as well as any other theory.
9. That with the proviso that electrical energy is a rhythmic manifestation of energy — tending to repel itself and therefore to keep upon the surface of material which is susceptible to it, and hence to expand a free atom — many of the electrical and magnetic phenomena of matter become more conceivable.
10. That the effect of light in hastening the attainment of chemical equilibrium, and the possibility of storing and emitting light energy possessed by material, may be interpreted in a similar way.
11. That the careful consideration of all these and other facts leads to a somewhat new conception of the relation between gravitation and chemical affinity, as well as between matter and luminiferous ether. This conception involves simply an antithesis of contracting and expanding tendencies, and is thus founded entirely upon an energetic basis.

12. That the idea is capable of throwing light upon the periodic system, and the genesis and permanence of the elements.

13. That it may be applied even to such astrophysical problems as the cause of the sun's heat.

The scientific world will hail with delight the carrying out of this programme. It may be well to take account of stock first. At the present moment the matter stands as follows. Postulating a new property for an atom does not necessarily interfere with any results obtained without that assumption, and may help to explain phenomena not previously accounted for. *W. D. B.*

On the practical attainment of the thermodynamic scale of temperature. *J. Rose-Innes. Phil. Mag.* [*6*] 2, *130* (*1901*).—This paper follows from the author's two previous papers. The present one is the result of an attempt to provide a sufficiently simple method of reducing to the thermodynamic scale. The method of treating the differential equations requires the knowledge of the Joule-Thomson effect, and the isothermal compressibility at one temperature only. After showing how the fundamental equations can be integrated, the theory is applied to N. and H. where it is shown that three constants are required in order to represent the experimental values, and hence the resulting formula is, as the author points out, only empyrical. The thermodynamic correction for the constant volume gas thermometer is found, and a comparison with Chappuis' results seems to point to a source of error in his work. In working out the correction to the constant pressure gas thermometer it is shown that it is considerably larger than the constant volume type. *H. T. B.*

The law of physical chemical processes. *G. N. Lewis. Zeit. phys. Chem.* 38, *205* (*1901*). — Instead of the Clausius formula,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{Q}{(v_1 - v_2)T},$$

the author deduces the formula

$$\left(\frac{\partial P}{\partial T}\right)_p = \frac{Q}{v_1 T},$$

where v_1 is the molecular volume of the vapor and P, the total pressure on the liquid, is kept constant. [The tacit assumption is made that the vapor pressure is not changed when compressing a liquid by a piston permeable to the vapor and impermeable to the liquid]. The author next introduces and advocates the conception of "fugacity" which is the tendency of a substance to pass out of the phase in which it is. For an ideal gas the fugacity is equal to the pressure. Incidentally the author concludes that the heat capacity of a gas is

$$\frac{Q}{T} + R \log p$$

and not the entropy. *W. D. B.*

Argon and its companions. *W. Ramsay and M. W. Travers. Zeit. phys. Chem.* 38, *641* (*1901*).—Reviewed (5, 319) from Proc. Roy. Soc. 67, 329 (1900).

A new laboratory barometer with automatic zero. *B. Woringer. Zeit. phys. Chem.* 38, *326* (*1901*).—The instrument works on the principle of the automatic burettes where an overhead siphon draws off the liquid until the short arm is exposed. If barometers and manometers are all of the same-sized glass tubing, a single adjustable vernier can be used for all. *W. D. B.*

Modification of Hempel's gas-apparatus. *T. W. Richards. Proc. Am. Acad.* 37, *273* (*1901*). — The author describes a home-made modification of an absorption pipette which has stood the test of laboratory work. He further recommends the use of a 50 cc burette with a water jacket as a measuring apparatus. *W. D. B.*

One-Component Systems

On the physical isomerism of thallium picrate. *W. O. Rabe. Zeit. phys. Chem.* 38, *175* (*1901*). — Thallium picrate occurs in a yellow modification stable above 46° and a red modification stable below 46°. The density of the yellow form is 2.993 and of the red form 3.164, both at 17°. *W. D. B.*

The specific gravity of cuprous iodide. *W. Spring. Zeit. anorg. Chem.* 27, *308* (*1901*). — Schiff obtained a value of 4.41 for the specific gravity of cuprous iodide, while a redetermination by the author gives 5.631. The importance of this lies in the fact that cuprous iodide is now seen to be formed from the elements with contraction, whereas Schiff's figure called for twenty-four percent expansion. *W. D. B.*

The equation of state and the theory of cyclical motion. *J. D. van der Waals. Zeit. phys. Chem.* 38, *257* (*1901*). — A discussion of the modification of the gas law made necessary by assuming a gas under given temperature and volume to be a system in cyclical motion. *W. D. B.*

Note on the isothermals of fluids and in particular of hydrogen. *E. H. Amagat. Phil. Mag.* [*6*] 2, *651* (*1901*). — The author draws attention to the fact that the isothermals for hydrogen, which were shown in his earlier work to be straight lines, and as such quoted by Rose-Innes, have been shown in a later work to be curved. This latter work extended to much higher pressures, and is, therefore, more trustworthy. In the present note he insists that "the isothermals for all bodies including hydrogen show a perfectly distinct curvature." *H. T. B.*

The thermal properties of isopentane compared with those of normal pentane. *J. Rose-Innes and S. Young. Phil. Mag.* [*6*] 2, *208* (*1901*). — It is shown that the departure from Boyle's law in the case of isopentane bears a constant ratio to the departure for normal pentane at the same volume and temperature. This simple law the author claims yields results within the experimental errors. *H. T. B.*

The theoretical evaluation of the ratio of the specific heats of a gas. *J. H. Jeans. Phil. Mag.* [*6*] 2, *638* (*1901*). — It is pointed out that the variation of the value of γ from the Maxwell-Boltzmann theorem of the partition of energy might be attributed to an interaction between matter and ether, a slight interaction being sufficient to cause a modification of the theorem. The present paper is an attempt to study this point, and to obtain a value of the constant in agreement with observation. In the general theory upon which the results are based one kind of freedom, either vibration or rotation in addition to the freedom to move in space is accorded the molecules. The transfer of energy takes place by collisions between the molecules, and in addition a transfer is imagined to take place by æther vibrations. From the theoretical deductions the ratio of the specific heats should come 1 2/5. As an example, it is found that air is almost completely regular, the value of γ being 1.4040 at 0° C, and 1.4031 at 100° C. Oxygen, hydrogen, nitrogen, and carbon monoxide are cited as instances of regular gases. As an instance of an irregular gas the author, of course, studies CO_2. *H. T. B.*

Two-Component Systems

On remarkable phenomena near the critical point of partially miscible liquids. *J. Friedländer. Zeit. phys. Chem.* 38, *385* (*1901*). — The author has studied the opalescence which often appears just before or just as a liquid separates into two phases, and finds that it is not a time phenomenon. There is a marked increase of viscosity at this point and it is probable that the two maxima coincide. The system benzene, water and acetic acid, showed a marked increase in viscosity as the point of clouding was reached. *W. D. B.*

The solubility of manganous sulphate. *T. W. Richards and F. R. Fraprie. Proc. Am. Acad.* 36, *509* (*1901*). — The results confirm those of Cottrell (4, 637) as against the measurements of Linebarger. *W. D. B.*

New determinations of copper-tin, copper-zinc, and tin-zinc alloys. *E. Maey. Zeit. phys. Chem.* 38, *289* (*1901*). —The author has determined the densities of copper-tin alloys containing 28–100 percent tin, of copper-zinc alloys and of tin-zinc alloys over the whole range. The alloys were prepared by fusing in a porcelain crucible, but no details are given as to rate of cooling or as to the inhomogeneity of the samples. *W. D. B.*

The specific volume as a characteristic of chemical compounds in metallic alloys. *E. Maey. Zeit. phys. Chem.* 38, *292* (*1901*). — The author plots the specific volumes against the percentage concentrations and draws conclusions as to the existence of compounds from the form of the resulting compounds. The weak point in the argument is that the possible existence of solid solutions is ignored, which is the more unfortunate since brasses and bronzes almost certainly come under this head. *W. D. B.*

The thermochemistry of alloys of copper and zinc. *F. J. Baker. Zeit. phys. Chem.* 38, *630* (*1901*). — The heat of formation of the alloys was determined by dissolving in aqueous solutions of ferric and ammonium chlorides or of cupric and ammonium chlorides. All the alloys of copper and zinc are formed with evolution of heat. The maximum heat of formation occurs with an alloy having the composition $CuZn_2$ and equals 10143 cal per gram-molecule. The author thinks there exists possibly a compound of the formula CuZn. There is no comparison made with the conclusions reached by other methods and the possibility of solid solutions is overlooked. The value of the work therefore depends exclusively on the experimental results. *W. D. B.*

Isotherms for mixtures of hydrochloric acid and ethane. *N. Q. Gzn. Zeit. phys. Chem.* 39, *14* (*1901*). — The author has determined the pressure-volume-temperature relations for four mixtures of hydrochloric acid and ethane. This is a system in which a maximum pressure occurs. *W. D. B.*

Isobaric aqueous solutions. *J. A. Groshans. Zeit. phys. Chem.* 38, *163* (*1901*). — By isobaric solutions the author understands equimolecular solutions of substances having the same 'density number.' It is found that such solutions have equal densities. *W. D. B.*

On the calculation of the heats of dilution from Kirchhoff's formula. *F. Jüttner. Zeit. phys. Chem.* 39, *76* (*1901*). — The author discusses Kirchhoff's formula for the relation between heat of dilution and the change of the percentage lowering of the vapor-pressure with the temperature, showing the discrepancy that has existed between theory and experiment. He himself tests the formula by measurements at the boiling temperature and the freezing temperatures. In two cases, KCl and KNO_3 in water, the difference between the calculated and experimental results was less than fifty percent. *W. D. B.*

Studies on the thermochemistry of very dilute solutions. *H. v. Steinwehr. Zeit. phys. Chem.* 38, *185* (*1901*). — When a reaction absorbs heat, an electric lamp is put into the calorimeter and the electrical energy measured, which is necessary to keep the temperature constant. When the reaction involves heat the lamp is put in a second identical calorimeter and the electrical energy measured, which is necessary to duplicate the results in the first calorimeter. The temperature change is measured with a thermopile. The bulk of the data are to be found in the author's doctor thesis. *W. D. B.*

Multi-Component Systems

On reciprocal salt pairs, III. *W. Meyerhoffer. Zeit. phys. Chem.* 38, *307* (*1901*). — A discussion of the freezing-point relations in the case of two salts which form two others by a mathematical reaction. Some experiments with $BaCO_3$ and K_2SO_4 show that this is the stable pair. Attention is drawn to the ease with which theoretically instable phases may occur and to the possibility of this being realized on a large scale in the deposition of minerals.

W. D. B.

On an acid triple salt. *W. Meyerhoffer and F. G. Cottrell. Zeit. anorg. Chem.* 27, *442* (*1901*). — The authors have prepared the salt $KHMg(SO_4)_2 2H_2O$ and have determined the concentration of the solution in *equilibrium* with it and with schönite at 25°. *W. D. B.*

The formation of tachhydrite. *J. H. van't Hoff, F. B. Kenrick and H. M. Dawson. Zeit. phys. Chem.* 39, *27* (*1901*). — Reviewed (3, 508 and 5, 530) from Sitzungsber. Akad. Wiss. Berlin, 1897, 508; 1899, 557.

On the behavior of some fluorides of the heavy metals in solution. *A. Jaeger. Zeit anorg. Chem.* 27, *22* (*1901*). — The author has investigated the solubility of mercuric and cupric oxides and of cadmium fluoride in hydrofluoric acid of varying concentrations. From the mass relation with mercury, the author concludes that hydrofluoric acid has the formula H_2F_2. Lead hydroxide is sparingly soluble in dilute hydrofluoric acid and practically insoluble in concentrated acid.

W. D. B.

The decomposition of mercurous chloride by dissolved chlorides. *T. W. Richards and E. H. Archibald. Proc. Am. Acad.* 37, *347* (*1902*). — When mercurous chloride is treated with solutions of calcium, barium, sodium, and hydrogen chloride, mercury goes into solution as mercuric salt. From the increase in solubility with increasing concentration of the soluble chloride, the authors conclude that the mercury is present as part of the bivalent anion, $HgCl_4$. Cadmium chloride solution has no effect on mercurous chloride.

W. D. B.

The thermodynamics of concentrated solutions. *A. Schükarew. Zeit. phys. Chem.* 38, *543* (*1901*). — The author starts from the Gibbs equation between the chemical potentials, pressure and temperature and postulates that no definite relation between dm_1 and dm_2 exists in cases where no known reactions occur according to the law of definition and multiple proportions. He then deduces an equation which describes admirably the distribution of iodine between two solvents as observed by Jakowkin. Very remarkable results are also obtained for the distribution of ether between rubber and water and of β-naphthol between naphthalene and water. Very satisfactory results are also obtained for the precipitation of one salt by another. The author's conclusions rest on the gratuitous hypothesis that

$$m^2 \frac{d\mu}{dm} = \text{const}$$

for each substance in every solution, an assumption known not to be true.

W. D. B.

On the chemical processes in the system: ether, water, hydrochloric acid. *F. Jüttner. Zeit. phys. Chem.* 39, *56* (*1901*). — Elaborate calculations to show that ether combines with hydrochloric acid to form a hydrochloride soluble in water. While this may be true, the reasoning is not very convincing. The implied conclusion, p. 59, that less hydrochloric acid is absorbed when there is a homogeneous solution of ether, water and hydrochloric acid than when this is not so, seems extremely improbable. The chances are very strong that the author has not studied states of equilibrium.

W. D. B.

The condition of dissolved substances as deduced from distribution experiments. *A. Hantzsch and A. Vagt. Zeit. phys. Chem.* 38, *705* (*1901*). — In a number of cases the distribution ratio does not vary with the temperature, in others it does. The authors decide that the variation occurs when the solute forms molecular compounds with one of the solvents. Variations with the concentration are attributed to the same cause. The experiments on the distribution of mercuric chloride between toluene and water show a continuous change of the distribution ratio with the concentration, but the authors decide, nevertheless, that the ratio is practically constant. The distribution of bromine between water and air varies very much with the temperature between 0° and 60°, and therefore the authors conclude that bromine forms hydrates with water which are decomposed by rising temperature. On the other hand at 25° bromine in water follows Henry's law and therefore the authors conclude that there is complete hydration at that temperature. They do not state how this conclusion is to be reconciled with the preceding one that there is marked dehydration at all temperatures above 0°. *W. D. B.*

On the theory of solutions. *W. Nernst. Zeit. phys. Chem.* 38, *487* (*1901*). —The author discusses the effect of the assumption that the presence of other substances affects the application of Henry's law. As he postulates that the partial pressure of water vapor depends on the concentrations of the dissolved substances, he misses the significance of the relative solubilities. The article also contains an abusive polemic against Arrhenius. *W. D. B.*

On cobalt sulphide. *W. Herz. Zeit. anorg. Chem.* 27, *390* (*1901*). — When cobalt sulphide which has stood for a day and a half is treated with 0.5 *n* HCl, hydrogen sulphide is formed and cobalt goes into solution. If the cobalt sulphide be filtered and allowed to stand on the filter for fourteen days exposed to the air, no hydrogen sulphide is formed when this precipitate is treated with 0.5 *n* HCl. On the other hand, cobalt sulphate goes into solution. *W. D. B.*

On the isomorphism between the salts of bismuth and of the rare earths. *G. Bodman. Zeit. anorg. Chem.* 27, *254* (*1901*). — Lanthanum, didymium and yttrium nitrates form two sets of solid solutions with bismuth nitrate. Since bismuth sulphate does not crystallize from water, only the series with an excess of lanthanum, didymium or yttrium sulphate could be obtained. When the specific volumes of the crystals are plotted against the percentage composition, straight lines are obtained. *W. D. B.*

Quantitative precipitation of metals by organic bases. *W. Herz. Zeit. anorg. Chem.* 27, *310* (*1901*). — Experimental data are given to show the accuracy obtainable when copper, magnesium or zinc is precipitated by guanidine or piperidine. Piperazine does not give complete precipitation. Tetramethyl ammonium hydroxide gives complete precipitation, but the precipitate is so gelatinous as to make this reagent unsatisfactory. *W. D. B.*

The oxides of cobalt. *E. Hüttner. Zeit. anorg. Chem.* 27, *81* (*1901*).— An analysis of the cobalt "peroxide" precipitated at the anode shows that it is really the oxide Co_2O_3. Oxidation of $Co(OH)_2$ by potassium persulphate, ammonium persulphate, chlorine or iodine gave a hydrated Co_2O_3. With sodium hypochlorite a substance of variable composition was obtained, containing more oxygen. This is presumably a mixture of the peroxide CoO_2 and the oxide Co_2O_3. When iodine is added to the sulphate solution and then caustic potash, the peroxide CoO_2 is obtained. *W. D. B.*

Velocities

On the law of the action of invertine. *V. Henri. Zeit. phys. Chem.* 39, *194* (*1901*). — The author finds that the inversion of cane sugar in presence of invertine may be described by the formula

$$dx/dt = k\left(1 + \frac{x}{A}\right)(a - x),$$

where A is the initial concentration of the cane sugar and $A - x$ the concentration of the time t. The constant is smaller the greater the initial concentration of the sugar, but the product of the two is not absolutely constant.

W. D. B.

The reaction velocity for bromine and ethyl alcohol. *S. Bugarszky. Zeit. phys. Chem.* 38, *561* (*1901*). — Bromine acts on ethyl alcohol to form ethyl acetate and hydrobromic acid according to the equation

$$2C_2H_5OH + 2Br_2 = CH_3CO_2C_2H_5 + 4HBr.$$

The experiments were carried on in alcoholic solution containing one-fifth water. The alcohol concentration may be considered constant and the reaction velocity was found to be directly proportional to the concentration of bromine. The hydrobromic acid formed combines with bromine to form HBr_3. This disturbing effect was eliminated by adding mercuric bromide. *W. D. B.*

On the rate of decomposition of ammonium nitrite. *K. Arndt. Zeit. phys. Chem.* 39, *64* (*1901*). — The decomposition of ammonium nitrite is apparently due to the action of undissociated ammonium nitrite on nitrous acid set free by hydrolysis. In consequence traces of ammonia decrease the reaction velocity enormously, while traces of acid increase it. *W. D. B.*

On polymolecular chemical changes. *A. Schükarew. Zeit. phys. Chem.* 38, *353* (*1901*). — The author has studied the reaction between ferric chloride and iodides. The reaction velocity depends approximately on the concentration of the iron salt and the square of the concentration of the iodide. The reaction between chromic oxide and the iodides is monomolecular as regards the chromic oxide while some of the iodides behave as though the reaction were monomolecular with regard to them, but others do not. *W. D. B.*

Investigations of the reaction during oxidation with gaseous oxygen. *W. Manchot and J. Herzog. Zeit. anorg. Chem.* 27, *397* (*1901*). — When cobaltous cyanide is oxidized by oxygen under constant pressure, the reaction is monomolecular. When ferrous oxalate, tartrate or citrate is substituted for the cobaltous cyanide, the results become unsatisfactory. The disturbing factor appears to be the oxygen made active during the reaction. When arsenious acid is added to the ferrous citrate solution to take up the active oxygen, the reaction becomes monomolecular for a constant pressure of oxygen.

W. D. B.

On the formation of active oxygen with ferrous oxide. *W. Manchot. Zeit. anorg. Chem.* 27, *420* (*1901*). — When ferrous sulphate in an atmosphere of oxygen is mixed with caustic potash solution containing much arsenious acid, the red color of the ferric hydroxide appears when practically double the amount of oxygen has been absorbed which is necessary to form the hydroxide. Ferrous iron makes active one of oxygen for every one taken up. *W. D. B.*

On the solution of metals, I. *T. Ericson-Aurén and W. Palmaer. Zeit. phys. Chem.* 39, *1* (*1901*) — The rate at which zinc dissolves in hydrochloric acid of different concentrations is not that required by a plain application of the mass law. It can be accounted for on the hypothesis that the rate is due solely to local galvanic action. It should be noted, however, that the only stirring was that produced by hydrogen bubbles so that the experiments as made are not conclusive. *W. D. B.*

The rate of solution of zinc in acid solution. *T. Ericson-Aurén. Zeit. anorg. Chem.* 27, *209* (*1901*). — When dilute acids act on zinc there is first an induction period during which bubbles of hydrogen form on and cling to the surface of the zinc. This changes later into a period during which gas is given off freely and the rate of attack remains nearly constant until the bulk of the zinc has been dissolved.

The rate of attack is probably due both to local galvanic action and to the direct action of the acid. The rate of attack increases with the concentration of the acid faster than the conductivity. With dilute acids the temperature coefficient is small, but it increases with increasing concentration of acid.

Non-electrolytes reduce the rate of attack, the reduction being roughly a function of the concentration and not of the chemical nature. The first addition of salts decreases the reaction velocity; a further addition increases it, a maximum being obtained if there is a maximum conductivity. *W. D. B.*

The paralysis of platinum catalysis by poisons. *G. Bredig. Zeit. phys. Chem.* 38, *122* (*1901*). — The author disputes the view of Raudnitz that prussic acid does not affect the catalytic agent because removal of the prussic acid restores the original condition. *W. D. B.*

Electromotive Forces

Pyrochemical Daniell cells. *R. Suchy. Zeit. anorg. Chem.* 27, *152* (*1901*). — The author measured the electromotive forces at different temperatures of the following cells containing fused salts: —

$$\mathrm{Pb} \mid \mathrm{PbCl_2} \mid \mathrm{AgCl} \mid \mathrm{Ag}$$
$$\mathrm{Zn} \mid \mathrm{ZnCl_2} \mid \mathrm{PbCl_2} \mid \mathrm{Pb}$$
$$\mathrm{Zn} \mid \mathrm{ZnCl_2} \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

In all three cases the electromotive force decreases with rising temperature. In the first two cases the change is linear, in the third it is linear above 580°. The values at 600° are 0.319, 0.269 and 0.427 V respectively. From these figures and from the measurements of the half-cells against chlorine, it appears that the potential differences between fused salts are not zero. The measurement of the cell

$$\mathrm{Pb} \mid \mathrm{PbCl_2} \mid c_1\mathrm{AgCl} + \mathrm{KCl},\mathrm{LiCl} \mid \mathrm{Ag}$$

showed that the electromotive force decreased with decreasing concentration of silver chloride, eventually changing its sign. If we assume complete dissociation of silver chloride in the most dilute solution 0.035 *n*, the dissociation of fused silver chloride calculates to 17 pct at 520°, 28 pct at 640°, 60 pct at 730°. *W. D. B.*

Investigations on the electromotive activity of elementary gases, II. *E. Bose. Zeit. phys. Chem.* 38, *1*; 39, *114* (*1901*).— In the first paper (5, 328) it was shown that the usual value for the hydrogen-oxygen gas cell is much too low, owing to the slow diffusion of the gases into the metal electrodes. Further experiments point to 1.139 V as the probable value. At the oxygen electrode there is equilibrium between water, oxygen and hydrogen peroxide. Hydrogen peroxide may give a higher potential than oxygen, and this potential holds constant for a long time. From the sudden change of the potential on heating, the author deduces the formation of an isomeric hydrogen peroxide, a reducing agent. *W. D. B.*

Investigations on the electromotive activity of elementary gases, III. *E. Bose and H. Kochan. Zeit. phys. Chem.* 39, *28* (*1901*). — A gold electrode in dilute sulphuric acid is sensitive to light when polarized with oxygen. Rays at the violet end of the spectrum lower the oxidation potential, those at the red end raise it. The total variation amounts to about 0.1 V. *W. D. B.*

Experiments on contact electricity. *O. Knoblauch. Zeit. phys. Chem.* 39, *225* (*1901*). — The author has made a number of experiments as to the sign of the charge when different substances are brought in contact with plates of platinum, paraffin, glass or sulphur. He believes that the all-important factor is the adhering layer of water, the sign of the charge being determined by the relative migration velocities of the ions. In cases where there are no ions, the relative dielectric constants must be taken into account — as has already been done by Coehn (3, 123). Experiments of Emich showed the presence of sulphuric acid on the surface of stick sulphur. *W. D. B.*

On cathodic polarization and formation of alloys. *A. Coehn. Zeit. phys. Chem.* 38, *609* (*1901*). — When the precipitating ion alloys with the cathode, the decomposition voltage should be lowered. With a mercury cathode zinc salts show the greatest tendency to form alloys. In diminishing sequence come cadmium, silver, copper, iron. Zinc shows a tendency to alloy with platinum and hydrogen with palladium. Hydrogen gives excess values with other cathodes which, however, fall below the value for visible precipitation of gas. The author concludes that the second decomposition point with potassium salts is due to the precipitation of KH_x and not of potassium. Ammonium salts behave like the salts of the alkali metals. *W. D. B.*

An experiment on the theory of the flowing electrode. *J. Bernstein. Zeit. phys. Chem.* 38, *200* (*1901*). — Successive instantaneous photographs of a flowing electrode and of the electrometer show that the potential difference forms almost instantaneously as the drop tears away and then decreases gradually. *W. D. B.*

On passive iron. *A. Finkelstein. Zeit. phys. Chem.* 39, *91* (*1901*). — Experiments on the polarization capacity of passive iron show that it is not covered with a non-conducting layer of oxide. The sharp anodic polarization curves are against the view of an oxide layer corresponding to lead peroxide. The electromotive force of an iron electrode varies with the ratio of ferric to ferrous iron in the solution, the total quantity of iron being constant. The author inclines to the view that passive iron is trivalent metallic iron while active iron is bivalent metallic iron. This hypothesis accounts for many but not for all of the facts. *W. D. B.*

Correction. *H. Jahn. Zeit. phys. Chem.* 38, *125* (*1901*). — The author now admits that the experimental verification of his previous conclusions (5, 619) was unsound. The final conclusion is that the gas laws do not hold for so-called strong electrolytes and that we have no way of determining their dissociation even in dilute solutions. *W. D. B.*

The effect of a salt with a common ion on the electromotive force of concentration cells. *O. Sackur. Zeit. phys. Chem.* 38, *129* (*1901*). — The experiments were made to test a formula of Abegg and Bose (5, 417). The authors claim an average discrepancy of 0.0003 V which looks well; but means a large percentage error. The authors conclude further that the migration velocities do change with the concentration, but that this variation is not enough to account for the discrepancies observed when applying the dilution law to strong electrolytes. *W. D. B.*

The electrical behavior of chromium when dissolving in acids. *E. Brauer. Zeit. phys. Chem.* 38, *441* (*1901*). — When an oscillating and a non-oscillating piece of chromium are connected in acid, the electrical and the hydrogen curves correspond in time, though of course not absolutely in form. If the acid solution be made to flow past the electrodes at a sufficient rate of speed the oscillations practically cease. Very pure chromium gives no oscillations. Addition of sulphur or arsenic to the acid tends to produce oscillations.

W. D. B.

The thermomagnetic and thermoelectric properties of crystalline bismuth. *L. Lownds. Phil. Mag.* [*6*] 2, *325* (*1901*). — The present work is an extension of the work of van Everdingen on the verification of the theory of thermomagnetic phenomena discovered by Ettingshausen and Nernst. A plate of bismuth was used cut from a large crystal, so that the chief crystallographic axis lay in the plane of the plate and parallel to its length. The longitudinal and transversal thermomagnetic phenomena, and the thermoelectric force with relation to copper are studied. *H. T. B.*

On the electrical resistance of bismuth in a strong magnetic field. *G. C. Simpson. Phil. Mag.* [*6*] 2, *300* (*1901*). — The author shows by a very nice arrangement of apparatus that the change in resistance in bismuth in a magnetic field for alternating currents may be represented by an alternating E. M. F. set up in the bismuth, and works out equations showing the magnitude and phase for frequencies between 10 and 60 per second. In addition he considers that his results reconcile the contradictory results of Sadovsky, and Wachsmuth and Bamberger, although the experiments are not yet entirely completed.

H. T. B.

Electrolysis and Electrolytic Dissociation

The electrolysis of fused lead iodide and lead chloride. *G. Auerbach. Zeit. anorg. Chem.* 28, *1* (*1901*). — Experiments with fused lead iodide showed marked irregularities of current yield at 700°. The cause for this was not discovered; but analysis of the anode solution proved that there was no measurable formation of PbI_4.

Experiments were made with fused lead chloride to determine whether the evolution of chlorine followed Faraday's law. In addition to the expected difficulties due to diffusion through the electrolyte, it was found that the carbon anode absorbed large quantities of chlorine. After eliminating these sources of error as completely as possible, a current efficiency of 99.1 percent was obtained at the anode.

Special experiments to test Lorenz's formula for the relation between depolarization and current efficiency showed that the formula did not describe the facts with absolute accuracy.

A study of the cathode solutions by means of polarized light proved that the so-called fogs are really solutions of lead in lead chloride and are not suspensions. The same is true for cadmium in cadmium chloride. *W. D. B.*

Quantitative determination of bismuth by electrolysis. *K. Wimmenauer. Zeit. anorg. Chem.* 27, *1* (*1901*). — After a general study of the methods proposed for the electrolytic determination of bismuth, the author recommends the use of bismuth oxide dissolved in concentrated nitric acid or of bismuth nitrate dissolved in dilute glycerol solution. In either case it is important to keep the electrolyte well stirred. The author does this by rotating the anode.

W. D. B.

On the solvent and dissociating action of liquid cyanogen and liquid hydrocyanic acid. *M. Centnerszwer. Zeit. phys. Chem.* 39, *217* (*1901*). — Salts are practically insoluble in liquid cyanogen and what does dissolve shows no conducting power. In liquid prussic acid potassium iodide and $S(CH_3)_3I$ dissolve readily and conduct about four times as well as in water. *W. D. B.*

On the alkali salts of hydrogen peroxide in aqueous solutions. *H. T. Calvert. Zeit. phys. Chem.* 38, *513* (*1901*). — In alkaline solutions hydrogen peroxide forms salts of which the anion is univalent $O_2 + nH_2O$. The migration velocity of this anion is 48.5. The solubility of potassium chlorate is increased by the addition of hydrogen peroxide. *W. D. B.*

Dissociation relations with ternary electrolytes. *K. Drucker. Zeit. phys. Chem.* 38, *602* (*1901*). — The author calculates that HSO_4 as ion is not present in appreciable concentration in sulphuric acid solution more dilute than tenth-molecular. Oxalic acid behaves differently. *W. D. B.*

The classification of acidimetric and alkalimetric indicators. *J. Wagner. Zeit. anorg. Chem.* 27, *138* (*1901*). — The author proposes and discusses a classification of indicators along the following lines: —

A. Indicators with univalent characteristic ion.
    1. With univalent characteristic anion.
    2. With univalent characteristic cation.
B. Indicators with multivalent ion.
    1. With positive and negative ion.
    2. With univalent and bivalent anion or cation. *W. D. B.*

ON THE RELATIVE VELOCITIES OF THE IONS IN SOLUTIONS OF SILVER NITRATE IN PYRIDINE AND ACETONITRILE[1]

BY HERMAN SCHLUNDT

Although the velocities of the ions have been extensively investigated in aqueous solutions, the relative ionic velocities in non-aqueous solutions is a subject that has been given but limited study. Hittorf[2] made some determinations of transference numbers in alcoholic solutions. He investigated solutions of zinc chloride, zinc iodide, and cadmium iodide in absolute ethyl alcohol, and also made a determination with cadmium iodide dissolved in amyl alcohol. Lenz[3] also worked with solutions of cadmium iodide in ethyl alcohol, and extended his investigations to solutions of this salt in various mixtures of alcohol and water. Determinations of transference numbers with solutions of potassium iodide and potassium chromate in mixtures of alcohol and water were also made by Lenz. More recently Campetti[4] studied the influence of the solvent upon the migration velocities of the ions. He investigated solutions of lithium chloride and silver nitrate in water, methyl alcohol, and ethyl alcohol, and found that the solvent often exercises considerable influence upon the migration velocities. The results of Hittorf and Lenz likewise show this. Mather's[5] determination of the relative velocities of the ions in a tenth-normal solution of silver nitrate in ethyl alcohol concludes the list of investigations on transference numbers in non-aqueous solutions.

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[1] This paper was presented before the Wisconsin Academy of Letters, Sciences and Arts, in a preliminary form, December 27, 1901.

[2] Pogg. Ann. 106, 551 (1859). Also Ostwald's Klassiker der exacten Wissenschaften No. 23, p. 105.

[3] Mém. Ac. Imp. St. Petersb. 30, No. 29, p. 34 (1882). Also Ostwald. Lehrbuch d. allgemeinen Chemie, II Auflage, p. 618.

[4] Nuovo Cimento, 35, 226 (1894). Reference. Zeit. phys. Chem. 16, 165 (1895).

[5] Am. Chem. Jour. 26, 473 (1901).

Apparently no attempts have heretofore been made to determine transference numbers in solvents other than water and the alcohols. This work was accordingly undertaken with the view of determining transference numbers in other solvents that yield solutions which conduct fairly well and at the same time to ascertain, in a general way, the effect of increasing dilution upon the relative velocities of the ions.

For several reasons solutions of silver nitrate in pyridine and methyl cyanide were chosen for this investigation. These solutions conduct well, and the volumetric estimation of silver by Volhard's excellent method is rapid and accurate. To me the silver nitrate solutions in pyridine appeared of special interest. Pyridine, as is well known, forms definite compounds with silver nitrate., i. e., silver nitrate crystallizes out with pyridine of crystallization from its solutions forming the compounds $AgNO_3.2C_5H_5N$ and $AgNO_3.3C_5H_5N$. In perusing Hittorf's classical researches on migration velocities, it was noted that the relative velocity of the cation increased with increasing dilution, as a rule, in solutions of such salts as show a marked affinity for water, i. e., salts which, in the anhydrous state, are strongly hygroscopic, and which, for the most part, crystallize out with water of crystallization. Copper sulphate and ferric chloride are good examples. On the other hand, salts showing relatively weak affinity for water, yield transference numbers for the cation, which vary but little, or decrease with increasing dilution. Potassium chloride and silver nitrate will serve as examples. Since pyridine and silver nitrate have a strong mutual affinity, we should expect the transference number of the cation in solutions of silver nitrate in pyridine to increase with increasing dilution, analogous to the behavior of solutions of salts which have a marked affinity for water. The experimental results which follow will show this to be the case.

Apparatus and method

Several preliminary tests were made with various simple forms of apparatus, such as had been successfully used by other investigators in their researches on ionic velocities in aqueous solutions. A tenth-normal solution of silver nitrate in pyridine served for this preliminary work. These tests showed that such forms of apparatus in which the solution remains in contact with rubber stoppers or rubber connections during the test were not well suited owing to the reducing effect of the rubber. The portion of the solution near the rubber stoppers gradually becomes turbid and, upon standing, finely-divided silver settles. The solvent effect of pyridine upon rubber is also harmful. The form of apparatus devised by Loeb and Nernst[1] is free from this objection, and since good results were obtained with it, this apparatus was used for most of the subsequent tests. Two sizes of this apparatus were used, — one of about 30 cc capacity for the concentrated solutions electrolyzed, and another of about 60 cc capacity for the more dilute solutions, — tenth- and fortieth-normal.

A disk of Kahlbaum's pure silver served as anode, and a bar of silver as cathode. For further details regarding the apparatus the reader is referred to the article of Nernst and Loeb.

The apparatus was connected in series with a silver voltameter, a Weston milliammeter, and a resistance for regulating the current strength. A set of twelve storage batteries or a 110 volt dynamo furnished the current. During electrolysis the apparatus was kept in a large reservoir of water in which the temperature did not vary more than half a degree as indicated by a thermometer strapped to the apparatus.

The amount of solution used in the several tests was determined by weighing the apparatus with fittings, then introducing the solution, and weighing again. The weighings were made to the nearest milligram for solutions stronger than tenth-normal, and to the nearest centigram for the tenth-normal and more dilute solutions.

Before beginning electrolysis the cell was placed in the bath for about fifteen minutes to equalize temperatures. After electrolysis the solution was transferred to three tared flasks pro-

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[1] Zeit. phys. Chem. 2, 948 (1888).

vided with well fitting stoppers, and weighings of each made. The differences gave the quantities of solution taken for the anode portion, the unchanged middle layer, and the cathode portion respectively, exclusive of the residue remaining in the apparatus. The weight of the residue was obtained by weighing the apparatus containing it and subtracting from the weight thus obtained the weight of the complete, empty apparatus previously ascertained. The weight of the residue plus the weight of the cathode portion in the weighing flask gave the total weight of the portion of the solution about the cathode. The sum of the weights of the three samples and the residue should equal the amount of solution originally weighed out in the apparatus. The check was never perfect, the sum being several milligrams less, even for solutions electrolyzed at 0°, and in the solutions transferred at room temperatures the differences amounted to a few centigrams. This loss, which was evidently due to evaporation during the transfer of the solution from the apparatus to the weighing flasks, was divided in proportion to the weights of the respective samples, and each sample was allotted its share of the loss.

The samples were then analyzed. The middle layer, which should show no change in concentration, was subjected to analysis first. When it differed more than one percent from the original solution in strength, the experiment was entirely rejected, and no further analyses were made. In cases where the change in concentration of the middle layer (which is comparatively small) was one percent or less, it was considered a part of the anode portion of the solution, when stronger than the original, and a part of the cathode solution when weaker. In the several experiments the middle layer generally showed no change in concentration.

The duration of the electrolysis, the current strength employed, the temperature, etc., are noted in the tabulated statement of results.

Preparation and analysis of solutions

The silver nitrate used was of the c. p. variety. To obtain it perfectly dry and neutral, it was fused. After powdering, it was kept dry in a desiccator. The pyridine used was twice dehydrated with fused caustic potash and distilled. The sample used distilled between 114°–116° under a pressure of 742 mm. I am indebted to Prof. Kahlenberg for the sample of acetonitrile used. It had been carefully dehydrated by him with phosphorus pentoxide, and distilled from phosphorus pentoxide. Its boiling-point was 81.0° under a pressure of 739 mm.

The various solutions electrolyzed were prepared the day before using. When silver nitrate is dissolved in methyl cyanide a slight reddish-brown precipitate was obtained, which, when filtered off and dissolved in nitric acid, shows the presence of silver, but the amount of precipitate was too small to warrant further investigation.

The strength of the solutions was determined volumetrically by Volhard's method, using standard solutions of ammonium sulphocyanate. Different strengths of ammonium sulphocyanate solutions were employed. They were standardized by titrating weighed quantities of metallic silver dissolved in nitric acid, and also by titration of weighed samples of silver nitrate in aqueous solution. Comparison of the solutions generally employed — fortieth- and fiftieth-normal — with a hundredth-normal silver nitrate solution, and titration of the silver deposits obtained in the voltameter during electrolysis, showed that the cyanate solutions remained of the same strength for a long time.

The solutions of silver nitrate in acetonitrile were analyzed by distilling off the nitrile from a weighed sample, as completely as possible, on a water-bath.[1] The residue was diluted with water and titrated. Whenever the so-called middle layer differed from the original solution in strength by one percent or more, a second determination of the strength of the original solution was made. Generally the strength of the middle layer checked well with that of the original solution. To guard against mistakes in the observation of the end of the reaction, the scheme of

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[1] Not all the acetonitrile distils at this temperature, a syrupy liquid remaining.

Nernst and Loeb was followed. One cc of the *n*/100 $AgNO_3$ solution was added after the titration was believed to be complete, and cyanate solution again added till the color of the indicator appeared.

In the analysis of the solutions of silver nitrate in pyridine a somewhat different course had to be pursued. During the distillation of these solutions some decomposition of the pyridine takes place, and violent decomposition — combustion — occurs toward the end of the operation. These decomposition products color the aqueous solution of the residue to such a degree as to interfere somewhat with the sharpness of the end reaction in titration. But the silver may be accurately determined by adding an excess of nitric acid to the original pyridine solution, diluting with water, and titrating as in aqueous solutions. The pyridine nitrate in the dilute solutions does not interfere in the least with the titration, as the following comparative tests show. Five samples of silver nitrate were weighed out; three of these were dissolved in pyridine and two in water. The solution of ammonium thiocyanate used in these titrations was approximately twenty-fifth-normal. The results obtained are recorded in the following table:

TABLE I.

No.	Grams $AgNO_3$	Solvent	NH_4CNS required	NH_4CNS per gram $AgNO_3$
1	0.4000	Water	58 08 cc	145.2 cc
2	0.2001	"	29.02	145.0
3	0.3003	Pyridine	43.58	145.1
4	0 2000	"	28.98	144.9
5	0.2006	"	29.12	144.9

The pyridine was recovered by concentrating the solution of pyridine nitrate, and then adding a large excess of crude caustic potash. The alkali layer was removed by means of a separatory funnel, and the pyridine purified as previously described.

In analyzing the three portions into which the original solution in the apparatus was divided after electrolysis, it was not deemed necessary to take the entire samples for the analysis, in the case of most of the solutions of silver nitrate in pyridine. Since the middle layer is comparatively small, the whole of it was generally titrated. The anode and cathode solutions were weighed in tared flasks to get the weight of the total solution of each. In working with the normal and half-normal solutions, a 2 cc sample was removed from the weighing flask containing the anode solution, and after weighing the flask with its remaining contents, a second sample of two cc was removed, and another weighing made. The procedure with the cathode solution was the same. The two pairs of samples thus obtained were titrated as before described, and from the results obtained the number of cubic centimeters of ammonium sulphocyanate required for the total solution was calculated. With the tenth-normal solutions one sample of 10 cc was taken from each, the anode and cathode solutions, and its weight and strength determined as before. With the fortieth-normal solutions the entire solutions were used for the analysis.

The method of calculating the transference numbers and some other details will appear in the following example.

An example

The relative velocities of the ions were calculated by Hittorf's well-known method.[1] The following example illustrates the method. An approximately tenth-normal solution of silver nitrate in pyridine was prepared, and its strength accurately determined by titrating two samples:

Sample	Weight	NH_4CNS required	1 g. solution required
1	9.923	40.70 cc	4.101 cc NH_4CNS
2	10.580	43.38	4.100 " "

One cc of the NH_4CNS solution[2] used is equivalent to 4.191 mg of $AgNO_3$ or 2.6624 mg Ag. From these data the strength of the original solution was calculated as follows:

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[1] Pogg. Ann. 98, 6 (1856). Also Ostwald's Klassiker No. 21, p. 38.

[2] It is about fortieth-normal.

The quantity of $AgNO_3$ in 1 g of the solution =

$$4.1 \times 4.191 = 17.18 \text{ mg.}$$

The quantity of Ag in 1 g of the solution =

$$4.1 \times 2.6624 = 10.92 \text{ mg.}$$

Hence the amount of pyridine in 1 g of solution =

$$1 - 0.01718 = 0\ 98282 \text{ g.}$$

And the silver with 1 gram of pyridine $= \frac{10.92}{0.98282} = 11.11$ mg.

The amount of the above solution taken for electrolysis was 63.715 grams. The solution was electrolyzed for 240 minutes, at 0°, with a current of 6 milliamperes as indicated by the ammeter, the potential difference between the electrodes being 39 volts. The silver deposited in the voltameter amounted to 96.4 mg.

The anode portion of the solution weighed	19.710 g
The middle layer of the solution weighed	5.701 g
The cathode portion of the solution weighed	37.836 g
The residue in the apparatus weighed	0.460 g
Total weight	63.707 g

The loss is so small that it is negligible. The following tabulated data show (1) the amounts of each portion taken for analysis, (2) the number of cubic centimeters of NH_4CNS required, (3) the number of cubic centimeters calculated for the entire sample, and (4) in the last column the actual number of cubic centimeters of NH_4CNS used in titrating the entire samples.

Solution	Sample	NH_4CNS required	NH_4CNS per gram	Total NH_4CNS calculated	Total NH_4CNS found
Middle	5.701 g	23.33 cc	4.09 cc	23.33 cc	23.33 cc
Anode	10.120	52.45	5.182	102.14	102.10
Cathode	9.891	35.28	3.568	135.00	134.85
Residue	0.460	1.15	——	1.15	1.15
			Totals	261.62 cc	261.43 cc

The whole amount of solution taken when multiplied by the NH_4CNS equivalent of one gram gives a check on the

TABLE II.

Solvent : Pyridine

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Experiment number	Temperature	Time in minutes	Current in milliamperes	E. M. F. in volts	Silver in voltameter mg.	Solution electrolyzed				Anode portion of solution					Ag migrated out mg.	Cathode portion of solution					Ag migrated in mg.	Cation	
						Approximate strength	100 parts contain		Ag with 1 g. solv't mg.	Weighs grams	Contains			Ag content of original		Weighs grams	Contains			Ag content in original		*n* anode	*n* cathode
							$AgNO_3$	Solvent			$AgNO_3$	Solvent	Ag				$AgNO_3$	Solvent	Ag				
1	23	330	7	3.5	170.3	*n*	15.107	84.893	113.06	15.410	2.481	12.929	1.5763	1.4616	55.6	17.330	2.465	14.865	1.5660	1.6802	55.7	32.6	32.7
2	18.5	360	6	11	161.0	*n*/2	8.090	91.910	55.93	23.744	2.075	21.669	1.3180	1.2119	54.9	——	——	——	——	——	—	34.1	—
3	23	240	8	7	130.8	"	8.146	91.854	56.35	12.466	1.140	11.326	0.7240	0.6382	45.0	18.236	1.361	16.875	0.8646	0.9509	44.5	34.3	34.0
4	0	310	8	7	168.8	"	8.147	91.853	56.36	11.341	1.087	10.254	0.6900	0.5777	56.5	18.198	1.321	16.877	0.8392	0.9512	56.8	33.5	33.6
5	19	225	12	—	168.2	*n*/10	1.724	98.276	11.18	61.460	1.217	60.243	0.7738	0.6736	68.0	——	——	——	——	——	—	40.4	—
6	21	300	6	23	126.2	"	1.717	98.283	11.11	17.647	0.423	17.224	0.2687	0.1913	48.8	36.185	0.502	35.683	0.3189	0.3963	48.8	38.7	38.7
7	0	240	6	39	96.4	"	1.717	98.283	11.11	19.710	0.429	19.281	0.2718	0.2142	38.8	38.296	0.570	37.726	0.3619	0.4191	39.2	40.2	40.6
8	22	205	4	39	57.8	*n*/40	0.435	99.565	2.765	14.220	0.1131	14.11	0.07186	0.3901	24.95	41.22	0.1278	41.09	0.0812	0.1136	25.4	43.2	43.9
9	22	300	2	24	37.7	"	0.436	99.564	2.768	22.150	0.129	22.02	0.08180	0.6094	16.84	41.75	0.1485	41.60	0.0943	0.1152	16.8	44.7	44.5
Solvent : Acetonitrile																							
10	18	360	10	3	233.2	*n*	18.554	81.446	144.73	9.170	1.885	7.285	1.1978	1.0543	89.7	14.434	2.494	11.940	1.5840	1.7281	89.1	38.5	38.2
11	19	270	7.5	5	125.3	11*n*/40	5.648	94.352	38.03	9.181	0.626	8.555	0.3973	0.3253	53.3	14.470	0.709	13.761	0.4506	0.5233	52.6	42.4	42.0
12	17	240	8	11	123.5	*n*/11	2.095	97.905	13.69	15.574	0.432	15.142	0.2750	0.2073	55.8	32.202	0.574	31.628	0.3644	0.4329	55.0	45.2	44.5
13	19	—	8	—	76.4	*n*/35	0.588	99.412	3.735	12.395	0.136	12.258	0.0864	0.0458	35.8	34.670	0.140	34.530	0.08875	0.1290	36.15	46.9	47.3

total volume of NH_4CNS required, 63.715 × 4.1 = 261.2 = cc NH_4CNS required on the basis of the strength of the original solution. The results checked quite as well in the other experiments that were performed.

From the foregoing data the transference number for the silver ion was calculated from the anode portion of the solution as follows:

The quantity of $AgNO_3$ in the anode portion = 102.1 × 4.191 = 427.9 mg, which contained 271.8 mg Ag. The quantity of pyridine was evidently 19.710 − 0.428 = 19.282 grams. The silver with this amount of pyridine originally = 19.282 × 11.11 = 214.2 mg. To this amount of silver must be added the silver which went into solution from the anode. Hence 214.2 + 96.4 or 310.6 mg represents the amount of silver that would have been found present if no silver had migrated out during electrolysis. But the quantity of silver actually found in the anode portion was 271.8 mg; consequently the amount of silver that migrated out was 310.6 − 271.8 = 38.8 mg. The transference number for the Ag-ion therefore is $\frac{38.8}{96.4}$ = 0.402 = 40.2 percent.

From the data on the cathode solution we find, by a similar calculation, that 39.2 mg of silver have migrated in during the electrolysis. Hence the transference number of the Ag-ion = $\frac{39.2}{96.4}$ = 0.406 = 40.6 percent.

The silver deposit on the cathode was bright and adhered well in the case of pyridine solutions of silver nitrate whose strength was tenth-normal or greater, while in the fortieth-normal solutions the deposit was gray and spongy. The silver deposits from the acetonitrile solutions was bright, crystalline, and loosely adhering.

Experimental results

The following table gives the data obtained in the several experiments, and the transference numbers for the cation calculated therefrom. The strength of the current is given in milliamperes in the fourth column. These numbers are the current readings observed on the ammeter used, which was graduated to milliamperes, and must be taken to indicate the approximate current strength.[1] Column 5 gives the potential differences between the electrodes. These were measured by closing for an instant a shunt circuit containing the voltmeter. Columns 15 and 21 give the amounts of silver in the silver nitrate which, before electrolysis of the solution, was dissolved in the quantities of solvent indicated in columns 13 and 19. These figures are obtained by multiplying the number of grams of solvent by the amount of silver with one gram of solvent found in column 10. The last two columns — 23 and 24 — give the transference number of the cation as calculated from the portions of the solution about the anode and cathode respectively.

In the experiments numbered 2 and 5 an apparatus resembling one of Bein's simpler forms[2] was used. A fortieth-normal solution of thiocyanate was used for most of the titrations; but for the analysis of the dilute solutions employed in experiments 8 and 13, a hundredth-normal solution of thiocyanate was used. In experiment 10 — normal silver nitrate in acetonitrile — the analyses of the solutions were made with a tenth-normal solution of thiocyanate.

Table III. gives the relative velocities of the silver ion, at different concentrations in solutions of silver nitrate in water, methyl alcohol, ethyl alcohol, acetonitrile, and pyridine. The

TABLE III.

Transference number of the cation multiplied by 100

Solvent	Volume in liters containing one gram-molecule of $AgNO_3$							
	0.42	1	2	4	10	16	35	40
Water	53.2	50.0	48.3	47.3	—	—	—	47.5
Acetonitrile	—	38.3	—	42.2	44.8	—	47.3	—
Pyridine	—	32.6	34.2	—	39.0	—	—	44.0
Methyl alcohol	—	—	—	—	—	53.3[3]	—	—
Ethyl alcohol	—	—	—	—	40.5[1]	49.0[4]	—	—

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[1] From the amount of silver deposited in the voltameter the exact current strength in amperes could of course be deduced.

[2] See Fig. 5. Zeit. phys. Chem. 27, 25 (1898).

transference numbers in aqueous solutions are taken from the work of Hittorf, and those in the alcoholic solutions are from the determinations of Campetti[1] and Mather[2]. Campetti's original article was not available, and as none of the various abstracts of his paper mention the concentration at which he worked, the position of his results in the table is uncertain.

Concluding remarks

From Table III. it appears that there is considerable difference in the relative velocities of the ions, in solutions of silver nitrate of the same concentration, in different solvents. The results also indicate that with increasing dilution the relative velocities apparently converge to the same value, about 0.47 for the cation, in the different solvents. But the experimental evidence at hand on this point is still too meager to make the general statement that with increasing dilution the relative velocities of the ions of a substance dissolved in different solvents approach the same value.

In aqueous solutions of silver nitrate we see that the velocity of the cation decreases with increasing dilution, while in the solutions of pyridine and acetonitrile the opposite holds true. In this respect, these non-aqueous solutions of silver nitrate behave like certain salts in aqueous solutions, copper sulphate, for example. Moreover, when the transference numbers of the various salts studied in aqueous solutions at different concentrations are classified, it appears that those salts which show a marked affinity for the solvent, as a rule, yield transference numbers for the cation which increase with increasing dilution; and again, solutions of salts which show but slight variation, or a decrease in velocity of the cation with increasing dilution, have a relatively slight affinity for the solvent.

Silver nitrate has a pronounced affinity for acetonitrile and pyridine, the rise in temperature being especially marked when silver nitrate is dissolved in pyridine.[3] From the analogous be-

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[1] Campetti. Abstract Zeit. phys. Chem. 16, 165 (1895).

[2] Mather. Am. Chem. Jour. 26, 473 (1901).

[3] The thermal effects are now being investigated in this laboratory.

havior of these solutions with respect to the variation of the transference numbers with the dilution to aqueous solutions of salts which show a marked affinity for water, and from the contrast of behavior of silver nitrate solutions in water on the one hand, and in pyridine and acetonitrile on the other, it appears that the affinity of the solvent for the dissolved substance must receive due consideration in any explanation of these phenomena.

These variations of the transference numbers with the dilution may be explained by assuming the presence of various complex ions in the solutions; thus, for example, A. A. Noyes[1] cites the case of barium chloride,—a salt in which the velocity of the cation increases with increasing dilution,—and states in explanation of this change in velocity with the dilution that it is necessary to assume that there are present a considerable quantity of complex negative ions formed by the union of one or more chlorine ions with one or more chloride molecules, e. g. $BaCl'_3$ or $BaCl''_4$, and that these dissociate with increasing dilution. For the opposite behavior of the cation, i. e., decrease in relative velocity with increase of dilution, as is the case of aqueous solutions of silver nitrate, we must on this basis assume the existence of complex positive ions in the solution, and that these dissociate with increasing dilution. For solutions of such salts as show little or no change in the velocities of the ions with the dilution, we should have to say that but few complex ions exist; or, assuming their existence, the number of each kind, positive and negative, is about the same, and that they dissociate at about the same rate with increasing dilution. To explain the opposite behavior of the solutions of silver nitrate pointed out above, in different solvents, on this basis, it is necessary to assume the existence of complex positive ions in aqueous solutions, and complex negative ions in the pyridine and acetonitrile solutions. But the assumed existence of these various complex, free ions in the different solutions of silver nitrate under consideration must be ascribed to the influence of the solvent. In fact the results in Table III. illustrate well the

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[1] Jour. Am. Chem. Soc. 23, 37 (1901).

important rôle of the solvent in ionization phenomena. Moreover in view of the parallelism here pointed out between the affinity of solvent and dissolved substance and the change of the transference numbers of the ions with the dilution, it seems to me that the true explanation for these variations in the ionic velocities lies in a complex union of solvent and dissolved substance, and not in the assumption of several kinds of complex, free ions of the solute.

During the progress of this work Professor Kahlenberg offered helpful suggestions for which I desire to express my thanks.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
Feb. 14, 1902.

ON THE INVERSION OF ZINC SULPHATE

(SECOND PAPER)

BY H. T. BARNES AND H. L. COOKE

In a previous paper[1] one of the authors has shown that the temperature of inversion represented by

$$ZnSO_4 \cdot 7H_2O \rightleftarrows ZnSO_4 \cdot 6H_2O + H_2O,$$

when measured by the electrical method, differs considerably from the same point measured by solubility determinations. There seems little reason to doubt the electrical determination since the results of Jaeger[2] give an independent verification of the point. The solubility measurements of Callendar and Barnes[3] for zinc sulphate have also been completely verified by E. Cohen,[4] and have thus added a second independent verification of this temperature. It was suggested in the first paper[5] on this subject that the presence of the mercurous sulphate in the Clark cell used for the electrical determinations caused a lowering of the inversion temperature. This seemed all the more probable as it had been previously shown that the mercurous sulphate was to a certain extent soluble, and exerted a small influence on the E. M. F. of the Clark cell. To show this, cells of special design were constructed, similar to the H-form of cell, with electrodes separated by a long narrow tube, and these compared with cells of the usual test-tube type with the zinc rod not far removed from the paste of mercurous sulphate.

In addition an H-form of cell was made with a mass of zinc placed in the shank between the two limbs to collect the mercurous sulphate that diffused over from the positive to the negative limb. In both these experiments the cells with zinc elec-

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[1] Jour. Phys. Chem. 4, 1 (1900).

[2] Wied. Ann. 63, 354 (1897).

[3] Proc. Roy. Soc. 62, 150 (1897).

[4] Proc. Roy. Soc. of Amsterdam, 334 (1900).

[5] l. c. p. 19.

trode shielded from the diffusing mercurous salt had a higher E. M. F. than those not so protected. Since then further experiments have been made, which show the solubility of the mercurous sulphate in the zinc sulphate solution, and an attempt made to measure the diffusivity. For this latter an H-form of cell was constructed with a glass tap between the electrodes which could be opened and closed at will. Although no very definite quantitative results have as yet been obtained, a measurable effect was noticed.[1]

The temperature of inversion as measured by the Clark cell, i. e. 38.75° C, differs so widely from the same point measured by the solubility determinations, which is 39.95° C, as to suggest some influence due to the solubility of the mercurous sulphate. It was decided therefore to make some experiments to test this point electrically and to arrange the conditions so as to avoid the presence of mercurous sulphate. Two inversion cells were constructed for comparison in the H-form (Fig. 1) with in-

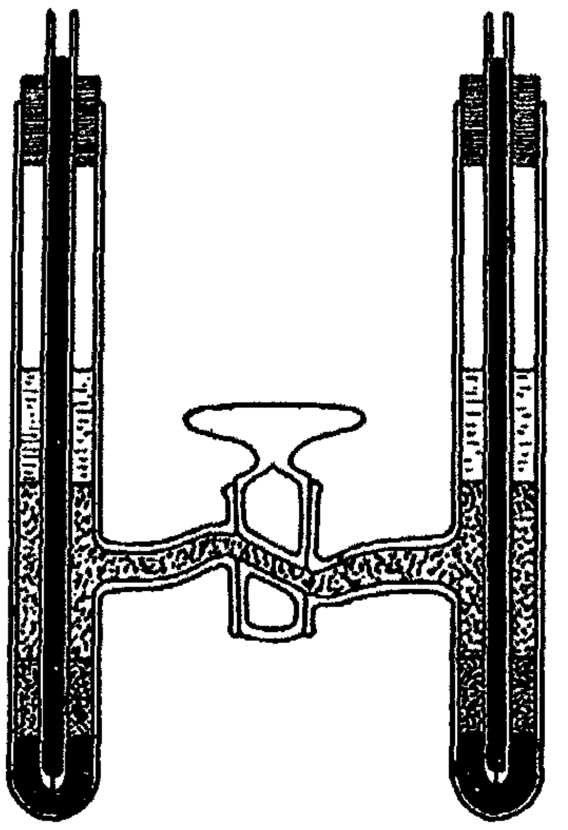

Fig. 1

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[1] These experiments, one of the authors (H. T. B.) carried out with Dr. E. Cohen by his courtesy in his laboratory in Amsterdam.

tervening glass tap. In one of the cells both limbs were filled with a 10 percent zinc amalgam and a mixture of zinc sulphate crystals, and in the other both limbs were filled with mercury, mercurous sulphate, paste zinc sulphate crystals and solution. In both of these cells the E. M. F. was zero: when both limbs contained either phase at all temperatures, when each limb contained a different phase at the inversion temperature.

Cohen's early experiments[1] were available for an inversion cell similar to our second, which contained the heptahydrate in one limb and the hexahydrate in the other limb in the presence of the mercurous sulphate, but we found on inspection that the temperature at which the cell gave zero E. M. F. was not sufficiently precise for our purpose.

Our method of procedure for the experiments with our two types of cells was very simple. The glass tap was closed and the crystals in one limb inverted from the heptahydrate to the hexahydrate by immersing in a water-bath at a temperature between 55° and 60° C, keeping at the same time the other limb containing the heptahydrate just below the inversion temperature. The cell was then removed to a thermostat near the inversion temperature, and so arranged that by disconnecting the regulator the temperature could be varied by small amounts up or down the scale. As soon as sufficient time had been allowed for the two limbs of the cell to attain the temperature of the bath the glass tap was opened and the E. M. F. of the cell measured. Since either phase can remain metastable over a considerable range, it was possible to make observations several degrees above and below the inversion temperature, and the true temperature obtained by interpolation. By varying the temperature sufficiently the change in the limb containing the metastable salt could be observed by the return of the E. M. F. of the cell to zero on the inversion to the stable form.

The difference of potential between the two ends of the cell was measured on the potentiometer described in the first paper.[2]

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[1] Zeit. phys. Chem. 15, 53 (1894).

[2] l. c. p. 4.

Since these differences were small and changed sign at the inversion temperature the electrical connections were made as shown in the diagram (Fig. 2) so that a change in sign could be

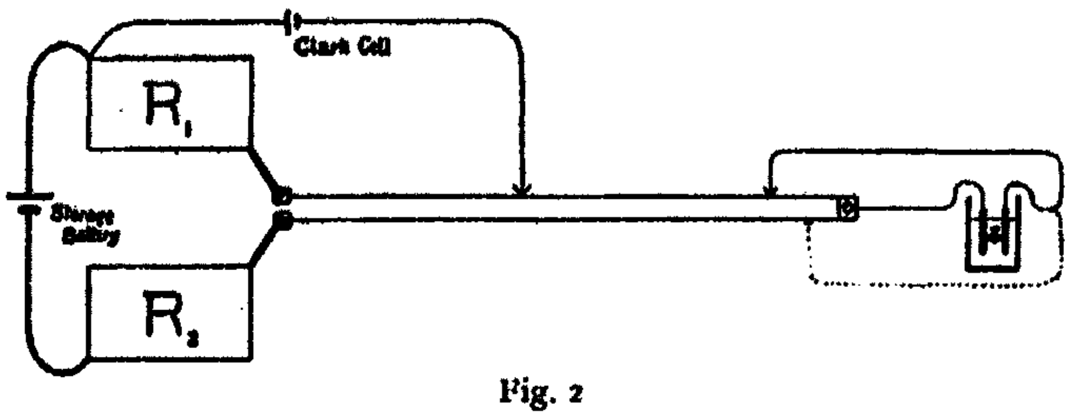

Fig. 2

measured immediately. One pole of the cell was permanently fastened to a point on the bridge-wire, and the other passed to sliding contact which could be placed on one wire or on the other depending on the polarity of the cell. One centimeter of the bridge-wire corresponded to 1/10 of a millivolt and the galvanometer was capable of detecting a shift of one millimeter on the wire. This gave ample accuracy in the measurements. For the method of measurement and adjustment of this form of instrument for small differences of potential the first paper should be consulted.

In our experiments with the second inversion cell containing the mercurous sulphate, the method of inverting one limb and the electrical measurements were exactly the same as those just described. Since the E. M. F. of the cell results from the difference in the solubility of the two hydrates, sufficient time had to be allowed on a change in temperature for the solution to assume its normal strength. The temperature was therefore varied slowly and by small increments. No great error is likely to have arisen from a want of saturation or supersaturation since a large quantity of crystals was always present. From the experience with the "crystal" Clark cell in which the solution is always in contact with the solid crystals, the "lag" is exceedingly small and quite negligible for the temperature ranges we worked with. Nevertheless this point could not be overlooked and care was taken to obviate it. Crystals were placed in the narrow tube connecting the two limbs so as to ensure saturation there, and when the salt was inverted the entire limb up to the glass tap was immersed in the hot bath. The two limbs could be kept separated for an indefinite time by keeping the tap closed, and since the level of the liquid remained the same in the two limbs there was no passage of solution from one to the other when the tap was opened for a measurement.

The following table contains the result of the observations. The differences of potential are expressed in millivolts, the change in sign occurring at the inversion temperature.

TABLE OF OBSERVATIONS

Inversion cell without mercurous sulphate

E. M. F. in millivolts	Temperature
−0.15	39.77° C
0.00	38.62
+0.25	36.92
+0.40	36.00
+0.56	35.17
−0.55	41.61
−0.69	42.12

Inversion cell with mercurous sulphate

−0.14	40.0
−0.17	40.0
−0.14	39.5
−0.11	39.0
−0.04	38.0
−0.03	38.3
+0.02	37.5
+0.07	37.3
+0.08	37.0
+0.02	37.9
−0.05	38.4

From an inspection of the table it will be seen that the inversion temperature in the case of the two cells is very nearly the same and both are below the temperature given by the solubility determinations. A small difference exists in the results by the two cells, and shows, we believe, an effect produced by the presence of the mercurous sulphate. It cannot be said, however, that so large a difference as exists between the temperature as measured on the Clark cell and as measured by the solubility determinations can be ascribed to the mercurous sulphate, but must be looked for elsewhere. As it has been shown conclusively that the mercurous sulphate goes into solution in the cell a small effect might be expected, but it does not seem to be enough to account for the discrepancy in question.

In conclusion we may state that we are continuing the investigation, and hope to be able to communicate further results in a later paper.

McDonald Physics Building,
McGill University, Montreal,
March 6, 1902

SYNTHETIC ANALYSIS OF SOLID PHASES

BY WILDER D. BANCROFT

Except in the rare instances where a solid phase is in equilibrium with a liquid phase of the same composition, the usual method of analysis requires the preliminary isolation of the solid in a pure state. This is not always easy. There may be danger of dissociation if dealing with a compound containing at least one volatile component. There may be difficulty in removing the mother-liquor, as in the case of alloys.

This latter difficulty has been partially obviated by van Bijlert,[1] who added a third component, known not to enter into the solid phase, and estimated the amount of mother-liquor clinging to the crystals from the quantity of this third substance apparently present in the crystals. This process involves removing the solid phase from the solution, and is also open to error owing to the possibility of a change in the composition of the mother-liquor while removing the crystals.

Being interested in the study of alloys, I have reversed the process of van Bijlert and determine the composition of the solid phase from the change in the composition of the solution from which it separates. Let us suppose that we have three substances, A, B, and C, and we wish to determine whether the solid phase is pure A, pure B, a compound of these two, or a solid solution containing A and B only. We start with a solution containing x_1 grams of A, y_1 grams of B per gram of C. We let this solution cool to some convenient temperature, pipette off a portion of the solution and analyze. If the solution contains x_2 grams of A and y_2 grams of B per gram of C, the solid phase contains $x_1 - x_2$ grams of A and $y_1 - y_2$ grams of B. If $x_1 - x_2 = 0$, the phase is pure B; if $y_1 - y_2 = 0$, the phase is pure A. If the two differences are neither of them zero, the ratio gives the mean composition of the phase. The only

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[1] Zeit. phys. Chem. 8, 343 (1891).

limitations are that there shall be but one solid phase and that the component C shall not form part of it. It is, of course, possible that the solid solution in equilibrium with a certain liquid phase might happen to have a composition corresponding to a compound. A second analysis with different initial and final concentrations will enable one to distinguish between these two possibilities, since the composition of the solid phase will vary if a solid solution and will remain constant if a compound.

For the sake of simplicity, it has been assumed that the initial concentrations were such as to have everything in solution at some accessible temperature. If this were essential, the method would be applicable only to systems in which there was a marked change of concentration with the temperature. This is not necessary, and the initial concentrations may be those of the system regardless whether a homogeneous solution is or is not formed. The only limit to the accuracy of analysis to be obtained by this method is that the mass of the solid phase shall not be so great as to make it impossible to draw off enough solution for analysis. It is not essential that the system shall be in equilibrium when the solution is drawn off, nor that the solution shall be free from the solid phase, though it is desirable to have as little of the solid phase as possible in the mass to be analyzed in order to make the difference between the initial and final concentrations as large as may be. If there were enough solid phase in suspension, this difference might even become zero.

So far, we have assumed that the third component does not form part of the solid phase. This assumption has been made as a preliminary convenience; but it is not essential. The method is equally applicable to systems in which ternary compounds occur. Wherever it is not known definitely that the third component does not enter into the solid phase, a graphical method is the best for interpreting the results. If we plot the initial and final concentrations in a triangular diagram and connect the points by a straight line, the composition of the solid phase is represented by some point lying in the extension of that line. If we make a second analysis, with different initial and final concentrations, and plot these results, the composition of the solid phase is represented by some point lying in the extension of the line connecting these two points. The actual composition of the solid phase is therefore given by the point of intersection of these two lines, in case the solid phase is not a solid solution. If the lines meet outside the diagram, the solid phase must be a solid solution; in other cases, where the analysis shows the presence of more than one component, a solid solution may be present, but a second analysis will settle the question if it is at all doubtful.

To illustrate this there is given in Figure 1 a schematic

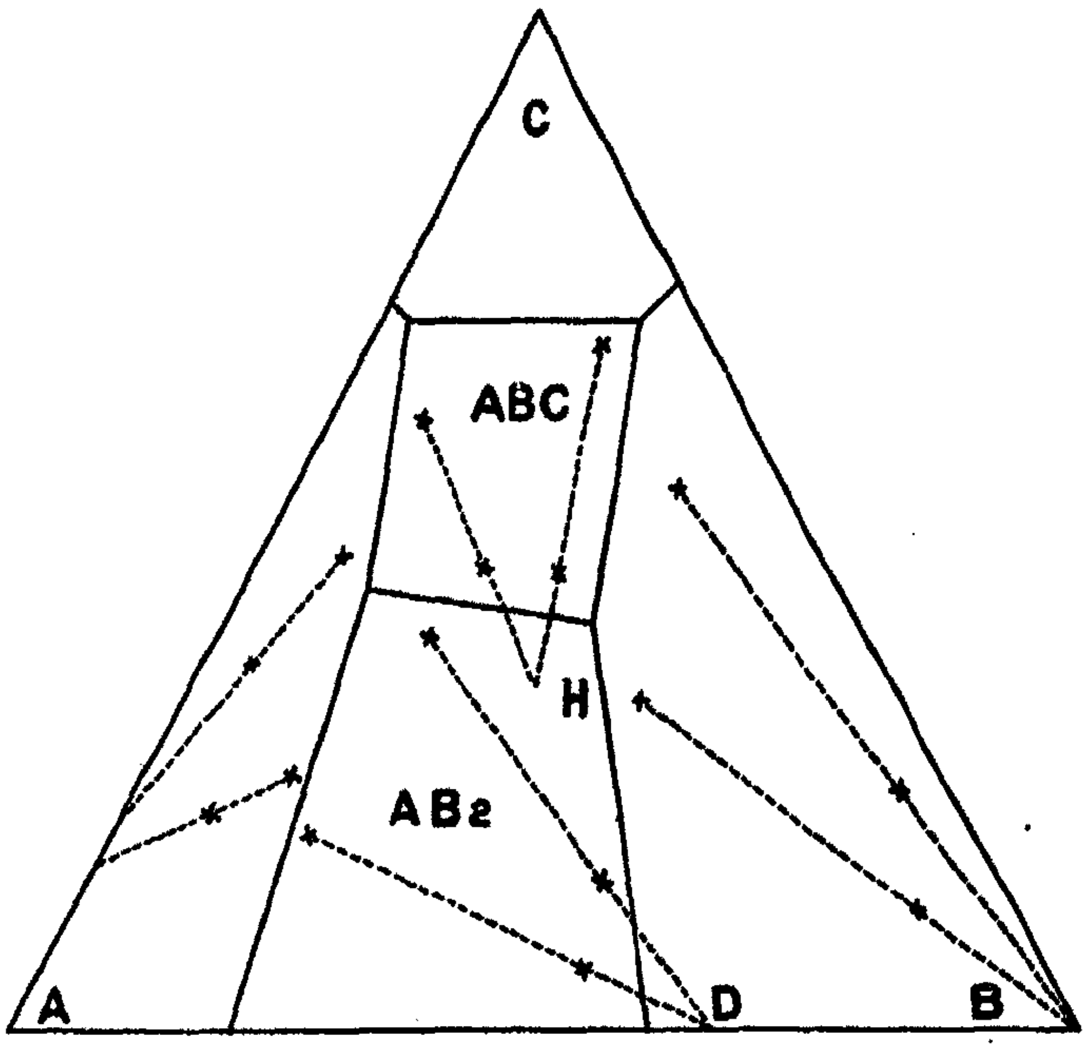

Fig. 1

diagram for a system made up of three components A, B, and C, in which the substances A and C form two series of mix-crystals, and there are two compounds, AB_2 and ABC, neither of them stable at its melting-point. The continuous lines show the boundary curves and the crosses, the initial and final concentrations in the crystallization experiments. In the field in which pure B is solid phase, the dotted lines meet in the corner representing one hundred percent B. In the field for the compound AB_2, the dotted lines meet at the point D, which represents the compound AB_2. In the field for the ternary compound, the lines intersect at H and the solid phase therefore has the composition ABC, represented by the point H. In the field in which we should expect to find pure A as solid phase, the dotted lines as drawn do not intersect at all. From the upper line we might suspect that we were in the field for a compound A_4C. The second dotted line shows that the solid phase is a solid solution of C in A. If the solid phase had been mix crystals containing A, B, and C, as in the case of copper and iron sulphates in water, the two lines would have intersected inside the diagram, but a third crystallization experiment would have given another line cutting the other two but not passing through the point of intersection.

Where one is dealing with inorganic substances, a direct analysis of the solution will usually be the simplest and the most accurate method. Cases may easily occur, however, where a direct analysis is very difficult or inadvisable. Under these circumstances a zero method can be employed. We start with a saturated solution at some definite temperature and then determine any convenient property, such as density, conductivity, boiling-point, or acidity, etc. We next add one or more components in the proportions in which we believe them to occur in the solid phase, and keep the solution at the adopted temperature until equilibrium has been reached. If we have been right in our guess as to the composition of the solid phase, the solution will be entirely unchanged because the added component or components will have separated as the solid phase. If we have been wrong, the composition of the solution will have changed. The accuracy of the analysis depends on the accuracy with which we can detect small changes in the concentration of the solution. This general principle of keeping the concentration of the solution constant by adding to it the phase which is being removed has previously been applied successfully in this laboratory by Dr. Carveth to the analysis of the vapors given off by a mixture of two volatile liquids.

When we are dealing with alloys there is a possibility of applying the zero method in another form. If we determine the temperature-time cooling curve, we shall get a break where the first solid phase separates, another at the boundary curve where the second solid phase separates, and a third at the eutectic point where the third solid phase separates. If we melt the mass and add one or more components in the proportion in which they occur in the solid phase, we shall raise the temperature at which the first break occurs and leave the other two unchanged. If we add one or more components in a different proportion from that in which they occur in the solid phase, we shall change the temperature at which the upper two breaks occur, while the temperature of the third remains unchanged. The accuracy with which we can make our analysis depends on the accuracy with which we can pick up our boundary curve. There are several serious difficulties. There is a possibility of superfusion and of the intermediate formation of instable phases, a phenomenon which we know to be serious in the case of steel and which may be serious with other alloys. Then, the more of the solid phase we add the greater the accuracy of the analysis for a given error in determining the boundary curve; but the larger the mass of the solid phase the less marked will be the break at the boundary curve and the greater the error in determining the temperature at which this occurs. There is no doubt but that the method can be used to determine the composition of a compound. Whether one can use it to distinguish between a pure metal and a solid solution containing less than one percent of the other substance is not so certain. It becomes largely a question of the delicacy of the recording apparatus.

One of the most important points in regard to a method of analysis is the accuracy to be obtained. The amount of solid phase which will interfere with drawing off a portion of the liquid phase will vary with the relative densities of the two phases and the form of the crystals, and cannot therefore be stated generally. From Charpy's experiments on alloys[1] a mixture containing 75 g of tin, 30 g of lead, and 45 g of bismuth should give at about 125°, 100 g of solid tin and a solution containing 25 g of tin, 30 g of lead, and 45 g of bismuth. Taking the most unfavorable case and throwing all the error on the tin and lead, we will assume that our final analysis shows 25.25 g of tin and 29.75 g of lead to 45 g of bismuth. This would mean that the solid phase contained 49.75 g of tin and 0.25 g of lead. In other words, an error of one percent in the determination of the tin in the solution means an error of one-half of one percent in the composition of the solid phase.

From Seidell's experiments[2] on the solubility of sodium sulphate, sodium chloride and water, a mixture of 94.25 g Na_2SO_4, 8.15 g NaCl, and 190 g H_2O should give at 25° a solution containing 23.15 g Na_2SO_4, 8.15 g NaCl and 100 g H_2O. Here an error of one percent in the amount of sodium sulphate means an error of about the same amount in the water to salt in the hydrated salt. As a matter of fact, an error of this magnitude is not permissible.

There are two things to be noticed about hydrated salts. If one adds the anhydrous salt to the solution, there is the theoretical possibility that it may become hydrated on the surface only and that equilibrium may be reached only after a very long time. Experiments that have been made in this laboratory show that this difficulty does not occur with sodium sulphate or barium chloride when these substances are added as powder, and slowly. The second point to be noticed is that the occlusion of mother-liquor in the crystals introduces no error in case the occluded liquid has the same composition as the solution.

In this paper I have described a method of synthetic analysis whereby the composition of a solid phase may be deter-

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[1] Comptes rendus, 126, 1569 (1898).

[2] Am. Chem. Jour. 27, 52 (1902).

mined without removal from the solution. When the zero method is used, it is not necessary to know either the initial or final composition of the solution. This method should prove serviceable with alloys, efflorescent compounds, basic salts and substances like many double salts which are decomposed by the pure solvent.

Cornell University

A DERIVATION OF THE PHASE RULE

BY J. E. TREVOR

Although several forms of Gibbs's derivation of the phase rule have been presented in recent years, I venture in the present paper to offer another, in the hope that its simplicity will entitle it to consideration.

1. The case of n constituents

Let us first consider a phase-system having n independently variable "components", each one being a component of each of the phases of the system. At equilibrium, the energy of each of the r coexistent phases is a function of the volume, the entropy, and the component-masses, of the phase,

$$\mathrm{E}_i(v_i, \eta_i, m_{i1}, m_{i2}, \dots, m_{in}). \qquad (i = 1, 2, \dots, r).$$

By differentiation of these functions, we find expressions for the "intensities" that correspond to these variables (the "extensities"), i. e., for the pressure, the temperature, and the chemical potentials of the components,

$$(1) \quad \begin{cases} p = \phi_{i1}(\overline{v_i}, \overline{\eta_i}, c_{i1}, c_{i2}, \dots, c_{in}), & (i = 1, 2, \dots, r) \\ \theta = \phi_{i2}(\overline{v_i}, \overline{\eta_i}, c_{i1}, c_{i2}, \dots, c_{in}), & \\ \mu_1 = \phi_{i3}(\overline{v_i}, \overline{\eta_i}, c_{i1}, c_{i2}, \dots, c_{in}), & \\ \dots & \\ \mu_n = \phi_{i(n+2)}(\overline{v_i}, \overline{\eta_i}, c_{i1}, c_{i2}, \dots, c_{in}). & \end{cases}$$

Here for the specific volumes, specific entropies, and specific component-masses or mass "concentrations", of the phases we introduce the notation

$$\overline{v_i} = \frac{v_i}{\Sigma_j m_{ij}}, \quad \overline{\eta_i} = \frac{\eta_i}{\Sigma_j m_{ij}}, \quad c_{ij} = \frac{m_{ij}}{\Sigma_j m_{ij}}.$$

The first derivatives of the functions E_i may be regarded as functions of these variables, since the functions E_i are homogeneous and of the first degree in their variables.

Differentiation of the functions E_i yields primarily, of course, $(n+2)r$ equations for the phase intensities p_i, θ_i, μ_{ij}; but between these functions obtain the $(n+2)r$ conditions of equilibrium,

$$\begin{cases} p_1 = p_2 = \dots = p_r = p \\ \theta_1 = \theta_2 = \dots = \theta_r = \theta \\ \mu_{11} = \mu_{21} = \dots = \mu_{r1} = \mu_1 \\ \dots \\ \mu_{1n} = \mu_{2n} = \dots = \mu_{rn} = \mu_n, \end{cases}$$

which serve for the elimination of the phase intensities, whereby we obtain the $(n+2)r$ equations (1). The only further independent relations between the variables of (1) are the r equations

$$(2) \qquad \sum_j c_{ij} = 1.$$

We introduce the nr concentrations c_{ij}, and therefore also these equations (2), instead of restricting ourselves to functions of the $(n-1)r$ ratios of the component-masses, in order that our set of variables shall include the phase-concentrations of all the components.

Relating to our system of r coexistent phases, we have above the

$$(n+2)r + r$$

equations (1) and (2), between

$$(n+2)r + (n+2)$$

variables. Of these variables, therefore, the number that remains independent is the difference of these two numbers, or

$$n + 2 - r.$$

It appears, that is to say, that of the variables

$$\begin{matrix} p, & \theta, & \mu_1, & \mu_2, & \dots, & \mu_n, \\ \bar{v}_i, & \bar{\eta}_i, & c_{i1}, & c_{i2}, & \dots, & c_{in}, \end{matrix} \qquad (i = 1, 2, \dots, r)$$

the number remaining independently variable, the variance v of the system, is

$$v = n + 2 - r.$$

This is the phase rule for the case in question.

It may be, however, that certain of the components are absent from certain of the phases. This fact will be expressed by q equations

$$m_{ij} = 0.$$

The effect of these equations is to cause q of the concentrations c_{ij} to disappear from the set of variables, and q of the equations

$$\mu_j = \phi_{i(j+n)},$$

of the set of equations (1), to disappear from among the equations between them. Further, whenever the number of the components of a phase reduces to unity, an *additional* concentration disappears from the set of variables, and an additional equation,

$$\sum_j c_{ij} = 1,$$

vanishes. The number of disappearing equations being thus equal, in either case, to the number of disappearing variables, the number of variables remaining independent is still, as before,

$$n + 2 - r.$$

The above result, but with reference to a smaller set of variables, is obtained by means of the above line of reasoning if we start from any one of the sets of auxiliary fundamental functions,

$$\begin{array}{llllll} \mathrm{F}_i(v_i, & \theta, & m_{i1}, & m_{i2}, & \ldots, & m_{in}) \\ \mathrm{G}_i(p, & \eta_i, & m_{i1}, & m_{i2}, & \ldots, & m_{in}) \\ \mathrm{H}_i(p, & \theta, & m_{i1}, & m_{i2}, & \ldots, & m_{in}). \end{array}$$

2. The case of $n + h$ constituents

The case considered in the foregoing is not wholly general. It may be that the number of substances whose masses vary in the phases of the system exceeds the number of independently variable components of the system as a whole. Denoting the phase-masses of the former substances, the "constituents", by

$$A_{i1}, \; A_{i2}, \; \ldots, \; A_{i(n+h)}, \qquad (i = 1, 2, \ldots, r)$$

and supposing provisionally that each of the $n+h$ constituents is a constituent of each phase, we have for the energies of the r phases,

$$E_i(v_i, \eta_i, A_{i1}, A_{i2}, \ldots, A_{i(n+h)}),$$

functions which are homogeneous and of the first degree in their variables. Differentiation of these functions yields expressions for the intensities, writing λ_j for the chemical potential of the j-th constituent,

$$(3)\quad \begin{cases} p = \psi_{i1}(\overline{v_i}, \overline{\eta_i}, C_{i1}, C_{i2}, \ldots, C_{i(n+h)}) \qquad (i = 1, 2, \ldots, r) \\ \theta = \psi_{i2}(\overline{v_i}, \overline{\eta_i}, C_{i1}, C_{i2}, \ldots, C_{i(n+h)}) \\ \lambda_1 = \psi_{i3}(\overline{v_i}, \overline{\eta_i}, C_{i1}, C_{i2}, \ldots, C_{i(n+h)}) \\ \ldots \\ \lambda_{n+h} = \psi_{i(n+h+2)}(\overline{v_i}, \overline{\eta_i}, C_{i1}, C_{i2}, \ldots, C_{i(n+h)}). \end{cases}$$

Here again the notation includes *specific* extensities, namely,

$$\overline{v_i} = \frac{v_i}{\Sigma_j A_{ij}}, \quad \overline{\eta_i} = \frac{\eta_i}{\Sigma_j A_{ij}}, \quad C_{ij} = \frac{A_{ij}}{\Sigma_j A_{ij}};$$

and here again the phase-intensities are replaced by the equilibrium values of the intensities with reference to the system as a whole, by means of the equations representing the conditions of equilibrium. The only further relations between the variables of (3) are the r equations

$$(4)\qquad \sum\nolimits_j C_{ij} = 1,$$

and h equations between some or all of the λ_j's.

Relating to our system of r coexistent phases, we have above

$$(n+h+2)r + r + h$$

equations between

$$(n+h+2)r + (n+h+2)$$

variables. Of these variables, therefore, the number that remains independent is the difference of these two numbers, or

$$n + 2 - r.$$

It appears, that is to say, that of the variables,

$$\begin{array}{llllll} p, & \theta, & \lambda_1, & \lambda_2, & \ldots, & \lambda_{n+h} \\ \overline{v}_i, & \overline{\eta}_i, & C_{i1}, & C_{i2}, & \ldots, & C_{i(n+h)}, \qquad (i = 1, 2, \ldots, r) \end{array}$$

the number remaining independently variable, the variance v of the system is

$$v = n + 2 - r.$$

It may be, however, that certain of the constituents are absent from certain of the phases. This will be expressed by q equations

$$\Lambda_{ij} = 0.$$

The effect of these equations is to cause q of the concentrations C_{ij} to disappear from the set of variables, and q of the equations

$$\lambda_j = \psi_{i(j+2)},$$

of the set of equations (3), to disappear from among the equations between them. Further, whenever the number of the constituents of a phase reduces to unity, an additional concentration disappears from the set of variables, and an additional equation

$$\sum_j C_{ij} = 1$$

vanishes. The variance thus remains in any case

$$v = n + 2 - r,$$

as before. The phase rule, that is to say, is true generally.

Here, as for the simpler case treated under the first caption, the same result, but with reference to a smaller set of variables, is obtained by the same reasoning if we set out from any one of the sets of auxiliary fundamental functions,

$$\begin{array}{l} F_i(v_i, \ \theta, \ \Lambda_{i1}, \ \Lambda_{i2}, \ \ldots, \ \Lambda_{i(n+h)}) \\ G_i(p, \ \eta_i, \ \Lambda_{i1}, \ \Lambda_{i2}, \ \ldots, \ \Lambda_{i(n+h)}) \\ H_i(p, \ \theta, \ \Lambda_{i1}, \ \Lambda_{i2}, \ \ldots, \ \Lambda_{i(n+h)}). \end{array}$$

The treatment under this second caption, The Case of $n + h$ Constituents, may be regarded as the general derivation of the phase rule. That under the first is a particular case of it, and may be looked upon as merely introductory.

Cornell University

LIMITATIONS OF THE MASS LAW

BY WILDER D. BANCROFT

Nernst[1] and Luther[2] have shown that the dissociation of a compound in solution can be deduced from the dissociation in the vapor provided Henry's law holds for the compound and its dissociation products. If we have a compound AB dissociating into A and B, let c_1, c_2 and c_3 be the concentrations of AB, A and B in the vapor phase and let c_1', c_2', c_3' be the corresponding concentrations in the solution phase, the solvent being one in which no polymerization occurs. If the solubility relations of AB, A and B are given by the equations

$$(1) \qquad c_1 = k_1c_1', \qquad c_2 = k_2c_2', \qquad c_3 = k_3c_3',$$

and if the equation for equilibrium in the vapor phase is

$$(2) \qquad Kc_1 = c_2c_3,$$

the equation for equilibrium in the solution phase will be

$$(3) \qquad K\frac{k_1}{k_2k_3}c_1' = c_2'c_3'.$$

This would seem to show that a solvent has no effect on the form of the equilibrium equation so long as it does not change the molecular weights of the reacting substances and does not form compounds with them. There is one assumption, made explicitly by Nernst and by Luther, which does not hold in all cases. They have assumed Dalton's law: that each substance in the vapor phase is absorbed proportionally to its partial pressure and independently of the nature of the other absorbed substances. In many cases this is not true. The presence of benzene in alcohol or acetone decreases the absorption of water and vice versa. Salicylic acid precipitates water from aqueous acetone at 0°. In other words, the solubility coefficient varies

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[1] Zeit. phys. Chem. 6, 36 (1896); 8, 110 (1897); 28, 487 (1901).

[2] Ibid. 26, 317 (1898).

with the nature and concentration of the other substances present.

We will therefore take up the case where the relations $c_2 = k_2c_2'$ and $c_3 = k_3c_3'$ hold for A and B by themselves but not for A and B together. Ignoring any disturbing effect on the compound we shall have

$$(4) \qquad c_1 = k_1c_1', \qquad c_2 = k_2c_2'f_2(c_2'), \qquad c_3 = k_3c_3'f_3(c_3').$$

The equation for equilibrium in the solution phase becomes

$$(5) \qquad \mathrm{K}\frac{k_1}{k_2k_3}c_1' = c_2'f_2(c_2')\cdot c_3'f_3(c_3').$$

In a case of this sort, the equilibrium would not be represented by the usual equation and the experimental data might be more accurately reproduced by an equation with fractional exponents. Chloral hydrate is a case where the dissociation products, chloral and water, are only partially miscible and the change of the dissociation with the concentration in acetone solution, for instance, must be different from that of the dissociation of aniline acetate. We are not limited to a case where the dissociation products precipitate one another. Take the case of chloral hydrate in chloroform solution. Since water is very sparingly soluble in chloroform, the partial pressure of water vapor will vary with the amount of undissociated chloral hydrate present and this will introduce a special complication.

We see therefore that even in cases where the molecular weight of each reacting substance is constant and where Henry's law holds absolutely for each reacting substance taken singly, the orthodox mass law equation will not apply in the solution if any one of the reacting substances influences the partial pressure of any of the other reacting substances either positively or negatively.

In the cases where Dalton's law may be assumed to hold, the effect due to the nature of the solvent will be seen in the change of the equilibrium constant, the more soluble system increasing at the expense of the other. This seems at first sight to be contradicted by the fact that a reaction runs practically to an end in the other direction when one of the reacting substances is practically insoluble. This apparent discrepancy is due to the introduction of a new phase.

Let the equation for the dissociation of the compound AB in a given solvent be

$$Kc_4' = c_5'c_6', \tag{6}$$

and then let us change to a solvent in which the solubilities of A and B are unchanged, but in which AB is 1/D times as soluble. We shall then have, if the solution remains unsaturated,

$$KDc_4'' = c_5''c_6''. \tag{7}$$

If we let y be the amount of AB which has changed over into the dissociation products, we may write the last equation

$$KD(c_4' - y) = (c_5' + y)(c_6' + y). \tag{8}$$

If the solution in the first solvent had been saturated with respect to AB, we should have written equations 7 and 8 as follows:

$$Kc_4' = c_5'c_6' = H \tag{9}$$

$$KDc_4'' = c_5''c_6'' = H, \tag{10}$$

where H is a constant. If we let x be the amount of AB which has precipitated and y, as before, the amount which has changed into the dissociation products, equation (10) becomes

$$KD(c_4' - x - y) = (c_5' + y)(c_6' + y) = H. \tag{11}$$

A comparison of equations 9 and 11 shows that they can hold simultaneously only when y is zero. In other words, there will be increased formation of the dissociation products when the solution is first unsaturated and no increase when it is saturated with respect to the compound. The tendency to form the more soluble system is therefore consistent with Berthollet's law.

Cornell University

NEW BOOKS

Thermodynamique et Chimie. *By P. Duhem. 16 × 25 cm; pp. ix + 496. Paris: A. Hermann, 1902.* — The chemist of to-day will admit more or less regretfully that his mathematical knowledge is too restricted to understand the volumes of the celebrated French physicist, but this book will cause him to change his opinion, for the author has expressed his ideas in the simplest language he knows.

Actuated by the desire to make thermodynamics as helpful and necessary to chemistry as it has been to physics, and knowing that exactness is equivalent to clearness, he has enunciated in the first chapter the fundamentals to applied thermodynamics. These discuss force and work, quantity of heat and inner energy, chemical calorimetry, reversible changes in their bearing on equilibria and the principles of chemical statics. The reader whose training has not gone beyond the confines of elementary calculus, may find these as well as the subsequent chapters of the book not merely intelligible, but pleasurably intelligible.

There is then given a simple non-mathematical explanation of the phase rule, in which the limitations and fundamental hypotheses are discussed. The author now introduces an innovation by dealing with multivariant systems of three, four, and five components; and then univariant and invariant systems with one or more components. The order of the subsequent chapters is: displacement of equilibrium by various energy factors, bivariant systems, mixed crystals, optical antipodes, and metallic alloys, critical state, chemical mechanics of the perfect gas, capillary action in relation to apparent false equilibria, false equilibria, systems unequally heated, and chemical dynamics in relation to explosions.

The subject matter contains much that is very interesting and well presented, of which the best cases are those in which the author has himself done pioneer work — the critical state of mixtures and false equilibria. Instances of the latter are met at every turn, showing that the author has (and with perfect right) regarded it of very great importance. The illustrations have been chosen from the classic as well as the more modern cases; of the latter there are treated optical antipodes, isomorphous mixtures, and the theory of iron and steel. Colloidal solutions are not discussed.

It is difficult to understand why Duhem has chosen the order used in this book. It is certainly one which would be extremely difficult to employ with any one who is being introduced to the subject. Why one should be launched on the stormy sea of three components is not apparent when it is difficult to get complete bearings with one-component systems. There is also lacking in this, as in other works, a sharp distinction as to the variables which are of prime importance in determining states of equilibrium and those whose efficiency is secondary. In the science of chemistry the accuracy of all instruments whether experimental or mathematical must always be regarded. In the first development of the phase rule this was not considered necessary; at the present it is and in the future must become increasingly so. Only then can the limitations of the rule be clearly defined and its effectiveness as a system of attack increased.

Duhem has not employed the theorem of Le Chatelier in its most effective form; the Tammann theory on the velocity of phase formation and the fact that chemists are intensely interested in the study of phase separation as well as formation have not been regarded.

These, however, are minor points which will be differently emphasized by different teachers. The work is good and well adapted for the serious study of all teachers of chemistry, especially those who lament the chaotic state of most methods of presentation.

H. R. Carveth

The Elements of Physical Chemistry. *By Harry C. Jones. 14 × 21 cm; pp. xi + 565. New York: The Macmillan Company, 1902. Price: bound, $4.00.*—The headings of the chapters are: atoms and molecules; gases; liquids; solids; solutions; thermochemistry; electrochemistry; photochemistry; chemical dynamics and equilibrium; measurements of chemical activity.

This particular arrangement calls for a number of forward references. One striking instance is the discussion of the dilution law before the mass law. There seems to be no reason for this in the historical development of the subject and it certainly is not justifiable. In the preface, the author states that he has devoted a relatively large portion of the book to the discussion of the results in physical chemistry obtained before 1885. This is a feature which the reviewer greets with pleasure. In fact, more could have been introduced without harm. Gladstone's work on the spectra of salt solutions is interesting both in regard to the evidence it brings in favor of the electrolytic dissociation theory and the evidence against that same theory.

There are a few slips in the book. It is misleading, p. 11, to state that carbon, boron, and silicon follow the law of Dulong and Petit at 600° without stating that some of the so-called normal elements have become abnormal at that temperature. It is unfair, p. 88, to quote Ramsay's views in 1881 when he has since withdrawn them specifically and emphatically. In discussing Trouton's law, p. 105, it would make things easier for the student if the relation were limited specifically to the boiling-point at atmospheric pressure. Where two liquids are partially miscible, it is not necessarily true that the lower boiling solution, p. 173, passes off more rapidly. This is necessarily true only when the masses are expressed in molecular weights and not in grams. It would have been instructive to have shown the way in which fractional distillation depends on the difference between the vapor concentrations and the liquid concentrations, instead of giving the concentration-pressure curves for the liquid only. It is a pity, p. 207, to imply that the variation from Raoult's formulation for the molecular lowering of the freezing-point is due, in the case of water, to polymerization. It is more serious not to show, pp. 231, 281, that N in the van't Hoff-Raoult formula, refers to the molecular weight of the solvent as vapor and not to its molecular weight as liquid. All reference to the heat of dilution has been omitted, and the author therefore finds himself compelled to assume, p.

239, that the molecular weight of barium is 75.7 when dissolved in mercury. It is hardly justifiable, p. 276, to cite Küster's experiments on ether, rubber, and water, and on water, β-naphthol, and naphthalene, and to omit all reference to Küster's work on starch, iodine, and water, and to Walker and Appleyard's experiments on silk, picric acid, and water. The use of θ instead of Q for a quantity of heat seems ill-advised. Ostwald has long since admitted that the experiment, p. 367, did not demonstrate the existence of free ions in a solution. There is no objection to describing Hess as the father of thermochemistry and Raoult as the father of all cryoscopic work if one so wishes; but it seems like overdoing the parental relation to say, p. 319, that the theory of Clausius will be recognized to be the father of the Theory of Electrolytic Dissociation.

There are many interesting facts in the book and it will be valuable for reference. The volume shows a marked improvement over any previous publication by the author. The scope is wide and though the execution falls short of the plan, this is a defect which can be remedied. If the author would arrange his matter more systematically and would correct the errors of detail, the second edition should make a very satisfactory text-book.

Wilder D. Bancroft

The Experimental Study of Gases. *An account of the experimental methods involved in the determination of the properties of gases, and of the more important researches connected with the subject. By Morris W. Travers. 14 × 22 cm; pp. xiii + 323. New York: The Macmillan Company, 1901.* — "The manipulation of gases has been the object of attention at various epochs of chemical history. Scheele collected his gases in bladders; Priestley, unconsciously imitating Mayow, brought the pneumatic trough into use; and Bunsen devised processes still employed in analysis of gases. The device of Sprengel's pump, and later that of Töpler, has placed a new instrument at the disposal of chemists; and the ingenious methods of Hampson and Linde of producing liquid air in quantity has made it possible to deal with gases as easily, if not more so, as with liquids. In the research on the gases of the helium series a number of workers, including Lord Rayleigh, and Drs. Collie and Travers, have made use of apparatus, a description of which does not always appear in the original papers on the subject, but which will be found treated of in this volume. Dr. Travers has also taken the opportunity of tabulating the more important constants relating to gases, and what is perhaps of still greater moment, of directing the attention of chemists and physicists to lacunae in knowledge, which suggest subject for research."

The subdivisions of the book are: the fundamental gas laws; mercury pumps; stop-cocks, etc.; collecting and storing gases; preparation of pure gases; reading instruments; measurement of volume; calibration, etc.; gas analysis; composition of atmospheric air; gases of the helium group; determination of density; relationship of temperature, pressure, and volume over limited ranges of pressure; relations of temperature, pressure, and volume over wide ranges of pressure and temperature; liquefaction of gases; manipulation of liquefied gases; vapor-pressure and critical constants; solubility of gases in liquids; specific heats; effusion, transpiration, and diffusion; refractivity; spectrum analysis; methods of maintaining a constant temperature.

Wilder D. Bancroft

Vorlesungen über theoretische und physikalische Chemie. *By J. H. van't Hoff. Zweite Auflage. Erstes Heft: Die chemische Dynamik. 15 × 23 cm; pp. xi + 251. Braunschweig: F. Vieweg und Sohn, 1901. Price: paper, 6 marks.*—The second edition does not differ materially from the first. What changes have been made antedate the work of Bodenstein on false equilibria so that the chapter relating to this stands as first written. *Wilder D. Bancroft*

Anorganische Fermente. *By Georg Bredig. 16 × 24 cm; pp. 99. Leipzig: Wilhelm Engelmann, 1901.*—This is a recapitulation in book form of the author's work on the preparation of colloidal metals by means of the arc and of the work on the analogy between the action of these metals on hydrogen peroxide and the behavior of ferments. This pamphlet is much more convenient for reference than the original papers. *Wilder D. Bancroft*

Liquéfaction des Mélanges gazeux. *By F. Caubet. 16 × 25 cm; pp. 170. Paris: O. Hermann, 1901.*—This thesis contains a general discussion of the phenomena connected with the vaporization and condensation of two liquids or gases. The author has himself studied the behavior of mixtures of carbon dioxide and sulphur dioxide, of carbon dioxide and methyl chloride, and of methyl chloride and sulphur dioxide. More than one-third of the book is taken up with the tabulated data. The work is most valuable in increasing our knowledge in regard to retrograde condensation. *Wilder D. Bancroft*

Apuntes de Quimica. *By Pedro N. Arata. Third edition. Three volumes. 14 × 19 cm; pp. 309, 335, 319. Buenos Aires: Libreria Italiana "Dante Alighieri," 1901.*—We are used to translating text-books from German into English for the benefit of our students; but translations from the Spanish are not common. This book from South America is a remarkably comprehensive one, and students with this work as a text-book should be well-equipped if they have really mastered all within the covers. The first half of the first volume is largely physical chemistry and the author discusses—in very condensed form—the general properties of matter, the theory of vortex rings, the gas laws, the critical phenomena, rotation of the plane of polarized light, surface tension, viscosity, crystallography including solid solutions, solutions and solubility, osmotic pressure and vapor pressure relations, determination of molecular weights, laws of definite and multiple proportions, periodic law, valence and structure formulas, thermochemistry and dissociation, contact electricity, electrolysis, electrolytic dissociation theory, mass law, phase rule, physiological action of elements. The second half of the first volume deals with manipulation and methods in organic chemistry, together with directions for making forty-five organic compounds.

After this preliminary mental and manual drill, the author expounds the chemistry of the aliphatic compounds in the second volume and the chemistry of the cyclic compounds in the third volume. The portion dealing with alkaloids is made very complete for the benefit of students of pharmacy. It is not surprising that three editions have been called for in ten years.

Wilder D. Bancroft

Lições de Estereochimica. *By Alvaro José da Silva Basto. Edited by Alvaro de Mattos. Second edition. 17 × 23 cm; pp. xiii + 135. Coimbra, Portugal: França Amado, 1901.* — This volume is based on lectures given at the university. The first chapter is introductory and shows the insufficiency of plane structure formulas. The second deals with the stereochemistry of carbon, exclusive of the benzene derivatives. The constitution of benzene forms the subject of the third chapter, while the last chapter is devoted to the stereochemistry of nitrogen. *Wilder D. Bancroft*

The Analysis of Air and Water. *Reprints of Science Classics, I. (Edited by C. E. Linebarger.) 15 × 20 cm; pp. 31. Chicago: The School Science Press, 1902. Price: paper, 10 cents.* — This is the first of a series analogous to Ostwald's Klassiker. The following announcement is made in regard to the series:—

"The laboratory method of science teaching, at first applied to supplement the text-book, has proved so valuable that the text-book work has in a measure become subordinate to the laboratory work. In the laboratory the student comes in direct contact with the facts of science, and uses his text-book mainly to supplement and correlate what he has learned in the laboratory. The text-book, however, too often proves inadequate. From his experience in getting knowledge at first hand in the laboratory the student comes to feel a desire to get his knowledge of matters which from lack of time and facilities he cannot study by laboratory methods, also at first hand; he wants to consult the original sources of knowledge of the facts given in the text. The value of "supplementary reading," as it is called, is universally recognized in the study of history and literature. It gives the student a breadth and power impossible otherwise. And so it would be in the study of science, if the original sources of information were readily accessible.

"To meet this want is the object of the series of "*Reprints of Science Classics.*" These consist of collections from the writings of the pioneers of science, so edited as to be within the comprehension of the beginner in science. They embrace the sciences of BIOLOGY (BOTANY, ZOOLOGY and PHYSIOLOGY), CHEMISTRY, PHYSICS, ASTRONOMY, PHYSIOGRAPHY, etc., and are accompanied with copious notes, reproduction of cuts and plates, biographical sketches and other matter calculated to arouse interest and hold attention. Each "*Reprint*" is edited by a man who is a teacher as well as a scientist. It is believed that the study of such "*Reprints*" cannot fail to inculcate more of the true scientific spirit into science education and to make it more and more of a training for power."

Very appropriately the first number of this series consists of selections from Lavoisier. *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 genesis of the elements. *P. Hellström. Zeit. anorg. Chem.* 29, *95* (*1901*). — The author considers it a remarkable coincidence that there are seven (eight) groups according to the periodic law and that there are seven groups of crystal forms. By assigning a definite crystalline group to each group in Mendelejeff's table, he believes that everything can be explained from valency down or up. *W. D. B.*

On a new element, europium. *E. Demarçay. Comptes rendus,* 132, *1484* (*1901*). — By fractional crystallization with the double magnesium nitrates in nitric acid solution, the author has separated from a gadolinium earth an oxide with an atomic weight of about 151 and a characteristic spectrum. This new element has been named europium. *W. D. B.*

The unit of the atomic weights. *T. W. Richards. Zeit. anorg. Chem.* 28, *355* (*1901*). — A discussion of the relative merits of hydrogen and oxygen as standard. It seems a pity that the author should have weakened his otherwise excellent argument by an appeal to authority. He argues that the oxygen standard must be accepted because a majority of chemists have voted in favor of it. If there is one thing that is absolutely certain in this world, it is that an appeal to authority is out of place in scientific matters. *W. D. B.*

On neutral affinities. *L. Spiegel. Zeit. anorg. Chem.* 29, *365* (*1902*). — The author believes that ammonia is to be considered as an electrically indifferent substance with a pair of neutralizing (positive and negative) affinities. The nitrogen can therefore become pentavalent only when a positive and a negative radical can be added simultaneously. Platinum tetrachloride is looked upon as a substance with two pairs of neutral affinities. It can therefore take up two more negative radicals and only two, forming K_2PtCl_6. Werner's coordinate number would then be the sum of the active affinities and of the neutral affinity pairs. *W. D. B.*

One-Component Systems

The melting-point of manganese. *W. C. Heraeus. Zeit. Elektrochemie,* 8, *185* (*1902*). — The melting-point was determined in an atmosphere of carefully purified hydrogen in a special Heraeus electric furnace. The metal was placed in an alumina vessel and a melting-point of 1245° C. was obtained. This may be slightly inaccurate owing to the detrimental effect of hydrogen on the thermocouple. An atmosphere of nitrogen could not be used because manganese burns in this gas at about 1210°–1220°. *W. D. B.*

On some allotropic modifications of inorganic compounds. *W. Herz. Zeit. anorg. Chem.* 28, *342* (*1901*). —Nickel sulphide, when first precipitated, redissolves readily in hydrochloric acid. On standing, it loses its power. It oxidizes in the air much more readily than cobalt sulphide. Chromium hydroxide, when first precipitated, is readily soluble in sodium hydroxide, but this is no longer the case after the substance has been dried in vacuum for a few days. On the other hand, there is no inversion point when zinc oxide is heated and the color changes from white to yellow. *W. D. B.*

Two-Component Systems

On the alloys of aluminum and magnesium. *O. Boudouard. Comptes rendus*, 132, *1325* (*1901*). — From the freezing-point curve there would appear to be two compounds, $AlMg_3$ and AlMg. *W. D. B.*

On the silver subhalides. *K. Emszt. Zeit. anorg. Chem.* 28, *346* (*1901*). —Vogel believed that the precipitates obtained by the action of silver nitrate on the cuprous halides were the subhalides of silver, Ag_4X_2, and not a mixture $2Ag + 2AgX$. The author finds that nitric acid, sodium thiosulphate and mercury react with the precipitates as though they were mixtures and not compounds. *W. D. B.*

On the dissociation of chloral hydrate and chloral alcoholate in solutions. *L. Bruner. Bull. Acad. Sci. Cracovie*, 1901, *464*. — Boiling-point determinations with chloral alcoholate in ether, acetone, methyl iodide, ethyl bromide and carbon bisulphide as well as with chloral hydrate in ether and acetone showed that the molecular rise was rather too small than too large. It is doubtful whether this proves anything in regard to dissociation because the solute or its dissociation products might easily be present in the vapor. When chloral hydrate is added to boiling chloroform, methyl iodide, ethyl bromide, or carbon bisulphide, the boiling-point falls and then rises. The author attributes this to the formation of water which slowly distils off; but a slow distillation of this sort would appear to be incompatible with accurate measurements, especially when the solute is volatile. Freezing-point determinations in nitrobenzene and *p*-toluidine showed no dissociation. As dissociation would probably raise and not lower the freezing-point, this is inconclusive. Experiments with $C_6H_4Br_2$ and $C_{10}H_8$ in boiling chloral hydrate gave values from which a heat of vaporization was calculated which agreed fairly with the experimental value.

W. D. B.

Multi-Component Systems

On the solubility of silver sulphate and mercury sulphate. *K. Drucker. Zeit. anorg. Chem.* 28, *361* (*1901*). —The author has determined the solubility of silver sulphate and of mercurous sulphate in water and in solutions of sulphuric acid and of potassium sulphate. The solubilities in water at 25° are 11.71×10^{-4} for mercurous sulphate and $2\ 57 \times 10^{-2}$ for silver sulphate. In the sulphuric acid and potassium sulphate solutions, the solubility is less in each case than in water, but the amount of the change does not conform to the theory. *W. D. B.*

The experimental verification of a law of chemical mechanics. *H. Pélabon. Comptes rendus*, 132, *1411* (*1901*). — The author has studied the reduction of mercury sulphide by hydrogen when hydrogen in excess acts on mercury sulphide, when mercury is present in excess, and when hydrogen sulphide acts on mercury in excess. The experiments were carried out at 440°. *W. D. B.*

On the reduction of silver chloride by hydrogen, and the reverse reaction. *Jouniaux. Comptes rendus*, 132, *1270* (*1901*). — Above 500° the reaction between silver chloride and hydrogen is reversible. From the equilibrium pressures at different temperatures the author calculates a heat of reaction of −6790 cal, while Berthelot found −7000. *W. D. B.*

Action of bases and acids on the salts of amines. *A. Colson. Comptes rendus*, 132, *1563* (*1901*). — The action of piperidine on ammonium chloride sets free ammonia and the action of ammonia on piperidine hydrochloride sets free ammonia. *W. D. B.*

Physical-chemical studies on aqueous ammonia solutions. *F. Goldschmidt. Zeit. anorg. Chem.* 28, *97* (*1901*). — Attempts to determine the amount of hydration of ammonia, from a study of the partial pressures when urea is added to the water, proved futile, presumably because the urea affects the solubility of ammonia in water irrespective of any hydration. The addition of ammonia to solutions of salts of the alkali metals decreases the conductivity and this decrease seems to depend but slightly on the nature of the salt. When ammonia is added to halide solutions of substituted ammonias more marked changes are observed, due doubtless to the partial displacement of the substituted ammonia. *W. D. B.*

On cuprous chloride. *M. Gröger. Zeit. anorg. Chem.* 28, *154* (*1901*). — When cuprous chloride is washed with water in the dark it goes over into cuprous oxide and hydrochloric acid. In the light up to thirty percent of metallic copper may be formed. *W. D. B.*

On the behavior of hydrochloric acid solutions of metastannic acid toward hydrogen sulphide. *G. Jörgensen. Zeit. anorg. Chem.* 28, *140* (*1901*). — The action of hydrogen sulphide on a solution of metastannic acid in dilute hydrochloric acid precipitates chiefly $Sn(OH)_2$ mixed with more or less sulphide. Experiments showed that this precipitate, when digested long enough with a large excess of hydrogen sulphide, was converted completely into sulphide. *W. D. B.*

The action of mannite on bismuth nitrate. *L. Vanino and O. Hauser. Zeit. anorg. Chem.* 28, *210* (*1901*). — The following results are obtained: —

When bismuth nitrate is triturated with a sufficient quantity of mannite, clear aqueous solutions can then be prepared which can be mixed with almost any amount of water without decomposition.

In these solutions there is a slow reaction taking place which replaces nitric acid successively and completely by mannite.

Intermediate and end-products can be isolated, all readily soluble in caustic potash or soda, and some in water. *W. D. B.*

The laws of Gay-Lussac and the dissociation of gaseous compounds. *A. Ponsot. Comptes rendus,* **132**, *1401* (*1901*).—The author concludes that an equilibrium which is not displaced by changing pressure is not displaced by changing temperature, a conclusion which is obviously false. *W. D. B.*

Chemical actions in dissolved or gaseous systems. *A. Ponsot. Comptes rendus,* **132**, *1551* (*1901*).—"The real or virtual formation of the system which tends to exist alone at infinite dilution and which decreases when the solvent is removed, decreases the vapor pressure of the solvent." *W. D. B.*

On ferrite solutions. *F. Haber. Zeit. Elektrochemie,* **7**, *724* (*1901*).—By analysis with stannous chloride, the author succeeds in showing that the change caused by heating an electrolytically prepared solution of ferrate is actually a change to ferrite and nothing else. *W. D. B.*

The neutralization of phosphoric acid. *M. Berthelot. Comptes rendus,* **132**, *1277* (*1901*).—When an aqueous solution of phosphoric acid is neutralized with lime water, there is precipitated $CaHPO_4$. On standing in contact with lime water, this precipitate slowly takes up lime, apparently forming Ca_2PO_4OH. *W. D. B.*

Action of disodium phosphate on silver nitrate. *M. Berthelot. Comptes rendus,* **132**, *1449* (*1901*).—The study of the action of varying quantities of silver nitrate on disodium phosphate leads to the following results:

$$3Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + Na_2HPO_4 + 3NaNO_3.$$

All the silver is precipitated and carries down about five percent of NaH_2PO_4. The solution is alkaline with methyl orange and acid with phenolphthaleine.

$$3Na_2HPO_4 + 6AgNO_3 = 6NaNO_3 + 2Ag_3PO_4 + H_3PO_4.$$

The silver is not entirely precipitated and the precipitate contains some sodium. The solution is acid to methyl orange and to phenolphthaleine; but only about one and one-half times as much alkali is needed with phenolphthaleine as with methyl orange, showing that the acid is not exclusively phosphoric acid as required by the approximate equation.

$$3Na_2HPO_4 + 9AgNO_3 = 3Ag_3PO_4 + 9HNO_3.$$

The silver is not entirely precipitated and the precipitate is not entirely Ag_3PO_4. The solution is acid to both indicators and requires practically the same amount of alkali with each, after precipitation of the dissolved silver, showing that the free acid is mainly nitric acid. *W. D. B.*

Simultaneous action of two bases on phosphoric acid. *M. Berthelot. Comptes rendus,* **132**, *1517* (*1901*).—The pair of bases has always been so selected that one gives a soluble salt with phosphoric acid and the other an insoluble salt. *W. D. B.*

Velocities

The reaction between nitric and hydriodic acids. *A. Eckstädt. Zeit. anorg. Chem.* **29**, *51* (*1901*).—Two very disturbing factors were found to be the presence of traces of ferric oxide in the distilled water and unknown "germs" in the air. Even after eliminating these disturbances, it was not possible to calculate a reaction velocity constant for the reaction between nitrous acid and hydriodic acid, between nitric acid and hydriodic acid, or between nitric acid, nitrous acid and hydriodic acid. Ferrous salts act as catalytic agents, presumably through the formation of a ferrohydriodic acid. Other metals, such as copper and manganese, have no effect. *W. D. B.*

Pseudo-catalytic oxidation. *C. Engler and L. Wöhler. Zeit. anorg. Chem.* 29, *1* (*1901*). — For the case where half the oxygen is made active, the authors write the following equation on the assumption of an intermediate peroxide:

$$AO_2 + B = AO + BO.$$

Under the same assumption, for the case where the catalytic agent so-called does not appear to change, we have the equation

$$AO_2 + 2B = A + 2BO,$$

which may of course take place in two stages. The authors discuss three styles of oxygen transferrers:

1. The noble and semi-noble metals and their oxides.
2. Oxides and salts of metals with readily changing valence.
3. Organic ferments.

In all these cases, the authors believe that an intermediate product is formed, this product being probably PtO_2 or PtO_2H_2O in the case of platinum black. *W. D. B.*

On chromic chloride. *P. Rohland. Zeit. anorg. Chem.* 29, *159* (*1901*). — The change of the anhydrous insoluble violet chromic chloride into the soluble modification is very much accelerated by the metals K, Na, Mg, Al, Zn, Cd, Sn; markedly accelerated by the metals Fe, Ni, Pb; slightly accelerated by the metals Sb, Bi, Au, Hg, Ag; and not accelerated by platinum or gold. The author believes that the real accelerating agent is chromous chloride, which is formed to a greater or lesser extent by the action of the different metals on chromic chloride. *W. D. B.*

On the rate of solution of solids, II. *L. Bruner and S. Tolloczko. Zeit. anorg. Chem.* 28, *314* (*1901*). — The authors show that the rate of stirring has an effect on the rate of solution and also that practically invisible solid particles may be thrown off, which play havoc with the experimental results if not guarded against. Contrary to the view of Drucker (5, 416) the rate of solution is independent of the volume. The structure of the solid has an effect. *W. D. B.*

On the rate of solution. *K. Drucker. Zeit. anorg. Chem.* 29, *459* (*1902*). — A reply to Bruner and Tolloczko (preceding review) in which the author states that he does not consider their criticisms well founded. *W. D. B.*

Electromotive Forces

The nitrogen-hydrogen gas cell. *E. Baur. Zeit. anorg. Chem.* 29, *305* (*1902*). — Nitrogen and hydrogen electrodes in a solution of ammonium nitrate in ammonia have an electromotive force of about 0.6 volt and ammonia is formed when a current passes. Experiments on decomposition voltages gave no sharp value; but the value is in the neighborhood of 0.6 volt. *W. D. B.*

The hydrogen-chlorine gas cell. *E. Müller. Zeit. Elektrochemie*, 7, *750* (*1901*). — The author gives his reasons for not accepting the conclusions of Akunoff (5, 269). He believes it more than probable that the first decomposition voltage in the case of hydrochloric acid refers to the formation of hypochlorous acid and not to chlorine. *W. D. B.*

On the equilibrium relations at gas electrodes. *E. Bose. Zeit. Elektrochemie*, 7, *817* (*1901*). — Attention is called to the fact that the oxygen electrode in sulphuric acid is a very uncertain thing since there appear to be two hydrogen peroxides there, and there may be persulphuric acid. At the chlorine electrode there is hypochlorous acid. The author proposes naming an electrode after the substance which is added or removed in order to keep near equilibrium. *W. D. B.*

Contribution to the theory of lead accumulators. *E. Abel. Zeit. Elektrochemie*, 7, *731* (*1901*). — The author shows that the lead accumulator can be considered as a concentration cell with respect to quadrivalent lead.

W. D. B.

On electrolytic short circuits in concentration cells. *O. Sackur. Zeit. Elektrochemie*, 7, *781* (*1901*). — The potential difference between two differently concentrated solutions of the same salt can be reduced practically to zero, according to Nernst, by adding to each solution equal quantities of a salt with a common ion. This is called an "electrolytic short circuit". The author has tested the formula of Abegg and Bose for a number of cases and finds the theory confirmed to within several tenths of a millivolt. This seems pretty satisfactory, but it must be remembered that any variation from the theory would probably fall within the same limits, so that the experiments are conclusive only so long as one is certain about the correctness of the premises.

W. D. B.

Recent work on accumulators of other metals than lead. *S. v. Lascynski. Zeit. Elektrochemie*, 7, *821* (*1901*). — The author discusses the silver peroxide, the nickel oxide, iron oxide and cadmium electrodes. As a laboratory experiment only he takes up the cell

$$NiO \mid K_2CO_3 \mid ZnCO_3.$$

W. D. B.

On contact electromotive force and the theory of ions. *E. Rothé. Comptes rendus*, 132, *1478* (*1901*). — The author has determined the electromotive forces corresponding to the maximum surface tension of mercury in hydrochloric acid and sulphuric acid solutions. The values increase with increasing concentration. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Experiments on the preparation of aluminum. *F. Haber and R. Geipert. Zeit. Elektrochemie*, 8, *1*, *26* (*1902*). — By melting a bath of cryolite, aluminum fluoride and alumina in a small carbon crucible by means of the arc and then electrolyzing with six to ten volts and fifty amperes, it was possible to get 4 to 5 g aluminum. The method was not satisfactory because the contents of the crucible solidified in the course of an hour. The later experiments were carried on in a larger vessel and with a current of 300-400 amperes. The potential difference is seven volts, running up to ten as the alumina is consumed. The authors obtained a very pure aluminum even though they did not use purified alumina. In a discussion with H. Goldschmidt they make the point that most of the silica in European aluminum comes from the carbon anodes and that the exceeding purity of the American aluminum is due largely to the high-grade anodes used. *W. D. B.*

On the current and energy efficiencies in the electrolytic production of alkali hypochlorites and chlorates. *F. Foerster and E. Müller. Zeit. Elektrochemie*, 8, *8* (*1902*). — The addition of chromate and the use of platinum black electrodes have made it possible to make hypochlorite containing 23 g bleaching chlorine per liter with a current efficiency of 95 percent. The platinum black electrodes, besides increasing the efficiency, lower the voltage by nearly one volt. By adding small amounts of hydrochloric acid every little while after the hypochlorite concentration reaches its maximum the authors have obtained an efficiency of 94 percent for chlorate on a run lasting seventy hours. At the end of twenty-four hours there had been a current efficiency of 98 percent at a mean voltage of 3.66 V. This corresponds to 12.5 kilowatt hours per kilogram of chlorate, a most remarkable showing which might possibly be further improved by working at a lower current density. *W. D. B.*

Electrochemical reduction of ketones. *K. Elbs. Zeit. Elektrochemie*, 7, *644* (*1901*). — The electrodes are lead; the anode solution is a soda solution or ten percent sulphuric acid. The cathode solution consists of the ketone dissolved in aqueous alcohol to which has been added 2 percent sodium acetate or one percent sulphuric acid. The current density is 0.5-1.5 amp/qdm and the temperature 50°-90°. In alkaline solutions aliphatic ketones give a mixture of alcohol and pinacone, while aromatic ketones give secondary alcohols. In acid solutions, aromatic ketones give pinacones. The yield is sometimes as high as ninety percent. *W. D. B.*

The electrolytic formation of perchlorates. *F. Winteler. Zeit. Elektrochemie*, 7, *635* (*1901*). — The formation of perchlorate from chlorate increases with increasing anode density and with falling temperature; it is practically independent of the concentration of perchlorate and chlorate until that of the latter becomes very small. Starting from chloride, no perchlorate is formed until the major part of the chloride has been changed to chlorate. The perchlorate appears the sooner, the more favorable the conditions for its formation.
W. D. B.

On the electrolytic oxidation of *p*-toluylic acid. *H. Labhardt and R. Z. Schoche. Zeit. Elektrochemie*, 8, *93* (*1902*). — In alkaline solution *p*-toluylic acid can be oxidized to terephthalic acid, though not quantitatively. With a high current density at the anode the oxidation efficiency is higher but the oxidation runs too far. With a lower current density, a purer terephthalic acid is obtained, but with a lesser electrical efficiency. Increase in the concentration of the *p*-toluylic acid and of the alkali increases the efficiency. A smooth platinum anode works much better than an anode of mercury, gold, silver, copper, iron, or nickel. *W. D. B.*

On the electrochemical behavior of acetylene. *A. Coehn. Zeit. Elektrochemie*, 7, *681* (*1901*). — The decomposition voltage of a caustic potash solution is lowered by passing in acetylene at the anode. By careful regulation of the voltage, it was possible to obtain a quantitative yield of formic acid. Similar experiments with sulphuric acid gave a quantitative formation of acetic acid, the acetylene forming aldehyde spontaneously in presence of sulphuric acid. *W. D. B.*

On alkyl ammonium amalgams. *F. Crotogino. Zeit. Elektrochemie*, 7, *648* (*1901*). — The author electrolyzed substituted ammonium oxalates in presence of a flowing mercury cathode. With methyl amine an amalgam was obtained which yielded methyl amine hydrochloride when treated with hydrochloric acid. With dimethyl ammonium oxalate an amalgam was obtained which gave methyl amine hydrochloride and ethane, but no dimethylamine hydrochloride. No amalgam could be obtained with trimethyl or tetramethyl ammonium oxalate. *W. D. B.*

On the electrolytic formation of alkali ferrates. *W. Pick. Zeit. Elektrochemie*, 7, *713* (*1901*). — The author sums up his results as follows: —

Every iron forms ferrate when made anode in concentrated alkali solutions, cast iron most readily, next steel, and least readily wrought iron.

Pieces of wrought iron or steel, which do not at first yield ferrate, can be made to do so by making them alternately anode and cathode for a few seconds at a time or by a long continued weak anodic polarization in concentrated alkali.

Iron, which has served in the formation of ferrate, has a dark color, is passive, and is very resistant to rusting. The current yield of ferrate is better in caustic soda than in caustic potash. The yield increases with increasing concentration of the electrolyte.

With a current density of 0.1 amp/qdm in caustic soda the yield is 47 percent for cast iron, 26 percent for steel, and 14 percent for wrought iron; in caustic potash the corresponding figures are thirty-seven, thirteen and two.

Raising the temperature increases the yield of ferrate. Iron, electrolytically precipitated in a Classen platinum dish, gives practically no ferrate at 0°, a sixteen percent yield at 30°, and eighty to one hundred percent yield at 70°.

The yields of ferrate and of oxygen sum up one hundred percent. Ferrite is therefore not formed primarily. The potential difference ferrite ⟷ ferrate is about -0.78 V, that of concentrated alkali against active iron about $+0.6$ V. Both values change but slightly between 0° and 70°. The potential of the passive iron, which has been used for forming ferrate shows about the same potential against ferrate solution at low temperatures as the value for ferrite ⟷ ferrate; at higher temperatures it changes by several tenths of a volt towards the cathode side. *W. D. B.*

On the electrolytic reduction of aromatic nitro compounds to amines. *A. Chilesotti. Zeit. Elektrochemie*, 7, *768* (*1901*). — The author publishes experiments to test the Boehringer process in which small amounts of a tin, copper, or iron salt are added to the cathode chamber. The reduction is to the amine, and current efficiencies of 70-90 percent are obtained. This phenomenon is thought to be due to the chemical reduction of phenyl hydroxylamine by the finely divided tin or copper precipitated by the current. *W. D. B.*

On electrolytic chromium. *B. Neumann. Zeit. Elektrochemie*, 7, *656* (*1901*). — Within certain definite limits of current density, temperature and concentration, chromium can be precipitated from an aqueous solution of the chloride, sulphate or acetate. In some instances a current efficiency of 85 percent was obtained. *W. D. B.*

Simultaneous precipitation of iron and nickel from mixed sulphate solutions. *F. W. Küster. Zeit. Elektrochemie*, 7, *688* (*1901*). — From a mixed solution of nickel and iron sulphates, nickel alone precipitates provided the voltage be kept low enough. With increasing current density, iron appears in small amounts, suddenly jumping to a high value and then falling off a little. The author makes the tentative suggestion that possibly a compound is precipitated, Fe_2Ni for instance. *W. D. B.*

The quantitative determination of cadmium. *E. H. Miller and R. W. Page. Zeit. anorg. Chem.* 28, *233* (*1901*). — After a comparison of the different methods of determining cadmium, the authors conclude that the electrolytic determination in cyanide solution is the best provided that an excess of potassium cyanide is not used and that other salts are not present. *W. D. B.*

Electrolytic separation of cobalt and nickel. *D. Balachowsky. Comptes rendus*, 132, *1492* (*1901*). — The mixture of cobalt and nickel is dissolved in acetic acid. For every 0.3 g of metal there is added 3 g ammonium sulphocyanate, 1 g of urea and 1-2 cc. ammonia to neutralize the excess of acid. The solution is made up to 100 cc and electrolyzed with a potential difference not exceeding one volt and a current density of not less than 0.8 amp/qdm. The temperature is 70°-80° and the nickel is precipitated as sulphide. *W. D. B.*

On the electrochemical behavior of nickel ammonium sulphate. *W. Pfanhauser. Zeit. Elektrochemie*, 7, *698* (*1901*). — The author sums up some of his results somewhat as follows:

The addition of ammonium sulphate to a solution of nickel sulphate causes the formation of the complex double salt, $(NH_4)_2Ni(SO_4)_2 + 6H_2O$, and increases the specific conductivity of the solution.

In concentrated solution the double salt dissociates chiefly into $2\overset{+}{NH_4}$ and $Ni(SO_4)_2$. In more dilute solution the complex anion dissociates further. If stirring is eliminated there will be decomposition of the double salt at the cathode and formation at the anode where the double salt often crystallizes.

At the anode the nickelous sulphate is oxidized to nickelic sulphate, which generates a counter-electromotive force. The nickelic sulphate, being instable, decomposes, precipitating black $Ni(OH)_3$.

When low current densities are used, the precipitation of nickel is not a

primary reaction. With increasing current density, primary precipitation of nickel may occur, the metal coming down as a powder. By stirring, one can of course use a higher current density than otherwise; also by heating.
W. D. B.

Periodic phenomena during electrolysis. *K. Koelichen. Zeit. Elektrochemie*, 7, *629* (*1901*). — When a solution of an alkali sulphide is electrolyzed, under suitable conditions, periodic phenomena are obtained, due to the alternating precipitation and dissolving of sulphur at the anode. *W. D. B.*

On the constitution of semi-complex salts as shown by transference experiments. *E. Rieger. Zeit. Elektrochemie*, 7, *863*, *871* (*1901*). — By semi-complex salts the author means salts which show more or less of the properties of the components in dilute solution. With potassium mercuric iodide, potassium silver iodide, potassium mercuric cyanide, potassium zinc cyanide, potassium cadmium cyanide, potassium ferro-oxalate and potassium ferri-oxalate, the nobler metal concentrates at the anode. With potassium copper sulphate, copper passes to the cathode, but the transference number is distinctly smaller than it would be if no copper were present as part of the anion. *W. D. B.*

An apparatus illustrating ion velocities and transference. *B. D. Steele. Zeit. Elektrochemie*, 7, *729* (*1901*). — The author has devised an apparatus differing somewhat in construction from those of Müller, Kohlrausch, and Miller and Kenrick. *W. D. B.*

A modified Moissan furnace. *L. Liebmann. Zeit. Elektrochemie*, 8, *125* (*1902*). — The essential feature of the furnace is that it consists of two kinds of stone, an outer infusible and a replaceable inner layer of a Hildesheim stone which is soft enough to be easily cut. The inner stone, in which the fusion takes place, is used but once and costs ten pfennigs each time. *W. D. B.*

Sensitiveness of the higher vegetables to the useful action of potassium salts. *H. Coupin. Comptes rendus*, 132, *1582* (*1901*). — Experiments with Bordeaux wheat show that the beneficial effects of potassium salts are noticeable in the following concentrations in grams per gram of solution: carbonate 0.000,000,1; phosphate 0.000,000,25; sulphate + 0.000,000,8; chloride 0.000,003; nitrate 0.000,004. *W. D. B.*

Contributions to the constitution of inorganic compounds, IV. *A. Werner and C. Herty. Zeit. phys. Chem.* 38, *331* (*1901*). — Conductivity determinations of metal ammonia salts. In many instances the conductivity of the solution increases on standing. The article also contains a polemic against Petersen. *W. D. B.*

On the number of ions in metal ammonia compounds. *E. Petersen. Zeit. phys. Chem.* 39, *249* (*1901*). — A reply to Werner and Herty (preceding review). *W. D. B.*

On neutral salts. *K. Arndt. Zeit. anorg. Chem.* 28, *364* (*1901*). — The author believes that salts like NaCl and KCl are really slightly acid in solution and that salts like sodium sulphate are slightly alkaline in solution. Starting from this hypothesis, the author attempts a qualitative explanation of the action

of the neutral salts on sugar inversion, etc. The difficulty is that this hypothesis cannot account for more than the sign of the effect. It is much more likely that the effect is connected with the change of solubility of the catalytic agent.
W. D. B.

On the validity of the mass law for strong electrolytes. *H. v. Steinwehr. Zeit. Elektrochemie*, 7, *685* (*1901*). — Figures are given to show that the dilution law holds for strong electrolytes provided we take into account the change of the internal pressure and the contraction. *W. D. B.*

On the dissociation of strong electrolytes. *O. Sackur. Zeit. Elektrochemie*, 7, *784* (*1901*). — A general review of the recent discussions of the dilution law. The author has made some measurements on the conductivity of mixed electrolytes and finds the observed values always lower than the calculated ones.
W. D. B.

Studies in neutralization. *M. Berthelot. Comptes rendus*, 132, *1377* (*1901*). — A general discussion of indicators with special reference to the titration of organic acids. *W. D. B.*

On artificial graphite and on platinum iridium as anode materials. *F. Foerster. Zeit. Elektrochemie*, 8, *143* (*1902*). — Experiments with Acheson graphite showed that it was scarcely attacked in eight percent caustic soda at 20°, slightly attacked in sodium chloride solution and readily attacked in sulphuric acid solution. The electrodes contain no humus and are preferable to carbon anodes at all times. The author believes that the platinum iridium electrodes of Heraeus are preferable to graphite for the manufacture of chlorate.
W. D. B.

On diaphragms. *M. LeBlanc. Zeit. Elektrochemie*, 7, *653* (*1901*). — A new diaphragm material is described, differing but slightly in composition from the one obtained before (5, 273), but having a much lower electrical resistance. The material allows rapid diffusion; but this can be checked without affecting the electrical resistance appreciably by saturating the walls with a solution of water glass and a soluble salt, and then treating with an acid. Since the rate of diffusion decreases inversely as the square of the ratio of the diameters and the conductivity only inversely, a fine-pored diaphragm may be almost impervious to diffusion and yet offer very slight resistance to the current. Something of this sort seems to have been approximated experimentally. *W. D. B.*

Dielectricity and Optics

Determination of the dielectric constants of some substances of the pyridine and piperidine series by Drude's method. *R. Ladenburg. Zeit. Elektrochemie*, 7, *815* (*1901*). — Eighteen substances were studied. Replacement of hydrogen lowers the dielectric constant, the lowering being greater the more carbon there is in the alkyl group, and the nearer the replacing group is to the nitrogen.
W. D. B.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA.]

MOLECULAR ATTRACTION[1]

BY J. E. MILLS

In 1887 van 't Hoff first applied the gas law $PV = RT$ to solutions and showed that the molecules of a dissolved substance exert the same pressure, as osmotic pressure, that a gaseous molecule would exert under the same conditions of volume and temperature. Now, so rapidly has evidence accumulated, the law is almost universally accepted as true for moderate ranges of concentration. If the dissolved substance dissociates, the number of molecules in the solution must be increased, ($PV/i = RT$, i being the van 't Hoff coefficient), but the principle underlying the law remains unchanged — a dissolved molecule exerts the same pressure as would a gaseous molecule under similar conditions.

Since a gaseous molecule exerts pressure because of its translational energy, it seems a necessary conclusion that if a dissolved molecule exerts an equal pressure its translational energy must be the same. Mechanically it is quite impossible that the dissolved molecules should have and maintain a different average amount of translational energy than is possessed by the molecules of the solvent. So we reach a conclusion, which has been expressed by others,[2] that the average translational energy of gaseous and liquid molecules must at the same temperature be equal.

A study of the specific heat of gases makes it clearly probable, and the conclusion is widely accepted, that the total energy of a gaseous molecule, exclusive of the energy which holds the molecule together and of extraneous forces, is proportional to

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[1] Taken from the author's thesis presented to the Faculty of the University of North Carolina for the Degree of Doctor of Philosophy.

its translational energy. At least this seems to be true until we approach the temperature where the molecule is broken apart. It appears reasonable therefore to conclude that the total energy *per se* of a molecule must be the same in the liquid as in the gaseous state, the temperature being the same. If at a given temperature a given weight of gas represents more energy than the same weight of the substance as a liquid, the extra energy of the gas must be energy of position only. It cannot be held to be energy of motion so long as the gas law $PV = RT$ be found true for solutions without surrendering all that is essential in the kinetic theory of gases.

Upon this belief the following work is based and the assumption is justified by the result.

The energy which is added to change a liquid into a gas must then be spent solely in overcoming the external pressure and in altering the distance apart of the molecules. (Unless the molecule breaks apart also or nears the point of disruption.)

Denoting the energy spent in overcoming the external pressure by E_1 this energy can be calculated from the equation

$$E_1 = 0.024\,P(V - v) \text{ cals}, \tag{1}$$

where P is the pressure in atmospheres,[107] and V and v the volumes after and before expansion. The calorie was assumed to be from 0° to 1° C, because most of the data used was referred to that standard. Rowland's value of the therm, as corrected by Day,[2] was used, 41.88×10^{10} ergs from 15° to 16° C, and the specific heat of water at 0° C was taken to be 1.007 referred to the specific heat of water at 15° as unit.[3]

The energy spent in overcoming the molecular attraction is denoted by E_2 and the total "latent" heat supplied by L. Therefore we have

$$L - E_1 = E_2. \tag{2}$$

In the theory of liquids it is usual to consider molecular action upon any individual molecule as limited to a certain sphere around that molecule. Imagine such a molecular sphere. If the molecules contained therein are very numerous we can suppose them evenly distributed around the central molecule. Suppose an expansion of the system to take place so that the molecules formerly contained in the sphere are now evenly distributed throughout a larger sphere. Let v and V represent the volumes of the two spheres and n the number of molecules. Then the distance between the molecules of the two spheres are $\sqrt[3]{v/n}$ and $\sqrt[3]{V/n}$ respectively. Now assuming that the attraction between the molecules varies inversely as the square of the distance apart of the molecules we can derive a means of testing the assumption as follows:

Let a certain molecule be distant from the central molecule by $x\sqrt[3]{v/n}$ before expansion. After expansion the same molecule must be distant $x\sqrt[3]{V/n}$. The energy spent in moving this molecule against the attraction of the central molecule is from mechanics,

$$(3)\qquad m\mu\left(\frac{1}{x\sqrt[3]{v/n}}-\frac{1}{x\sqrt[3]{V/n}}\right)=\frac{m\mu}{x}\left(\frac{1}{\sqrt[3]{v/n}}-\frac{1}{\sqrt[3]{V/n}}\right).$$

where m is the mass of the molecule and μ the absolute attraction at unit distance from the central molecule.

If we in turn consider similarly the energy spent in moving each molecule of the sphere and sum up, we have for the total energy necessary to overcome the attraction of the central molecule in producing the given expansion

$$(4)\qquad E_m=m\mu\left(\frac{1}{\sqrt[3]{v/n}}-\frac{1}{\sqrt[3]{V/n}}\right)\left(\frac{1}{x}+\frac{1}{x_1}+\cdots+\frac{1}{x_{n-2}}\right).$$

This latter factor we will call c'.

This expression represents the energy E_m spent by the molecules of the mass in moving away from a single molecule during a given expansion. Hence to get the total energy of expansion for a given mass M we must multiply the above expression by one-half the number of molecules, since of each pair of molecules compared one molecule only is considered moved. This gives

$$E_M=\frac{nm\mu}{2}c'\left(\frac{1}{\sqrt[3]{v/n}}-\frac{1}{\sqrt[3]{V/n}}\right).$$

Letting d and D represent the densities corresponding to volumes v and V we have putting

$$v = \frac{M}{d} = \frac{nm}{d}, \ V = \frac{nm}{D}, \ nm = M, \ \frac{c'}{2} = c,$$

$$E_M = \frac{M\mu c}{\sqrt[3]{m}}(\sqrt[3]{d} - \sqrt[3]{D}), \tag{5}$$

where E_M is the energy necessary to produce the expansion in mass M from density d to D, m being the molecular weight of a molecule and μ its absolute attraction. c is an unknown constant.

If we consider this last equation to hold during the change of volume of a liquid into a gas at temperature T then we have referring to equation 2,

$$L_T - E_{1T} = \frac{M\mu c}{\sqrt[3]{m}}(\sqrt[3]{d_T} - \sqrt[3]{D_T}), \text{ and at } t, \tag{6}$$

$$L_t - E_{1t} = \frac{M\mu c}{\sqrt[3]{m}}(\sqrt[3]{d_t} - \sqrt[3]{D_t}),$$

the subscripts signifying the temperature of the observation. Now making the supposition that n remains constant with the temperature, we obtain the ratio of the two equations

$$\frac{L_T - E_{1T}}{L_t - E_{1t}} = \frac{\sqrt[3]{d_T} - \sqrt[3]{D_T}}{\sqrt[3]{d_t} - \sqrt[3]{D_t}}, \tag{7}$$

an equation in which all of the quantities can be measured and *which therefore affords an experimental test of the assumption that the molecular attraction varies inversely as the square of the distance from the molecule and does not vary with the temperature.*

The result of this test is shown in Table I. Columns 1–7 contain the data with the citations of authority. No actual determination of the density of the gas could be obtained for CH_3OH, C_2H_5OH, $(C_2H_5)_2O$, CS_2, C_6H_6, and CCl_4 at the desired temperatures. The density was therefere calculated for these gases from the equation

$$D = \frac{0.01227\, p.m}{t}, \tag{8}$$

based on the gas laws and the density of hydrogen $0.0_4898765$.[59] The error thus introduced is probably very small, since for the indicated pressure the gases, if normal, obey the gas laws closely. Column 9 gives E_i calculated from equation 1. Column 10 gives the two temperatures T and *t* concerned in the calculations which follow on the same line. The ratio of $(L_T - E_{iT})/(L_t - E_{it})$ is given in column 11 and the ratio of $(\sqrt[3]{d_T} - \sqrt[3]{D_T})/(\sqrt[3]{d_t} - \sqrt[3]{D_t})$ is given in column 12.

Of the twenty ratios shown in columns 11 and 12, from ten different substances, only three, N_2O, from −20° to 0°, and from −20° to 20°, SO_2, from 0° to 65°, fail to agree by as much as six percent. The agreement of the ratios shown may be regarded on the whole as quite satisfactory, since eight measurements, some of them difficult, enter into each calculation, thus making the probable error of observation quite large.

It will be noticed, however, that within the limits for which equation 7 is tested we are really getting on both sides of the equation the ratios of two numbers which are very nearly equal, and from this standpoint the agreement might appear to be quite accidental. It becomes necessary therefore to look at the subject from a different point of view.

If the ideas which have been presented are correct, then at temperature T, $L_T - E_{iT}$ represents the energy required to produce a given change in the density of the substance. At temperature *t* a different change in the density of the substance occurs. How much latent heat will now be required to produce this new change in the density, if the law of attraction is the inverse square of the distance? Or, in other words, the internal latent heat of a substance changes with the temperature. How much of the change can be accounted for on the supposition that it is caused solely by the corresponding changes in the density of the body, the attraction to vary as described, viz., inversely with the distance apart of the molecules?

We must have $(L_T - E_{iT}) - (L_t - E_{it}) =$ change in internal latent heat with the temperature, as an observed fact simply. Since from equation 7

TABLE I.

1 Substance	2 Molecular weight	3 Temperature, °C.	4 Pressure in atmospheres	Authority	5 Density of the liquid	Authority	6 Density of the gas	Authority	7 Latent heat	Authority
Water, H_2O	17.88	0°	0.006	5	0.99987	6	0.0_5475	7	597.6	8
		100	1		0.95865		0.0_3606		535.0	
		200	15.38		0.900		0.0_2795		464.3	
Methyl alcohol, CH_3OH	31.78	0	0.037	9	0.816	12	0.0_4531		289.17	15
		66	1	10	0.748	13	0.00115		265.67	16
		100	3.165	11	0.7135	14	0.00331		246.01	15
Carbon dioxide, CO_2	43.66	—25	17.12	17	1.025	18	0.044	18	72.23	19
		0	35.40		0.905		0.097		56.86	20
		22.04	61.75		0.725		0.220		31.80	19
Nitrous oxide, N_2O	43.74	—20	23.14	21	0.996	22	0.044	22	66.90	23
		0	36.08		0.902		0.081		59.50	
		20	55.30		0.755		0.151		43.25	
Ethyl alcohol, C_2H_5OH	45.68	0	0.016	24	0.8075	26	0.0_4336		236.5	28
		78.2	1	25	0.7374	27	0.00160		205.7	29
Sulphur dioxide, SO_2	63.6	0	1.52	30	1.434	33	0.00447	33	91.45	34
		30	4.56	31	1.352		0.0136		80.5	
		65	12.11	32	1.245		0.0361		68.4	
Ethyl ether, $(C_2H_5)_2O$	73.48	0	0.243	35	0.736	37	0.0_3802		93.75	39
		34.9	1	36	0.696	38	0.00293		88.88	40
Carbon disulphide, CS_2	75.56	0	0.168	41	1.295	43	0.0_3572		89.75	45
		46.2	1	42	1.225	44	0.00291		85.24	46
Benzene, C_6H_6	77.4	0	0.034	47	0.899	49	0.0_3119		109.00	51
		80.4	1	48	0.813	50	0.00268		93.18	52
Carbon tetrachloride, CCl_4	152.62	0	0.043	53	1.631	55	0.0_3298		52.00	57
		76.5	1	54	1.480	56	0.00536		46.35	58

TABLE I.—(*Continued*)

Substance	8 Latent heat calculated	9 E_1	10 Temperature, °C.	11 $\frac{L_T - E_{1T}}{L_t - E_{1t}}$	12 $\frac{\sqrt[3]{d_T} - \sqrt[3]{D_T}}{\sqrt[3]{d_t} - \sqrt[3]{D_t}}$	13 Observed	14 Calculated	15 Observed minus calculated	16 $L - E_1$	17 $\sqrt[3]{d} - \sqrt[3]{D}$
Water, H_2O	....	30.34	0, 100°	1.15	1.09	71.9	47.2	24.7	567.3	0.9831
	559.7	39.57	0, 200	1.35	1.285	149.0	125.6	23.4	495.4	0.9014
	487.7	45.99	100, 200	1.18	1.18	77.1	78.4	—1.3	418.3	0.7655
Methyl alcohol, CH_3OH	....	16.81	0, 66	1.11	1.12	27.53	28.55	—1.02	272 36	0.897
	264.65	20.84	0, 100	1.22	1.205	49.20	46.31	2.89	244.83	0.803
	248.90	22.85	66, 100	1.10	1.08	21.67	17.76	3.91	223.16	0.7445
Carbon dioxide, CO_2	....	8.94	—25, 0	1.29	1.29	14.25	14.21	0.04	63.29	0.655
	56.90	7.82	—25, 22	2.33	2.21	36.18	34.79	1.39	49.04	0.508
	33.19	4.69	0, 22	1.81	1.72	22.93	20.58	2.35	27.11	0.295
Nitrous oxide, N_2O	....	12.07	—20, 0	1.10	1.21	5.06	9.52	—4.46	54.83	0.6456
	55.04	9.73	—20, 20	1.51	1.71	18.61	22.72	—4.11	49.77	0.5335
	39.14	7.03	0, 20	1.37	1.41	13.55	13.20	0.35	36.22	0.3781
Ethyl alcohol, C_2H_5OH	....	11.71	0, 78	1.18	1.14	34.13	28.29	5.84	224.79	0.899
	211.54	15.04							190.66	0.786
Sulphur dioxide, SO_2	....	8.14	0, 30	1.15	1.11	10.78	8.31	2.47	83.31	0.963
	82.97	7.97	0, 65	1.375	1.29	22.73	18.77	3.96	72.53	0.867
	73.67	7.82	30, 65	1.20	1.16	11.95	10.46	1.49	60.58	0.746
Ethyl ether, $(C_2H_5)_2O$	....	7.26	0, 34.9	1.07	1.09	5.77	7.15	—1.38	86.49	0.8100
	87.50	8.16							80.72	0.743
Carbon disulphide, CS_2	....	7.06	0, 46.2	1.07	1.09	5.69	6.57	—0.88	82.69	1.007
	84.35	8.23							77.01	0.927
Benzene, C_6H_6	....	6.90	0, 80	1.21	1.15	17.85	13.60	4.25	102.1	0.916
	97.43	8.93							84.25	0.794
Carbon tetrachloride, CCl_4	....	3.50	0, 76.5	1.16	1.15	6.61	6.33	0.28	48.50	1.110
	46.63	4.46							41.89	0.965

$$L_t - E_{1t} = \frac{(L_T - E_{1T})(\sqrt[3]{d_t} - \sqrt[3]{D_t})}{\sqrt[3]{d_T} - \sqrt[3]{D_T}},$$

we also have

$$L_T - E_{1T} - \frac{(L_T - E_{1T})(\sqrt[3]{d_t} - \sqrt[3]{D_t})}{\sqrt[3]{d_T} - \sqrt[3]{D_T}}$$

= change in internal heat calculated upon the supposition that the attraction varies as the inverse square of the distance apart of the molecules. Or combining the two equations,

$$(9) \qquad (L_T - E_{1T}) - (L_t - E_{1t}) =$$

$$L_T - E_{1T} - \frac{(L_T - E_{1T})(\sqrt[3]{d_t} - \sqrt[3]{D_t})}{\sqrt[3]{d_T} - \sqrt[3]{D_T}}.$$

In Table I., column 13 gives the observed differences as shown by the left-hand side of the above equation. Column 14 gives the calculated change in the latent heat as shown by the right-hand side of the equation. Column 15 gives the differences between the two values, the calculated being subtracted from the observed.

In eight out of twenty comparisons the error is more than three cals. But in only three cases, H_2O, 0° to 100° and 0° to 200°, C_2H_5OH, 0° to 78°, is the error more than five cals. The following points are to be noted:

1. By the subtraction the sum total of the error introduced by all of the measurements is left in the result. This tends to magnify an error *relatively* small.

2. A study of the measurements entering into the calculation and a comparison of these and similar measurements which have been made will show that an error of three cals is easily within the limits of error of the measurements as taken. Even an error of four cals is not excessively large. For instance different measurements of the latent heat of water at 0° and at 100° show an error by difference of twenty-one cals. Alcohol, which shows the next largest variation in column 15, shows similarly a possible error of 6.5 cals. As to N_2O, the third largest variation, an inspection of the density curve as taken, shows that the measurements are irregular and somewhat uncertain.

3. The attraction was assumed constant, while it may vary slightly with the temperature owing to a loosening of chemical bonds, etc.

4. No allowance was made for molecular association or dissociation. Even if such a dissociation is caused by the attraction which we are considering, yet if it persisted in the gaseous state it would modify the value of E_i and would thus produce quite an appreciable effect. Moreover n would become variable, not a constant, and the method employed to calculate the average distance apart of the molecules would not hold good.

5. The fact that in the case of N_2O and H_2O agreement is reached in one case would seem to indicate either an error in some measurement (for the other cases) or else the existence of some temporary condition, as molecular association, causing the variation.

6. *The general correspondence of the two sets of values is too marked to be accidental.* In the case of water certainly, and probably in several other cases, the disagreement is too pronounced to be laid upon the experimental error. It may be that one or several of the causes above-mentioned are sufficient to explain the discrepancy. See also the remark on page 231.

Column 8, Table I., contains the latent heat calculated from the equation

$$(10) \qquad L_t = \frac{(L_T - E_{iT})(\sqrt[3]{d_t} - \sqrt[3]{D_t})}{\sqrt[3]{d_T} - \sqrt[3]{D_T}} + E_{it},$$

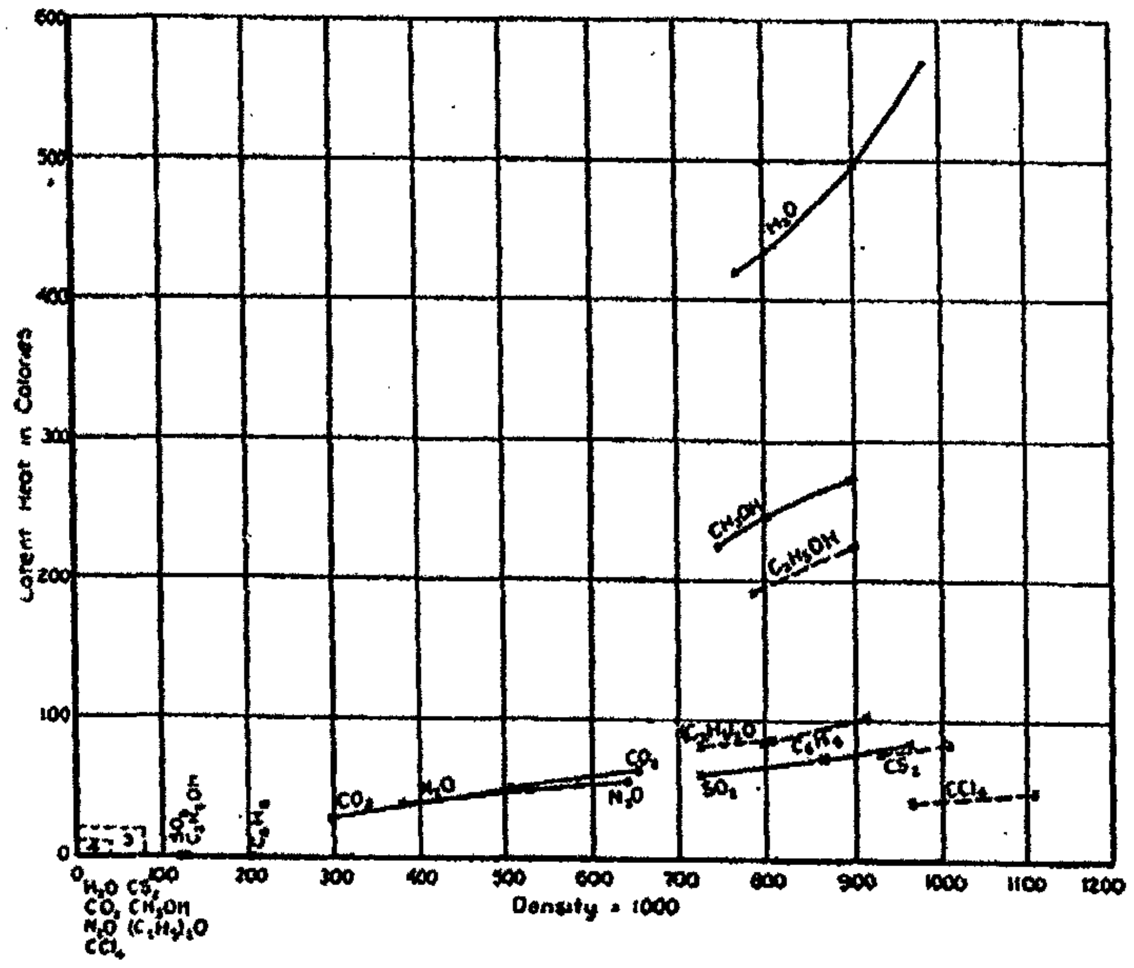
obtained by solving equation 7 for L_t. The observed latent heat used in this calculation is that given in column 7 for the temperature which corresponds to the blank in column 8.

By reference to equation 6, and the supposition there made, it will be seen that $\frac{M\mu c}{\sqrt[3]{m}}$ = constant, and we can therefore write the equation

$$(11) \qquad L_T - E_{iT} = C(\sqrt[3]{d_T} - \sqrt[3]{D_T}).$$

But this is the equation of a *straight line through the origin of coordinates* if $L - E_i$ and $\sqrt[3]{d} - \sqrt[3]{D}$ be regarded as the variables. This gives us a method of showing to the eye the approximation of the formula.

In Diagram 1, $L - E_1$ (Table I., column 16) are plotted as ordinates and $\sqrt[3]{d} - \sqrt[3]{D}$ (Table I., column 17) as abscissae. When three observations are shown, as in the case of N_2O, H_2O, CO_2, SO_2, and CH_3OH, the dots are connected by a heavy line. *It will be seen that the curvature of these lines is but slight.*



When only two observations were available the observations are connected by a dotted line. If these lines are prolonged, four, H_2O; CO_2, N_2O, CCl_4, will enter the small square outlined around the origin. Three others, CS_2, CH_3OH, $(C_2H_5)_2O$, come within the second square, and the end, if prolonged of SO_2, C_2H_5OH and C_6H_6 are shown by dots. *The diagram shows how strikingly improbable is the supposition that the relations given are accidental.*

Since equations 7, 9, 11 are but altered expressions of the same fact, we cannot regard them as helping to confirm each other. They only serve to emphasize the agreement originally shown (equation 7). But if we can confirm the above results by an altogether different line of argument then we very much increase the probability that both the original hypothesis and the conclusions derived therefrom are true.

Such a confirmation we can obtain by the help of a theorem by Crompton,[60] where the following relation holds,

$$(12) \qquad L_T = 2RT \log_e \frac{d}{D},$$

the notation being the same as that already used.

The equation is very neatly derived on theoretical grounds quite different from the above assumptions. (Crompton considers the change in density as due to pressure alone, then doubles the amount of energy required, in order to keep the substance in that state without the excess of pressure.)

In confirmation of this result the following observed and calculated latent heats were given:

Substance	Temperature. °C	Latent heat observed	Latent heat calculated
N_2O	−20°	66.90	70.93
	0°	59.50	58.77
	20°	43.25	42.36
CO_2	−25°	72.23	71.91
	0°	57.48	54.26
	22°.04	31.80	31.06
SO_2	0°	91.2	97.17
	30°	80.5	86.05
	65°	68.4	70.03

The calculated latent heats show an undoubted correspondence to the observed values and the lack of exact agreement is attributed by Mr. Crompton to molecular association.

It seemed that the theory was hardly well enough established by the published results shown above to warrant its use for the purpose in view, where it could not be checked by experiment. As a preliminary to its use a further examination of the theory was undertaken. The value for the gases N_2O, SO_2, and CO_2 given above were recalculated from the data used in

TABLE II.

1 Substance	2 Molecular weight[1]	3 Temperature, 0° C.	Authority	4 Density of liquid	Authority	5 Density of gas	6 Latent heat observed	Authority	7 Latent heat calculated
Water, H_2O	17.88	0°	Refer to Table I.	Refer to Table I.		Refer to Table I.	597.6	Refer to Table I.	733.0
		100					535.0		601.7
		200					464.3		489.7
Methyl alcohol, CH_3OH	31.78	0					289.17		325.36
		66					265.67		270.69
		100					246.01		246.99
Carbon dioxide, CO_2	43.66	—25					72.23		70.00
		0					56.86		54.68
		22.04					31.80		31.60
Nitrous oxide, N_2O	43.74	—20					66.90		70.62
		0					59.50		58.87
		20					43.25		42.22
Ethyl alcohol, C_2H_5OH	45.68	0					236.5		236.5
		78.2					205.7		184.7
Sulphur dioxide, SO_2	63.6	0					91.45		96.88
		30					80.5		85.72
		65					68.4		73.67
Ethyl ether, $(C_2H_5)_2O$	73.48	0					93.75		99.36
		34.9					88.88		89.76
Carbon disulphide, CS_2	75.56	0					89.75		109.21
		46.2					85.24		99.86
Benzene, C_6H_6	77.4	0					109.00		123.46
		80.4					93.18		102.17
Carbon tetrachloride, CCl_4	152.62	0					52.00		60.27
		76.5					46.35		50.36

TABLE II.—(*Continued*)

1 Substance	2 Molecular weight[4]	3 Temperature. 0° C.	Authority	4 Density of liquid	Authority	5 Density of gas	6 Latent heat observed	Authority	7 Latent heat calculated
Acetic acid, $C_2H_4O_2$	59.56	118.1°	61	0.935	62	0.00187	84.9	63	139.73
Ethyl formate, $C_3H_6O_2$	73.46	54.0	64	0.870	65	0.00276	99.3	66	99.99
Methyl acetate, $C_3H_6O_2$	73.46	56.3	67	0.8836	68	0.00274	102.1	69	101.39
Ethyl acetate, $C_4H_8O_2$	87.36	75.2	70	0.8292	71	0.00308	86.68	72	87.23
Methyl propionate, $C_4H_8O_2$	87.36	79.5	73	0.8445	74	0.00304	84.15	75	88.92
Propyl formate, $C_4H_8O_2$	87.36	81.2	76	0.8242	77	0.00303	85.25	78	89.16
Ethylidene chloride, $C_2H_4Cl_2$	98.16	57.6	79	1.1100	80	0.00364	67.02	81	75.33
Ethyl propionate, $C_5H_{10}O_2$	101.26	98.6	82	0.7975	83	0.00334	77.1	84	78.69
Isobutyl formate, $C_5H_{10}O_2$	101.26	98.5	85	0.7806	86	0.00335	77.0	87	78.78
Methyl butyrate, $C_5H_{10}O_2$	101.26	101.9	88	0.8026	89	0.00331	77.25	90	79.65
Propyl acetate, $C_5H_{10}O_2$	101.26	102.0	91	0.793	92	0.00331	77.3	93	79.46
Ethyl butyrate, $C_6H_{12}O_2$	115.16	119.6	94	0.770	95	0.00360	71.5	96	71.64
Ethyl isobutyrate, $C_6H_{12}O_2$	115.16	110.1	97	0.7726	98	0.00369	69.2	99	69.61
Isobutyl acetate, $C_6H_{12}O_2$	115.16	116.5	100	0.765	101	0.00363	69.9	102	70.86
Methyl valerate, $C_6H_{12}O_2$	115.16	116.3	103	0.7767	104	0.00363	69.95	105	71.06

Table I., and below (Table II., column 7) are given the values obtained. They are practically the same as those given by Mr. Crompton. Also the values for water for which data was found at the temperatures 0°, 100°, 200° C are added. For all the other substances shown below the *calculated density of the gas is used* (equation 8), because the substance could be assumed, within the limits of pressure used, to obey the gas laws very accurately, provided molecular association did not take place. If there was such association Crompton's theory, unmodified as to the molecular weight, could not be used properly and hence *this calculation introduces no new assumption.*

Columns 1 to 4 show the data used and cite authority except for the substances already given in Table I. Column 5 contains the calculated density of the gas, the pressure being taken as one atmosphere. Column 6 gives the observed latent heat, and Column 7 the calculated.

Twenty-five gases are shown and forty comparisons are obtained. In twenty-one of these comparisons the agreement is within five percent. In ten others within ten percent. Nine are off more than ten percent. This would not seem to be a very good agreement, but several points must be noticed. The calculated latent heats are usually the largest, in every case where the theoretical density is used, except C_2H_5OH at 78.2° C and $C_3H_6O_2$ (methyl acetate) at 56.3° C. This was to be expected since the theoretical density of the gas used would be somewhat too small. Again it will be noticed that the agreement is better if the comparisons at the boiling-points of the substances are alone considered. There are twenty-two such observations, and of these fourteen are within five percent of agreement and only four above ten percent. These four are H_2O, CS_2, C_2H_5OH, and $C_2H_4O_2$, and except CS_2, they are liquids whose molecules are supposed to be associated. The amount of molecular association of a liquid has been found to increase with decrease of temperature, and this would explain the fact that the agreement is not so good at temperatures below the boiling-point. (For molecular association causes an energy change not contemplated by Crompton's formula. Besides, if the association persisted in the gaseous state it would cause a variation from the calculated density of the gas. This latter observation does not apply where the observed density of the gas is available.)

It would seem that Crompton's theory can be regarded as giving very approximately correct results when molecular association does not take place.

If we consider any gas, it is reduced to the liquid state by pressure and by the molecular attraction. In nature of course the two, pressure and attraction, act jointly and continuously. But theoretically we can separate their action, since mechanically all forces are independent of each other Legitimately then, we can consider a liquid at its critical temperature as reduced to that density: First, by the action of a pressure; second, by the action of molecular attraction. Accordingly the theoretical density of the gas at its critical temperature and under its critical pressure was calculated from equation 8. *The gas would be reduced to that condition if there were no molecular attraction. The remainder of the condensation, to the actual density, must be the work of the attraction alone.*

If the attraction obeys the law already assumed, viz., the inverse square of the distance, and if this attraction be supposed not to vary with the temperature, we can use equation 7 to calculate the energy expended at the critical point by the attraction in changing the gas from its theoretical to its observed density. (This energy we will call L_T). The theoretical density of the gas at the critical temperature $D_T = \frac{0.01227 p_T \cdot m}{T}$, from 8.

Likewise

$$E_{,T} = 0.024 \cdot \left(\frac{1}{D_T} - \frac{1}{d_{,}}\right) p_T = 0.024 \left(\frac{T}{0.01227\, p_T m} - \frac{1}{d_T}\right) p_T,$$

from 1.

Substituting these in equation 7, we have

$$(13) \quad L_T - 0.024 \left(\frac{T}{0.1227\, p_T m} - \frac{1}{d_T}\right) p_T =$$

$$\left(\frac{\sqrt[3]{d_T} - \sqrt[3]{\frac{0.01227\, p_T m}{T}}}{\sqrt[3]{d_t} - \sqrt[3]{D_t}}\right)(L_t - E_{,t}).$$

By the use of Crompton's theory, we can obtain another measure of the same amount of work and the two results should agree. In this case, again writing for D_T its value we have from equation 12,

$$(14) \qquad L_{tT} = \frac{2RT}{m}\left(\log_e d_t - \log_e \frac{0.01227\, p_T m}{T}\right),$$

where R = 1.958, or combining the two equations, transposing E_{tT}, and writing for $E_{,t}$ its value,

$$(15) \quad 3.916\, T/m\left(\log_e d_T - \log_e \frac{0.01227\, p_T m}{T}\right) - 0.024\left(\frac{T}{0.01227\, p_T m} - \frac{1}{d_T}\right)p_T =$$

$$\left\{\frac{\sqrt[3]{d_T} - \sqrt[3]{\frac{0.01227\, p_T m}{T}}}{\sqrt[3]{d_t} - \sqrt[3]{D_t}}\right\}\left\{L_t - 0.024\left(\frac{1}{D_t} - \frac{1}{d_t}\right)p_T\right\}.$$

Where D_t is also calculated (equation 8), the equation assumes a still more complicated form.

T is used above (13, 14, and 15) to represent the critical temperature only, though there would seem to be nothing in the method to prevent its application to other temperatures.

It will be recognized that the principle underlying the above equation 15 is briefly as follows: the change in density is due to the pressure and to the attraction. Crompton's formula calculates the total energy necessary to produce the change in density as if it were all produced by the pressure, because the law governing the change of pressure with the density is known. Equation 7 above gives the law governing the change of density with the attraction and enables the same amount of energy to be calculated as if the change were produced by the attraction. The two calculations must agree.

TABLE III.

1 Substance	2 Molecular weight	Critical[108]			6 Theoretical density of the gas	7 L_T per Crompton	8 E_{l}T
		3 Temperature °C.	4 Pressure in atmospheres	5 Density			
Water, H_2O	17.88	362.4°	197.5	0.429	0.0680	256.4	58.63
Carbon dioxide, CO_2	43.66	31.0	75.0	0.450	0.1322	33.37	9.64
Nitrous oxide, N_2O	43.74	35.9	74.0	0.410	0.1286	32.07	9.47
Ethyl alcohol, C_2H_5OH	45.68	236.8	64.23	0.300	0.0706	63.23	16.69
				0.288		61.47	16.47
Sulphur dioxide, SO_2	63.6	156.6	78.9	0.505	0.1433	33.24	7.57
Ethyl ether, $(C_2H_5)_2O$	73.48	193.4	37.16	0.245	0.0718	30.55	8.76
Carbon disulphide, CS_2	75.56	275.0	76.3	0.365	0.1290	29.49	9.18
Benzene, C_6H_6	77.4	289.3	52.6	0.355	0.0888	39.59	10.66
Acetic acid, $C_2H_4O_2$	59.56	321.5	57.1	0.4065	0.0712	68.62	16.14
Ethyl formate, $C_3H_6O_2$	73.46	233.9	48.93	0.315	0.0870	34.73	9.77
Methyl acetate, $C_3H_6O_2$	73.46	234.6	52.57	0.320	0.0933	33.36	9.58
Ethyl acetate, $C_4H_8O_2$	87.36	248.6	40.92	0.2993	0.0840	29.69	8.41
Methyl propionate, $C_4H_8O_2$	87.36	259 8	39.88	0.300	0.0802	31.51	8.74
Propyl formate, $C_4H_8O_2$	87.36	262.9	42.7	0.305	0.0854	30.58	8.64
Ethylidene chloride, $C_2H_4Cl_2$	98.16	254.8	52.45	0.419	0.1197	26.24	7.51
Ethyl propionate, $C_5H_{10}O_2$	101.26	277.5	34.64	0.286	0.0781	27.61	7.74
Isobutyl formate, $C_5H_{10}O_2$	101.26	278.2	38.29	0.288	0.0864	25.61	7.44
Methyl butyrate, $C_5H_{10}O_2$	101.26	278.0	36.02	0.291	0.0812	27.19	7.71
Propyl acetate, $C_5H_{10}O_2$	101.26	274.4	34.8	0.290	0.0790	27.51	7.69
Ethyl butyrate, $C_6H_{12}O_2$	115.16	298.5	30.24	0.276	0.0748	25.32	7.07
Ethyl isobutyrate, $C_6H_{12}O_2$	115.16	285.4	30.13	0.276	0.0762	24.41	6.87
Isobutyl acetate, $C_6H_{12}O_2$	115.16	292.5	31.4	0.281	0.0784	24.54	6.92
Methyl valerate, $C_6H_{12}O_2$	115.16	288.6	31.5	0.279	0.0792	24.03	6.83

TABLE III.—(*Continued*)

Substance	9 $L_T - E_{1T}$ per Crompton	10 $L_T - E_{1T}$ per equation 7	11 Translational energy at T	12 μ/c from equation 16	13 μ/c' from equation 17	14 Ratio
Water, H_2O	197.8	192.9	104.4	1458.3	123.21	11.8
Carbon dioxide, CO_2	23.73	24.43	20.46	334.46	31.97	10.5
Nitrous oxide, N_2O	22.60	21.77	20.75	321.86	33.48	9.6
Ethyl alcohol, C_2H_5OH	46.54 45.00	60.82	32.93	880.34	59.60 60.41	14.7
Sulphur dioxide, SO_2	25.67	22.87	19.85	334.30	33.85	9.9
Ethyl ether, $(C_2H_5)_2O$	21.79	22.55	18.67	449.87	42.50	10.6
Carbon disulphide, CS_2	20.31	17.34	21.31	349.35	42.88	8.1
Benzene, C_6H_6	28.93	28.50	21.37	463.53	43.75	10.6
Acetic acid, $C_2H_4O_2$	52.48	27.68	29.30	329.46	52.61	6.3
Ethyl formate, $C_3H_6O_2$	24.96	26.42	20.28	466.26	42.48	11.0
Methyl acetate, $C_3H_6O_2$	23.78	26.24	20.29	477.36	42.33	11.3
Ethyl acetate, $C_4H_8O_2$	21.28	22.99	17.53	441.56	39.59	11.2
Methyl propionate, $C_4H_8O_2$	22.77	22.70	17.92	422.97	40.44	10.4
Propyl formate, $C_4H_8O_2$	21.94	22.71	18.01	433.00	40.44	10.7
Ethylidene chloride, $C_2H_4Cl_2$	18.73	17.52	15.78	316.43	33.12	9.5
Ethyl propionate, $C_5H_{10}O_2$	19.87	20.82	15.96	419.16	38.45	10.9
Isobutyl formate, $C_5H_{10}O_2$	18.17	19.78	15.96	422.25	38.37	11.0
Methyl butyrate, $C_5H_{10}O_2$	19.48	20.61	15.98	418.23	38.25	10.9
Propyl acetate, $C_5H_{10}O_2$	19.82	21.01	15.87	420.51	38.05	11.0
Ethyl butyrate, $C_6H_{12}O_2$	18.25	19.51	14.58	413.32	37.06	11.1
Ethyl isobutyrate, $C_6H_{12}O_2$	17.54	18.66	14.23	399.66	36.22	11.0
Isobutyl acetate, $C_6H_{12}O_2$	17.62	18.90	14.42	404.95	36.49	11.1
Methyl valerate, $C_6H_{12}O_2$	17.20	18.52	14.31	402.57	36.31	11.1

TABLE IV.

1 Substance	2 Temperature °C	3 $L_T - E_{1T}$	4 c/μ	5 Ratio
Water, H_2O	0°	199.6	1508.8	12.24
	100	190.16	1437.2	11.66
	200	189.05	1428.8	11.59
Carbon dioxide, CO_2	−25	24.84	340.10	10.64
	0	24.82	339.78	10.62
	22.04	23.63	323.49	10.12
Nitrous oxide, N_2O	−20	20.25	299.29	8.94
	0	22.24	328.75	9.82
	20	22.83	337.56	10.08
Ethyl alcohol, C_2H_5OH	0	61.75	893.75	15.00
	78.2	59.90	866.93	14.54
	(Corres	ponding to	$\mu/c' =$	14.80
	60.41	Table III.	Col. 13)	14.35
Sulphur dioxide, SO_2	0	23.62	345.17	10.19
	30	22.83	333.72	9.86
	65	22.17	324.03	9.57
Ethyl ether, $(C_2H_5)_2O$	0	22.42	447.19	10.52
	34.9	22.69	452.55	10.64
Carbon disulphide, CS_2	0	17.24	347.32	8.100
	46.2	17.44	351.39	8.195
Benzene, C_6H_6	0	29.20	474.92	10.86
	80.4	27.80	452.14	10.34

The data used in Tables III. and IV. are given in Tables I. and II., and Table III., columns 1–5.

In Table III., column 9 contains the results calculated according to the left-hand side of equation 15, and column 10 contains the results calculated from the right-hand side of the equation. When the necessary data could be obtained for the latter calculation at several different temperatures, the results vary according to the data chosen, and the average is given. This variation is only slight, as will be seen from Table IV., column 3, where the unaveraged results are given, a result which necessarily follows from the agreement previously shown (equations 7, 9, 11).

The agreement of the two sets of values is very satisfactory. Out of a total of twenty-three comparisons only six lack agreement by more than two cals, and three of these six are within three cals of agreement. H_2O, C_2H_5OH, and $C_2H_4O_2$ show the worst agreement, and these have associated molecules at ordinary temperatures. The values for water really furnish a striking confirmation of the formula for the proportional error is small. Alcohol and acetic acid alone fail entirely of agreement.

The agreement obtained would seem to confirm the law of attraction assumed and also shows that the attraction for many substances remains constant with a change in the temperature.

By still another argument we can confirm the truth of the original formula 7 and the supposition upon which it is based. Using equation 6 and solving for μ we have for one gram of substance,

$$\mu = \frac{(L_t - E_{st})\sqrt[3]{m \cdot c}}{\sqrt[3]{d_t} - \sqrt[3]{D_t}}. \tag{16}$$

In a gas indefinite expansion takes place as the pressure is decreased. This shows that the attraction between the molecules cannot be great enough to make the paths of the molecules closed curves. In a liquid, while undoubtedly many molecules, whose velocity is above the average molecular velocity, are continually flying away from the surface, yet it must certainly be the case that most of the molecules are drawn back by the molecular attraction. There must be for each substance a certain temperature at which the molecular attraction, without outside pressure, is just strong enough to overbalance the kinetic translational energy of the average particle and cause it to return to the liquid or solid substance. At this point if the attraction varies inversely as the square of the distance between the molecules, we will have $v^2 = \frac{2\mu}{R}$, where v is the molecular velocity and is equal to $\sqrt{\frac{3R_cT}{m}}$, R_c being equal to 1.958, and R is the distance apart of the molecules and is equal to $c\sqrt[3]{m/d}$. Hence,

$$\mu = c' \, T\sqrt[3]{m/d_T}/m, \tag{17}$$

c and c' being unknown constants.

It is a common text-book idea that at the critical temperature the kinetic energy of the molecules of a liquid (gas) under the critical pressure just balances the attraction. The idea rests on the diminution and final disappearance of surface tension at the critical temperature, and the fact, that a liquid at its critical temperature may be changed to a gas without the addition of external energy, i. e., by an infinitesimal change in pressure, the heat of vaporization being zero. It must be at this point then that equation 17 holds good. On this assumption I have calculated $\frac{\mu}{c'}$ (Equation 17), and show the results in column 13, Table III. $\frac{\mu}{c}$ is also calculated from equation 16, and shown in column 12. Again where data were available at different temperatures the average only is shown in Table III. and each calculation is given in Table IV., column 4.

Combining the two equations 16 and 17, we have

$$\frac{(L_l - E_{il})\sqrt[3]{m}}{\sqrt[3]{d_l} - \sqrt[3]{D_l}} \Big/ T\sqrt[3]{m/d_T/m} = \frac{c'\mu}{c\mu},$$

or

$$m\,\frac{(L_l - E_{il})\sqrt[3]{d_T}}{(\sqrt[3]{d_l} - \sqrt[3]{D_l})T} = \text{constant}, \tag{18}$$

where T must be the critical temperature. This ratio is given in Table III., column 14, average results being given where *l* could represent more than one temperature, and the detailed results are shown in Table IV., column 5. The values obtained seem to approximate 11.0 Out of the twenty-three substances examined five, N_2O, C_2H_5OH, CS_2, $C_2H_4O_2$, and $C_2H_4Cl_2$, differ from the average constant by more than ten percent; and of these C_2H_5OH, $C_2H_4O_2$, and N_2O, CS_2, to a less extent have continually failed to agree with the theory and the molecules of C_2H_5OH and $C_2H_4O_2$ are known to be associated at ordinary temperatures.

We must examine a little further the supposition made that at the critical temperature the molecular attraction just balances the kinetic translational energy of the molecule. For if this be true, then the kinetic translational energy, E_3, of the molecule as calculated by the equation

$$(19) \qquad E_3 = 3/2RT = \frac{2.937\,T}{m},$$

for the critical temperature, should equal the attractive energy calculated from Crompton's formula (12) less E_2 (Table III., column 9) and equation 7. (Table III., column 10.) The kinetic energy thus calculated is shown in Table III., column 11. The agreement is not usually good, the kinetic energy being almost invariably several (two to six) cals too small, and failing entirely to agree in the case of H_2O and C_2H_5OH. The lack of agreement may be due partially to the measurements of the critical density which have been used, or to some influence exerted by the pressure, or to one of several other causes, but all my attempts to satisfactorily explain the divergence have so far proved futile. The values, columns 9, 10, 11, are of the same order of magnitude, and the disagreement shows some signs of regularity. Therefore I do not think that the lack of agreement necessarily will be found to offer a serious obstacle to what has preceded.

If the methods outlined in this paper hold true and if the discrepancies can be explained or brought into accord with the theory many lines of investigation are opened. The calculations involved, even with the help of tables, are time-consuming and laborious, and the necessary data are scattered and somewhat uncertain. Work has been undertaken along several lines, but the results are not yet understood or completed sufficiently to justify their publication. Attention will be called here only to one or two obvious applications of the ideas discussed.

Equations 16 and 17 afford a method of determining the relative attraction between the molecules and hence permit of a further study of the laws of attraction. This attraction appears to depend primarily upon the chemical nature of the molecule and not upon its mass. We may say therefore that *the molecular attraction appears to resemble the attraction of gravitation* *in that it varies inversely as the square of the distance apart of the attracting molecules and does not vary with the temperature. It differs from the attraction of gravity in being determined primarily by the construction of the molecule and not by its mass.*

Again the argument pursued might lead one to suspect that the entire increase of the specific heat of a liquid over that of a gas at constant volume must be spent in increasing the distance apart of the molecules. Investigation shows that this is not always, if it is ever, the case, and herein possibly lies the true cause of the discrepancies from the theory.

Again the law of attraction assumed does not lead to the gas equation given by van der Waals.

Again the foregoing work has an obvious bearing upon boiling-points, vapor pressures and Trouton's formula.

In conclusion I wish to acknowledge and here express my thanks for the encouragement, criticism, and helpful suggestion given me during the progress of this work by Dr. Chas. Baskerville.

Summary

Evidence is advanced to prove that

1. Molecular attraction varies inversely as the square of the distance apart of the molecules.

2. The absolute molecular attraction is only slightly affected by changes in temperature.

3. The molecular attraction depends primarily upon the chemical constitution of the molecule and not upon its mass.

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10. 1, p. 181. See Note 25.
11. Regnault, 1, p. 71.
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46, Buff, 3, p. 57. See Note 25.
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26.54 mm, Young, 1, p. 73.
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100.4, Berthelot and Ogier, 1, p. 348.
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74.6°, Andrews, 1, p. 349.
77°, Schiff, 1, p. 349.
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0.8368, at 79.9°, Elsässer, 3, p. 209.
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57.7°, Schiff, 1, p. 165.
80. 1.1070, at 56°, Ramsay, 3, p. 296.
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102.3°, Schiff, 1, p. 349.
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92. 0.7917, at 101.8°, Schiff, 1, p. 208.
0.7944, at 100.8°, Elsässer, 1, p. 208.
93. 77.3, at 102.3, Schiff, 1, p. 349.
94. 119°, Schiff, 1, p. 349.
119.8°, Schiff, 3, p. 211.
119.9°, Elsässer, 3, p. 211. See Note 25.
95. 0.7704, at 119.8°, Schiff, 3, p. 211.
0 7694, at 119.9°, Elsässer, 3, p. 211.
96. 71.5, at 119°, Schiff, 1, p. 349.
97. 110.1, Schiff, 3, p. 211.
110.1, Elsässer, 3, p. 211.
98. 0.7681, at 110.1°, Schiff, 3, p. 211.
0.7772, at 110.1°, Elsässer, 3, p. 211.
99. 69.2, at 110°, Schiff, 1, p. 349.
100. 1, p. 177.
101. 0.77080, at 116.3°, Elsässer, 3, p. 208.
0.7589, at 112.7, Schiff, 3, p. 208.
102. 69.9, at 116.8°, Schiff, 1, p. 349.
103. Schiff. 1, p. 349. See Note 25.
104. 0.7767, at 127.3°, Gartenmeister, 3, p. 212.
105. 69.95, at 116.3°, Schiff, 1, p. 349.
106. The critical data given was taken from 1, p. 84, by averaging the *observations*.
107. Density of mercury at 0° referred to water at 4° C = 13.5956. Average of Marek, 2, p. 95, Reguault, 1, p. 119, Volkmann, 1, p. 119. Standard gravity at Lat. 45° and sea-level = 980.5966, Helmert, 1, p. 6.

STUDIES IN VAPOR COMPOSITION, II.

BY H. R. CARVETH

A. INTRODUCTION

The Phase Rule, as formulated by Gibbs, has done more to present chemistry as a complete and systematic science than any other modern theoretical research, and many believe that its work has but begun. When its full scope is appreciated — the study of phases in all their interrelationships with regard to formation, separation, and identification, and the relations of the various components of the phases, — it will undoubtedly cause a revolution in many of our methods. Considering for the moment the separations which are ordinarily carried on in laboratory work, one must realize that they are to a very considerable extent carried on by unintelligent rule-of-thumb, the operator rarely understanding clearly where or why certain chemical operations are to be performed or to be suspended. If, however, he has a useful theory as his guide, he may at first work more slowly, but in the end he will necessarily gain much. From none of the works on laboratory practice or theoretical instruction can he obtain these. It is unfortunate, therefore, that the possible practical applications of Phase Rule results have not appealed more strongly to the workers in this field; it is with the object of keeping these in view, therefore that the writer has resumed work on the study of vapor composition, aiming to interpret, explain, or criticize known facts, while introducing a few new ones.

If, at the outset, one formulates from past experience that in any chemical work "Arbitrary conditions are not always the necessary conditions for equilibrium", he makes a statement which causes him to consider his experiment, its conditions and the result at which he is aiming. The conditions which prevail at equilibrium, especially the various condition factors, the interrelationships of the phases and their components, and the knowledge of their relative importance with regard to controlling influences must all be considered. Among the factors which are usually of prime importance are temperature, pressure, concentration, electromotive force, etc. — in other words, all 'natural' adjustments, striving to bring the systems to a state of rest or equilibrium, tend to involve a change in some of these terms. It may be possible in many cases to interfere with artificial adjustments and to arrive at a different final state — the same terms, however, are involved.

The same facts were all considered by Gibbs in his definition of 'state of equilibrium'. He found that in this condition the potentials of the various energies — heat, mechanical, chemical, or electrical — in the different phases must be equal. If they are not so, there is always present a transfer of energy, hence a velocity term and the tendency toward the equalization of these factors. In any case, therefore, where a system is isolated from surroundings so as to absorb no form of energy, it will be comparatively easy to determine by simple differential measurements of any of its condition factors, whether it is or is not in a state of equilibrium.

In the case, however, where the system is in interchange with its surroundings, there is as the guide the principle of action and reaction or the theorem of Le Chatelier, "Any change in a factor of equilibrium from without is followed by a reverse change of that factor from within the system." With these principles, one is in a position to consider in detail the effect of various artificial and arbitrary conditions on the final state of equilibrium.

B. ARTIFICIAL CONDITIONS

If one takes ice and salt at 0° C and brings them together (isolated completely from the surroundings) there is formed a solution; if a thermometer is inserted, it is found that the temperature falls, rapidly at first, and then more slowly. The tendency is undoubtedly toward the conditions characteristic of the invariant system ice, salt, saturated solution and vapor. Whether or not this is reached depends on a number of factors, of which the most important is the relative masses of salt and of ice. The controlling phases are the solids; the controlling energy is the heat of fusion and not the heat of solution; the volume change also adds an energy term. The temperature of the equilibrium point for the invariant system is striven for, but owing to the slowness with which energy and material transfer takes place when there is but slight difference in driving pressure, the velocity term has always to be considered, before conclusions are reached in regard to equilibrium.

If, however, one brings together water and salt at 0° C, it will be found that again there is interaction between the phases tending to the formation of solution saturated or unsaturated. The resultant equilibrium may be that of the bivariant, solution and vapor, or the univariant, salt, solution and vapor. The controlling factors are the relative masses of the phases, the physical state of the components, the heat of solution of the salt in the solution, and the volume changes. Here again the velocity term is found on close examination to fall away very rapidly when the final conditions of concentration and temperature are approached.

It is of course not stated that heat is the only energy concerned; in the cases cited there is also volume change, and therefore a mechanical work term concerned. Other forms may have to be considered. These energies may work in the same or in opposite directions, i. e., one be positive and the other negative in the striving for equilibrium.

Artificial conditions may be brought about just as well by the removal of the phases as by the addition of one or more phases, and the relations discovered will correspond in many cases to the two above cited. In much of the work with which chemists have to do, the operations are undoubtedly reversible. In many cases, however, the conditions for realizing complete reversibility have not been worked out, and perhaps never will be. In the present elementary state of the subject, it will be wiser to restrict the discussion to examples of the reversible type. In cases such as the above, the system may be regarded as enclosed in an envelope impervious to any form of energy; when, however, a phase is to be separated, energy of some kind must be supplied or withdrawn, and hence the above restriction must be dropped. This is also the case where one or more phases are being added continuously.

In all cases, therefore, where one is adding or withdrawing phases, there are changes in the energies of the system which proceed in a definite direction, either adding to or withdrawing from the energy store of each phase of the system. Equilibrium will be reached when the various factors of equilibrium concerned have assumed or been so controlled as to give a constant value. *So long, therefore, as these factors are changing while a phase is being added or being removed, equilibrium has not been attained.* Further the *direction toward which each of these tend, indicates the value toward which this term is tending in its attempt to reach a final state of equilibrium.* If one is dealing with any univariant system, it is only necessary to select arbitrarily *any* value of *any* variable, and *every* property and condition of the system must at once assume a definite and constant value: conversely, if on fixing one condition factor, all others are found definite and constant, one has to do with a univariant system. If the system is bivariant, the operator must hold constant any *two* conditions, in order to prevent change; conversely, if holding two condition factors constant prevents the system from changing, one has to deal with a bivariant system. Similar statements hold true for systems of any degree of variance. Moreover, the number of phases which may possibly be present at equilibrium indicates frequently a degree of variance different from the initial. It is in such cases that the changing values of the condition factors have a very definite significance. Since illustrations of these occur frequently in the body of the paper, no further reference is required here. It is evident, however, that the italicized statement is a direct deduction from the meaning of the Phase Rule.

The various condition factors of equilibrium, external —

such as pressure, temperature, and electromotive force — and internal — chemical and physical states and concentration — now assume the rôle of indicators of change.

Determinations of their values made roughly may in many cases give all the information desired; but, starting with arbitrary conditions, as one approaches the actual equilibrium conditions, the equalization of every one of these factors proceeds more and more slowly. There is met here therefore the distinctions between the requirements for differential and absolute measurements. Since these are approached hyperbolically from either side, it is but right to demand that all values given in quantitative phase work should give as far as possible the probable error as gauged by the method of working from the opposite directions. At present this is rarely or never done, even in methods which have been well developed, and which are to-day the ones most frequently used in laboratory work.

C. ARTIFICIAL CONDITIONS AND PASSAGE OF VAPOR BUBBLES

There are various methods of obtaining a rapid readjustment of material and energies in particular systems, but all require that the smallest parts of the different phases be brought into close contact frequently. The velocity of the transfer varies very much with the physical state of the phases in contact, being most rapid in gaseous and slowest in solid phases. One might rapidly shoot a salt through water without obtaining any indication whatever of equilibrium. A similar experiment might be performed with liquid or with a vapor or gas. The thoroughness with which these phases are mixed includes, therefore, the time of contact as one factor; the velocity term is always to be remembered.

All other factors which affect phases very unequally should also be considered; e. g., viscosity, capillarity, gravity, electrical stress, distortion, etc., may each exercise an effect. But some of these may be eliminated or kept constant so as to have no influence on the interrelation of the phases; it was on the assumption of this possibility that Gibbs's Phase Rule derivation holds good.

Of these, however, the action of gravity may not always be disregarded. Any object immersed in a liquid stands under a greater pressure than it would at the surface of the liquid. This excess pressure may cause a great difference in equilibrium factors. This will also be the case where one is dealing with the passage of any vapor or gas through a dense liquid; here, therefore, hydrostatic pressure may play a prominent rôle.

One-component systems

This effect of gravity is met in the study of vapor pressure relations of one-component systems. Sometimes in comparison with other factors the pressure value expressed numerically is negligibly small, but in most measurements it has to be considered. Kahlbaum,[1] when working on the vapor pressure of mercury by the dynamic method, found a difference in the temperature of vapor and liquid of 1.7° at $p = 28.77$ mm, but of 22.1° at $p = 0.87$ mm, and gave his results the correct interpretation. His demonstration that in using this method the layers of liquid differ more and more from the temperature of the vapor the greater the ratio of the hydrostatic to the external pressure is complete. In the light of his work, it seems necessary in speaking of the equilibrium between vapor and liquid to restrict ourselves to the phenomenon of equilibrium directly at the boundary surfaces of the two phases where theoretically the definite pressure and temperature prevail. The bubble of vapor could not remain in equilibrium with the denser liquid which surrounds it unless other forces (e. g., capillary) offset the density differences.

The disappearance of the bubble of vapor, or its expulsion from the liquid indicate the direction in which equilibrium may be found. Parting with its heat of condensation, it must raise the temperature of the liquid, or being expelled it must pass to a place where the pressure is less. Bubble passage, therefore, with its concomitant change in condition factors may therefore

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[1] Siedepunkte, p. 62.

be used in examining equilibrium conditions where a vapor phase is concerned.

Especial attention has been drawn to this effect of hydrostatic pressure to illustrate the foresight of Gibbs in his Phase Rule derivation, and also to call attention to a term which has been repeatedly overlooked in recent researches. Cases may be found where chemists working under reduced pressures, e. g., in molecular weight and vapor pressures, have given results as quantitative when this source of error has been entirely ignored.

Superheating is another difficulty which has been met in all vapor pressure work.[1] The heat supply is delivered at one place more rapidly than it is transferred to do the work of vaporization evenly and uniformly. Hence there is observed the reluctance to change which is almost invariably present when one phase is being transformed into another, and this shows itself in the raised temperature of the liquid. Various devices have been used to overcome this: for example, Faraday[2] advised the use of platinum foil cut by scissors into narrow strips so as to resemble a fringe, or silver, copper wire, filings, piece of cork or torn cartridge paper, and notes that the addition of some foreign substance lowers the boiling-point of concentrated sulphuric acid some degrees. LeGrand[3] in his work on the boiling-points of saturated saline solutions, which for that period was done with considerable accuracy, made use of platinum to prevent superheating. Yet more than sixty years later we meet the statement:[4] "As a fact no one prior to me has used filling material to carry out exact boiling-point determinations with thermometer inserted", and accordingly the former work has "durchaus missglückt". Does it seem strange that if it was necessary to prevent superheating to the extent of whole degrees, it was equally necessary to use as good means when measurements in thousandths of degrees were to be made?

That such a statement has been accepted without dispute

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[1] Ostwald's Measurements, p. 112.

[2] Faraday. Chemical Manipulation, 215 (1831).

[3] LeGrand. Ann. Chim. Phys. 59, 423 (1835).

[4] Beckmann. Zeit. phys. Chem. 21, 256 (1896).

shows only too plainly the little thought that has been devoted to overcoming the problem of superheating, and it is advisable to consider briefly its cause and the methods of its elimination. When heat is supplied to the surface in ordinary methods of heating, we have a layer of liquid which cannot rise above a certain temperature without change of state, impinging on a solid body such as glass, which varies in temperature between its internal and external surfaces. The cohesive force by which the water is held to the glass is different from that when in contact with a metal, and this force has to be overcome before vapor formation can take place at the surface of contact. The velocity of heat transfer is of course very different in the two cases. The bubble formation seems to take place more readily from a series of points than from a smooth surface — probably because the superheating is localized to a smaller area. The number of points has also a definite effect; this has been shown by Beckmann,[1] who found that addition of glass beads lowered the apparent boiling-point from 0.60° to 0.24° on his thermometer, and that further addition of beads had no further effect.

Besides the method of adding to the boiling solvent a material which causes more ready bubble formation by surface effects, the plan has been adopted to add material which held gas in its pores, e. g., charcoal, hydrogenized palladium, etc., or else to pass the gas directly into the boiling liquid. As the gas is evolved, it is surrounded by a layer of hot liquid which vaporizes into it as into a vacuum.

Another method, which has not received the attention which is its due, requires the passage into the liquid of the vapor having the same composition. Only when the thermometer indicates constancy is the boiling-point actually reached. Is it possible to have superheating by this method? Are the results obtained by these different methods the same?

In finding an answer to this question, use was made of an apparatus of the general form employed by McCoy in his molec-

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[1] Beckmann. Zeit. phys. Chem. 21, 239 (1898).

ular weight work, as shown in Figure 1. This apparatus for working with vapors has been employed very frequently in our subsequent work. Into the outer jacket B was put water and a number of platinum tetrahedra; into the inner tube C a Beckmann thermometer. After the temperature of the water had been raised to the boiling-point, a clip was slipped over the rubber tube at A, and the steam forced through the inner tube C. The thermometer soon assumed a steady reading at 50.7°. Water was now added to the inner tube. This was soon raised to its boiling temperature; successive readings at intervals of one minute commenced at 5.14° and differed as little as 0.001°, but rose steadily because of the increase in hydrostatic pressure as the vapor condensed. The water in the outer tube was now replaced by a salt solution boiling at 106.75° and the thermometer immersed to the same extent as before. The readings now indicated 5.140°, rising occasionally about 0.001° irregularly, and at the end of six minutes' reading 5.145°. These results are surprising in that they indicate the great velocity with which the heat transfer from the vapor bubble to the liquid takes place — that a vapor heated seven degrees above the liquid when entering does not exert any greater influence on the boiling-point than may be measured in thousandths of degrees under the conditions of the test.

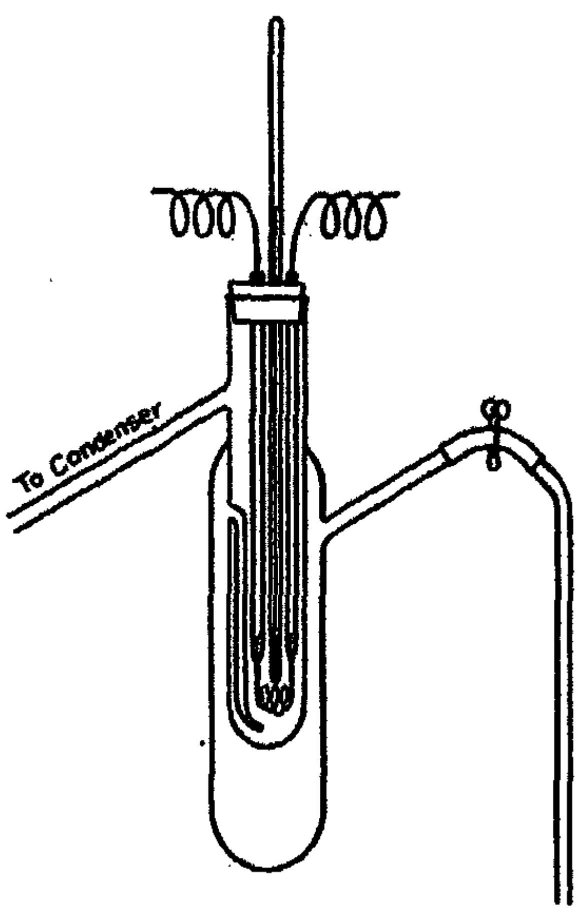

Fig. 1

To test further the velocity of transfer we have passed water vapor through a tube heated almost to redness and then into the inner tube of a large test-tube surrounded by a vacuum jacket. When steam was passed in very vigorously, the Beckmann reading (set differently from the one above) was 0.621°. When, however, the velocity of generation of the steam remaining constant, the long delivery tube was intensely heated, the thermometer indicated 0.672°. In other words, great superheating of the steam and consequent formation of very large bubbles of vapor raised the temperature 0.05°. The actual effect, therefore, of passing a vapor into its own liquid is the rapid equalization of temperature with concentration factors, the velocity term being sometimes very great.

Now the selection of a zero for differential measurements in phase work has become a problem of some importance since the introduction of the boiling- and freezing-point methods; the reproduction of the zero ought always to be a simple problem. Beckmann, in his original papers, has given us some data illustrating the difficulties in this direction. In his last paper[1] he gives a page of directions on the use of filling material, which in substance means that the material is to be added as long as the boiling-point falls. Several students, who were told to follow out these directions carefully, reported that the Beckmann method gave results from 0.1° to 0.2° higher than the vapor-heating method, with degree of immersion of the thermometer and other factors constant. On repeating the experiments myself, it was found that the Beckmann method might give values considerably higher than the other and that these might be selected as arbitrary zeros of reference, but that with care the boiling temperature obtained by the different methods might be found the same. We have never as yet found the indicated temperature of ebullition lower in the first than in the vapor-heating method. The latter seems therefore to indicate an automatic zero, which is certainly of great advantage.

The bearing of this relative or absolute zero on the test of purity of a body by reference to its boiling-point is obvious. When the thermometer is immersed in the liquid there is always present the hydrostatic pressure — which in a case cited above

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[1] Beckmann. Zeit. phys. Chem. 40, 135 (1902).

amounted to 0.1° —and the effect of superheating. Now in some cases, e. g., ethyl alcohol and water, this difference in the boiling temperature might indicate the presence of nearly 10 pct of water and 90 pct of alcohol in place of pure alcohol. In cases, therefore, where purity is determined by means of the boiling-point, it is advisable to determine the temperature of the vapor and check up by at least one more decisive analytical property.

Systems of two components, forming no compounds, both components volatile

After noticing that the vapor of A passed into liquid A raises the temperature of the latter to its boiling-point, one is interested in finding the temperature effects when the vapor of A is passed into liquid B or vice versa. Now a vapor containing nothing but A can be in equilibrium with no liquid except pure A (if we assume all substances volatile). The temperature toward which one will tend then on passing the vapor of A into B is the boiling temperature of pure A. If then one starts with liquid B at its boiling-point and passes in the vapor of A, the range of temperature will be from the boiling temperature of B to that of A. We first made this observation on substances showing a normal curve, e. g., acetone and water, making use of the apparatus shown in Fig. 1. The next mixture was that of ethyl alcohol and benzene, which showed a minimum temperature. It now seemed probable that the curve indicated the actual direction of temperature changes in passing from B to A. This will be the case if the transfer of energy and material takes place with very great velocity. As has been shown above, this was found to be the case with water vapor passed into liquid water, and later experiments showed the same with alcohol vapor into alcohol, etc.

A satisfactory arrangement of similar experiments for two-component systems is very difficult owing to the difference in composition of liquid and vapor. In lieu of such, it was decided that if various fluid pairs possessing abnormal boiling curves showed by this method the same minimum or maximum temperatures which was to be found by other methods, it was very probable that the same condition as to equalization of temperature and concentration prevailed as in the one-component systems.

Consequently a number of cases have been examined in this way. In every case where compounds are not formed it has been found that these temperatures do correspond — usually within less than 0.1°. The comparisons were made in each case with the same material which had been used with other methods. It is of course not strange if the material used by different observers gives different results, for the effect of slight impurities is very noticeable. Another factor which can not be ignored is the lag of the thermometer. When one considers that the time required to make a run from pure B to nearly pure A has been at times cut down to five minutes, it is certainly possible that the thermometer may not assume the equilibrium position for the temperature desired.

Another method of checking this minimum or maximum temperature was obtained by changing the positions of B and A. For example, passing the vapor of methyl alcohol into acetone at a pressure of 744 mm, the temperature fell from 55.9° to 55.35°, after which it rose again. The acetone in the inner tube was raised to its boiling-point by means of the electric heating coil shown in Fig. 1. When into a mixture of the alcohol and acetone, which started to evolve bubbles at 58°, the vapor of acetone was passed, the temperature fell to 55.32° when it began again to rise. The materials employed were the same which had been used by J. H. Pettit,[1] who found a minimum of about 54.80°, $p = 728.9$ mm. This agrees very well indeed with the results obtained above. With absolute alcohol and commercial benzene a minimum was found at 67.55°, $p = 743.8$; this was reproduced at 67.7° on interchange of position of the materials. With purest materials available the minimum was obtained at 66.60° at $p = 733.0$, the same result being obtained by reversal. This corresponds very well indeed with the result which Thayer[2] obtained by fractional distillation, viz., 66.7° at $p = 737$ mm.

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[1] Pettit. Jour. Phys. Chem. 3, 349 (1899).

[2] Thayer. Ibid., 2, 382 (1898).

On passing acetone into water, the temperature fell continuously from 98.8° to 61.1° in fifteen minutes. On taking out some of the solution from C and adding more acetone to the outer vessel, the temperature fell in about seven minutes to 57°. On passing water vapor into acetone, the thermometer had in two minutes indicated 58°, these three experiments indicating that the curve was of the normal type. Similarly, the passage of carbon bisulphide into benzene or vice versa showed that the curve was normal; thus confirming the results previously obtained by the dynamic method.[1] With hydrochloric acid and water, the maximum as obtained by both methods was 108.2° at $p = 748.3$ mm. This corresponds exactly with results which we have obtained on distilling the same acid. Results with other fluid pairs will be given later. The general conclusion is that the method of vapor heating gives results which conform to those obtained by the distillation method and that the probability is that when no compounds are formed, adjustment of concentration and temperature takes place with great rapidity. No measurements on the concentration at the minimum have yet been made.

Varying external pressures

No restriction whatever having been imposed as to the external pressure, it is apparent that the method may be applied in working at any pressures from very low pressures up to the critical point. Experiments of this nature could, taken in conjunction with concentration determinations, give us information as to the displacements of maxima or minima with the pressure and as to whether the normal curves ever became abnormal or vice versa. Not less interesting but far more difficult in realizing experimentally would be the examination of the effects at the critical pressures, the bearing on retrograde condensation, etc.

Dephlegmation

The bearing of the results obtained above on the theory of

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[1] Carveth. Jour. Phys. Chem. 3, 193 (1899).

dephlegmators is very readily seen. The following diagrams 2 and 3 show forms used in lecture illustration of the theory. The liter distilling flask A holds a mixture of two components (both volatile) as for example, acetone and water. When a series of bulbs cooled by the air (BBB, Fig. 2) is inserted between flask and condenser and the content of the flask is boiled, some vapor passing over is condensed in the first bulb. Very soon this blocks up the vapor inlet, and bubbles of vapor pass through the condensed liquid, which is soon raised to the boiling-point. In the next bulb condensation and bubble passage takes place and so on throughout the series. In every bulb the liquid therein contained is at its boiling temperature. The thermometers throughout the series indicate temperatures always lower and lower. The vapor passing over finally is very much richer in the more volatile component than the vapor initially condensed in the first bulb. Even without an experimental confirmation which has been given, one can easily see that a low velocity of distillation will favor better cooling, and hence better separation.

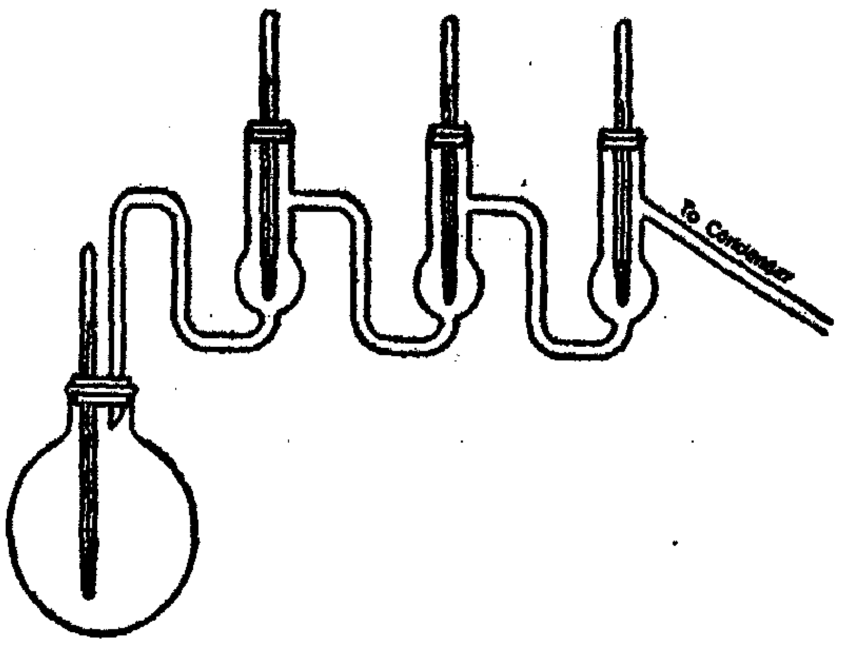

Fig. 2

This form of apparatus will not serve as a good laboratory form because the condensed vapor accumulates. The same objection holds for Fig. 3, which indicates merely an evolutionary stage, and which, it may be readily seen, is related in form to practically all the ordinary forms of dephlegmators. The Hempel, for example, would be considered as of essentially the same type, combining a great number of dephlegmators and surfaces of liquids in a very compact form.

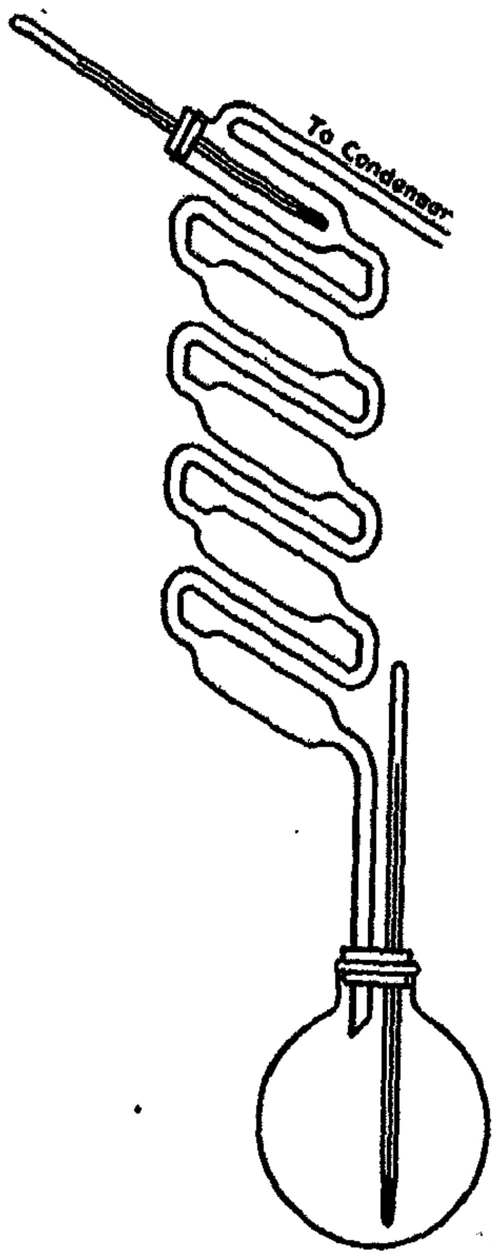

Fig. 3

For the complete removal of the more volatile component in a short space of time, it is better to have the liquid which is condensed fall slowly, coming into contact with the ascending current of vapor. Of course the greater the number of steps or phlegms holding liquid, with which the vapor comes into contact, the more nearly will the more volatile component distil over in a state of purity. A number of chemists still hold to the idea that cooling and passing the vapors *over* the condensed liquid is sufficient. The work of Brown[1] indicates that passage *through* the condensed liquid allows of better control and more efficient separation, although there is always the disadvantage that the condensed liquid accumulates in the still-head.

There have been at times very lively discussions as to the efficiencies of various forms of distilling apparatus, and numerous and ingenious works of the glassblower have been produced as new types.[2] From the practical as well as theoretical standpoint, it is desirable to have (1) an apparatus which is sufficiently cooled to allow of some condensation; (2) a very large number of intercepts holding liquid through which the vapor must be forced; and (3) provision for the return of the condensed liquid.

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[1] Brown. Jour. Chem. Soc. 37, 49 (1880).

[2] Compare Young. Ibid., 75, 699 (1899).

Insofar as (2) and (3) are concerned, these conditions are fulfilled in a very desirable manner by the Hempel column. In many cases, however, especially with liquids of high or low boiling-point, the first condition can not be controlled properly, the condensation being too much or too little. The result is that in many such cases fractionation is not carried on with satisfactory results. But by a proper control of the temperature of the rectifying column, it is possible to obtain separations which are exactly analogous with those obtained with ordinary mixtures and air cooling. A very decided objection to the Hempel form is, of course, the amount of liquid contained in the still-head.

It was at one time thought that the still-head should be kept at a constant temperature of the more volatile component and it is a matter of historical interest that the separation of benzene from toluene was effected in this manner.[1] With the still-heads of constant temperature which have been used, there have been so far as the writer is aware, no attempt to use a dephlegmating column, but rather to obtain the separation by fractional precipitation of the less volatile liquid by means of the cooling action of the walls. This has been done by Mansfield and by Brown,[2] who in this way obtained separations which were fairly satisfactory, but were not better (in the cases used) than could be obtained by a good dephlegmating apparatus.

Experiments have been carried on in this laboratory making use of still-heads of constant temperature surrounding a tube containing a large number of intercepts. It was found, however, that the completeness of separations varied more with the degree of heating the boiling liquid than with inconstancy in the temperature of the still-head. In every case, however, it was found possible by keeping the still-head temperature properly controlled, to obtain better separations. In preparation of pure substances it is usually well to keep the jacket a degree or so below the boiling temperature of the more volatile and exercise the same precautions as with the Hempel.

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[1] Mansfield. Ann. Chem. (Liebig) 69, 177 (1848).

[2] Compare Young. Jour. Chem. Soc. 75, 679 (1899).

Continuous distillation

In connection with separations by the agency of still-heads of constant temperature it seemed possible that by maintaining two parts of a system at different temperatures corresponding to the boiling temperatures of the component, one might be able to effect continuous separation, especially if use were made of dephlegmating intercepts. In 1900, Mr. Ira H. Derby experimented on mixtures of ethyl alcohol and water with an apparatus shown in Fig. 4. This consists of a long block-tin tube surrounded at its lower end A by the vapor of boiling water, at its upper end B by vapor from boiling alcohol, and filled with intercepts. The mixture to be distilled was slowly dropped in at C, the vapor passing off to the condenser at D, and the residue through a trap at E. Starting with a mixture containing 62 pct of alcohol by weight, the weight percent of alcohol in the distillate was found to be 90.6; with an initial mixture containing 40 pct, and the other conditions being improved, the distillate on three successive runs contained 90.6 pct, 93.7 pct, and 93.9 pct. The percentage of alcohol in the residue was found to average about 0.5 pct when working carefully. When one remembers the impossibility of separating water quantitatively from alcohol by distillation alone, the efficiency of this apparatus is striking indeed. It is a mere matter of increasing the

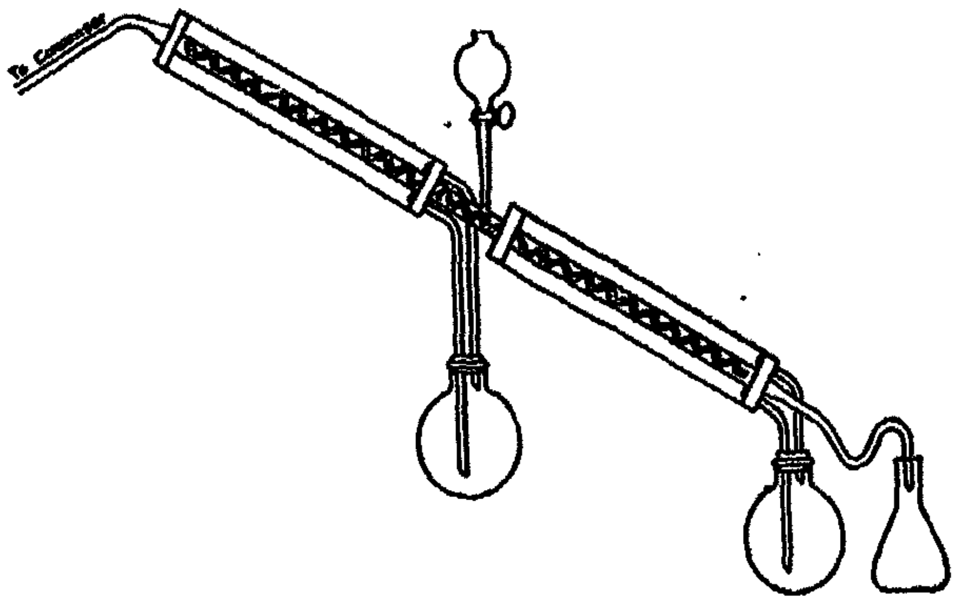

Fig. 4

length and diameter of the tube, the number of intercepts and the velocity of delivery in order to obtain a practical, complete and continuous separation. The problem of continuous fractional distillation for two components is shown by these experiments to be one capable of easy solution in technical work.

The actual velocity with which distillation was effected was in all these cases very low, due of course to the limitations in the size of the apparatus.

With regard to the total amount of heat required in operating by this continuous method, the following results were obtained, starting with an initial mixture of a 20 pct alcohol:

Number of run	1	2	3	4	5
Grams of distillate obtained	22.2	9.6	19	9	10.2
Weight pct alcohol in distillate	76.7	85.2	87	88.5	89.9
Time of run in minutes	157	60	173	79	90
Small calories required	16850	6470	11799	5337	5783
Small calories per gram distillate	759	674	621	593	567
Weight pct alcohol in residue	1.5	2.0	2.0	2.0	2.0

These results show the actual heat amounts required in a fractional separation. To obtain ideas as to the efficiencies we should require the value of the heat evolved when these various distillate mixtures as vapors are brought together with the condensate mixtures as liquids at their boiling-points — in other words, the sum of the heat of condensation and the heat of *solution*. It is seen that in accordance with this theoretical value, less heat is actually required to obtain a vapor of 89.9 pct than a vapor of 88.5 pct, 87 pct, 85.2 pct, or 76.7 pct. In other words, efficient dephlegmation works both in the direction of saving heat and in giving a purer product. Of course these experiments were performed under such conditions that all the heat supplied performed effective work. Despite the ingenuity of detail shown in Mr. Derby's calorimetric apparatus, it is not thought desirable to describe it here for this reason — that while one attempts to keep the upper half of the boiling tube at 78°, there must be within the dephlegmating tube a range of temperatures from the boiling-point of the mixture down to about 78°. For that reason the "constancy of temperature" signifies a range of some degrees. If, therefore, one wishes to make use of a temperature jacket, it is advisable to have the temperature slightly lower than the boiling temperature of the more volatile, since the velocity with which the vapor is actually passing has to be considered, and it is desirable to have as the uppermost layer of liquid in the dephlegmator, the pure volatile component which may not condense just at its boiling temperature. The actual temperature chosen is of course directly connected with the velocity of the distillation and should be the lower, the more rapid the distillation.

These experiments are, so far as the writer is aware, the only ones which give data as to the heat efficiency obtained with any particular form of distillation apparatus, and form part of the scheme required in the examination of any technical form. The work has not been continued further in this direction since it is apparent that the standards as to what constitutes efficiency in the laboratory vary with each problem of laboratory work.

If, however, one compared an apparatus of the continuous form with any discontinuous non-fractioning forms, in regard to efficiencies of any kind, the result would be to banish the latter from the factory as inefficient and unscientific.

Vapor composition

According to the phase rule, it is necessary with two components and two phases, to fix two variables in order to define the system for purposes of reproducing it. These may be t and p, t and c, or p and c. Now, in the ordinary methods of determining the composition of a vapor in equilibrium with a solution, this is not done. The vapor phase is usually removed at constant pressure, varying temperature and concentration, or constant temperature with varying pressure and concentration. Of course, the method of analysis may be such that the variation is very small, but this is rarely the case. After many practical difficulties in determination of vapor pressures with acetone water mixtures it occurred to us that better control and more accurate results could be obtained by maintaining two of these variables constant. The first idea was to pass into the solution kept at constant temperature a vapor from another solution, which vapor should be roughly of the composition corresponding to equilibrium with the first. This was rather difficult to carry out easily and successfully.

The plan was therefore tried of returning to the boiling liquid a liquid which had approximately the same composition as that which was being removed, and in the same amounts, using the constancy of the thermometer as the gauge of the concentration of the boiling liquid, so that the thermometer would stay constant so long as the heat supply remained constant. We have here therefore the exact analogy of the Beckmann method for boiling-point work, only that in addition to adding the vapor condensed, we are also removing it for purposes of analysis. This method has been found to work very well in practical work. In some preliminary work, it was found possible to keep the boiling-point of an acetone water mixture constant for fifteen minutes within ± 0.1° over a part of the curve where such a temperature variation indicated a concentration charge of 0.2 pct, where the concentration of liquid and vapor phases differed very widely.

In the case where analysis may be difficult, this now offers a synthetic method of determining vapor composition by distilling off a certain amount of vapor and adding to the boiling flask the same amount of liquid made up synthetically and then examining for equality of boiling-point.

The first method is to be preferred in cases where accuracy is desired. It is exactly analogous to the method discovered by Bancroft[1] for determining the composition of a solid phase separating, the details of which have been worked out by Browne.[2]

Cornell University, April, 1902.

[*To be continued.*]

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[1] Bancroft. Jour. Phys. Chem. 6, 178 (1902).

[2] Browne. Ibid. May, 1902.

ON THE STABILITY OF THE EQUILIBRIUM OF UNIVARIANT SYSTEMS

BY PAUL SAUREL

The following properties of the multiple point of an n-component system are well known:

At the temperature and under the pressure of the multiple point $n + 2$ phases can coexist in equilibrium. At the temperature and under the pressure of the multiple point the system of $n + 2$ phases admits of a continuous series of states of equilibrium in which the entropy and the volume of the system and the masses of the phases change, while the total thermodynamic potential of the system and the concentration of the phases remain unaltered. The state of equilibrium is completely determined if, in addition to the masses of the independent components, the volume and the entropy of the system be given.

If we represent the multiple point by a point in the temperature-pressure plane, there will pass through this point $n + 2$ curves, each of which represents the states of equilibrium of one of the $n + 2$ univariant systems which can be formed by suppressing one of the phases of the univariant system.

The multiple point divides each of these curves into two parts; along one of these parts the equilibrium of the corresponding univariant system is stable, while along the other part the equilibrium is unstable. The object of the present note is to establish the following two theorems which enable us to distinguish the stable from the unstable portions of the temperature-pressure curves.

I. Consider at the temperature and under the pressure of the multiple point a reversible change which increases the entropy of the invariant system, but which leaves its volume unchanged. During this change the masses of certain of the phases increase, while the masses of the others decrease. If the mass of the i-th phase increases, then the i-th univariant system, that is to say, the univariant system in which the i-th phase is lacking, cannot exist in stable equilibrium at temperatures higher than that of the multiple point. If, on the other hand, the mass of the i-th phase diminishes, then the i-th univariant system cannot exist at temperatures lower than that of the multiple point.

II. Consider at the temperature and under the pressure of the multiple point a reversible change which diminishes the volume of the invariant system, but which leaves its entropy unchanged. During this change the masses of certain of the phases increase while the masses of the others decrease. If the mass of the i-th phase increases, then the i-th univariant system cannot exist in stable equilibrium under pressures greater than that of the multiple point. If, on the other hand, the mass of the i-th phase diminishes, then the i-th univariant system cannot exist under pressures lower than that of the multiple point.

These two theorems are for invariant systems, the analogues of the theorems of Moutier and of Robin for univariant systems. They are due to Bakhuis Roozeboom.[1]

To establish the first theorem, consider at the temperature and under the pressure of the multiple point the i-th univariant system in equilibrium. If we keep the volume of the system fixed we can cause the i-th phase to appear either by increasing or by decreasing the entropy of the system. Suppose that an increase of entropy causes the i-th phase to appear. Denote the total thermodynamic potential, the entropy and the volume of the system in the first state of equilibrium by Φ_1, H_1, V_1, and in the second state of equilibrium by Φ_2, H_2, V_2. Then we have obviously the following relations:

$$\begin{aligned} \Phi_1 &= \Phi_2, \\ H_1 &< H_2, \\ V_1 &= V_2. \end{aligned} \tag{1}$$

If we take the system in the first state of equilibrium and if, without changing the concentrations, we change the temperature

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[1] Recueil des travaux chimiques des Pays-Bas, 6, 329 (1887). Die heterogenen Gleichgewichte, 1, 43 (1901).

T and the pressure Π, the change in the thermodynamic potential will be given by the equation

$$d\Phi_1 = -H_1 dT + V_1 d\Pi. \qquad (2)$$

In like manner, if we take the system in the second state of equilibrium and if, without changing the concentrations, we change the temperature and the pressure, the change in the potential will be given by the equation

$$d\Phi_2 = -H_2 dT + V_2 d\Pi. \qquad (3)$$

If we suppose that the change in temperature dT is positive, equations 1, 2, 3 yield immediately

$$\Phi_1 + d\Phi_1 > \Phi_2 + d\Phi_2. \qquad (4)$$

If we remember that at a given temperature and under a given pressure a system cannot be in stable equilibrium unless its thermodynamic potential has the smallest value possible at that temperature and under that pressure, it follows from inequality 4 that, at a temperature slightly higher than that of the multiple point and under a pressure equal to or slightly different from that of the multiple point, the *i*-th univariant system cannot be in stable equilibrium. This establishes the first part of Theorem I.

Suppose that at the temperature and under the pressure of the multiple point a decrease in the entropy of the system, kept at constant volume, is necessary if the *i*-th phase is to appear. Equations 1 are to be replaced by the following:

$$\begin{aligned} \Phi_1 &= \Phi_2, \\ H_1 &> H_2, \qquad (5) \\ V_1 &= V_2. \end{aligned}$$

If we suppose that dT is negative, equations 5, 2, 3 yield immediately inequality 4. It follows that, at a temperature slightly lower than that of the multiple point and under a pressure equal to or slightly different from that of the multiple point, the *i*-th univariant system cannot be in stable equilibrium. This establishes the second part of Theorem I.

Theorem II. can be established by a course of reasoning in all respects similar to that just given. Instead of the conditions 1 and 5 we now have to consider the conditions

$$\begin{matrix} \Phi_1 = \Phi_2, & & \Phi_1 = \Phi_2, \\ H_1 = H_2, & \text{and} & H_1 = H_2, \\ V_1 > V_2, & & V_1 < V_2. \end{matrix}$$

With the first set of conditions we take $d\Pi$ positive, with the second set negative. In each case we obtain inequality 4.

The demonstration which we have just given is entirely analogous to the demonstration which we have given[1] of the theorems of Moutier and of Robin.

New York, April 12, 1902.

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[1] Jour. Phys. Chem. 3, 548 (1899).

ON THE FUNDAMENTAL EQUATIONS OF THE MULTIPLE POINT

BY PAUL SAUREL

Consider a system of $n + 2$ phases formed by means of n independent components and denote by η_i, v_i the entropy and the volume of the unit of mass of the i-th phase, and by m_{ij} the mass of the j-th component which enters into the unit of mass of the i-th phase. If we denote by $d\Pi_i/dT_i$ the slope of the pressure-temperature curve of the i-th univariant system that can be formed from the invariant system, that is to say, of the univariant system that can be formed from the invariant system by suppressing the i-th phase, then at the multiple point the following equations[1] hold:

$$\begin{vmatrix} \frac{d\Pi_1}{dT_1}, & v_1, & m_{11}, & \dots, & m_{1n} \\ \frac{d\Pi_2}{dT_2}, & v_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{d\Pi_{n+2}}{dT_{n+2}}, & v_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix} = 0, \qquad (1)$$

$$\begin{vmatrix} \frac{dT_1}{d\Pi_1}, & \eta_1, & m_{11}, & \dots, & m_{1n} \\ \frac{dT_2}{d\Pi_2}, & \eta_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{dT_{n+2}}{d\Pi_{n+2}}, & \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix} = 0. \qquad (2)$$

In a previous note[2] we have shown that these equations of Riecke can be written in the form

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[1] Riecke. Göttinger Nachrichten, p. 223 (1890). Zeit. phys. Chem. 6, 268 (1890).

[2] Jour. Phys. Chem. 5, 170 (1901).

$$\sum_{i=1}^{n+2} \delta V_i \frac{d\Pi_i}{dT_i} = 0, \qquad \sum_{i=1}^{n+2} \delta H_i \frac{dT_i}{d\Pi_i} = 0, \qquad (3)$$

in which δV_i, δH_i denote the changes in the volume and the entropy of the i-th univariant system, corresponding to a certain reversible change of that system at the multiple point. It was shown that the reversible changes are such that

$$\sum_{i=1}^{n+2} \delta V_i = 0, \qquad \sum_{i=1}^{n+2} \delta H_i = 0, \qquad (4)$$

and it should have been pointed out that the $n + 2$ reversible changes used in defining δV_i and δH_i constitute, when taken in succession, a reversible cycle of the invariant system. Our result can accordingly be stated as follows:

Consider at the temperature and under the pressure of the multiple point a reversible cycle of the invariant system, which can be divided into $n + 2$ reversible changes, each of which involves the phases of one of the $n + 2$ univariant systems. During the i-th of these reversible changes, the volume and the entropy of the invariant system receive increments δV_i, δH_i. These increments satisfy not only equations 4, but also equations 3.

Riecke's equations can be put into another form, which is even simpler than that just given.

Denote by M_i the mass of the i-th phase, by $\mathfrak{M}_j$ the mass of the j-th compoment, and by H, V, the entropy and the volume of the invariant system. Then the following equations hold:

$$\sum_{i=1}^{n+2} M_i \eta_i = H, \qquad \sum_{i=1}^{n+2} M_i v_i = V,$$

$$\sum_{i=1}^{n+2} M_i m_{ij} = \mathfrak{M}_j, \qquad j = 1, 2, \ldots, n. \qquad (5)$$

Consider at the temperature and under the pressure of the multiple point a reversible change which leaves the volume unaltered. The preceding equations give us

$$\sum_{i=1}^{n+2} \eta_i \delta M_i = \delta H, \qquad \sum_{i=1}^{n+2} v_i \delta M_i = 0,$$

$$\sum_{i=1}^{n+2} m_{ij} \delta M_i = 0, \qquad j = 1, 2, \ldots, n. \tag{6}$$

From these equations 6, we obtain at once

$$\begin{vmatrix} \eta_1, & v_1, & m_{11}, & \ldots, & m_{1n} \\ \eta_2, & v_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_{n+2}, & v_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix} \delta M_i$$

$$= (-1)^{i+1} \delta H \begin{vmatrix} v_1, & m_{11}, & \ldots, & m_{1n} \\ \vdots & \vdots & & \vdots \\ v_{i-1}, & m_{i-1,1}, & \ldots, & m_{\ -1,n} \\ v_{i+1}, & m_{i+1,1}, & \ldots, & m_{i+1,n} \\ \vdots & \vdots & & \vdots \\ v_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix}. \tag{7}$$

The coefficient of δH in this equation is the same as the coefficient of $d\Pi_i/dT_i$ in equation 1. It follows from this without difficulty that equation 1 can be written in the form

$$\sum_{i=1}^{n+2} \delta M_i \frac{d\Pi_i}{dT_i} = 0. \tag{8}$$

Consider now at the temperature and under the pressure of the multiple point a reversible change which leaves the entropy unaltered. Equations 5 now give us

$$\sum_{i=1}^{n+2} v_i \delta M_i = \delta V, \qquad \sum_{i=1}^{n+2} \eta_i \delta M_i = 0,$$

$$\sum_{i=1}^{n+2} m_{ij} \delta M_i = 0, \qquad j = 1, 2, \ldots, n. \tag{9}$$

From these we obtain at once

$$\begin{vmatrix} v_1, & \eta_1, & m_{11}, & \dots, & m_{1n} \\ v_2, & \eta_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_{n+2}, & \eta_{n+2} & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix} \delta M_i$$

$$= (-1)^{i+1} \delta V \begin{vmatrix} \eta_1, & m_{11}, & \dots, & m_{1n} \\ \vdots & \vdots & & \vdots \\ \eta_{i-1}, & m_{i-1,1}, & \dots, & m_{i-1,n} \\ \eta_{i+1}, & m_{i+1,1}, & \dots, & m_{i+1,n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix}. \qquad (10)$$

The coefficient of δV in this equation is the same as the coefficient of $dT_i/d\Pi_i$ in equation 2. It follows that equation 2 can be written in the form

$$\sum_{i=1}^{n+2} \delta M_i \frac{dT_i}{d\Pi_i} = 0. \qquad (11)$$

The fundamental equations of the multiple point can accordingly be put into the form of equations 8 and 11. It should be remembered that in the first of these equations δM_i denotes the increment of M_i, due to a reversible change in which the volume is kept constant, while in the second δM_i denotes the increment of M_i due to a reversible change in which the entropy is kept constant.

New York, April 12, 1902.

NEW BOOKS

Cours d'électricité. *Tome I., Electrostatique, Lois d'Ohm, Thermo-électricité. By H. Pellat. 16 × 25 cm; pp. vi + 329. Paris: Gauthier-Villars, 1901. Price: paper, 10 francs.*—The present book is the first of a series of three volumes, containing the lectures delivered by Pellat at the Sorbonne. It is written in the well-known, clear-cut, French manner, and demands no further mathematical equipment than the usual elementary knowledge of the calculus. The volume before us treats of electrostatics, Ohm's law, and thermoelectrics, and is therefore particularly interesting in view of the valuable contributions which Pellat has made to electrostatics.

The presentation of the subject is original from a French point of view; it does not start out with Coulomb's law, but rather from the fundamental experiments in electrostatics considered apart from the law, which in fact is not directly true for heterogeneous media. It seems to the reviewer, however, that even if this method is new in France, it does not differ very essentially from the introduction to Maxwell's great treatise. The definition of a quantity of electricity is made by aid of Faraday's ice pail experiment. The delightful and leisurely descriptions given, however, are in marked contrast to the draft and stress which characterizes Maxwell's treatment. This chapter and the following on the electrostatic field, contain many new and striking experiments. A skilful introduction is made early in the book of Helmholtz's *Doppelschicht*, and the old potential notation of Volta is effectively revived. The appearance of the round Jacobian delta, here as in Poincaré's books, is evidence of its general introduction in France. A like indulgence of the reader in English books is remote enough.

In the next chapter, electrostatic principles and their consequences are discussed, the remarks grouping themselves around Poisson's equation and Gauss's theorem. To the reviewer, the inexorable consistency of this chapter is a trifle wearisome, and he is tempted to believe that the methods by which women proverbially reach conclusions may after all have something in their favor. At least one would like to be spared the labor of constructing diagrams in one's brain from tedious descriptions. Much may be said by the man of scholarly and dignified leisure, against the narrowness and rigidity of diagrams, and doubtless the other man who reasons about electricity as Euclid reasons about geometry, will agree with him. But with most of us, acquisition is always a more or less incidental matter; and one is grateful to get an idea, no matter how, if it is only attainable in a reasonable time. The chapter is very long. Much of it, particularly the treatment of the refraction of lines of induction, is well done.

The chapter on induction and capacity is shorter, but of the same nature, being virtually a review of the preceding. The subject is overhauled with a degree of detail that leaves no loophole for the student to exercise his own imagination or acuteness. The book is literally a lecture course.

After these introductory remarks, there follow several chapters on electrical machines, in which, as is usual in French text-books, large artistically executed figures accompany the text, while the explanations maintain the same degree of detailed thoroughness laid down in the preceding chapters. The reviewer would gladly dispense with many of these completed pictures, in favor of a greater wealth of diagrams inserted throughout the book. The orderly historical treatment presented throughout is attractive. One becomes impressed not only with the rapid progress of science, but with the more melancholy fact of how short-lived is the fame of really excellent work.

In the following chapter on energy, the discussion is made complete by the introduction of the heat effects within the condenser, discovered as to their nature by Pellat himself. It is curious that, in a book so rigorously logical, subjects like electrical oscillation and Joule's law should be introduced by an equation subsequently to be proved. Finally in the discussion of X-rays and allied phenomena, it seems inexcusable that all reference to the work of J. J. Thomson and his pupils, now so famous with us, should be omitted. The theory given of cathode ray phenomena, in which Villard's explanation in terms of the dissociation of water vapor is presented, together with the authors to whom the main discoveries are referred (not an English name appears), are all quite different from our own estimate of the more noteworthy researches and the chief thinkers on the subject.

Pellat's chapter on dielectrics is admirable. He has here embodied much of his own work with a judicious selection of fundamental experiments by others, like those of Boltzmann for gases. Nevertheless one misses a variety of familiar material as, for instance, the more recent experiments of Ayrton and Perry. The reviewer knows of no book in which the phenomenon of dielectric polarization and its consequences is so clearly put. The small chapter on Coulomb's law deduces it consistently from Gauss's theorem, a method the reverse of this being the more antiquated custom. Chapters follow on Ohm's and Kirchhoff's laws, and a final chapter on thermoelectrics. The method here is naturally that of the Thomson and Tait diagram, though more credit is given to original investigations like those of Magnus, Becquerel, and others, than is usually done.

Throughout its whole extent the book preserves a logical clearness of the first water, and yet one does not put it down without a feeling of disappointment. Shades of Lagrange and Poisson, of Fresnel and Fourier, of Carnot and Ampère, is it true that to-day at the Sorbonne a doctrine can be presented as new, which in English-speaking countries is almost ancient history?

C. Barus

Lehrbuch der Elektrochemie. *By Svante Arrhenius. Translated from the Swedish by Hans Euler. 14 × 21 cm; pp. viii + 305. Leipzig: Quandt and Händel, 1901. Price: bound, 8.75 marks.* — This is really a treatise on the electrolytic dissociation theory, and therefore includes a surprising amount of general physical chemistry. The headings of the chapters are: earlier electrochemical views; laws of Avogadro and van 't Hoff; vapor-pressure of solutions; boiling-point and freezing-point of solutions; general conditions of equilibrium; reaction velocities; electrolytes and electrolytic dissociation; conductivity of electrolytes; degree of dissociation, and dissociation constant; additive properties of solutions; equilibrium between several electrolytes; calculation of electromotive forces; potential difference between two substances; oxidation and reduction cells, secondary cells; electrolytic analysis; the electric current as a source of heat.

When we consider the amount of ground to be covered in about three hundred pages, it is obvious that the subject can only be outlined, and this is actually the case. This is rather an advantage than otherwise, because there is real need of a book which will give the student a preliminary general view of the subject, leaving him to fill in the minor details later. As it is, the author calls attention in a mild way to a number of discrepancies which are usually passed over in silence. He points out that the so-called "solubility product" is not a constant because the solubility of the undissociated salt is affected by the presence of other substances. He shows that the difference between the decomposition voltage for the halogen acids and their sodium salts is not the same as the difference between the corresponding values for the oxygen acids and their sodium salts. He does not lay much stress on —0.560 V as the absolute value for the normal calomel electrode. In many respects it is a very satisfactory little book. There are two faults to be found with it. There are no references to the literature, and the body of the text dates back to 1897, the time when the author lectured the subject at Stockholm. In many respects, therefore, the book is some five years or more behind the times.

Wilder D. Bancroft

Grundriss der qualitativen Analyse *vom Standpunkte der Lehre von den Ionen. By Wilh. Böttger. 15 × 22 cm; pp. xii + 248. Leipzig: Wilhelm Engelmann, 1902. Price: bound, 7 marks.* — In the preface the author says: "In preparing this book I have tried to present the theoretical relations between the chemical processes in an easily intelligible form and as nearly exactly as is possible. By a strictly logical application of the relations thus obtained, I hope to have established their significance and the importance of a knowledge of them.

"In addition to the theory of the ions, I have laid special stress on the fundamental law of chemical equilibrium, the mass law. The great importance of this law, even for qualitative experiments, is pointed out wherever possible."

The first part of the book deals with the detection of the metals of the six groups in the usual order. The detection of the acids comes next. There is a chapter on blowpipe analysis, one on the preparation of solutions for analysis, and a final chapter on the rarer metals, thallium, gold, and the platinum metals being included under this head.

The author has done his work well and the really interesting question is as to the advantage of rewriting qualitative analysis in the language of the dissociation theory. In certain respects, there is a distinct gain. We see at once why potassium ferrocyanide does not behave in some ways like a ferrous salt, and why mercuric chloride and mercuric nitrate show differences which are not characteristic of some other chlorides and nitrates. It is important to lay stress on the qualitative effect of mass action and on the reversibility of reactions; but this can be done just as well when speaking of sulphate as of sulphate ions. On the other hand, there are distinct disadvantages. When we add a salt with a common ion we usually get a decrease in solubility, but this is not general and we have no way of predicting whether there will be an increase or decrease of solubility in any particular case. The important thing for the student to know is that both cases occur and that we add an excess of the precipitating substance when this causes a decrease of solubility, and that we do not add an excess when this causes an increase in solubility. Further, the important thing to the student is the qualitative side and not the quantitative side. He adds an excess of the precipitating agent when this causes a decrease of solubility quite irrespective whether this decrease can or can not be expressed algebraically. It is not too much to say that there is no single case in qualitative analysis where the precipitation takes place according to the formula written by the author, and consequently it is a mistake to lay stress on the formula. It is an additional mistake to apply the dilution law to sodium chloride. It is simpler, but it is not true. It also will not help physical chemistry to account for the solubility of lead sulphate in concentrated sulphuric acid by referring to the concentration of $\overline{HSO}_4$. Every chemist who is not overwhelmed by a theory knows that lead sulphate is soluble in liquid sulphuric acid just as potassium nitrate is soluble in liquid nitric acid, mercuric chloride in liquid methyl alcohol, sodium chloride or sugar in liquid water. The reviewer believes that no chemist can work with maximum efficiency unless he is familiar with the general principles of what we are forced to call physical chemistry; but he does not believe that there is anything to be gained by mis-stating facts.

These criticisms do not apply to this book alone. The author is not to blame because he has written down things which are generally accepted by physical chemists as true. There is scarcely a text-book on physical chemistry which does not contain the same and worse errors of fact. We have been so carried away by the beauty and the apparent simplicity of the electrolytic dissociation theory that we have rather lost our grip on the facts and no longer distinguish very clearly between what is proved and what is not proved.

While the reviewer believes that the future text-book on qualitative analysis will contain much less dissociation theory than this one, he recommends this book to teachers, if only to learn what the other extreme is.

Mercurous chloride, p. 19, is not affected by light when pure and dry.

Wilder D. Bancroft

The Elements of Physical Chemistry. *By J. Livingston R. Morgan. Second edition, revised and enlarged. 12 × 18 cm; pp. x + 352. New York: John Wiley and Sons, 1902. Price: bound, $2.00.* —The first edition of this book has already been reviewed in this Journal (3, 234). A shorter notice of the new edition will therefore suffice. The present volume when compared with the earlier one shows many minor alterations in the text; the major changes are a shifting of the chapter on the Rôle of the Ions in Analytical

Chemistry, and the addition of a chapter of problems. There is no doubt that the book could be studied with profit, but it is uncritical in a field where a critical attitude of mind is the best fruit of study. Furthermore we find here, as indeed in almost all works under the same title, one side of the subject developed at the expense of the rest. The present book is written from the standpoint of the theory of electrolytic dissociation; so the phase rule is disposed of in five pages. It does come with something like a shock, however, to find in a work revised in 1902, the same blithe statements about the connection between normal osmotic behavior and electrical conductivity which Arrhenius could properly make fifteen years ago.

The added chapter of problems will unquestionably render the book more useful by giving the student a kind of drill which other texts do not provide.

A. P. Saunders

A Text-Book of Inorganic Chemistry. *By A. F. Holleman. Translated by Hermon C. Cooper. 14 × 22 cm; pp. viii + 458. New York: John Wiley and Sons, 1902. Price: bound, $2.50.*—A notice of the Dutch original and of the German translation of this book has already appeared in this Journal (4, 621). The arrangement and the contents of the present translation are substantially the same.

The work as a whole is a very admirable one, and by its completeness and modern point of view comes into comparison with the similar works of Ostwald and Erdmann. It may be said to be less modern than Ostwald and less complete than Erdmann; but considering its smaller size, it bears comparison with those works well, and is certainly one of the very best text-books in our language. By this is not meant that it is free from faults, for it has many,—some due to the author and some to the translator. Being only about half as large as the works just mentioned, it suffers much from compression, especially in the theoretical parts, the treatment of the fundamental laws of chemical combination as well as of the more mathematical aspects of theoretical chemistry being often far too condensed.

In the matter of translation, while the English is generally clear and good, there are words here and there which sound somewhat more than quaint. Such is, among others, the phrase "a piercing odor" (pp. 9, 71, 84), as a translation of "stechend"; so "plurivalent" is to the reviewer's ear unusual, and not to be preferred to the more customary "multivalent"; "polyvalent" as of mixed etymology, the translator has apparently intentionally avoided; nevertheless he does use "pentivalent" so spelled, which is something worse than doubtful, as is also "tetrivalent". The phrase "spectral analysis" is substituted for the more usual "spectrum analysis"; "a reflective surface of mercury" appears on p. 51; "momentarily" renders "momentan" on pp. 16 and 83; "estimation" occurs on p. 64 where "estimate" would be correct; on p. 166 stands the very awkward phrase "as yet no compounds of argon have been able to be prepared"; "hydrogele" occurs throughout the book many times instead of "hydrogel", and on p. 262 "phosphorus bronze" for "phosphor bronze". Errors of this kind, so far as they are errors, are not few. Evident omissions are on the other hand not many; certainly the work of Chapman on the melting-point of red phosphorus should have been cited. Of actual misprints the following may be noted: — LiO_2 instead of Li_2O on p. 293; following the German edition, the melting-point of potassium nitrate is given (p. 310) at 238° in place of 338°; the name "Tamman" is so mis-spelled.

To atone for these defects, the student will find much which is often not included in books of this size; so reaction velocity, the phase rule, osmotic pressure, thermochemistry, Le Chatelier's rule, Henry's law, and many such topics come in for discussion, though there is no general treatment of oxidation and reduction processes. On the whole, as will be seen, a pretty complete programme for a book of only 450 pages.

In general appearance and clearness of type the book does not compare favorably with the German edition. *A. P. Saunders*

Übungsbeispiele für die elektrolytische darstellung chemischer Präparate. *Zum Gebrauch im Laboratorium für Chemiker und Elektrochemiker. By Karl Elbs. 14 × 20 cm; pp. vii + 100. Halle: Wilhelm Knapp, 1902. Price: 4 marks.* — The author gives directions for oxidizing chromium sulphate to chromic acid, for preparing sodium hypochlorite, potassium and sodium chlorates, potassium and sodium bromates, potassium iodate, potassium perchlorate, ammonium persulphate, cuprous and cupric oxide, lead white, lead disulphate, and for the recovery of copper from brass. The organic preparations include the electrolysis of acids, the preparation of aniline, phenyl hydroxylamine derivatives, azoxy and azo compounds, hydrazo compounds, and benzidines, diamines and amino phenols, the reduction of carbonyl compounds and the oxidation of alcohol to iodoform.

Each experiment is accompanied by a general discussion of the reaction and of the conditions, making the little volume a very satisfactory one. The student will have some difficulty in making out what the author means by "Stoffausbeute". *Wilder D. Bancroft*

Die Elektrolyse des Wassers, ihre Durchführung und Anwendung. *By Viktor Engelhardt. (Monographien über angewandte Elektrochemie. Band I.). 16 × 24 cm; pp. xii + 117. Halle: Wilhelm Knapp, 1902. Price: 5 marks.* — This is the first of a series of "Monographs on Applied Electrochemistry." The editor outlines his plan somewhat as follows: "It is intended to present as complete and as exact reports as possible on single branches of applied electrochemistry, the first volume of which now appears. These monographs are not to be merely a general statement of the present condition of the particular branch of applied electrochemistry with which they deal, but are to be extensive special reports from which one can also gather an idea of the historical development and a good knowledge of the more important patents. The effort will be made to overcome, so far as possible, the secretiveness prevailing in technical circles and to furnish data in regard to construction and operating expenses, in regard to existing factories, etc."

This is a most excellent plan, and the list of collaborators promises well for the future numbers. Certainly every one will wish the editor success in his undertaking.

As the title shows, the first number of the series is on the electrolysis of water. This choice was made rather on account of the historical importance of the subject than for its technical importance. It is, however, a good selection; because it does give us a relatively simple case.

The technical processes are divided into three classes, those which furnish hydrogen and oxygen separately, those which furnish them without separation, and those which furnish oxygen alone. Under the first head, the author distinguishes between processes where there is a porous non-conducting diaphragm; where there is a solid non-conducting diaphragm; and where there is a conducting diaphragm. The division in which the mixed gases are formed is devoted exclusively to a discussion of voltameters. The processes which furnish oxygen alone can be divided into those in which there is depolarization at the cathode and those in which there is a precipitation of metal at the cathode.

Hydrogen and oxygen are used in the oxy-hydrogen blow-pipe for high temperatures, and for working metals where the presence of carbon would be disadvantageous. They are used for lighting purposes as the lime-light. Experiments have also been made to use the mixed gases for explosives; but this is not a commercial success as yet.

Hydrogen alone is used for balloons, and the electrolytic hydrogen weighs only about half as much as the gas obtained by the action of acids on zinc. The hydrogen-air flame is used largely for lead-burning and for welding aluminum. With a modified Welsbach burner, this flame gives a brilliant light and has the advantage of not contaminating the air.

While the practical uses for hydrogen are somewhat limited, there is no doubt but that every reduction in the price of oxygen will be followed by a largely increased demand for it. *Wilder D. Bancroft*

Über anorganische Colloide. *By Alfred Lottermoser. (Sammlung Chemischer und chemisch-technischer Vörträge. VI. Band, 5/6 Heft. 16 × 25 cm; pp. 161-240. Stuttgart: Ferdinand Enke, 1901.* — The author discusses the formation of colloidal hydroxides, sulphides, elements, halides, and miscellaneous compounds. The monograph contains a number of most interesting facts, but there is a distinct failure to appreciate relative values. Bredig's work on colloids receives less than a page; van Bemmelen's work is dismissed with a word, as "being outside the scope of the paper"; there is no reference to Hardy; and few will understand about the reversible formation of sol and gel under the influence of alkali. The pamphlet is valuable for what it brings; but it does not justify its title. *Wilder D. Bancroft*

Grundriss einer Geschichte der Naturwissenschaften, *zugleich eine Einführung in das Studium der grundlegenden naturwissenschaftlichen Litteratur. By Friedrich Danneman. I. Band. Erläuterte Abschnitte aus den Werken hervorragender Naturforscher aller Völker und Zeiten. Zweite Auflage. 14 × 28 cm; pp. xv + 422. Leipzig: Wilhelm Engelmann, 1902. Price: paper 8, bound 9 marks.* — The appearance of a second edition of this work may be taken to indicate that it has found something of the welcome it deserves. It consists of selected passages from original works, — "sources," — which range chronologically in the present edition from Aristotle to Heinrich Hertz, and in subject-matter from Copernicus's description of his heliocentric universe and

Bessel's measurement of our distance from the star *61 Cygni*, to Dalton's atomic hypothesis and Pasteur's account of the organisms in the atmosphere.

The book is published by the same firm which brings out Ostwald's *Klassiker der exakten Wissenschaften*, and it might seem as if that series had already covered the ground; but they are meant for the specialist alone, while this collection will appeal to any one who has an intelligent interest in the history of the sciences. This is mainly because the editor has managed by judicious omissions to give in five or ten pages what is essential in each case, without making the text too discontinuous.

The contents, if classified by subject, would fall out roughly as follows:—botany 8, zoology 10, physics 20, astronomy 10, chemistry 15, general science 6.

To those teachers of language who have looked in vain for suitable reading matter in scientific German, the book will be a boon; nothing could be better for the purpose than some of these brief papers; and they have in most cases been so far modernized by the editor as to remove all obscure archaisms. On the whole the collection is one to be most cordially recommended. The present edition is larger than the first by ten new articles.

It may be well to say that the unbound volume falls to pieces when the pages are cut, so that intending buyers will do well to get bound copies.

A. P. Saunders

Ostwald's Klassiker der exacten Wissenschaften.

No. 119. Heft II. Versuch über die Hygrometrie. Von Horace Bénédicte de Saussure. 170 pp. 2.40 marks.

No. 124. Abhandlungen zur Thermodynamik. Von. H. Helmholtz. Herausgegeben von Max Planck. 83 pp. 1.40 marks.

No. 125. Untersuchungen über Salpeter und den salpetrigen Luftgeist, das Brennen, und das Athmen. Von John Mayow. Herausgegeben von F. G. Donnan. 56 pp. 1 mark.

No. 126. Experimental-Untersuchungen über Elektricität. Von Michael Faraday. Herausgegeben von A. J. v. Oettingen. IX.-XI. Reihe. 106 pp. 1.80 marks.

No. 128. Experimental-Untersuchungen über Elektricität. Von Michael Faraday. Herausgegeben von A. J. von Oettingen. XII. und XIII. Reihe. 113 pp. 2 marks.

Leipzig: Wilhelm Engelmann, (1901).

We greet with pleasure the appearance of further volumes in Ostwald's series of well-edited and inexpensive reprints of scientific classics. The one on hygrometry completes the publication of Saussure's papers. The collection of Helmholtz's publications on the thermodynamics of chemical processes includes the paper of 1877 on the electromotive forces of concentration currents, the famous paper of 1882 in which the theory of free energy is formulated, and the two subsequent publications under the same general title. The editor, Planck, has corrected the numerous errors of the original texts, and has added very helpful and brief annotations. Mayow's work has been carefully retranslated from the original Latin, and is likewise well annotated. The remaining volumes of the present lot continue Faraday's experimental researches. Containing now one hundred and twenty-eight volumes, this admirable series has become notable in extent as well as in quality. *J. E. Trevor*

First Book of Qualitative Analysis. *For studies of water solution and mass action. By Albert B. Prescott and Eugene C. Sullivan. Eleventh edition, entirely rewritten. 13 × 20 cm; pp. 148. New York: D. Van Nostrand Company, 1902. Price: bound, $1.50, net.* — "To enable the beginner in the qualitative laboratory to deal with chemical change in the light of present studies of WATER SOLUTION and the mass action has been the main purpose in preparing this edition. With this intent the little book has been written anew throughout. It was first published by one of the authors in 1879, and designed then as now for classes taking a short course in qualitative practice.

"In this edition as in the one first issued, the object is not so much analysis as it is chemistry; not detective method for its own sake so much as it is a personal acquaintance with the character of the chemical elements and with the nature of chemical change. A suitable course in qualitative chemistry is found to be a favorable avenue by which to approach the vantage grounds of science."

The "solubility-product" confronts us and the authors speak of ions when they mean acid or basic radicals. The following quotations may be interesting. "Reducing agents change Fe''' to Fe'' (p. 73)." "The ferrocyanides and ferricyanides contain neither the ferrous nor the ferric ion in appreciable quantity, as is evident from the fact that they do not yield the ordinary reactions of ferrous or ferric salts (p. 71)." "Reducing agents effect the reverse change [of ferricyanides into ferrocyanides] (p. 112)." This may help the student, but then again it may not. *Wilder D. Bancroft*

Methods of Gas Analysis. *By Walther Hempel. Translated from the third German edition, and considerably enlarged, by L. M. Dennis. 12 + 18 cm; pp. xix + 490. New York: The Macmillan Company, 1902. Price: bound, $2.25.* — The earlier German and English editions of this valuable and suggestive work by one of the greatest authorities on gas analysis are well known to all who are interested in the subject. In the present new translation of the last German edition, to quote the translator's preface, "the work has been thoroughly revised, both by the author and the translator, and has been changed to such an extent that this translation may indeed be regarded as a fourth edition of the book." The net addition amounts to about one hundred pages.

Many of these changes and additions will prove very acceptable; for example, the enlargement in variety of gases and mixtures discussed (including the "noble gases" and bacterial decomposition-products) and the extension of gas-volumetric methods to the analysis of a larger number of solid substances. One of the changes will however be greatly regretted by some, namely, the omission of the old apparatus for exact analysis pictured on page 47 in the English edition of ten years ago. In spite of the mortality of the many rubber connections (the cause of its omission), this apparatus is one of unusual completeness and fitness for its purpose.

The reviewer finds also with regret several evidences of haste in writing and in translating. The most serious is the statement on page 77: "If the gases are saturated with moisture when measured, corrections for the tension of aqueous vapor are unnecessary." This statement is not true as applied to the measurement of changing pressure in constant volume, and the ingenious "correction tube" designed to eliminate changing conditions does not remedy the essential difficulty. The tension of aqueous vapor is always such a stumbling block to the novice that this mistake is peculiarly unfortunate. The question is correctly treated on page 69 of the old English edition. Other evidences of haste are the confusing statements about the solubility of helium on page 169, and the statement on page 474 that 1 cc of carbon dioxide weighs 0.00196633 gram. This last number is likely to convey a false impression of accuracy;—for the last three figures have no significance unless latitude and the serious deviations from the gas law are considered. Latitude alone might cause variations from 0.001961 to 0.001968.

The arrangement of the book is likewise an evidence of haste, being somewhat scattered and inconvenient; and one regrets that the table of atomic weights should be based upon $H = 1$ instead of upon the international standard $O = 16.000$.

But these are, after all, matters of detail, which when recognized can do no serious harm. As one would have expected, the book is full of value, and should be in the hands of every one who has to deal chemically or physically with aeriform material. *T. W. Richards*

Indicators and Test-Papers. *Their source, preparation, application, and tests for sensitiveness, Designed for the use of chemists, pharmacists, and students. By Alfred I. Cohn. Second edition, revised and enlarged. 12 × 18 cm; pp. ix + 267. New York: John Wiley and Sons, 1902. Price: bound, $2.00.*—The second edition contains in an appendix an account of the following indicators: alizarine-green B; ammoniacal copper solution; coralline-malachite green; diazoparanitraniline-propylmetacresol; iron isopyrotritarate; iron salicylate; patent blue L; perezol; potassium ferrocyanide with ammonium molybdate; sodium alizarine sulphonate. *Wilder D. Bancroft*

L'Industrie des Acides minéraux. *Encyclopédie scientifique des Aide-Mémoire). By Leon Guillet. 11 × 18 cm; pp. 182. Paris: Gauthier-Villars. Price: paper, 2.50 francs; bound, 3 francs.*—This number of the *Encyclopédie scientifique des Aide-Mémoire* deals mainly with the manufacture of sulphuric, hydrochloric, and nitric acids, although about one-third of the work is devoted to other inorganic acids—hydrofluoric, sulphurous, arsenious and arsenic, boric and liquid carbonic. Several chapters contain statistics as to imports and exports, taxes and freight. Some of the more recent processes, as the contact method for sulphuric, and the Valentine and Guttman-Rohrmann for nitric acid, are described and compared.

The book has been condensed too much for American technical students; it adds one more to the list of descriptive chemical works which it is desirable, but not necessary, to have as a convenient reference book. *H. R. Carveth*

Die Preisbewegung von Chemikalien seit dem Jahre 1861. *By Karl Grauer. (Sammlung Chemischer und chemisch-technischer Vorträge, VII. Band; 2-4 Heft). 16 × 24 cm; pp. 29 to 130. Stuttgart: Ferdinand Enke, 1902.*

Price: 1.20 marks. — The author discusses first the changes in price of a number of the important chemicals, pointing out the causes for the particular variations. He next considers the general causes affecting the chemical industry as a whole. Under this head the author groups: cost of production; supply and demand; patents; trusts. While most products have fallen in price enormously since the sixties, there is very little change in the case of fuming sulphuric acid, crude hydrochloric acid, iodine, potassium iodide, mercury and mercuric chloride. White arsenic, methyl alcohol and absolute alcohol are higher in price. The pamphlet is a most excellent one and should be read by all chemists.

Wilder D. Bancroft

Electromagnets; their design and construction. *By A. N. Mansfield.* (*Van Nostrand's Science Series, No. 64.*) *9 × 14 cm; pp. 155. New York: D. Van Nostrand Company, 1901. Price: boards, 50 cents.* — A preliminary chapter on history and classification is followed by one on the properties of the magnetic circuit and by one on materials of construction and formulas for winding. Tractive and attractive electromagnets are next discussed and then electromagnets for alternating currents. The book closes with an appendix of useful information. *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

Comments on self-acting mercury pumps. *G. W. A. Kahlbaum. Drude's Ann.* 6, *590* (*1901*). — The author discusses at some length the usefulness of the Sprengel pump, and the various precautions necessary for its efficient working. He emphasizes the fact that the speed of working depends entirely on the proper adjustment of the inflowing and outflowing mercury. This has to be regulated for each pump. To avoid the breaking of the fall tubes, which is the most common source of annoyance in this form of pump, an inner tube of steel is placed so as to receive the inflowing mercury. In conclusion some hints are given for the construction of an efficient pump. *H. T. B.*

Aluminothermic welding by means of an automatic outflow. *H. Goldschmidt. Zeit. Elektrochemie,* 7, *935* (*1901*). — The crucible containing iron and thermite has a hole in the bottom covered with an iron plate. This is either melted through by the mass in the crucible or is pushed up by means of a lever as soon as the contents of the crucible are liquid. In this way the molten iron comes out first and the alumina afterwards. Steel rails can be welded in place by this process, and it can be used successfully to mend broken shafts at sea. *W. D. B.*

The significance of changing atomic volume, I. *T. W. Richards. Zeit. phys. Chem.* 40, *169* (*1902*). — Review (6, 146) from Proc. Am. Acad. 37, 3 (1901).

Reply to the remarks of Felgentraeger. *T. Middel. Drude's Ann.* 6, *214* (*1901*). — The author points out that the explanation of Felgentraeger of the change in sensitiveness with temperature in the balance used by Richarz and Krigar-Menzl (6, 65) is partially correct, but that his numbers are incorrect. He also replies to the criticism made by Felgentraeger to some of his observational data. *H. T. B.*

One-Component Systems

On the so-called anomaly in oxygen at low pressures. *M. Thiesen. Drude's Ann.* 6, *280* (*1901*). — The deviation from Boyle's law at a pressure of 0.7 mm, which was discovered by Bohr, forms the subject of the present paper. The author gives a lengthy criticism of the work that has been done on the subject, which, taken with his own work, leads him to doubt the existence of any anomaly. The deviations which have been observed he considers to be more likely due to errors of experiments. *H. T. B.*

On the expansion of porcelain and glass at high temperatures. *L. Holborn and E. Grüneisen. Drude's Ann.* 6, *136* (*1901*). — By the method previously used, the authors determine the thermal expansion of Berlin porcelain, and the hard Jena thermometer glass (59^{III}). Peculiar interest is attached to their measurements for the former material on account of the recent work of Chappuis and Harker on the boiling-point of sulphur (5, *148*). By using the formula obtained by the authors, and recalculating Chappuis and Harker's results for their air thermometer measurements, the boiling-point of sulphur is lowered half a degree, which brings it more into agreement with Callendar and Griffiths' experiments. Simple parabolic formulas are obtained for capillary tubes and rods of hard Jena glass. *H. T. B.*

Two-Component Systems

On the factor *i* as a function of the concentration in moderately dilute solutions. *A. Smits. Zeit. phys. Chem.* 39, *385* (*1893*). — The author uses a sensitive two-liquid manometer with water and aniline as the liquids. It was found that the molecular lowering of the vapor pressure passes through a minimum for NaCl and H_2SO_4 at about 0.5 mol. With KNO_3 the value decreases rapidly with increasing concentration, while it increases slowly with sugar. Experiments on boiling-points with a special silver boiling-flask and also with a modified McCoy apparatus showed a similar result. At 56° and at 74° no minimum was found with NaCl. The author reaches the conclusion that "molecular weight determinations in moderately dilute solutions offer no clue as to the dissociation of a solute." The author believes in sticking to the electrolytic dissociation theory, but in supplementing it by arbitrary assumptions in regard to the polymerization of the undissociated substance. *W. D. B.*

On solutions of inorganic salts in water. *W. Biltz. Zeit. phys. Chem.* 40, *185* (*1902*). — The apparent discrepancies between the osmotic phenomena with highly dissociated inorganic salts and the requirements of the mass law can be explained by the assumption of the occurrence of certain chemical reactions during the process of solution, chief among which is hydration, with the formation of complexes and with hydrolysis as next in importance. The magnitude of the discrepancy is in general dependent on the greater or lesser tendency of the ions of the salt in question to form complexes. If this tendency is very small, there is a good agreement between the requirements of the mass law and the experimental data. *W. D. B.*

On the determination of molecular weights, V. *E. Beckmann. Zeit. phys. Chem.* 40, *129* (*1902*). — A general discussion of some of the principles connected with the boiling of liquids by bubbling in vapor. The author then describes in detail a modification of the McCoy apparatus designed by himself. He is not prepared to admit that the thermometer readings are any more accurate with this form than with the old, nor does he believe that there is any real saving of time. The new method takes less solvent in the boiling tube.

W. D. B.

On the chemical dynamics of nickel carbonyl. *A. Mittasch. Zeit. phys. Chem.* 40, *1* (*1902*). — At ordinary temperatures the reaction between nickel and carbon monoxide is a reversible one. With change of pressure the change of equilibrium is represented fairly accurately by the formula $KC_1 = C_2^4$. The value of K varies however very much with the nature and state of the metallic nickel. While this unexpected result may be due to surface tension phenomena, it is impossible to establish this beyond question. With nickel dust there was the least decomposition. The calculation of the heat of reaction from the displacement of the equilibrium with the temperature gave a value which does not agree at all with that obtained directly. No explanation was found for this discrepancy.

The decomposition of nickel carbonyl is a monomolecular reaction, while the formation is a reaction of the third order and not of the fifth. The reaction velocity is very much affected by the presence of air, hydrogen sulphide, mercury, etc. A few special experiments were made to determine whether measurable amounts of nickel dicarbonyl could be obtained, but the results were all negative. *W. D. B.*

The physical chemistry of sulphuric acid. *O. Sackur. Zeit. Elektrochemie,* 8, *77* (*1902*). — This is a discussion of the contact process for making sulphuric acid with special reference to the fact that SO_3 is absorbed more rapidly by a 98 percent acid than by any other concentration. The author considers this acid of constant boiling-point as a mixture of H_2SO_4, $H_2SO_4H_2O$ and SO_3. There being no free water there is nothing to polymerize the SO_3; and it therefore reacts directly with the monohydrate, forming the anhydrous acid. *W. D. B.*

The liquefaction of mixtures of gases. *F. Caubet. Zeit. phys. Chem.* 40, *257* (*1902*). — Translated from the author's doctor thesis (6, 196).

On the change in volume and density of liquids by the absorption of gases. *E. Wenzel. Drude's Ann.* 6, *520* (*1901*). — The absorption of hydrogen, oxygen, sulphur dioxide, carbon dioxide, and ammonia are studied. The results show that for the less absorbent gases the law of proportionality between the increase in volume and the quantity of absorbed gas is substantiated, while for strongly absorbed gases the law does not hold. The specific gravity of the absorbed gas is found to be greater than the gas in the liquid condition. *H. T. B.*

Multi-Component Systems

On the solubility of ammonia in salt solutions as shown by measurement of partial pressure, I. *R. Abegg and H. Riesenfeld. Zeit. phys. Chem.* 40, *84* (*1902*). — The solubility of ammonia in salt solutions varies with the nature and concentration of the salt. The change with the concentration of the salt is not linear, but the authors consider it as linear because that simplifies the mathematical relations. With anions which have an affinity for water, the solubility of ammonia decreases. The reviewer believes that the careful and accurate study of the behavior of one salt would have been more profitable than the superficial and inaccurate measurements actually recorded. *W. D. B.*

The occlusion of magnesium oxalate by calcium oxalate and the solubility of calcium oxalate. *T. W. Richards, C. F. McCaffrey, and H. Bisbee. Zeit. anorg. Chem.* 28, *71* (*1901*). — The authors show that anything which increases the amount of undissociated magnesium oxalate increases the amount of occlusion. The precipitated calcium oxalate takes up magnesium oxalate on standing in contact with the solution. Calcium oxalate is soluble to the extent of about six milligrams per liter at 18°. The precipitate should therefore be washed with a solution of ammonium oxalate in water. *W. D. B.*

On the state and properties of colloids. *P. D. Zacharias. Zeit. phys. Chem.* 39, *468 (1902).* — The author believes that the process of dyeing consists usually in the absorption of a colloidal dye-stuff by a colloidal fiber. The author assumes that colloids have an enormously high molecular weight because they affect the vapor-pressure of the water so slightly. This conclusion falls to the ground if the colloids are not appreciably soluble in water. He also looks upon Henry's law as an interesting generalization, having no necessary connection with the molecular weight of the solute. There is therefore nothing to trammel the author in his speculations, and he reaches no conclusions which can be tested experimentally. There are consequently no difficulties.

W. D. B.

Action of hydrogen peroxide on potassium metavanadate. *L. Pissarjewsky. Zeit. phys. Chem.* 40, *368 (1902).* — When hydrogen peroxide acts on KVO_3 or on molybdic acid the heat of reaction increases until the ratio of hydrogen peroxide to the other substance is two to one, when it becomes constant. With tungstic acid there is no sharply marked point. *W. D. B.*

Osmotic Pressure and Diffusion

The diffusion of hydrogen through palladium. *A. Winkelmann. Drude's Ann.* 6, *104 (1901).* — The determination of the diffusion of hydrogen through palladium and the dependence on pressure is the object of the author's work. It is found that the diffusion varies with some power of the pressure, and it is suggested that dissociation takes place and that only hydrogen in the atomic state passes through the metal. This seems to be substantiated by the results of Holtsema. The experimental results seem best explained on the assumption that the diffusion is proportional to the dissociated molecule. At atmospheric pressure one square cm of palladium, 0.0102 mm thick, allowed in one second 0.0080 cc of H to pass. Graham's results for glowing platinum are a little greater; but, as the author points out, the metal was heated much higher in Graham's experiments. *H. T. B.*

Velocities

On catalysis. *W. Ostwald. Zeit. Elektrochemie,* 7, *995 (1901).* — This is an address delivered at Hamburg. Four types of catalysis are distinguished: the overcoming of supersaturation; catalysis in homogeneous systems; catalysis in heterogeneous systems; action of enzymes. In the discussion of an explanation of catalytic agent, it is now admitted that there are probably some cases in which the formation of intermediate products leads to an increased reaction velocity. *W. D. B.*

Electromotive Forces

The electromotive force of the hydrogen-chlorine gas cell. *E. Müller.*

Zeit. phys. Chem. 40, *151* (*1902*). — The electromotive force of the hydrogen-chlorine gas cell in normal hydrochloric acid is 1.3660 volts at 25°. The change of the electromotive force with the concentration of the acid is not at all in accord with the calculated change; but the discrepancy may be due in large part to direct hydrolysis of the chlorine and consequent increase in the concentration of hydrochloric acid. The electromotive force appears not to depend on the previous history of the chlorine. *W. D. B.*

Remarks on electrode potentials. *F. Haber. Zeit. Elektrochemie*, 7, *1043* (*1901*). — The author objects very properly to the log K in the formula for potential differences with oxidizing or reducing agents because one never knows what substances are taken as forming and what as disappearing. He proposes to refer everything either to the hydrogen electrode standard or to the −0.560 of the calomel electrode, writing the concentration of the reduction products in the numerator and of the oxidation products in the denominator. He also discusses the heat effects. *W. D. B.*

On the electric properties of alloys of copper and cobalt. *G. Reichardt. Drude's Ann.* 6, *832* (*1901*). — The author describes a series of experiments on alloys of copper and cobalt, which he carried out in a similar way to the experiments of Feussner on alloys of copper and nickel. Very small quantities of cobalt are found to exert a large influence on the electric properties of copper. An alloy of from 3 to 5 percent of cobalt produces a diminution of the temperature coefficient of the copper to 0.00077, which is found to be a minimum value. A maximum thermoelectric force of 33 microvolts against pure copper is found for the same strength of alloy. The specific resistance of the alloy is a maximum between 0 and 10 percent of copper, while for this strength the thermoelectric force is a minimum. No practical utility can be expected from a copper-cobalt alloy, but the author suggests that a mixture of from 1 to 2 percent of cobalt could be employed for thermojunctions, which would have the advantage not possessed by other materials of a high melting-point and low specific resistance. The cobalt alloys show magnetic properties, which is contrary to the experience with nickel alloys. It is pointed out as a matter of interest that two such closely allied elements as Ni and Co should show such widely differing properties when alloyed with copper. *H. T. B.*

The temperature coefficient of the susceptibility of salt solutions of the iron group with special reference to iron chloride. *H. Mosler. Drude's Ann.* 6, *84* (*1901*). — The object of the present work is to determine the correctness of the temperature coefficient of the susceptibility as given by Plessner and by Jäger and Meyer. The method of measurement is the one proposed by G. Wiedemann, and consists in measuring the turning moment of a vessel containing the liquid suspended in a magnetic field. The relation between temperature and concentration shows some curious changes, accounted for by the author's supposition of hydrolyzation. This he attempts to prove by solution in alcohol, but other complications prevent any results from being obtained. In conclusion it is shown that the results of Jäger and Meyer stand in close accord, and that the results of Plessner are too high compared with the present experiments.

H. T. B.

Remarks to the paper by J. Koenigsberger on the susceptibility of water. *G. Jäger and St. Meyer. Drude's Ann.* 6, *870* (*1901*). — The authors point out that they used three methods for determining their field strength, and that their communications have not all been seen by Konigsberger. *H. T. B.*

Electrolysis and Electrolytic Dissociation

On electrolytic refining in Germany. *H. Danneel. Zeit. Elektrochemie*, 8, *137* (*1902*). — A brief account of the firms producing electrolytic sodium, copper, silver, gold, platinum, nickel, bismuth, tin and zinc. Some of the author's statements in regard to the Papenburg works have been questioned, Zeit. Elektrochemie, 8, 177 (1902). *W. D. B.*

On the cathodic behavior of iron in ammonium nitrate solution and on a new ferro-ferric oxide. *A. Kaufmann. Zeit. Elektrochemie*, 7, *733* (*1901*). — Haber had found that, when a concentrated ammonium nitrate solution was electrolyzed at a low temperature with a low current density and an iron cathode, the iron dissolves and a golden yellow solution is formed from which an amorphous black oxide precipitates on heating. This has been confirmed and the author shows that that oxide has the composition $2FeO.3Fe_2O_3$. It was found further that metallic iron is attacked by a saturated solution of ammonium nitrate in ammonia, gas being given off and a golden yellow solution formed. This takes place more readily the more finely divided the iron. In the resulting ferro-ammonium nitrate solution, the iron is present as part of a complex cation. On heating this solution the new oxide is precipitated. *W. D. B.*

The electrolysis of alkali chloride solutions with carbon anodes. *L. Sproesser. Zeit. Elektrochemie*, 7, *971*, *987*, *1012*, *1027*, *1071*, *1083* (*1901*). — This is an investigation of carbon anodes, consisting of retort carbon, special anode carbon, and a French graphite. Acheson's graphite was not included in the test. Except in one case, the loss on coking was less than 1.5 percent, showing the absence of any large amount of volatile hydrocarbons. The amount of ash varied from 0.4 percent to 5.90 percent. The ash always contained Fe_2O_3, Al_2O_3 and SiO_2. The porosity varied from 11 to 28 percent, the retort carbons being the least porous.

Experiments on the electrolysis of neutral potassium chloride solutions showed that the yield of hypochlorite is always less with carbon anodes than with platinum anodes, and that oxygen is evolved at a much earlier stage. The decomposition of the carbon anodes in the electrolysis of alkali chloride solutions is essentially an oxidation process and the chief product is carbonic acid. In a few instances, there was a partial chlorination, but the importance of this is very slight. In addition to the loss by combustion, there is also a loss through mechanical disintegration which may, in some cases, exceed the loss due to chemical action. There is no essential difference in the behavior of carbon anodes due to the presence or absence of a diaphragm.

In sulphuric acid solutions, all the carbon anodes were attacked badly, over ninety percent oxidation taking place. In caustic soda solutions, the action is much less at temperatures below 25°, though there is no difference at 55°. The author draws the following conclusions:

1. The oxidizing action of electrolytic oxygen on carbon is dependent on the natural qualities of the carbon, on the temperature which affects the velocity of the reaction between carbon and oxygen, and on the potential of the oxygen.

2. There is no direct relation between the electrolytic oxidation of carbon in sulphuric acid or sodium hydroxide solutions and the rate of oxidation in chloride solutions.

The porosity of the anode carbons is a very serious item, since the solution in the mass of the electrode may have most of the chloride removed electrolytically and then we have an oxidation analogous to that in the sulphate or hydroxide solution. *W. D. B.*

The electrolytic reduction of *o*-nitro-anthraquinone to *o*-amido-anthraquinone. *J. Möller. Zeit. Elektrochemie*, 7, *741* (*1901*). — The cathode solution consists of 1 g nitro compound, 270 g alcohol and 30 g concentrated sulphuric acid The anode solution was sulphuric acid (1 : 10). Platinum electrodes were used and a diaphragm; the cathode density was 1 amp/qdm and the voltage 3–3.5 volts. About 70 percent of the theoretical yield was obtained. *W. D. B.*

The electrolytic reduction of *o*-nitro-anthraquinone in alkaline solution and of 1, 5 and of α-dinitro-anthraquinone in acid solution. *J. Möller. Zeit. Elektrochemie*, 7, *797* (*1901*). — In alcoholic sodium acetate solution with a nickel wire cathode *o*-nitro-anthraquinone can be reduced to *o*-amido-anthraquinone just as in acid solutions (preceding review). When dissolved in acetic acid and sulphuric acid, the 1,5 dinitro-anthraquinone can be reduced to the corresponding diamido-anthraquinone. Under similar conditions the *α*-dinitro-anthraquinone reduces to *α*-diamido-anthraquinone. *W. D. B.*

Electrolytic reduction of nitrites. *B. Suler. Zeit. Elektrochemie*, 7, *831, 847* (*1901*). — The author has investigated the effect of concentration, current density and temperature when potassium nitrite is electrolyzed with a zinc cathode. Increasing the concentration increases the yield of ammonia and decreases the yield of hydroxylamine. Increasing the current density decreases the yield of both. Increasing the temperature plays havoc with the yield of hydroxylamine and is not favorable to the yield of ammonia. *W. D. B.*

Mossy tin and tin crystals by electrolysis. *W. Pfanhauser, Jr. Zeit. Elektrochemie*, 8, *41* (*1902*). — With high concentration of stannous chloride and low current densities, there is no formation of mossy tin. When the current density exceeds 1 amp/qdm tin crystals are formed. Experiments showed that the time after which these crystals appear increases with decreasing current density. A curve is given to illustrate this, but the other conditions are not specified, so that it is doubtful whether any one could duplicate the results. The author believes that mossy tin and tin crystals both result from insufficient tin at the cathode, the bad precipitate occurring when other cations are present and the crystals when tin alone is there. *W. D. B.*

Experiments on the permanency of platinum-iridium anodes for electrolysis of alkali chlorides. *P. Denso. Zeit. Elektrochemie*, 8, *147* (*1902*). — Experiments with platinum-iridium electrodes, only 0,007 mm. in thickness, show that the loss of weight is a question of a fraction of a milligram and that these electrodes are therefore admirably suited for technical work. *W. D. B.*

Pyrogenic reactions and syntheses by means of the electric current. *W. Löb. Zeit. Elektrochemie*, 7, *903* (*1901*). — The author is studying the effect of electrically heated wires on different liquids and vapors. With chloroform and other chlorine carbon compounds, there is always a precipitate of carbon on the wire, so that the nature of the wire ceases to be a factor. The chief products of the dissociation of chloroform are hydrochloric acid, perchlorethylene, perchlorethane and perchlorbenzene. The belief that dichlormethylene, CCl_2, is an intermediate product, is strengthened by the facts that presence of water causes formation of carbon monoxide, and that presence of aniline causes formation of triphenylguanidine.

Carbon tetrachloride decomposes with liberation of chlorine. Perchlorethylene, perchlorethane, and perchlorbenzene are also formed. In presence of water there is a considerable formation of carbon monoxide. *W. D. B.*

On the direct combination of chlorine with carbon. *W. v. Bolton. Zeit. Elektrochemie*, 8, *165* (*1902*). — When chlorine is passed through the arc, no reaction products can be isolated, though the carbon electrodes show signs of wear. When the chlorine in a narrow closed vessel is exposed to the action of the arc, traces of benzene hexachloride are formed. When a larger vessel is used, hexachlorethane is formed. *W. D. B.*

Researches with platinum resistance and petroleum ether thermometers. *L. Holborn. Drude's Ann.* 6, *242* (*1901*). — The present paper is a contribution from the Reichsanstalt, being one of a series of papers by the author. The comparison of the platinum thermometer with the H-thermometer is carried down to the temperature of liquid air. A comparison of the nitrogen and hydrogen thermometer scales is also made at the low temperature and shows that the former reads 0.5° lower at − 190° C. A comparison of the platinum and nitrogen thermometers at high temperatures shows that the equation deduced by Callendar for reducing the reading of the platinum to the nitrogen scale is correct from 400° down to − 78°, but ceases to hold down to − 190°. A determination of the boiling-point of oxygen gives − 187.7° for 76.0 cm. Some experiments are described on the petroleum ether thermometer which gave good results. *H. T. B.*

Conductivity of mixed solutions of electrolytes. *H. Wolf. Zeit. Elektrochemie*, 8, *117*; *Zeit. phys. Chem.* 40, *222* (*1902*). — The following conclusions are drawn:

1. The conductivity of a mixture is always less than the sum of the conductivities of the single electrolytes.

2. This decrease of conductivity is to be referred to a decrease in the migration velocities in consequence of the changed viscosity and to a change in the dissociation owing to the change in the solvent. The first effect is in general more important than the second.

3. The conductivity of the mixed solutions is further determined by the sohydric tendency, in consequence of the chemical reactions which take place.

W. D. B.

A simple liquid resistance for laboratory purposes. *R. Abegg. Zeit. phys. Chem.* **8**, *43* (*1902*). — This consists essentially of a U-tube in which the resistance is varied by sliding a glass rod up or down. *W. D. B.*

Dielectricity and Optics

On the Maxwell law $K = n^2$ in its bearing on the molecular structure of substance. *A. Batschinski. Zeit. phys. Chem.* **38**, *119* (*1901*). — The author claims that the dielectric constant K equals the square of the refractive index only when the conducting particles are not in contact. Where aggregation takes place, the value of K may exceed n^2. These aggregations are not to be confused with molecular association. *W. D. B.*

A small contribution to the ammonium question in aqueous solution. *G. Bredig. Zeit. Elektrochemie*, **7**, *767* (*1901*). — The electrical absorption of pyridine or betaine in water is much greater than would be expected from the behavior of the components or from the conductivity. This is presumptive evidence in favor of a hydrate in solution. *W. D. B.*

The spectrum of cyanogen. *E. C. C. Baly and H. W. Syers. Phil. Mag.* [*6*] **2**, *386* (*1901*). — The experiments described in the present paper were made to see whether the pure cyanogen spectrum could be obtained free from the carbon spectrum. In accomplishing this the authors have added a great deal of evidence to prove that the Swan spectrum is that of carbon monoxide, and the carbon oxide spectrum that of carbon dioxide. *H. T. B.*

The spectra of hydrogen and some of its compounds. *John Trowbridge. Phil. Mag.* [*6*] **2**, *370* (*1901*). — It has been shown by the author that the so-called line spectrum of hydrogen cannot be considered apart from the spectrum of water vapor. From the results of the author's investigations with high tension electrical discharges he comes to the conclusion that hydrogen is an insulator, and that the passage of electricity through hydrogen, nitrogen and oxygen and their gaseous compounds is conditioned by the water vapor present. *H. T. B.*

Action of solar radiation on silver chloride in presence of hydrogen. *Jouniaux. Comptes rendus.* **132**, *1558* (*1901*). — While silver chloride and hydrogen do not react perceptibly in the dark at temperatures below 200°, the reaction takes place at ordinary temperatures in direct sunlight, the rate being approximately proportional to the lighted surface of the silver chloride. *W. D. B.*

Physiological action of radium rays. *H. Becquerel and P. Curie. Comptes rendus*, **132**, *1289* (*1901*). — Very serious burns, followed by mortification, were the result of exposing the skin for some time to radium rays. *W. D. B.*

Note on accidental double refraction in liquids. *B. V. Hill. Phil. Mag.* [*6*] **2**, *524* (*1901*). — A continuation of the study of double refraction in solutions of gelatine and gum-arabic in water, when subjected to a strain. Jellies were used too dilute to bear their own weight, and the experiments given in the paper are for these enclosed in thin-walled brass tubes. *H. T. B.*

A method of preparing colored flames. *Stscheglayew. Zeit. phys. Chem.* 39, *111* (*1901*) —The problem which the author set himself was to prepare a uniformly-colored steady-burning flame. He does this by blowing air under high pressure through a salt solution, getting a flame corresponding in shape to a blowpipe flame. *W. D. B.*

Contributions to the knowledge of cathode rays. *W. Seitz. Drude's Ann.* 6, *1* (*1901*). — The modern theory of cathode rays being a stream of negatively charged particles or electrons is the standpoint from which the author starts out to study them. The reflection of the rays and the relation between the reflected and incident ray are determined for different materials. The absorption of the rays in metal layers shows that it depends largely on the E. M. F. Lenard's law of absorption is found to be only a first approximation. The velocity of the rays is found to be 0.703×10^{10}. *H. T. B.*

On the action of Becquerel rays on bacteria. *E. Aschkinass and W. Caspari. Drude's Ann.* 6, *570* (*1901*). — It was found for the *micrococcus prodigiosus* that the two types of Becquerel rays from radium differ entirely in their action. The penetrating rays were found to have no effect at all, while the rays easily absorbed were found to exert an important influence in checking the development of the organism. *H. T. B.*

On the pressure of light. *P. Lebedew. Drude's Ann.* 6, *433* (*1901*). — In order to measure the ponderable force exerted by light rays, the author observes the deflection of an exceedingly delicate suspension upon which the rays impinge. The chief source of error which had to be overcome was that due to the ordinary radiometer action. This was to the author's satisfaction reduced to a minimum by working with an exceedingly high vacuum. The energy of the rays was measured in a calorimeter. The result of the work shows that light rays exert a pressure equal to 0.000038 dyne. Recently E. F. Nichols, working with a bolometer method, has shown this force to be equal to 0.000105 dyne. The measurements agree very well with the value calculated from the theory of Maxwell and Bartoli, and thus give an important experimental verification of the theory. The experimental difficulties of the investigation are numerous but are overcome exceedingly well, and the result taken in conjunction with Nichols' work forms a very valuable contribution. *H. T. B.*

A critical study of dark radiation. *O. Lummer and E. Pringsheim. Drude's Ann.* 6, *192* (*1901*). — The authors have shown in another place that the equation of Wien for a spectral radiation is not a general law, and does not accurately represent the facts from their work on radiation from black bodies for long waves. This is contrary to the results of Paschen, and the theory of Wien and Planck. They point out that the small systematic variation from the theoretical equation may be due to errors of experiment in their work, and in the work of Rubens and Kurlbaum, but it would be a matter of theoretical interest if these variations were real. *H. T. B.*

On the radiation from black bodies. *F. Paschen. Drude's Ann.* 6, *646* (*1901*). —This is a reply to the criticism of the author's work to be found in the recent papers of Lummer and Pringsheim. *H. T. B.*

On the dependence of the absorption of a gas in particular of carbon dioxide on pressure. *K. Ångström. Drude's Ann.* 6, *163* (*1901*). — The author makes a study of the absorption of ultra-red rays in carbon dioxide. As sources of heat he uses an Argand burner, a large Bunsen burner and an electrically heated spiral. The latter give him a temperature of 300° C. The effect of pressure and density of the gas is determined, and the influence of the absorbing layer. It is found that an increase of 19 percent in the absorption results from an increase in the pressure from 1 to 4 atmospheres.

It is found that the increase in absorption results in an increase in width of the absorption band, which agrees with the results of Kayser and Paschen. The results of Arrhenius also show that the absorption is a function of the density and absorbing layer.

The author discusses the suggestion of Arrhenius that the varying quantity of CO_2 in the atmosphere produces a difference in the absorption, and comes to the conclusion that the change in the absorption with pressure is so small as not to be influenced by the small fluctuations in the earth's atmosphere.

H. T. B.

Crystallography, Capillarity and Viscosity

A new method for determining the surface tensions of liquids. *W. H. Whatmough. Zeit. phys. Chem.* 39, *129* (*1901*). — The author uses a modification of the Simon-Jaeger method. The concentration surface tension curves for mixtures of liquids may have as many forms as the concentration-pressure curves. The surface tension of solutions containing two salts can be calculated with great accuracy when the values for the binary solutions are known.

W. D. B.

Capillary constants of organic liquids. *P. A. Guye and A. Baud. Comptes rendus,* 132, *1481* (*1901*). — From the surface tension constants, the authors conclude that phenetol, anisol, ethyl acetate, nitrobenzene and benzonitrile are monomolecular as liquids, while *m*-cresol is polymerized. *W. D. B.*

Capillary constants of organic liquids. *P. A. Guye and A. Baud. Comptes rendus,* 132, *1553* (*1901*). — Two oximes and four methanes have been studied. All six appear to be polymerized in the liquid state. *W. D. B.*

On the molecular surface energy of solutions. *D. Pêkar. Zeit. phys. Chem.* 29, *433* (*1902*). — Special experiments showed that in a number of cases the molecular surface energy of a solution could be regarded as an additive property, though not to the extent of permitting calculation of the critical temperature of the solution. The bahavior of sulphur in various solvents is considered to point to the existence of S_8 in solution. *W. D. B.*

On the surface tension of liquid air. *L. Grunmach. Drude's Ann.* 6, *559* (*1901*). — Liquid air, varying in strength of oxygen from 49.9 percent to 76.7 percent was found to have a surface tension of 11.61 to 12.63. The specific cohesion was found to be independent of the percentage composition and in the mean equal to 23.2. The method of measurement was by capillary waves. The results agree well with Knipp's measurements, using capillary tubes.

H. T. B.

SYNTHETIC ANALYSIS IN TERNARY SYSTEMS

BY A. W. BROWNE

In a recent article[1] Professor Bancroft has suggested a new method for analyzing the solid phase appearing in three component systems without removing it from the mother-liquor. In the following pages are described several experimental applications of this method to the analysis of the solid phase separating from aqueous solutions.

The method may be applied in either of two ways: (1) as a direct method, and (2) as a zero method.

In the first case, the solid phase under consideration is allowed to separate out in quantity, the composition of the original solution in terms of the three components having been previously determined by chemical analysis. Then, after the appearance of the solid phase, the composition of the mother-liquor is similarly determined. From the two series of values the composition of the solid phase may be computed; either arithmetically, or by a graphical method involving the use of the triangular diagram.

A simple illustration of the mode of applying the direct method is afforded by the case of an aqueous solution of sodium sulphate and sodium chloride. If the concentration of the former salt is sufficiently great and that of the latter sufficiently small, crystals of sodium sulphate with ten molecules of water will appear on cooling the solution from say 33° to 21°. Now suppose that analysis of the solution prior to the appearance of the crystals shows the percentages of the three components, sodium sulphate, sodium chloride, and water, to be respectively a, b, and c; and that analysis of the mother-liquor after the ap-

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[1] Jour. Phys. Chem. 6, 178 (1902). The same principle has been applied in an only slightly different form by Keutuer. Zeit. phys. Chem. 39, 658 (1902). The first mention is to be found hidden away in a paper by Schreinemakers. Zeit. phys. Chem. 11, 81 (1893).

pearance of the crystals shows the percentages to be a', b', and c'. Since no sodium chloride separates out, we may reduce the percentages, for purposes of comparison, to the basis $b = b' = 1$. Then $\frac{a}{b}$, $\frac{c}{b}$ are the amounts of sodium sulphate and water, respectively, in the original solution; and $\frac{a'}{b'}$, $\frac{c'}{b'}$ are the amounts in the mother-liquor. The excess of the amount of each component in the original solution over that in the mother-liquor is proportional to the amount of that component in the solid phase. Therefore $\frac{a}{b} - \frac{a'}{b'}$ represents the amount of sodium sulphate, and $\frac{c}{b} - \frac{c'}{b'}$ the amount of water in the crystals. The quotients of these expressions, respectively, by M and M′, the molecular weights of sodium sulphate and water, represent the relative number of molecules of the two components present in the solid phase. And finally, by dividing the second quotient by the first, we obtain an expression

$$\frac{M(cb' - c'b)}{M'(ab' - a'b)}$$

for the number of molecules of water to one of sodium sulphate.

This illustration deals with a solid phase in which only two of the three components are present. When all three components are present, the calculation of the final result from the analytical data may be accomplished in an equally simple way. In either event, however, the graphical method described below may be preferable because of its even greater simplicity.

In the second case, the composition of the mother-liquor in terms of the three components is determined, after some of the solid phase to be examined has appeared in the system. Then a considerable quantity of material supposedly identical in composition with the newly separated solid phase is added. After equilibrium has been re-established at the same temperature as before, the composition of the mother-liquor is again determined. If the composition is found to be the same in both cases, — within the limits of experimental error — and has not been altered by the addition of the new material, then the solid phase originally separating out is identical in composition with the substance added.

Instead of determining the composition of the mother-liquor by analysis, we may measure some physical property which is a function of the concentrations of the components, such as the electrical conductivity, or the vapor tension of the solution for a given temperature, or the boiling-point for a given pressure. If the measurements made before and after the additions of the new material are the same, it is to be inferred that the substance added is of the same composition as the solid phase under examination.

As an illustration of the mode of applying the zero method may be taken the simple case of an aqueous solution of barium chloride and hydrochloric acid. Since any change in the percentages of the other two components would cause a change in the percentage of the hydrochloric acid (unless the change should be such that the sum of the percentages of the two components should remain constant), it is necessary to find the percentage of the acid only, by titration with standard alkali in order to obtain a fixed point of reference. This is done after a quantity of the solid phase has been allowed to separate out, and the system has been carefully brought to equilibrium at a certain temperature, read to at least tenths of a degree. A considerable quantity of either the hydrated barium chloride or the anhydrous salt, together with an amount of water equivalent to the two molecules is now added. After equilibrium has been reached at the same temperature as before, the percentage of acid is again determined. If this percentage is found to be the same as that previously obtained, then the concentration of the other two components must have remained unaltered except in the one above-mentioned case. Therefore the two components barium chloride and water must be present in the solid phase in the same ratio as in the material added; i. e., in the ratio $BaCl_2 : 2H_2O$.

It is not necessary that the new material added shall have the exact composition of the solid phase under consideration, else the zero method would be of value only as a means of confirming data otherwise obtained. Different known amounts of one or more of the components known or supposed to be present in the solid phase may be successively added, the effect of each addition upon the composition of the solution being determined by one of the above-mentioned ways after the system had come to equilibrium. For example, if a salt is known to crystallize from solution with a number of molecules of water, the number may be readily ascertained by adding, to a system containing a quantity of the solid phase in question, a portion of the anhydrous salt, together with an amount of water equivalent to one or more molecules. If it is found, after a sufficient time has elapsed for the hydration of the anhydrous salt added, that the composition of the solution is not the same as it was before the addition of any new material, then another water equivalent is added. This process is repeated until the solution is brought back to its original composition. The total number of water equivalents added is then equal to the number of molecules of water of crystallization.

There are numerous possibilities regarding the composition of a solid phase appearing in a three-component system. Among the simplest of these are the following. The phase may be (1) a pure component, (2) a binary compound of components, (3) a binary solid solution, (4) a ternary compound, (5) a ternary solid solution, (6) a solid solution of one component in a compound of the other two, (7) a solid solution of two binary compounds, and (8) a solid solution of two ternary compounds.

As actually occurring instances of the forgoing we have, under proper conditions: (1) potassium chloride separating from the system potassium chloride, hydrochloric acid and water; (2) sodium sulphate with ten molecules of water from the system sodium sulphate, sodium chloride and water; (3) a solid solution of potassium sulphate and ammonium sulphate from the system potassium sulphate, ammonium sulphate and water; (4)

a hydrated ferric chloride with hydrochloric acid of crystallization from the system ferric chloride, hydrochloric acid and water; (5) a solid solution of potassium nitrate, sodium nitrate and silver nitrate from the system potassium nitrate, sodium nitrate and silver nitrate;[1] (6) a solid solution of hydrated ferric chloride and ammonium chloride from the system ferric chloride, ammonium chloride and water; and (7) a solid solution of the heptahydrates of zinc sulphate and ferrous sulphate from the system zinc sulphate, ferrous sulphate and water. A well-authenticated instance of the eighth case is not at hand.

The method in either of its forms may be applied to the above and to all other cases in which a solid phase separates from a three-component system. Since the application in any case is fairly typical, it has been thought sufficient for the purposes of the present paper to consider cases coming under the first three heads only.

Experimental work

(I.) The solid phase is a pure component.

The system studied was potassium chloride, hydrochloric acid and water. The zero method was employed.

A saturated solution of potassium chloride in presence of hydrochloric acid was made by placing about 150 grams of the "C. P." salt, 225 grams of water, and 60 grams of concentrated hydrochloric acid in a flask fitted with a stopper provided with a perforation for the thermometer. The flask was gently warmed and then allowed to stand for 45 minutes, being frequently shaken to facilitate the establishment of equilibrium. The proportions of the components had been chosen with a view to having the salt present in considerable excess. Two samples were now pipetted off from the clear solution at the temperature 22.3°, and weighed. The amount of hydrochloric acid present was determined by titration with half-normal sodium hydroxide solution, with methyl orange as indicator.

After introducing about 150 grams of additional potassium

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[1] On the basis of the fact that potassium and sodium nitrates, and sodium and silver nitrates, respectively, form solid solutions.

chloride and bringing the system to equilibrium as before, the concentration of hydrochloric acid was determined in two new samples taken from the flask at the above temperature.

Results were as follows:

No. of analysis	Weight of sample	Weight of HCl	Percent HCl	Average pct. HCl
1*a*	20.317 gr	1.4404	7.091	7.085
b	16.016	1.1335	7.078	
2*a*	11.338	0.8034	7.086	7.082
b	8.805	0.6231	7.078	

The agreement between the two values in the last column indicates that the solid phase present in the system was identical in composition with the material added. It was therefore the pure component potassium chloride.

(II.) The solid phase is a binary compound of components.

(*a*) The system studied was sodium sulphate, sodium chloride and water. The direct method was applied.

An attempt was first made to obviate the necessity of determining analytically the composition of the original solution by determining it synthetically. Suitable quantities of anhydrous sodium sulphate, decrepitated sodium chloride and water were weighed accurately to milligrams, into an Erlenmeyer flask. The system was brought to equilibrium at about 34°, the flask being frequently shaken, and allowed to stand some time in a water-bath at this temperature to effect as nearly as possible the complete solution of the sodium sulphate. The flask was now allowed to cool to a temperature of about 21°, with the result that a quantity of solid phase appeared. After equilibrium had been re-established, a sample was taken from the clear solution and divided into different portions, which were analyzed for chlorine and sulphuric acid by precipitation respectively with silver nitrate and barium chloride. From the data furnished by these analyses, the percentages of sodium chloride and sodium sulphate were computed. The percentage of water was found by difference. By the arithmetical method described above, the number of molecules of water present in the crystals for every molecule of the anhydrous sodium sulphate was calculated. Results were as follows:

Component	Percentage composition of	
	Solution (by synthesis)	Mother-liquor (by analysis)
NaCl	2.14	3.05
Na_2SO_4	28 15	21.07
H_2O	69.72	75.88

Water of crystallization for $Na_2SO_4 = 9.7 \pm 0.05$ molecule.

This result was not quite as satisfactory as had been hoped. The error may have arisen from either or both of two sources: (1) incomplete hydration of the anhydrous sodium sulphate, caused perhaps by the formation of a protective coating of the hydrate upon the particles of the anhydrous salt; or (2) the presence of some impurity in either the sodium sulphate or the sodium chloride weighed out at the start.

To test whether or no the error arose from incomplete hydration, a second experiment was performed similar to the first in every respect except that extra precaution was taken to insure complete hydration. The anhydrous salt was very finely powdered, and sifted little by little into the flask containing the weighed amount of water. After each small addition of the salt the flask was vigorously shaken, to prevent caking of the material during the process of hydration. Furthermore, such proportions of the components were chosen that the sodium sulphate was almost completely dissolved at a higher temperature. Analyses and calculations were made in the same way as before with the following results:

Component	Percentage composition of	
	Solution (by synthesis)	Mother-liquor (by analysis)
NaCl	11.70	14.96
Na_2SO_4	17.68	10.13
H_2O	70.62	74.91

Water of crystallization for $Na_2SO_4 = 9.7 \pm 0.05$ molecule.

The agreement between these two results obtained under conditions for which the probability of error as the result of incomplete hydration was widely different, eliminates the possible influence of that source, and points toward the alternative influence of some impurity in the salts used. Both of the salts were so-called "C. P." preparations, but had not been further purified by me. Care had been taken thoroughly to dehydrate the sodium chloride before weighing. Some little turbidity had been noticed in the solution, however, when the sodium sulphate was sifted into the flask, and trouble had not been taken to remove the insoluble material with a view to introducing a correction. This impurity would have the effect of making the apparent concentration of the sodium sulphate in the original solution greater than the actual, and that of the water, since it was determined by difference, smaller than the actual concentration. Thus the final result would be too small, as is illustrated in both experiments.

In the third experiment, further trouble from this source was avoided by determining the composition of the original solution, as well as that of the mother-liquor, by analysis. The procedure in this case was as follows: About 41 grams of sodium chloride, 61 grams of anhydrous sodium sulphate and 50 grams of water were warmed, with frequent shaking, until all the salt went into solution. When the solution had cooled to about 34° it was given a thorough final shaking, to insure uniformity of composition. Four samples were now pipetted off: two into small weighed flasks, and two into weighed "pigs" of the sort used in solubility work. The chlorine content of the first pair was determined as in the preceding experiments; and in the second pair the amount of water was determined by evaporating the solution to dryness and heating the residue until the dehydration of the sodium sulphate was complete. From the results for chlorine the percentage of sodium chloride was calculated as before, and the percentage of sodium sulphate was found by difference.

The remainder of the solution, cooled to about 21°, was treated with a minute crystal of the decahydrate of sodium sulphate. Abundant formation of crystals occurred almost instantaneously. Samples were taken from the clear mother-liquor — after sufficient time had elapsed for the establishment of equilibrium, and after this had been further insured by thorough shaking — and analyzed as above for chlorine and water.

Results were as follows:

Component	Percentage composition of	
	Solution (by analysis)	Mother-liquor (by analysis)
NaCl	10.82	13.53
Na_2SO_4	16.11	9.12
H_2O	73.07	77.35

Water of crystallization for $Na_2SO_4 = 10.0 \pm 0.05$ molecule.

This satisfactory result shows that the purity of the salts had been rightly questioned. If the first two experiments were to be repeated, all difficulty such as here experienced could of course be avoided by dissolving the salt in water, and recrystallizing after the removal of extraneous insoluble material by filtration.

(2) The system studied was barium chloride, hydrochloric acid and water. The zero method was applied.

About 500 grams of hydrated barium chloride, 50 grams of hydrochloric acid and 400 grams of water were placed in a stoppered Erlenmeyer flask provided with a thermometer, as in the preceding experiments. The flask was slightly warmed and shaken vigorously to insure saturation of the solution, and then allowed to cool, 21.3° being the final temperature read from the thermometer after the system had reached equilibrium. The proportions of the three components had been so chosen that the salt was present in considerable excess at this temperature. As in the preceding case, by determining the percentage of hydrochloric acid a fixed point for the system may be obtained, since this percentage may be regarded as a function of the other two. A pair of samples was therefore pipetted off from the solution, and the percentage in question determined by titration with half normal sodium hydroxide.

The system is now divided as nearly as possible into two equal parts, each of which contained about the same quantity of solution and crystals. To each of these portions, contained as before in a stoppered Erlenmeyer flask provided with a thermometer, a weighed amount of powdered, anhydrous barium chloride was slowly and carefully added. The anhydrous salt had been prepared by heating the hydrate in a large evaporating dish for a number of hours over a sand-bath. The salt was then powdered and heated again, until, at a temperature somewhat above 100° there was not the slightest visible trace of moisture deposited upon a cold watch crystal repeatedly held close over the salt. Into one of the flasks was now poured a weighed amount of water, slightly in excess of the amount required for the complete hydration of the anhydrous salt added; into the other was poured an amount slightly less than the corresponding theoretical amount for that flask. After a period of time sufficient for the temperature — which had risen about ten degrees during the hydration of the salt — to return to the starting point, 21.3°, two samples from each flask were analyzed for hydrochloric acid. In the first flask, to which the larger quantity had been added, a smaller percentage of acid was found than in the second. And now assuming — as is perfectly legitimate in this case — that the amounts of solution originally present in the two flasks were equal, or so nearly so that the error resulting from their difference is negligible, we may obtain by interpolation the percentage of hydrochloric acid when exactly the amount of water equivalent to two molecules is added. This was effected in practice by plotting excess (or shortage) of water in grams against the change produced in the concentration of the hydrochloric acid. The necessity for the division of the original solution into two parts, and for this subsequent procedure in the determination of the hydrochloric acid after the addition of the new material arises from the practical difficulty of adding the exact equivalent of water.

Results were as follows:

Before adding $BaCl_2 2H_2O$		Amounts added (in grams)		After adding $BaCl_2 2H_2O$		
No.	Pct. HCl	$BaCl_2$	H_2O	No.	Pct. HCl	Average
1	3.429	55.025	10.794	1*a*	3.387	
2	3.432	——	——	*b*	3.401	3.394
	——	——	——	2*a*	3.444	
Av'ge	3.431	58.751	9.858	*b*	3.439	3.442
				By interpolation		3.433

A comparison of the final percentage of acid obtained by interpolation with the percentage found at the same temperature before the addition of the new material, shows that the composition of the solution phase has not been altered. Therefore the solid phase originally present in the system must be identical in composition with the new material added, or must be a compound of barium chloride and water in the ratio $BaCl_2 : 2H_2O$.[1]

(3) The system studied was ferric chloride, hydrochloric acid and water. The direct method was applied.

About 250 grams of ferric chloride with twelve molecules of water were placed in an Erlenmeyer flask. A current of dry hydrochloric acid gas—obtained by adding concentrated sulphuric drop by drop to concentrated hydrochloric acid, and passing the gas through concentrated sulphuric acid contained in a Muencke wash-bottle — was passed into the flask until about half the salt had been liquefied. The generator was now removed, the solution diluted with about 25 cc of water, and the flask heated until the remainder of the solid had been melted. After the flask had been thoroughly shaken, a sample was pipetted into a small stoppered flask, quickly cooled to ordinary temperatures and weighed. It was then diluted to ex-

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[1] If the composition of the solid be assumed, to start with, then it would be possible to use the method in a case like this to ascertain the degree of completeness to which an anhydrous salt could be hydrated in a given time by bringing it into contact with water under such conditions that solution could not take place.

actly 200 cc and set aside for subsequent analysis. Immediately after the sample had been removed, the large flask was quickly stoppered and placed in a cold water-bath to prevent loss of water by evaporation. A minute crystal of the dodecahydrate of ferric chloride was added. A solid phase slowly separated out at about 15°. When this had appeared in considerable quantity, the flask was thoroughly shaken and a second sample obtained, which as before was diluted to 200 cc. In two ten cc portions of each of these samples the percentage of iron was determined gravimetrically by precipitating with ammonium hydroxide and weighing as ferric oxide. The precipitate had been thoroughly washed with hot water until no reaction could be obtained for chlorine in the filtrate. The filtrate, including wash-water, was then analyzed for chlorine. To calculate the percentages of the three components, the difference between the total percentage of chlorine found and the chlorine equivalent of the iron found was reduced to terms of hydrochloric acid. The percentages of ferric chloride and hydrochloric acid being then known, that of water was found by difference.

Results were as follows:

Component	Percentage composition of.	
	Solution (by analysis)	Mother-liquor (by analysis)
Fe_2Cl_6	47.25	44.63
HCl	4.46	5.41
H_2O	48.29	49.96

Water of crystallization for $Fe_2Cl_6 = 12.14 \pm 0.2$ molecule.

In the first attempt made to apply the method to the analysis of the solid phase appearing in this system, care was not taken to dilute the solution with a little water after leading in the hydrochloric acid gas. As a result some of the acid was lost by evaporation during the gradual separation of the solid phase (and the consequent increase in percentage of the acid in the solution) and the final result for the molecules of water of crystallization was rather high.

(III.) The solid phase is a binary solid solution.

The system studied was potassium sulphate, ammonium sulphate and water. The direct method was applied.

Quantities of the two salts were weighed out roughly in such proportions that both of them would separate out when the solution was allowed to crystallize. A saturated solution of the mixture was made at 90°, the potassium salt being dissolved first. The solution was brought to equilibrium at this temperature by thorough shaking. By means of a pipette which had been heated to about the temperature of the solution, a sample was quickly drawn, placed in a stoppered flask, cooled and weighed. The flask containing the original solution was also quickly stoppered, to prevent loss of water by evaporation, and cooled.

In two portions of the sample, total sulphuric acid was determined by precipitation as barium sulphate. In two other portions, total solid was determined by weighing the residue after the water had been evaporated off. To effect this evaporation, the samples were placed in solubility "pigs" and heated in a drying closet kept at about 100°, a slow current of air being drawn over them by means of a suction pump. The reliability of this method had been previously shown by analyzing a solution containing a known weight of the salt mixture.

The original solution had been cooled, in the meantime, and brought to equilibrium at 17°. A large mass of crystals had appeared. Samples of the mother-liquor were analyzed as above. From the two series of results were calculated the percentages of the three components, respectively, in the solution and in the mother-liquor. These are found to be as follows:

Component	Percentage composition of	
	Solution (by analysis)	Mother-liquor (by analysis)
H_2O	52.38	58.88
K_2SO_4	5.91	3.64
$(NH_4)_2SO_4$	41.71	37.48

Since no water separates out in this case, these percentages are reduced to terms of water equals one, and the other components compared as usual. The final result was as follows:

Number of molecules of $(NH_4)_2SO_4$ for each one of $K_2SO_4 = 4.13 \pm 0.05$.

So the two salts form a solid solution, though in this particular case the mixture chanced to be very nearly a molecular one.

Discussion of results

The graphical method of calculating the composition of the solid phase from the data obtained by analysis involves the use of the triangular diagram. For a complete general discussion of this form of diagram and the manner of its use, see an earlier paper by Professor Bancroft.[1]

There is obviously nothing to be gained by plotting the results obtained in the application of the zero method, for the final composition of the system is the same as the initial composition, and the composition of the solid phase is obtained by simply keeping a record of the new material added. When the direct method is applied, however, the triangular diagram affords a quick and easy method (1) of obtaining the composition of the solid phase from the results of analysis, and (2) of assigning the limits of error.

I

Either percentages or molecular weights of the three components may be used as the coordinates of the diagram. In each case it is of course required that the sum of the coordinates of any point on the diagram shall be equal to one hundred. Two points are located on the diagram by plotting the data obtained respectively for the original solution and for the mother-liquor. The straight line drawn through these two points also passes through a point, the coordinates of which show the composition of the solid phase. Obviously this point may not be definitely located by a single line of this sort. Starting from the point

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[1] Jour. Phys. Chem. 1, 403 (1897).

representing the composition of the mother-liquor after the separation of the solid phase, we may expect to find the desired point on any part of the line beyond the point representing the composition of the original solution. But if a second series of data be obtained, the line drawn through the two new points will intersect the first line at the point representing the composition of the solid phase. If molecular weights have been taken as the coordinates, the relative molecular proportions of the components present in the solid phase may be read directly from the diagram, where they appear as the coordinates of the point of intersection of the two lines. If percentages have been taken, the readings must be divided by the molecular weight of the respective components in order to obtain the molecular composition.

The solid phase is shown to contain one, two or all of the three components according as the intersection of the two lines is (*a*) at one of the vertices of the triangle, (*b*) at a point on one of the sides of the triangle, or (*c*) at a point within the triangle. In either of the first two cases one line would have been sufficient to locate the desired point could the assumption have been made at the outset that only one or two respectively of the three components would be present in the solid phase. In some cases this assumption is possible. Suppose for instance that a given salt is known to crystallize with X molecules of water. To evaluate X, a new "indifferent" component—that is, one known to form no compound with the two components already present—is added to the system. The line drawn through a single pair of points determined by analysis will now intersect one of the sides of the triangle at the point representing the composition of the solid phase.

Figures 1 and 2 illustrate the application of this graphical method to two of the experimental cases described above. It will be observed that in neither case the complete diagram is shown, but only that portion which is of particular interest in the case under consideration. The data were first roughly plotted on the full-sized diagram, in which of course each component is represented over a range from zero to one hundred molecular weights. Then, as the points located were found to have grouped themselves within the limits of a comparatively small portion of the entire diagram, that particular portion was enlarged, and the rest left out of account. Since in both cases only two of the components are present in the solid phase, the final result will be represented in each case by a point on the side of the triangle opposite the vertex, which in the complete diagram represents 100 molecules of the absent component. Care was taken, therefore, in selecting the limits of the smaller diagram, to retain in each case as one of the sides, a portion of the side of the larger diagram along which none of the component absent from the solid phase was present.

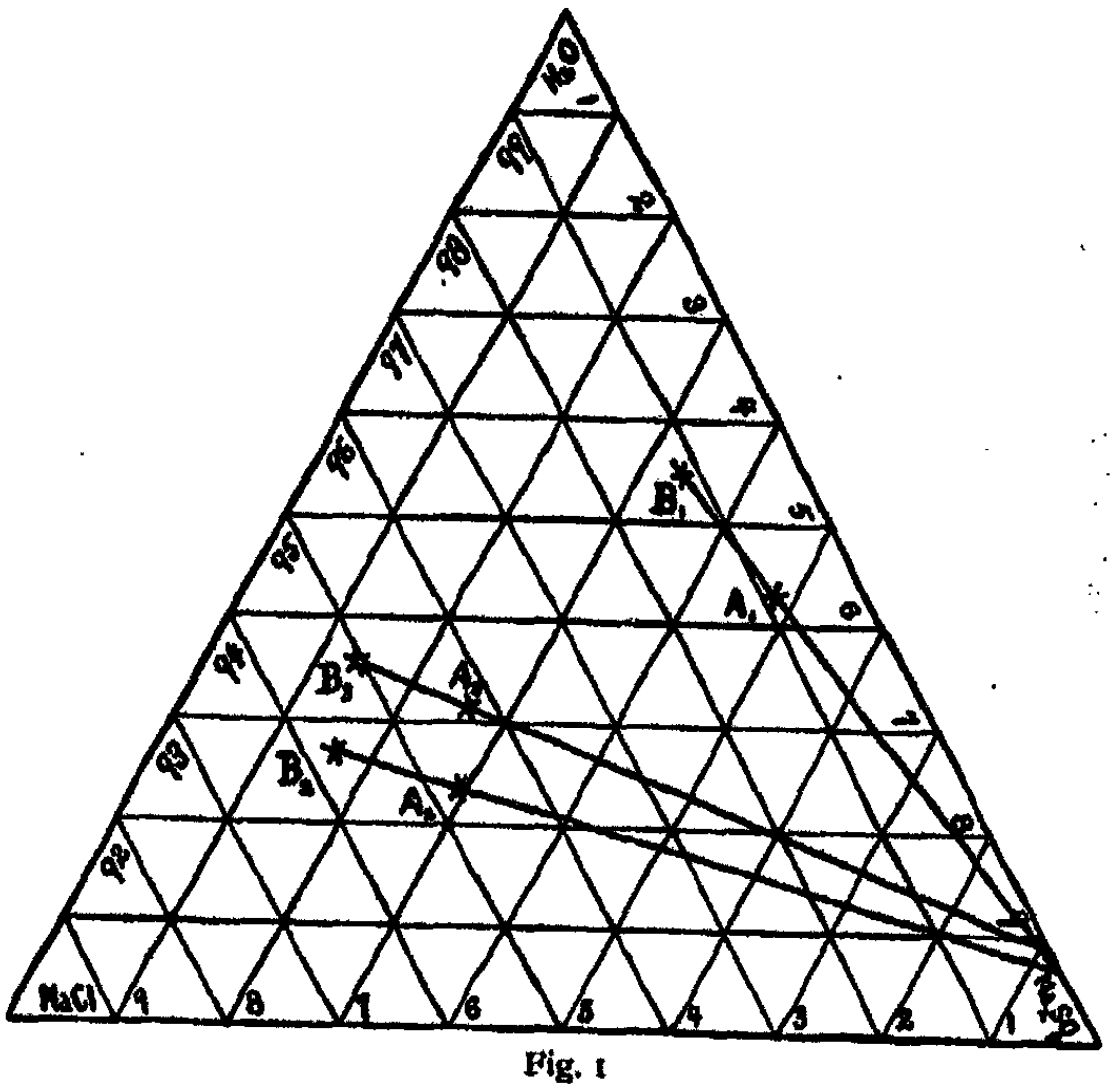

Fig. 1

In Fig. 1 are plotted the analytical data obtained for the system sodium sulphate, sodium chloride and water. The point

A_1 was located by synthesis, and B_1 by analysis after the solid phase to be studied had separated in sufficient quantity. The straight line drawn through these points intersect the right-hand side of the triangle at a point representing the system composed of 90.7 molecules of water for every 9.3 molecules of sodium sulphate. The quotient of the first of these values by the second gives 9.75, which is the number of molecules of water indicated by this experiment as present in the solid phase for every molecule of sodium sulphate. The points A_2 and B_2 were located respectively, by synthesis and analysis in the next experiment made upon this system, as described above. The line drawn through them intersects the side of the triangle, as nearly as may be read from the diagram, at the same point as does the line obtained in the former experiment. The points A_3 and B_3 were in the next experiment located by analysis, and the line

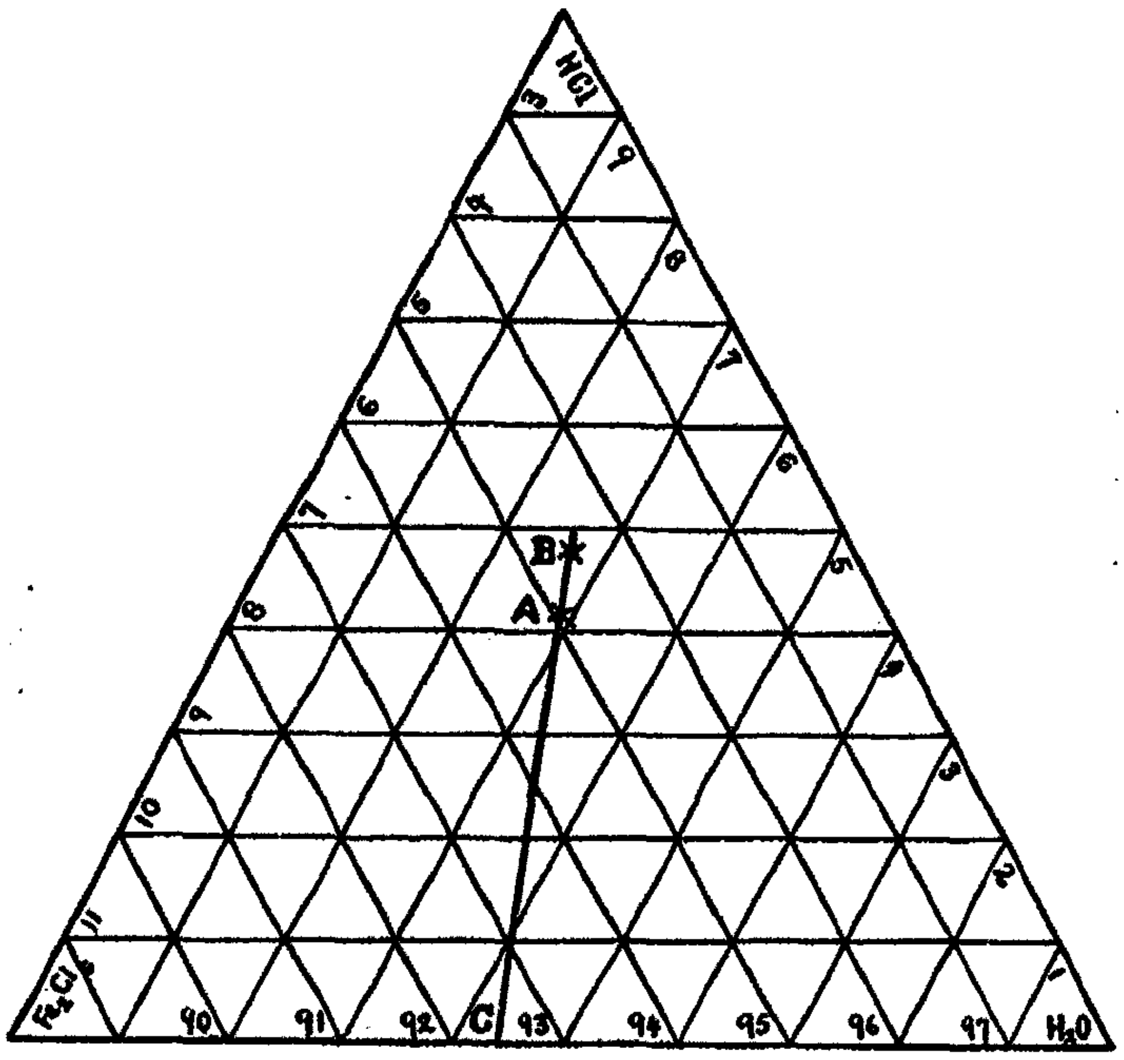

Fig. 2

drawn through them intersects the side of the point corresponding to 90.91 molecules of water and 9.09 molecules of sodium sulphate, or to 10.0 molecules of water for one of the salt.

In Fig. 2 are plotted the analytical data obtained for the system ferric chloride, hydrochloric acid and water. The point A shows the composition of the solution before the separation of the crystals, and the point B shows the composition of the mother-liquor after the crystals have appeared. The line drawn through the two points intersects the base of the triangle, along which are represented systems containing no hydrochloric acid, at the point C, the coordinates of which are respectively 92.4 H_2O and 7.6 Fe_2Cl_6. The quotient of the first of these values by the second is 12.16, which is the number of molecules of water indicated by the experiment as present in the solid phase for every molecule of ferric chloride.

2

By using the graphical method of expressing results it is possible with very little trouble to assign with considerable accuracy the limits of experimental error for any given case.

All error to which the final result in any case is subject arises of course primarily from the errors inherent in the methods of chemical analysis applied in the course of the experiment. If the percentages of the different components in a system under given conditions could be determined in the first place with absolute accuracy, the final result would be likewise absolutely accurate. But this is unfortunately not possible. And moreover, a small initial error in the chemical analyses may during the subsequent course of calculation be greatly multiplied in many cases.

If the probable errors involved in the determination of the composition of the system at each point considered be used as radii in describing circles respectively about the points, and if two tangents be drawn for each pair of circles, then the intercept between the intersections of these two lines with the side of the triangle represents the probable error of the final result.

By inspection of the diagrams shown in Fig. 3 it will be seen that the magnitude of this total error depends upon (1) the diameter of the circles, (2) the distance between the centers of the circles, (3) the distance of the circles from the side of the triangles toward which the tangents are drawn, and (4) the angle at which the straight line connecting the center intersects the side of the triangle. That is to say, the final error becomes smaller (1) as the error of the original chemical analyses and the accompanying calculations is diminished, (2) as the amount of solid phase allowed to separate from the system between the two points is increased, (3) as the concentration of the component absent from the solid phase becomes less at the point nearer the side of the triangle, and (4) as the change in the concentration of the component absent from the solid phase becomes greater between the two points. These last two considerations in their present form apply of course only to the cases in which but two

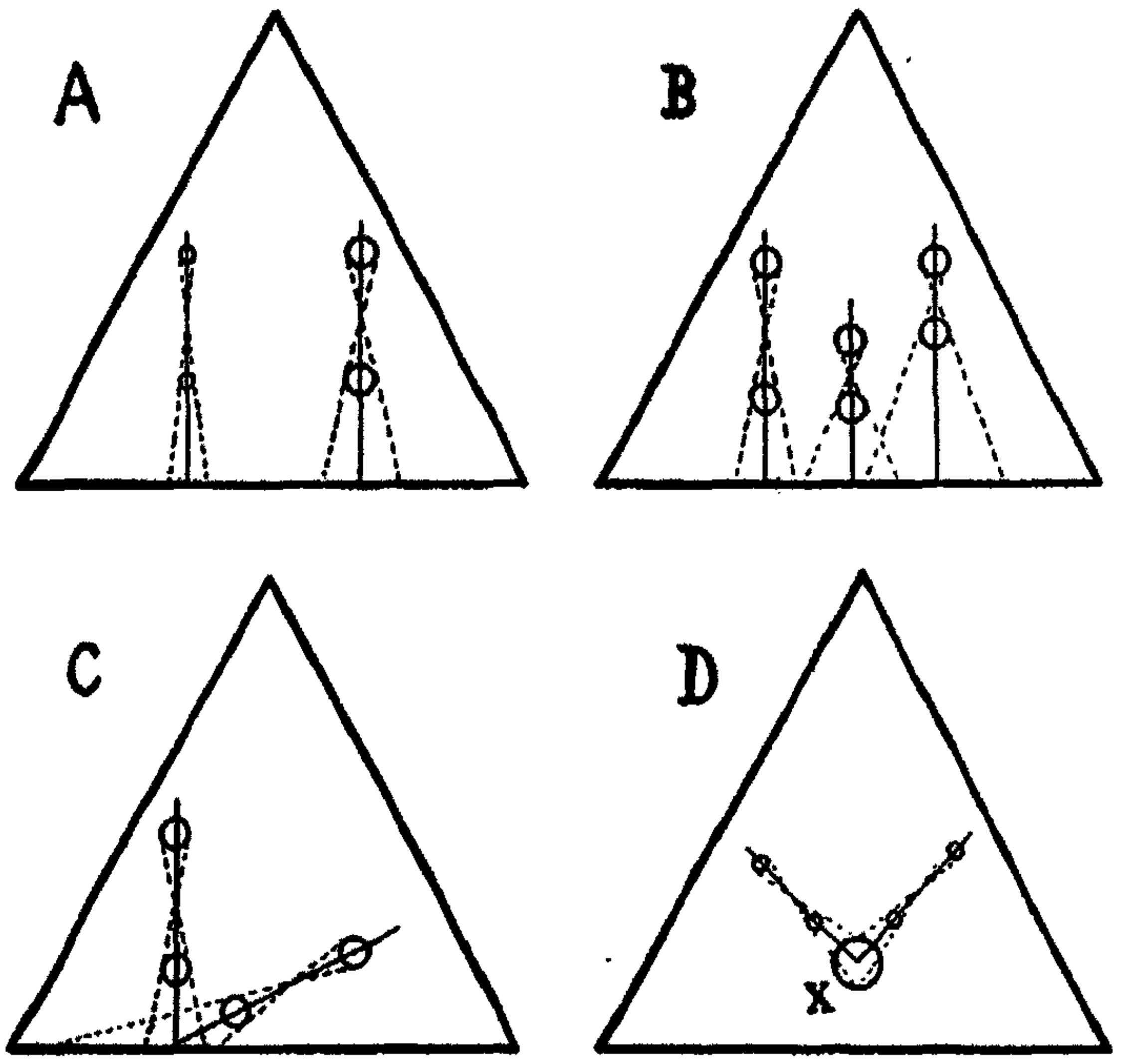

Fig. 3

components are present in the solid phase. When all three components are present the error will be minimized if, in addition to fulfilling the first two conditions mentioned above, the concentrations are so chosen that the two straight lines connecting respectively the pairs of points determined by analysis intersect each other at right angles. This is illustrated in the last diagram shown in Fig. 3, where X is the point representing the desired composition of the solid phase, while the circle drawn about this point as a center indicates the limits of experimental error. In all the diagrams in Fig. 3 the size of the circles has been exaggerated for purpose of clearness.

One of the experimental cases described in the preceding pages affords an excellent illustration of the influence of calculation in multiplying the error, even when all other conditions were rather favorable. This is the case of the system ferric chloride, hydrochloric acid and water, especially selected, because of the great opportunity for error, as the crucial test of the applicability of the new method of analysis. In changing the iron, which had been weighed as ferric oxide, to terms of ferric chloride, the original error was multiplied by at least two. A comparatively large error was therefore introduced into the value for hydrochloric acid, which was determined by difference, and also into the value for water, determined in this case by double difference. Obtaining the quotients of the values for the two other components, respectively, by that for the hydrochloric acid, caused still further multiplication of the error, a process which received its final impetus when one of these quotients was divided by the other to obtain the final result. This error called for comparatively large circles about the points located by analysis; so that although other conditions were not very unfavorable, as may be seen from Fig. 2, the probable error of the final result was comparatively large. It is of great importance, therefore, if any considerable accuracy is desired, that the percentages of at least two of the three components in each case be determined directly by analysis. Thus if the percentage of hydrochloric acid in the case just referred to could have been directly determined by titration, the final error would have been greatly diminished. This is impracticable, however, because of the tendency of the ferric chloride to hydrolyze under the conditions of the experiment.

The results obtained in the first two experiments upon the system sodium sulphate, sodium chloride and water have been published without reserve because of their value as an illustration of the applicability of the method even under adverse conditions of another sort; namely, when the initial composition of the system was determined by synthesis without the previous precaution of securing strictly pure components. The limits of error assigned in these two cases have reference only to the error which might have arisen in the course of the experiment as performed under normal conditions, and not to that introduced by the impurity of one of the components. These were the first experiments tried in applying the new method, and naturally the synthetic method was first resorted to, because of the smaller amount of time and labor involved.

In all of the above experiments, the analyses were conducted with little or no more pains than must be taken in ordinary careful analytical work, and two analyses only were made for each determination, of which the average was used in calculating results. No attempt whatever was made to introduce such refinements as are used for example in atomic weight work, the object of the experiments being a thorough test of the efficiency of the new method under ordinary laboratory conditions, rather than an exhibition of the high degree of accuracy attainable by the exercise of the greatest possible care in manipulation.

In the ordinary cases to which this method may come to be applied there will often be but little call for a high degree of accuracy in the final result, so that unusual refinements will become superfluous. If for example the problem be the analysis of a solid phase known to be a definite compound of two or more of the components, the final result need be accurate to such a degree only that there will be no doubt concerning the *molecular* composition of the solid phase. That is to say, if the solid phase is known to be, for instance, a hydrated salt containing x molecules of water, then would such a final result as 9.8 for x point unequivocally toward 10 as the desired number, even though so large a probable error as ± 0.2 molecule were involved in the experiment. If however the solid phase is known or thought to be a solid solution of any sort, regional determinations will not lead to so satisfactory a result. If the different components or compounds of components which are present in the solid solution do not happen to be present in approximately molecular proportions, then the regional datum will point toward the fact that the phase *is* a solid solution, but will be of no further value.

While this use of the method as a means of securing regional results for the composition of any solid phase in three-component systems would be no doubt of itself sufficient justification for this description of a few typical details of its application, it is by no means the only field of usefulness of the method. By the exercise of even ordinary care in conducting the analyses, results should be obtained in almost every case with a degree of accuracy equal to, and in the majority of cases, I think, much greater than that of, the results obtained by the method now in vogue of removing the solid phase from the system and analyzing it directly. To bear out this statement under conditions most unfavorable to the new method, direct analyses were made of the solid phase separating from the system ferric chloride, hydrochloric acid and water, at ordinary temperatures. A large portion of the crystalline mass was removed from the system and carefully dried with filter-paper. Two pieces were now cut out from the heart of the mass, each of which was quickly weighed and dissolved in water. The iron was weighed as ferric oxide and calculated to ferric chloride. The difference between this value and the total weight gave the amount of water, from which the number of molecules of water was readily calculated. This was found to be 11.88, a result about as far from the truth as was that obtained by the new method, and with a probable error more or less indeterminate because of the impossibility of ascertaining (1) the amount of mother-liquor which may have been occluded in the crystals, and (2) the degree of incompleteness (or overcompleteness) of the drying process, but probably of a magnitude just as great, if not greater, than that of the error to which the newer method was subject. This was undoubtedly an unfavorable case for both methods, since the error was in each case greatly enhanced by calculation, an effect much more pronounced in the case of the new method, however, than in the other. The amount of care exercised in conducting the analyses was as nearly as possible the same in both cases.

While I do not care to make any further claim for the accuracy of the method, because none of the experimental work yet performed has been carried out under conditions guaranteeing minimum error, I am not prepared on the other hand to decry the possibility of applying the method, under extremely favorable conditions, to work of greater dignity than that suggested in the preceding pages. If certain conditions were carefully fulfilled it might be practicable, for example, to use the method — either as a direct or as a zero method — in the determination of the atomic weight of an element, such as sulphur in the compound sodium sulphate, or phosphorus in the compound hydrogen disodium phosphate. In either case the ratio of the anhydrous salt to the water of crystallization, or that of the anhydrous to the hydrated salt could be used to obtain the desired result, assuming the atomic weights of the other elements involved.

If the direct method were used, care would have to be taken to exclude analytical processes involving the atomic weight of the element under consideration. If for example the atomic weight were to be determined by analyzing the decahydrate of sodium sulphate in the system sodium sulphate, sodium chloride and water, the percentage of sodium sulphate in the original solution and in the mother-liquor could not be determined by precipitating with barium chloride. The procedure followed in the last of the three experiments upon the system as described above could however be adopted. The method of calculation for this particular case is shown in the following equation:

$$\frac{x + m_1 + m_2}{m_3} = \frac{ab' - a'b}{cb' - c'b}, \tag{1}$$

in which m_1, m_2 and m_3 denote respectively the atomic weight of sodium taken twice, the atomic weight of oxygen taken four times, and the molecular weight of water taken ten times, while a, b, c, a', b', c' denote the percentages of the three components sodium sulphate, sodium chloride and water in the original solution and in the mother-liquor respectively. x represents the atomic weight of sulphur, and may be evaluated by solving the equation.

The zero method could probably be most advantageously applied to a case like the above by carefully measuring the electrical conductivity of an aqueous solution of sodium sulphate and sodium chloride at a certain temperature, adding a known weight of pure anhydrous sodium sulphate, and then diluting with known amounts of water until the conductivity at the same temperature became exactly the same as before. The final result would then be obtained by solving the equation:

$$\frac{x + m_1 + m_2}{m_3} = \frac{w_1}{w_2}, \tag{2}$$

in which x, m_1, m_2 and m_3 have the same significance as in (1); while w_1 and w_2 denote respectively the weights of anhydrous sodium sulphate and water added.

When either of these methods is used, the difficulties resulting (1) from occlusion of the mother-liquor by the solid phase, and (2) from the possibility of incomplete or overcomplete drying of the phase, difficulties which hitherto have constituted a stock objection to the use of hydrates in atomic weight work, would of course be entirely avoided.

The conditions to be fulfilled in securing maximum accuracy in the application of the direct method (most of which have been already alluded to above) are briefly as follows: (1) care in the selection of analytical methods which give as directly as possible the percentages of the different components, thus avoiding error-multiplying calculation; (2) extreme carefulness in conducting the analyses, including the introduction of all useful refinements, and the carrying out of a large number of analyses for each determination, so as to secure the most reliable average; (3) selection of temperature and concentration conditions so that (*a*) the largest possible amount of solid phase shall be allowed to separate out between the initial and final points determined by analysis, (*b*) the concentration of the component absent from the solid phase becomes as small as possible at the initial point, and (*c*) the change in concentration of the component absent from the solid phase becomes as great as possible between the two points.

The conditions to be fulfilled in order to secure maximum accuracy when the zero method is applied are too obvious to merit especial consideration.

The graphical method can only be applied satisfactorily to systems containing three or, at most, four components. An analytical treatment becomes necessary for the general case of *n* components, all of which may be present in the solid phase. Let A, B, C, D, etc., be the percentage concentrations in one initial solution, and let dA, dB, dC, dD, etc., be the changes in the percentage concentrations, as shown by analysis of the final solution. Let A_1, B_1, C_1, D_1, etc., and dA_1, dB_1, dC_1, dD_1, etc., be the corresponding values obtained from another initial and final solution. Let A_0, B_0, C_0, D_0 be the percentage concentrations of the unknown solid phase. If the percentage concentration of any component be higher in the initial solution than in the solid phase its percentage concentration will increase as crystallization proceeds, while it will decrease if the reverse be the case. From the two sets of analyses we get the relations:

$$
\begin{array}{cc}
\dfrac{dA}{dB} = \dfrac{A - A_0}{B - B_0} & \dfrac{dA_1}{dB_1} = \dfrac{A_1 - A_0}{B_1 - B_0} \\[2ex]
\dfrac{dA}{dC} = \dfrac{A - A_0}{C - C_0} & \dfrac{dA_1}{dC_1} = \dfrac{A_1 - A_0}{C_1 - C_0} \\[2ex]
\dfrac{dA}{dD} = \dfrac{A - A_0}{- D_0} & \dfrac{dA_1}{dD_1} = \dfrac{A_1 - A_0}{D_1 - D_0} \\[2ex]
\text{etc.} & \text{etc.}
\end{array}
$$

In these equations A_0, B_0, C_0, D_0, etc., are the only unknown quantities and can be determined by solving the equations. When a solution contains a large number of components, it seems probable that the zero method will give more satisfactory results than the direct method.

In concluding, I wish to express my sincerest thanks to Professor Bancroft for suggesting the line of work, and to acknowledge my grateful appreciation of the numerous invaluable suggestions he has kindly offered during its prosecution.

Cornell University

ON INDIFFERENT POINTS

BY PAUL SAUREL

If a bivariant or multivariant system is in equilibrium at a given temperature and under a given pressure, the state of equilibrium of the system is, in general, stable; the masses of the phases as well as their concentrations are determinate. However, at exceptional points, which Duhem has called indifferent points, the state of equilibrium of a bivariant or multivariant system is indifferent. At such a point the system can undergo, without change of temperature or pressure, a reversible change which changes the masses of the phases while leaving their concentrations unchanged.

Let us denote by n the number of independent components and by r the number of phases of the system. Let $\mathfrak{M}_j$ denote the total mass of the j-th component and let m_j denote the mean concentration of this component throughout the system, that is to say, let

$$m_j = \frac{\mathfrak{M}_j}{\sum\limits_{j=1}^{n} \mathfrak{M}_j}.$$

Finally, let m_{ij} denote the mass of the j-th component which is present in the unit of mass of the i-th phase. Then, as we have shown,[1] the necessary and sufficient conditions for an indifferent point are that each determinant of the order r that can be formed from the matrix

$$\begin{matrix} m_1, & m_{11}, & m_{21}, & \cdots, & m_{r1} \\ m_2, & m_{12}, & m_{22}, & \cdots, & m_{r2} \\ \vdots & \vdots & \vdots & & \vdots \\ m_n, & m_{1n}, & m_{2n}, & \cdots, & m_{rn} \end{matrix} \qquad (1)$$

should be equal to zero.

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[1] Jour. Phys. Chem. 5, 48 (1901).

It may perhaps help in making the meaning of this result clear if we state it in geometrical terms. But for this purpose it will be necessary first to recall a few elementary propositions in analytical geometry.

Consider a straight line. The position of any point on the line is determined by its distance from any fixed point of the line or more symmetrically by its distances from two fixed points of the line. Take two fixed points at a unit's distance apart and let x_1, x_2 denote the distances from the two fixed points to any given point on the line. Then we have not only

$$x_1 + x_2 = 1, \tag{2}$$

but also

$$A_1 x_1 + A_2 x_2 = 0, \tag{3}$$

in which A_1 and A_2 are constants. Equation 3 may be called the equation of a point. If a second point whose coordinates are y_1, y_2 is to coincide with the point x_1, x_2, we must have not only equation 3, but also the equation

$$A_1 y_1 + A_2 y_2 = 0. \tag{4}$$

From these two equations it follows that

$$\begin{vmatrix} x_1, & y_1 \\ x_2, & y_2 \end{vmatrix} = 0 \tag{5}$$

is the condition that the two points x and y coincide.

Consider next a plane. The position of any point in the plane is determined by its distances from two fixed intersecting lines or more symmetrically by its distances from three fixed lines forming a triangle. Take three fixed lines forming an equilateral triangle whose altitude is equal to 1, and let x_1, x_2, x_3 denote the distances from these three lines to any given point in the plane. Then it can be easily shown that

$$x_1 + x_2 + x_3 = 1. \tag{6}$$

It can also be shown that the equation of any line in the plane is of the form

$$A_1 x_1 + A_2 x_2 + A_3 x_3 = 0, \tag{7}$$

in which A_1, A_2, A_3 are constants. If we wish to express the fact that the three points x, y and z lie in the same straight line, we must write the equations

$$\begin{aligned} A_1x_1 + A_2x_2 + A_3x_3 &= 0, \\ A_1y_1 + A_2y_2 + A_3y_3 &= 0, \\ A_1z_1 + A_2z_2 + A_3z_3 &= 0. \end{aligned} \tag{8}$$

From these it follows that

$$\begin{vmatrix} x_1, & y_1, & z_1 \\ x_2, & y_2, & z_2 \\ x_3, & y_3, & z_3 \end{vmatrix} = 0 \tag{9}$$

is the condition that the three points x, y and z lie on the same straight line.

A point in the plane is determined by the intersection of two straight lines. Thus the position of a point is determined by the equations

$$\begin{aligned} A_1x_1 + A_2x_2 + A_3x_3 &= 0, \\ B_1x_1 + B_2x_2 + B_3x_3 &= 0, \end{aligned} \tag{10}$$

in which the A's and B's are constants. From these we find that

$$\frac{x_1}{\begin{vmatrix} A_2, & A_3 \\ B_2, & B_3 \end{vmatrix}} = \frac{x_2}{\begin{vmatrix} A_3, & A_1 \\ B_3, & B_1 \end{vmatrix}} = \frac{x_3}{\begin{vmatrix} A_1, & A_2 \\ B_1, & B_2 \end{vmatrix}}. \tag{11}$$

If we express the fact that a second point y coincides with the point x we shall find that y_1, y_2, y_3 satisfy equations 10 and 11. From this it follows at once that

$$\frac{x_1}{y_1} = \frac{x_2}{y_2} = \frac{x_3}{y_3}. \tag{12}$$

Accordingly when two points x and y coincide, the following conditions are satisfied:

$$\begin{vmatrix} x_1, & y_1 \\ x_2, & y_2 \end{vmatrix} = 0, \quad \begin{vmatrix} x_1, & y_1 \\ x_3, & y_3 \end{vmatrix} = 0, \quad \begin{vmatrix} x_2, & y_2 \\ x_3, & y_3 \end{vmatrix} = 0. \tag{13}$$

Consider finally an ordinary space of three dimensions. The position of any point in space is determined by its distances from three fixed planes which meet in a point or more symmetrically by its distances from four fixed planes forming a tetrahedron. Take four fixed planes forming a regular tetrahedron whose altitude is equal to 1, and let x_1, x_2, x_3, x_4 denote the distances from these planes to any given point in space. Then it can easily be shown that

$$x_1 + x_2 + x_3 + x_4 = 1. \tag{14}$$

It can also be shown that the equation of any plane in space is of the form

$$A_1x_1 + A_2x_2 + A_3x_3 + A_4x_4 = 0, \tag{15}$$

in which A_2, A_2, A_3, A_4 are constants. If we wish to express the fact that four points x, y, z and w lie in the same plane we must write the four equations

$$\begin{aligned} A_1x_1 + A_2x_2 + A_3x_3 + A_4x_4 &= 0, \\ A_1y_1 + A_2y_2 + A_3y_3 + A_4y_4 &= 0, \\ A_1z_1 + A_2z_2 + A_3z_3 + A_4z_4 &= 0, \\ A_1w_1 + A_2w_2 + A_3w_3 + A_4w_4 &= 0. \end{aligned} \tag{16}$$

From these it follows that

$$\begin{vmatrix} x_1, & y_1, & z_1, & w_1 \\ x_2, & y_2, & z_2, & w_2 \\ x_3, & y_3, & z_3, & w_3 \\ x_4, & y_4, & z_4, & w_4 \end{vmatrix} = 0 \tag{17}$$

is the condition that four points lie in the same plane.

A straight line is determined by two planes. Thus the equations of a straight line are

$$\begin{aligned} A_1x_1 + A_2x_2 + A_3x_3 + A_4x_4 &= 0, \\ B_1x_1 + B_2x_2 + B_3x_3 + B_4x_4 &= 0, \end{aligned} \tag{18}$$

in which the A's and B's are constants. If we wish to express the fact that three points x, y and z are on the same line, we must write equations 18 and the four analogous equations obtained by replacing x by y and by z. These equations may be written in two groups of three each. From the first group we find that

$$\frac{A_1}{\begin{vmatrix} x_2, & y_2, & z_2 \\ x_3, & y_3, & z_3 \\ x_4, & y_4, & z_4 \end{vmatrix}} = \frac{-A_2}{\begin{vmatrix} x_1, & y_1, & z_1 \\ x_3, & y_3, & z_3 \\ x_4, & y_4, & z_4 \end{vmatrix}}$$

$$= \frac{A_3}{\begin{vmatrix} x_1, & y_1, & z_1 \\ x_2, & y_2, & z_2 \\ x_4, & y_4, & z_4 \end{vmatrix}} = \frac{-A_4}{\begin{vmatrix} x_1, & y_1, & z_1 \\ x_2, & y_2, & z_2 \\ x_3, & y_3, & z_3 \end{vmatrix}} \qquad (19)$$

and from the second group we find that the B's are proportional to the same determinants. But this cannot be true since the A's and B's are not proportional. It follows then that

$$\begin{vmatrix} x_1, & y_1, & z_1 \\ x_2, & y_2, & z_2 \\ x_3, & y_3, & z_3 \end{vmatrix} = 0, \quad \begin{vmatrix} x_1, & y_1, & z_1 \\ x_2, & y_2, & z_2 \\ x_4, & y_4, & z_4 \end{vmatrix} = 0,$$

$$\begin{vmatrix} x_1, & y_1, & z_1 \\ x_3, & y_3, & z_3 \\ x_4, & y_4, & z_4 \end{vmatrix} = 0, \quad \begin{vmatrix} x_2, & y_2, & z_2 \\ x_3, & y_3, & z_3 \\ x_4, & y_4, & z_4 \end{vmatrix} = 0. \qquad (20)$$

Equations 20 are thus the conditions that three points x, y, and z lie on the same line.

A point is determined by three planes. Thus the equations of a point are

$$\begin{aligned} A_1x_1 + A_2x_2 + A_3x_3 + A_4x_4 &= 0, \\ B_1x_1 + B_2x_2 + B_3x_3 + B_4x_4 &= 0, \\ C_1x_1 + C_2x_2 + C_3x_3 + C_4x_4 &= 0. \end{aligned} \qquad (21)$$

From these equations we find that x_1, x_2, x_3, x_4 are proportional to certain determinants which it is unnecessary to write. If we wish to express the fact that a point y coincides with point x, we shall find that y_1, y_2, y_3, y_4 are proportional to the same determinants. It follows that

$$\frac{x_1}{y_1} = \frac{x_2}{y_2} = \frac{x_3}{y_3} = \frac{x_4}{y_4}. \qquad (22)$$

Accordingly when two points x and y coincide the following conditions are satisfied:

$$\begin{vmatrix} x_1, & y_1 \\ x_2, & y_2 \end{vmatrix} = 0, \quad \begin{vmatrix} x_1, & y_1 \\ x_3, & y_3 \end{vmatrix} = 0, \quad \begin{vmatrix} x_1, & y_1 \\ x_4, & y_4 \end{vmatrix} = 0,$$

$$\begin{vmatrix} x_2, & y_2 \\ x_3, & y_3 \end{vmatrix} = 0, \quad \begin{vmatrix} x_2, & y_2 \\ x_4, & y_4 \end{vmatrix} = 0, \quad \begin{vmatrix} x_3, & y_3 \\ x_4, & y_4 \end{vmatrix} = 0. \qquad (23)$$

We may extend this reasoning to space of more than three dimensions. Denote by $x_1, x_2, \ldots, x_n$ the n symmetrical co-ordinates of a point in a flat space of $n - 1$ dimensions. If two points x and y coincide it can be shown that every determinant of the order two that can be formed from the matrix

$$\begin{array}{cc} x_1, & y_1 \\ x_2, & y_2 \\ \vdots & \vdots \\ x_n, & y_n \end{array} \qquad (24)$$

is equal to zero. If three points x, y, and z lie on the same straight line it can be shown that every determinant of the order three that can be formed from the matrix

$$\begin{array}{ccc} x_1, & y_1, & z_1 \\ x_2, & y_2, & z_2 \\ \vdots & \vdots & \vdots \\ x_n, & y_n, & z_n \end{array} \qquad (25)$$

is equal to zero. If four points x, y, z and w lie on the same plane it can be shown that every determinant of the order four that can be formed from the matrix

$$\begin{array}{cccc} x_1, & y_1, & z_1, & w_1 \\ x_2, & y_2, & z_2, & w_2 \\ \vdots & \vdots & \vdots & \vdots \\ x_n, & y_n, & z_n, & w_n \end{array} \qquad (26)$$

is equal to zero.

Finally it can be shown that the necessary and sufficient condition that r points $x, y, z, w \ldots$ should lie in the same flat space of $r - 2$ dimensions is that every determinant of order r that can be formed from the matrix

$$\begin{array}{lllll} x_1, & y_1, & z_1, & w_1, & \dots \\ x_2, & y_2, & z_2, & w_2, & \dots \\ \vdots & \vdots & \vdots & \vdots & \\ x_n, & y_n, & z_n, & w_n, & \dots \end{array} \tag{27}$$

be equal to zero.

If we observe that the concentrations m_j and m_{ij} satisfy the conditions

$$\sum_{j=1}^{n} m_j = 1, \quad \sum_{j=1}^{n} m_{ij} = 1, \quad i = 1, 2, \dots, r, \tag{28}$$

it follows at once from the preceding discussion that we can state condition 1 as follows:

In order that a bivariant or multivariant system of r phases be at an indifferent point it is necessary and sufficient that the representative point of the system and the representative points of the r phases lie in the same flat space of $r - 2$ dimensions. In particular, for a two-phase system the representative points must coincide, for a three-phase system they must lie in the same straight line, for a four-phase system they must lie in the same plane.

The indifferent points of a bivariant or multivariant system form a series which is analogous to the series of states of equilibrium of a univariant system. At the indifferent point which corresponds to a given temperature there are a determinate equilibrium pressure and determinate equilibrium concentrations. In general, in passing from an indifferent point to an adjacent indifferent point, the equilibrium concentrations of the phases change. In general, then, in passing from an indifferent point to an adjacent indifferent point, it will be necessary to change the mean concentrations m_j. However, the mean concentrations m_j can be kept constant if the equilibrium concentrations of the indifferent point vary with the temperature in such a manner that the point, line, plane or $r - 2$ dimensional flat which they determine always contains the point which the mean concentrations m_j determine. Thus, for a two-phase system, the concentrations of the two phases must remain equal. This will surely be the case if one of the phases is a phase of fixed composition. For a three-phase system, it is necessary that the line determined by the concentrations of the three phases always pass through the point determined by the mean concentrations m_j. This will surely be the case if two of the phases are phases of fixed composition. For a four-phase system it is necessary that the plane determined by the concentrations of the four phases always pass through the point determined by the concentrations m_j. This will surely be the case if three of the phases are phases of fixed composition.

The simultaneous values of the temperatures and pressures of the indifferent points of a given system of phases can be represented by a curve, the slope of which is given by Clapeyron's equation,[1]

$$\frac{d\Pi}{dT} = \frac{Q}{T\delta V}.$$

In this equation T and Π denote the temperature and the pressure, Q denotes the heat absorbed by the system during a reversible change at the indifferent point, and δV denotes the accompanying increase in volume. In general, as we pass along this curve we must change the mean concentrations m_j. In the special case, when the mean concentrations can be kept constant, the system behaves like a univariant system.

In conclusion it may be observed that in the case of systems consisting of three or more phases the indifferent point corresponding to a given temperature can occur in systems whose mean concentrations are different. For a three-phase system the point m_j can take any one of an infinite number of positions on a limited portion of a straight line. For a four-phase system the point m_j can take any one of an infinite number of positions on a limited portion of a plane.

New York, May 3, 1902.

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[1] Jour. Phys. Chem. 5, 54 (1901).

STUDIES IN VAPOR COMPOSITION, II.—(*Continued*)

BY H. R. CARVETH

Mechanical carriage of liquid particles

In most work on vapor composition there has been ignored the question as to whether or not very small particles of the solution are carried over with the vapor. If such actually takes place, the velocity of distillation will be found to have a definite effect on the concentration of the distillate. Preliminary experiments made by Mr. V. H. Gottschalk confirm my own — no appreciable effect has been observed under our experimental conditions. More accurate experiments on this subject are necessary before the exact conditions for avoidance of this trouble may be determined. The study of the action of baffle plates and other engineering subjects is intimately connected with this topic.

If it is possible to have distributed through a phase particles liquid or solid which by some physical property may be differentiated from other particles in the phase, it is necessary to examine such cases from the view point of theory. Recent work on the solution phase where colloids are present raises the question as to whether analogous cases for the vapor phase may not be found, i. e., where in a vapor phase there may be particles which are properly classified as liquid rather than vapor. Whether the effect on the properties will be as marked as on those of colloidal solutions is difficult to state; the problem still remains open.

Two components (one volatile), three phases — solid, liquid, vapor

When in addition to a solution and a vapor phase there is present a second solution or a solid phase, the system is univariant. If one starts with a solution (at its own vapor pressure) and a great excess of the solid phases and passe, in the vapor of the volatile component at atmospheric pressure, the system will tend to pass to the temperature at which three phases are in equilibrium at atmospheric pressure, and then to the temperatures at which the two phases, vapor and unsaturated solution, exist under the same pressure. When steam was passed into a solution of calcium chloride mixed with a considerable amount of the solid, the temperature as indicated by the thermometer rose continually until, as in one experiment performed in a silvered vacuum tube, the boiling-point of 165° ($p = 744$) was reached; after remaining at this point until the calcium chloride had all dissolved, the temperature fell, since the system was now striving toward the boiling-point of an infinitely dilute calcium chloride solution. The temperature rose, passed through a maximum and again fell; this, however, is not comparable to the other cases in this paper where the same phenomenon has been observed, because under the conditions chosen the range of temperature is not from the boiling-point of one substance to that of the other.

Any one who has ever attempted to determine with accuracy the boiling-point of saturated salt solutions will appreciate the effect of varying amounts of the solid phase present. The method of vapor heating proposed in this paper seems to offer a ready experimental method for such determinations. It will be found here, however, that the velocity of solution of some salts is very low and this may affect the observation, so that the actual maximum observed is not the highest temperature attainable, i. e., is not the true boiling-point of the solution. This should be most readily reached by slow passage of the vapor and safeguarding from too great loss of heat. Readjustment between the phases takes place more and more slowly the greater the number of phases concerned.

Some experiments on the variation in the boiling-point observable with saturated solutions were made for us by Mr. A. W. Browne. Making use of a saturated solution of ammonium sulphate, he found 1.65° (Beckmann) as the temperature at which the solid first started to appear. As more and more of the solid separated, the successive readings were 1.67, 1.70, 0.80, 0.30, and 0.20. When enough water had been added to form unsaturated solution, and the solution was evaporated until solid just appeared, the boiling-point (in a vessel of glass, nickel, or silver) rose to 1.68°, showing that the change due to volatilization of ammonia could by no means account for the difference. Experiments repeated under many varying conditions show that potassium and sodium sulphates, chlorides and nitrates, behave like the ammonium sulphate — the presence of freshly precipitated solid phase lowers the apparent boiling-point of the solution. Further experiments by Mr. J. E. Root, whose results may later be published, confirm this fact.

The regular Beckmann method has been used to determine the boiling-points of saturated solutions, but here again we have found the difficulty of the displacement of the zero reading with the velocity of heating. In work where one requires the true boiling-point for theoretical work, this Beckmann method will not do; we resorted therefore to the method of vapor heating.

For some time we made use of the apparatus shown in Fig. 1; more recently this has been modified as indicated in Fig. 5, the object being to avoid expensive breakage and to allow of better control. The modification consists in making the apparatus in two pieces instead of one as was previously done. The lower end of the vapor heater passes through the cork of a 500 cc distilling flask. The cork also carries a thermometer and a two-way stopcock, which serves either as a safety valve or as a means of adding more solvent. Into the inner tube was put pure salt, or saturated solution; into the distilling flask a solution of the same salt saturated at its boiling-point. The vapor from the latter passes into the inner vessel. In the case of ammonium sulphate, fifteen successive readings made over an interval of one and a half hours showed a maximum deviation from 1.53° to 1.55°, with an increase in barometric pressure of 1 mm. In this case electric heating was also employed at the same time that steam was being passed, but this was found not to be absolutely necessary, the extra supply of heat really serving to compensate for radiation loss.

Concentration by superheated vapor

That, by passing in the vapor at a higher temperature, the solution may be concentrated very appreciably has been demonstrated in the case where vapor from a very concentrated calcium chloride solution was passed into a solution of magnesium sulphate. The apparatus employed is shown in Fig. 5. The amount of effective work which can be performed depends on the differences of temperature and on the specific heat of the vapor. In this specific case the difference in temperatures of the vapors above the two solutions was about 20°, the specific heat of water vapor

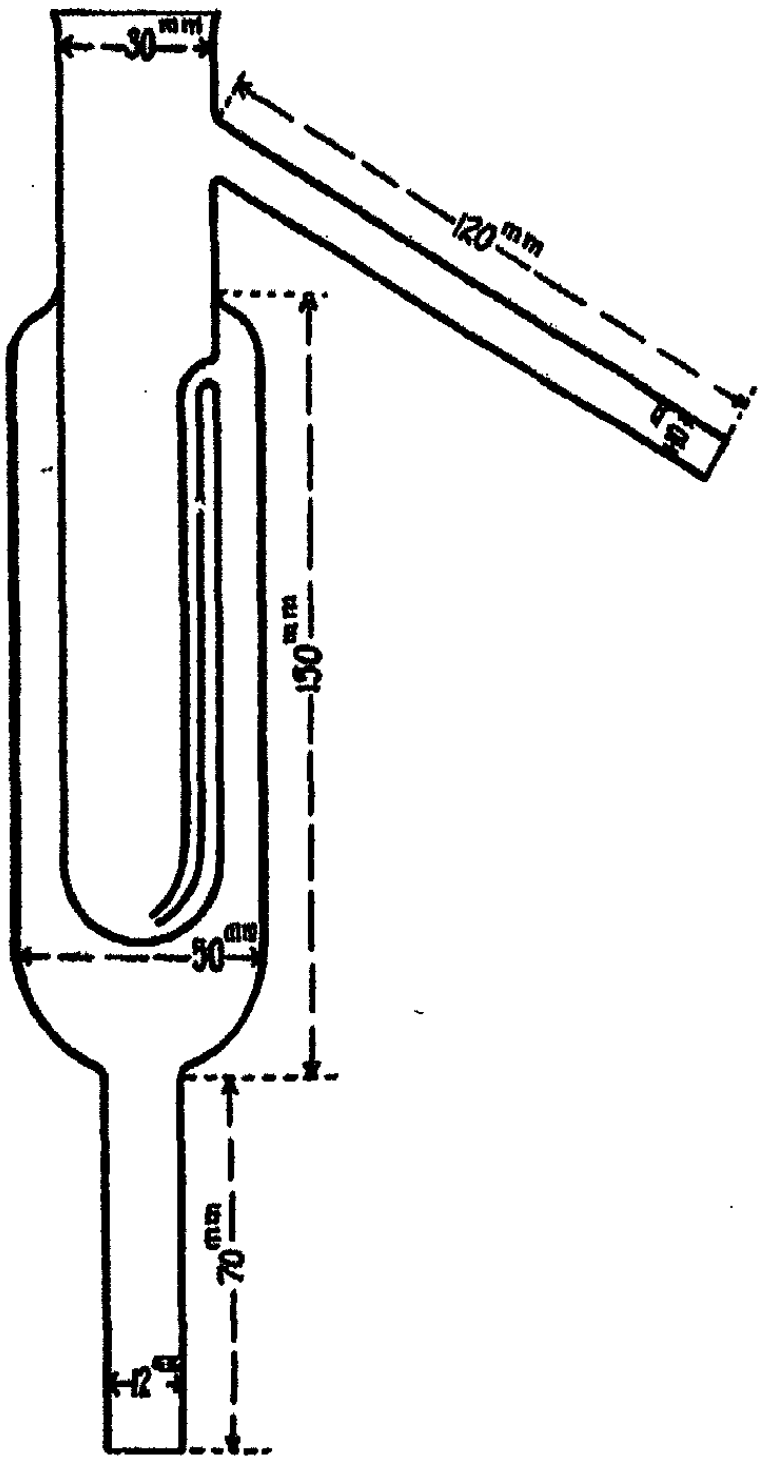

Fig. 5

about 0.39; as a consequence, one gram of water vapor given off by the chloride solution would, if no heat loss took place while it was being transferred, carry with it from the boiling solution in the inner tube more of the solvent by giving to it about 8 calories per gram of vapor passed in, thus concentrating the solution in the inner tube. The more effective the protection from radiation losses, the more efficient must be the concentration. The application of this method would be a useless waste of time were it not that it is the only one which has been tried in this laboratory by which it has been found possible to determine with any degree of accuracy the boiling-point of a saturated solution. It obviates the danger of superheating present in all work where glass vessels are heated over a free flame, does away with filling material and avoids the effects due to the presence of a solid phase. The readings are easily made, the maximum being chosen as the boiling-point, because it is coincident with the appearance of the solid phase which in this case where transparent vessels are employed is easily observable. While for very exact work it may not be allowable to consider this maximum temperature as the true boiling-point, because supersaturation may be present, nevertheless the probable error may be obtained by comparing the result with that obtained by the converse method of solution.

If so desired the very simple device of using a trap allows of the return to the outer boiling flask of the volatile component from the inner tube, thus making the concentrator perfectly automatic and allowing of excellent control. In this connection it might be mentioned that the very ingenious apparatus devised by Beckmann[1] may be applied to the method of determining vapor compositions by the boiling-point method employed by the author[2] for rough determinations. It is certain, however, that a vapor heater provided with a boiling vessel and trap will be far less fragile and just as serviceable as the new Beckmann type whether the apparatus be used for molecular weight or for vapor composition work.

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[1] Zeit. phys. Chem. 40, 145 (1902).
[2] Jour. Phys. Chem. 3, 193 (1899).

Of course one may employ steam more highly superheated in order to obtain more rapid evaporation if such is desirable. In such a case as this, superheated steam is passed into the outer jacket of the apparatus shown in Fig. 1, thence into the inner tube. Care must of course be taken not to have the water at such a temperature as to produce decomposition products. (In cases where calcium chloride solution is employed, it must not be forgotten that at its boiling temperature this solution gives off small amounts of hydrochloric acid.)

It is of course not necessary that the vapor of the solvent be used — any indifferent gas highly heated is also effective. In technical practice the superheated gas or vapor is frequently passed over, but rarely through the solution being concentrated. In the laboratory the method may be employed in increasing the velocity of evaporation where material of construction is expensive, e. g., in the volatilization of hydrofluoric acid from beakers which may not be heated externally. The extension of the method to the determination of physical constants is readily conceivable.

Two components, three phases — liquid, liquid, vapor

A few experiments have been made with liquids which are not thoroughly miscible even at the boiling-point. Chloroform, which was slightly impure, was passed into boiling water contained in the inner tube. The temperature fell in about twenty seconds to 57.9° ($p = 743.8$) and then rose slowly. On passing the mixed vapors of water and chloroform into boiling water the temperature had fallen at the end of two and one-half minutes to 58.4° ($p = 751.7$). In this case the impurities had a very marked effect.

With benzene in the inner tube and water in the outer, the benzene had evaporated completely before the thermometer became constant. With positions reversed, the final mixture in the inner tube boiled at 68.85° ($p = 745.2$). Naumann gives the value of 68.8° at $p = 741.5$.

The best conditions for observing the minimum correspond to those in the case of solid, solution and vapor, where the vapor from the system is passed into the same system held in the inner tube. This allows of a far more speedy readjustment of all condition factors, and is the one which should be used in all work where quantitative measurements are being made.

Two components — four phases

Starting with any invariant system, the mere increase of the volume of vapor will bring no change in the system. If, however, the vapor is capable of supplying heat, the change will be toward a univariant and then toward a divariant system. Among such cases would have to be considered the cryohydric, eutectic and inversion points — (1) solid solvent, solute, solution and vapor; (2) two solids, solution and vapor; (3) one solid, two solutions and vapor. When but one of the components is volatile, the phenomena as observed (e. g., constancy of temperature condition factors at invariant point) should be the same as those observable in simple heating or cooling work. When both compounds are volatile, the case is merely an extension of the three-phase system offering little more of interest.

Vapor pressures by differential methods

If into the outer vessel one puts always the system with the higher vapor pressure and into the inner that with the lower vapor pressure, and keeps the apparatus at constant temperature a bubble of vapor may not pass through the solution unless the driving pressure is equal to the external pressure plus the column of solution in the inner tube. Equilibrium is present when the bubble does not pass through. The method then offers a variation for the demonstration of differences of vapor pressures at constant temperature as well as differences in temperature at constant pressure; it is not, however, of such great practical service as the latter.

What constitutes a component?

The definition of a component is always given by reference to the number of limitations imposed on the possible number of constituents, every new condition lessening the number of components by one; e. g., if one has the four possible constituents, K, Na, NO_3 and Cl, with only one limitation — that K + Na =

$NO_3 + Cl$ for every phase, the number of components is three.[1] With a one-phase system the degree of variance cannot be told without imposing certain conditions: in other words, phase separation is most intimately associated with the definition of a component. *On the other hand, if it is found in separation work that certain limitations are present, the componency as well as the variance may be discovered.*

If the phase has been separated and a further readjustment takes place with measurable velocity in that or some other phase in equilibrium with it, it is known that equilibrium has not been reached, that possibly there is some change in the components of the system, and hence that the variance is not constant. While making any kind of measurement in a phase, e. g., the determination of any condition factor, it is frequently found that the element of time has to be very carefully considered. The unwritten opinion of chemists seems to be that when such a change takes place in a one-phase system, there is present some change — physical or chemical. As an instance, one might take the case of methyl alcohol and acetic acid. When mixed in equivalent parts, the solution is homogeneous and the physical properties definite, but after a time, the physical and chemical properties have changed, the velocity of change depending upon the temperature and other controllable factors. Among the properties whose change is most readily measurable is the vapor pressure. In this particular instance the boiling temperature will fall as time passes. If the boiling-point changes with the time, it is certain that some rearrangement has taken place in the solution, — in ordinary indefinite language, some physical or chemical change; the initial conditions were not those of equilibrium.

Velocity of readjustment

The velocity with which readjustment takes place now appears in a new light — as an indicator of rearrangement in the solution phase itself. When benzene was passed into alcohol, or water into the solution of a non-volatile salt, the readjustment

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[1] Cf. Phase Rule, p. 226.

took place with great rapidity. The chemical or physical constants or condition factors did not vary with the time, — e. g., if the liquid in the inner tube was taken out and boiled for a long interval, there was no change observable on bringing it back to its initial condition. This would not be the case if one passed methyl alcohol into acetic acid or vice-versa, or mixed and boiled the two materials. The study of velocity variations may indicate therefore whether one is dealing with a system in a state of equilibrium or not.

An article by Christiansen on the boiling-points of mixtures of chloral and water[1] showed that by his method of determining boiling-points, he could not reproduce the results, nor did he offer an explanation for the peculiar behavior. Other observers have studied the dissociation of chloral hydrate, obtaining contradictory results which Ostwald[2] records without offering explanation. Attracted by the difficulties of the subject, we attempted by means of the vapor heating method to rediscover the minimum which Christiansen had found. It was found that starting with chloral and water one minimum could be found very strongly marked, but that the whole course of the curve was very uncertain, maxima and minima occurring in great numbers, but not reproducible at the same temperature. This was probably due to the fact that in our endeavors to use small amounts of material, every operation changed the history of the chloral-water mixtures. The thermometer readings are not given as no attention was at that time paid to the thermal treatment of the mixture and reproduction is therefore impossible.

This now indicated very clearly that in the solution some readjustment was taking place and that some new factor, probably the formation of chloral hydrate, was exercising an influence. In such a case while one might, by referring to separation by crystallization or distillation, decide arbitrarily that the number of independent components was two, it is still conceivable that if the reaction velocity could be decreased the sys-

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[1] Jour. Phys. Chem. 3, 585 (1899).

[2] Ostwald. Lehrbuch, I, 201 (1891).

tem might on the same grounds be regarded as a three-component, water, chloral, and the compound.

A case exactly analogous to the above was discovered by Mr. V. H. Gottschalk while studying the system acetic anhydride and water. The curves obtained by the vapor heating method showed singular points at different temperatures according to the manner in which they were obtained. When conductivity was employed as the analytical agent, further examination showed that this was because the reaction velocity even at the boiling-point is low. This system may be regarded therefore not as a two but as a three-component system.

The bearing of this on the occurrence of more than one singular point in the boiling-point curve of a system is obvious. The curve for one component A and the compound AB might show a maximum, a minimum, or might be normal; the compound AB with the component B might also be abnormal or normal. Passing therefore from A to B and examining the boiling-points of mixtures in equilibrium, one might have numerous combinations, two minima and one maximum, two maxima and one minimum, etc. If more than one compound were formed, the number of singular points might be increased indefinitely.

If compounds may be formed and the measurement of the boiling temperature be made before equilibrium has been reached, the boiling curve for this instable condition may give one much information in regard to the formation or decomposition of compounds.

At present the only one case of a two-component system which seems to show both a maximum and a minimum is the fluid pair, sulphur dioxide and methyl chloride,[1] which however has not been examined from this point of view. *With the facts above known, one must insist that in the future work the first step in the examination of any binary system is an attempt to discover indication of change.*

Among typical cases of systems which are apparently two-

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[1] Caubet. Comptes rendus, 131, 108 (1900).

component, but are not truly such, may be cited: sulphur trioxide and water, chloral and alcohol, acetone and chloroform, carbon and sulphur. The compound may show a boiling-point lying higher or lower than either component or else intermediate thereto. In cases such as sulphur and chlorine one may have a series of compounds which may be isolated by resorting to different methods of separation, distillation alone not being at all conclusive since the compound may dissociate in the vapor. In such cases it is absolutely impossible to state what the number of components present may actually be, in order to foresee what may be observed under supposed circumstances. In examining such a case, however, care must be taken to ensure the presence of equilibrium conditions. Doubtless many of the peculiar relations found in phase separation by freezing, crystallization, etc., will later be traced back to the formation of compounds.

Three components — one volatile, two non-volatile

In this case the vapor is of constant composition. The study of the temperature changes with varying concentration may be followed very readily by means of the method of vapor heating. Unsaturated solutions may be carried to saturation by means of the superheated vapor, or molecular weight determinations may be carried out in the same solutions. This subject will in a subsequent paper be discussed in regard to its bearing on fractional crystallization.

The cases in three-component work which are of interest are those subject to easy control, i. e., univariant and divariant. One is also interested in the passage toward those, but until a trivariant is reached, the temperature changes in passing upward mean absolutely nothing.

Three-components, not reacting — two volatile

Given three components of which A and B are, and C is not, volatile, it is possible to learn much about the vapor compositions from a study of the boiling-point relations of saturated solutions. If one starts with a saturated solution of C in A at the boiling-point and passes in B as vapor, the thermometre indicates readings tending toward the temperature of ebullition of the saturated solution of C in B. The boiling curve as observed may be either normal or present a maximum or minimum. When the three-phase system changing from A and C to B and C shows a normal curve, we are always dealing with a bivariant system, the relation of A to B in the solution being different from what it is in the vapor. If three phases are present at the maximum or minimum, we know that we are really dealing with a univariant system because the removal of the vapor is done at definite temperature under definite pressure, and hence the concentration is determined. In other words, with an abnormal curve, the relation of A to B is at a definite point the same in the vapor as in the solution.

The various types which may be observed under this heading are:

(1) The binary pair of volatile components gives a normal curve, while the same system with a third component added to saturation may show a normal or abnormal curve.

(2) The binary pair may give a curve with maximum or minimum, while the ternary system may be either normal or abnormal.

In such systems the conditions which we wish to examine relate to the effect of the third non-volatile component on the concentration and temperature changes, on the vapor composition, and on the behavior on fractional distillation.

In the case where a binary pair giving a normal curve still gives a normal curve with a ternary system, it has been found that with the latter the boiling curve lies higher, and that the curve of vapor composition is displaced toward the side in which the non-volatile component is least soluble. This holds just as well in the case of unsaturated as with saturated solutions.[1]

The addition of the third component will therefore hinder the work of fractional dephlegmation if the substance added is more soluble in the more volatile and help if it is more soluble

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[1] Miller. Jour. Phys. Chem. 1, 633 (1897). Gaus. Zeit. anorg. Chem. 25, 236 (1901). Abegg und Riesenfeld Zeit. phys. Chem. 40, 84 (1902).

in the less volatile. For an example of the latter, the addition of sodium chloride to an acetone-water mixture helps in the separation by distillation, the sodium chloride being more soluble in water. The addition of a non-volatile organic body soluble in acetone and insoluble in water would hinder the separation by distillation.

When the binary pair giving the normal curve shows on the addition of a third component a maximum or minimum, a very peculiar displacement of the vapor composition curve would be indicated whose cause or significance is not at present fully understood. Peculiar solubility or reaction relations might lead to the discovery of such a case. If a maximum were present, fractional dephlegmation would give the more volatile over at first, the less volatile returning to the boiling flask. The indicated boiling-point in the flask might therefore rise, pass to a maximum and then fall again, in the course of a continued fractionation. In case a minimum were present the boiling-point might fall, pass through a minimum and then rise again. In the case of direct distillation, the boiling-point would rise to the maximum or the boiling-points of the saturated solutions of the components. In such cases the use of direct distillation as a means of separation is very ineffective compared with fractionation methods.

If the ternary system shows a normal curve while the binary is abnormal, the displacement in vapor composition produced by the addition of the third component is as marked as in the last case. On direct distillation, the boiling-point of the solution will rise continuously until the temperature remains constant where one is distilling over one pure component. Such a case may probably be obtained with calcium chloride, hydrochloric acid and water. The behavior on fractional dephlegmation may be examined in this fashion. The vapor contains continuously varying amounts of A and B (two-component system) which are dephlegmated by other continuously varying solutions of A and B. The temperatures indicated by the distilling vapor may, therefore, rise, pass through a maximum and then fall. If the normal curve shows a minimum, this mixture on fractionation distils over first of all and the boiling-point of the vapor rises continuously; the boiling-point of the solution itself may fall or may rise on fractionation.

The last two problematical cases considered offer far less of interest than the case where an abnormal binary curve remains abnormal in the ternary system. The displacement due to solubility effects is still present in this case. Direct distillation would of course result in the boiling-point rising continuously to the maximum point of the ternary system where the solution and vapor contain the same relative amounts of A and B. Dephlegmation of the vapor would again mean the passage of solutions of A and B into other solutions of A and B with the concomitant changes in the temperatures and concentrations of solution and vapor.

Dephlegmation in three-component work

It has already been seen that the fractioning column works by performing in one apparatus a very great number of fractionations. The question arises, can the displacement effected by the addition of a third component be increased by combining a number of fractionations into one more effectively than by the use of the fractioning column, working with a two-component system? Taking a specific case,—would the separation of hydrochloric acid and water by distillation be more effective if in addition to solid calcium chloride in the still, one put solid anhydrous salt in the still-head? Would the still-head itself be more effective than one containing glass beads alone? This case has not been tested. Experiments made with alcohol-water mixtures with lime in the still-head showed very little improvement over glass beads, the experimental conditions being exactly alike. In freeing carbon bisulphide from water, the use of lime in the column was very much more effective. This method is of course merely a variation of that employed frequently where for example the vapors are passed over metallic sodium as a dehydrating agent, only that in the latter case other decomposition products are formed. The method may be of advantage in certain specific cases, but is probably of restricted usefulness.

Dehydration by distillation

The ordinary method of dehydrating aqueous salts in an exsiccator salts holding water of crystallization depends on the distillation of water vapor from a place of higher to lower pressure. This takes considerable time, and the question arose whether it could not be performed more rapidly by direct distillation. The salt chosen was ferric chloride holding twelve molecules of water. This was put into the inner tube of the apparatus (Fig. 5) and benzene vapor passed through it; the vapor issuing was condensed, and dropped through a calcium chloride tube back into the flask containing the boiling benzene. In the first experiment, with 100 grams of the salt, the amount of water lost in one hour was six grams, or about 15 percent of the total water content. In the second run with 110 grams, the loss of water in two hours was 22 grams, or 50 per cent, the composition of the final mixture corresponding to the hexahydrate. In the third experiment 64 grams of the pentahydrate lost 4 grams in forty-five minutes, or about 30 percent of the total water content.

The substance which is to be used to carry over the water vapor depends on the stability of the salt. In this case we were unable to detect a trace of hydrochloric acid carried over by 50 grams of benzene. While the method is very rapid, its use is suggested mainly for the cases where rapid work or large amounts of material are required.

Three components — all volatile

In the case where the components are all miscible, the maximum number of phases being two, the system is trivariant; too many variables have therefore to be fixed to study the system from the view point of vapor heating. Schreinemakers[1] is examining such cases from another standpoint. The effect of the third component on the displacement of the maximum or minimum should prove very interesting; for example, might

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[1] Zeit. phys. Chem. 36, 257, 413, 710; 37, 129; 38, 227 (1901); 39, 485 (1902).

benzene, added to water-alcohol mixtures, not displace the vapor composition very decidedly? Even when a second liquid phase appears the system will in most cases be divariant. In connection with fractional distillation work, attention must be directed to one point — that it is perfectly feasible to separate by fractional distillation with steam or other immiscible solvent. In some cases the amount of liquid returned to the still may be too great, but this trouble is easily obviated.

The relation between displacement in vapor composition and catalytic or solvent action may be illustrated by reference to the action of hydrochloric acid on methyl alcohol. When the acid vapor is passed in, a very small amount of methyl chloride is formed. The presence of zinc chloride — a dehydrating agent — increases the velocity of the reaction to a great extent. This is probably not due to solubility alone, but might also be attributed to re-arrangement produced by the presence of the salt, e. g., formation of unstable compounds. It may later be found that even where no new chemical product is formed, the addition of the third component exercises an effect not of solubility alone, but also of re-activity. It follows naturally that the question of yield is influenced very decidedly by the displacements due to solubility effects.

Multi-component systems

Like all others these have first to be examined in regard to their reactivity. This determined, the same conditions hold which have been applied above in determining the significance of changing factors.

Vapor heating method applied in other work

The apparatus described in Figs. 1 or 5 may be applied in laboratory work for several purposes. In the first place it is a serviceable form for the checking of thermometers at the boiling-points of various liquids. The method needs no further description. It may also be used to find the purity of a volatile substance in exactly the same manner as is indicated by the thermometer placed at the head of a Hempel column. In cases where the substance shows a maximum or minimum boiling-point with another substance easily obtained in a pure state, the method may be employed to test the purity of the reagents because here we have another fixed point. This was shown by experiments on chloroform and water (p. 326). It has also been used in this laboratory for the detection of volatile acids or bases given off by a boiling solution, the solution formed in the inner tube there reacting upon the reagent or else being withdrawn for testing afterward. In this way it has been possible to easily detect ammonia and hydrochloric acid in the hydrolyzed solutions of various salts containing them, e. g., ammonium acetate, or sulphate, zinc chloride, magnesium chloride, etc. For this work, the heating produced by the absorption militates somewhat against the use of the apparatus.

Summary

In this paper on applied Phase Rule work, it has been shown how by the examination of condition factors there have been discovered practical and simple experimental methods:—

(1) For the rapid determination of the general course of a boiling curve for mixtures of two volatile components;

(2) For the exact determination of vapor composition;

(3) For concentrating solutions and determining the exact boiling-points of solutions, saturated or unsaturated; hence a modified apparatus for molecular weight determination by the vapor heating method.

(4) For dehydration of salts and liquids;

(5) For the displacement of maximum or minimum boiling-points, and the examination of this displacement.

The study has shown the rational method for the avoidance of superheating; has discussed the ideal form of dephlegmators, indicating their action; has described for the first time the method of continuous separation by distillation, and shown that economy of operation and purity of product go hand in hand; has indicated the necessity of looking for velocity terms before undertaking any study involving the separation of phases; and in general has shown how three- and multi-component systems may at times be referred back to systems of a smaller number of components.

To his students, especially Mr. Ira W. Derby, the writer wishes to express his thanks for hearty co-operation; to Professor Bancroft for suggestion and kindly criticism he is deeply indebted.

Cornell University

NOTE ON THE OPTICAL ROTATORY POWER OF CANE-SUGAR WHEN DISSOLVED IN AMINES

BY GUY MAURICE WILCOX

In a recent investigation[1] it was shown that pyridine solutions of cane-sugar have a much higher rotatory power than aqueous solutions of the same strength. It seemed of interest to determine the effect of other solvents on the optical activity of sugar. At the suggestion of Prof. Kahlenberg the solubility of sugar in some of the amines was tried, and it was found that sugar dissolves in isopropylamine, allylamine, and amylamine more readily than it does in pyridine. Especially is this true in the case of allylamine, in which sugar dissolves until a thick syrup is formed. When the solvents were evaporated from the solutions, crystals were deposited which did not lose materially in weight when heated to 90° in an oven, or when desiccated for several days over sulphuric acid. They therefore consisted of pure sugar and were not compounds of sugar and the solvents used.

Before determining the effect of these solvents on the rotatory power of sugar, it was desired to find out whether drying sugar by heat caused any change in its rotation. A quantity of the best loaf sugar was thoroughly pulverized in a mortar. Part of it was spread on a large evaporating dish and dried in an oven at 90° for about two hours. Another part was dried for several days over strong sulphuric acid. Ten percent solutions in water were prepared from each portion and from the undried sugar. Several measurements of the rotation in a tube two dcm long were made with a Landolt-Lippich polariscope manufactured by Schmidt and Haensch, and the following average results were obtained: Sugar dried by heat gave a rotation of 8.501°; sugar dried over sulphuric acid, 8.503°; undried sugar, 8.500°. These variations are within the limits of experi-

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[1] G. M. Wilcox. Jour. Phys. Chem. 5, 587 (1891).

mental error. The average density of the solutions was 1.0222, whence $[\alpha]_D^{25°}$ was found to be 66.53°.

In the experiments with amines heat-dried sugar was used. As only small quantities of the solvents were on hand, measurements were made in a one dcm tube. This tube was provided with a water jacket and had an opening in one side, through which the bulb of a thermometer could be placed directly in the solution. The allylamine was obtained from Schuchardt and had been dried for some time with fused caustic potash. It appeared perfectly clear and was used without further preparation. A series of three solutions gave the following results:

Percent sugar	Density	$\alpha_D^{25°}$	$[\alpha]_D^{25°}$
6.25	0.795	3.75	75.5
12.50	0.826	7.75	74.9
25.00	0.898	16.63	74.1

A considerable decrease in the specific rotation is noticeable as the concentration increases.

The amylamine was of Kahlbaum's make. It was dried with fused caustic potash and redistilled, nearly all passing over between 95.7° and 97° at a pressure of 746 mm. Sugar is less soluble in this than in allylamine. The solvent itself was found to be optically active, giving a negative rotation of 0.58° in a tube one dcm long. After correction for this, the following results were obtained:

Percent sugar	Density	$\alpha_D^{25°}$	$[\alpha]_D^{25°}$
3.125	0.7602	1.25	77.0
6.250	0.7754	3.09	75.7
12.500	0.8060	6.79	73.1

The isopropylamine came hermetically sealed in a glass tube from Schuchardt and was used as obtained without redistilling. As only a small quantity was at hand, a single solution was prepared and carefully measured. The following result was obtained:

Percent sugar	Density	$\alpha_D^{25°}$	$[\alpha]_D^{25°}$
6.25	0.749	3.45	73.7

It is evident that sugar in all three of these solvents, as in pyridine, has a much higher specific rotatory power than when dissolved in water.

On account of the low boiling-point of the solvents (except the amylamine) and the extremely pungent and disagreeable odor when heated, no effort was made to determine the effect of change of temperature upon the rotation of these solutions.

Since these solvents are formed from ammonia by substitution, the effect of ammonia on the rotatory power of sugar is of interest in this connection. Ost[1] found that sugar dissolved in strong ammonia solution has its rotatory power increased. Two determinations of the rotation of a 10 percent solution of sugar in 25 percent ammonia were made to test this and gave an average of 69.1 as the value of $[\alpha]_D^{25°}$. Stronger solutions of ammonia could not well be used at ordinary temperatures.

For comparison with the rotation of sugar in water and in pyridine the above results are graphically represented in the accompanying figure. The data for the aqueous solution were obtained from the work of Tollens,[2] those for the pyridine solution from the article already mentioned.[3] Franklin and Kraus[4] found that sugar is very soluble in liquid ammonia. A determination of its specific rotation in this solvent would be of interest. It has not yet been attempted, although the experimental difficulties one would encounter are not insurmountable.

Curve I is for sugar in pyridine. Curves II and III show the rotation of sugar in amylamine and allylamine. Curves IV and V give the rotation in isopropylamine and in 25 percent ammonia. Curve VI is for the aqueous solution of sugar.

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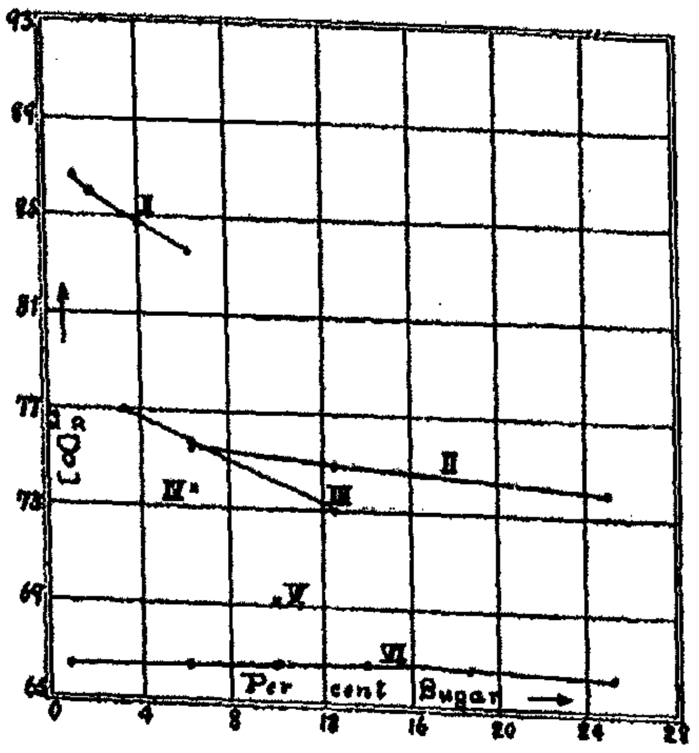
[1] Neue Zeit. für Rübenz. Ind. 9, 42.

[2] Ber. chem. Ges. Berlin, 17, 175 (1884).

[3] G. M. Wilcox. l. c.

[4] Am. Chem. Jour. 20, 825 (1898).

All these solvents which cause the rotation of sugar to increase are strong bases. While these organic bases and ammonia increase the rotation of sugar, the hydroxides and the salts of the alkali metals, when added to aqueous sugar solutions, cause the rotatory power to decrease. Sugar is known to have slightly acid properties, and although, apparently, no crystallizable compounds are formed in the cases above investigated, the rotatory power clearly indicates that loose compounds of sugar with the solvents do exist in the solutions.



Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
May, 1902.

NEW BOOKS

Le Mixte et la Combinaison chimique. *By P. Duhem. 14 × 23 cm; pp. 207. Paris: C. Naud, 1902.* — If we bring together sugar and water, the sugar will disappear and we shall have a syrupy liquid which is not pure water. One way of looking at the matter is to assume that we have a mechanical mixture of molecules of sugar and of water. With a microscope of fabulously high power we could see the particles of sugar between the water particles just as we can distinguish oats from corn when the two are mixed in a peck measure. Another way is to say that we have neither water nor sugar present, but a new substance having properties differing more or less completely from those of the components. Since we can get back pure water and pure sugar from this new substance, we must recognize the potential existence of water and sugar in the mixture or solution though denying the actual existence of either. The first of these views was held in early times by the Greek atomistic philosophers under Epicurus, and is set forth clearly in the verses of Lucretius. The second view was held by the peripatetic philosophers and was formulated by Aristotle.

In this volume under consideration, Duhem has traced the development of the conception of a mixture or solution from the days of the Greeks to the present time. Through the Middle Ages the views of the peripatetic philosophers predominated; but there came a change with the seventeenth century. Both Bacon and Descartes held the atomistic view though their conceptions differed in some details from those of Epicurus. In the eighteenth century, the influence of Newton was felt and the assumptions of mutual attractions and repulsions were introduced to account for phenomena which Descartes had explained by assumptions in regard to the shape of the atoms. A kinetic theory was substituted for a dynamic theory.

The developments of the nineteenth century are: the law of conservation of mass, the law of definite and multiple proportions, the definition of an element and of a compound, the relation between the chemical formula and the equivalent weights, the structure formula without and with stereochemistry, the conception of valence. Duhem outlines this growth of chemical science without postulating or denying the existence of atoms. The fact that this can be done leads to the question of the usefulness of the atomic theory at all. According to Duhem, the only point in favor of the atomic theory is that it makes the law of definite and multiple proportions appear as a necessary consequence and not as a most surprising and unexpected fact.

The real reason, in Duhem's mind, for rejecting the atomic hypothesis, is to be found in the success following the application of thermodynamics to chemistry. While the atomic theory has unquestionably been of great importance in enabling us to prepare and to classify an enormous number of compounds, it has not been of value in leading to new laws. Duhem sketches the growth of "chemical mechanics based on thermodynamics" and shows that the only distinction which can be made thermodynamically between a compound and a solution is that the former follows the law of definite and multiple proportions while the latter does not. In other words, a solution is a substance of variable composition in which certain constituents are potentially though not actually present. We have come back to the view of Aristotle.

While this is more or less true, Duhem goes farther than many people will care to follow. The following paragraph, p. 193, is an instance of this : —

"Are the elements forming a substance with variable composition merely mixed together? Are they partly combined, and is the chemical compound thus formed mixed with an excess of the free components. For chemical mechanics based solely on the principles of thermodynamics, these questions have no meaning."

As it stands, this statement is too extreme. We do not know and we do not much care whether hydriodic acid contains hydrogen and iodine as such or not; but we are very much interested in the question whether a vapor having the composition of hydriodic acid is entirely hydriodic acid or is a mixture of hydriodic acid, hydrogen and iodine. It is not correct to say "chemical mechanics based solely on the principles of thermodynamics" cannot distinguish between these two cases. In one case, the system will behave like a one-component system; in the second case, more or less like a two-component system. The difference is more marked if we take calcium oxide and carbonic acid in equivalent quantities. Duhem recognizes this himself and admits, on page 195, that the question asked on page 193 is legitimate, provided we can determine the "internal potentials" of the substances actually present.

What Duhem is trying to prove and what he has really brought out clearly is that the present trend of scientific thought in chemistry is away from special hypotheses in regard to matter. To this extent we have approached the point of view of Aristotle.

The book is a most interesting and welcome bit of work. Although nominally intended for students of philosophy, it will appeal primarily to chemists and should be read by all chemists.

Wilder D. Bancroft

The Practical Methods of Organic Chemistry. *By Ludwig Gattermann. Second authorized American translation from the fourth German edition, by William B. Schober. 12 × 18 cm; pp. xv + 356. New York: The Macmillan Company, 1901.* — "In preparation of this new edition, advantage has been taken of the opportunity offered to correct a number of errors in the first edition and to make the text a reproduction of the fourth German edition of Professor Gattermann's book. In many cases the laboratory directions have been improved, a number of new illustrations have been added, and the Special Part now includes methods for the preparation of glycol, dimethylcyclohexenone, *s*-xylenol, phenyl hydroxylamine, nitroso benzene, *p*-tolyl aldehyde (Gattermann-Koch synthesis), salicylic aldehyde (Riemer and Tiemann's oxyaldehyde synthesis), cuprous chloride, the decomposition of inactive mandelic acid into its active constituents, and a zinc dust determination. The preparations of acetylene and acetylene tetrabromide have been omitted."

The laboratory manual of Gattermann is a standard work and has stood the test of actual use in the laboratory. It is not unfair to assume that it comes very near to realizing the organic chemist's idea of a laboratory manual. The author has done what he tried to do with great success — barring the chapter on fractional crystallization, which is hopelessly behind the times. The question is whether the present high standard of laboratory manuals for organic chemists cannot profitably be raised still higher. The main objects of the laboratory course, as at present given, are to give the student practice in manipulation and familiarity with the properties of the substances handled. This is necessary, but it is not necessary to stop here. The student should learn more about the conditions. If there is no time to study these in the laboratory, they should be given in the text of the manual. Let us take the first experiment in the book, the synthesis of ethyl bromide. The student is told to add 90 g of alcohol without cooling to 200 g sulphuric acid, then to cool and add 75 g of ice-water and afterwards 100 g of finely pulverized potassium bromide. The mixture is subjected to distillation, which must not be too slow. If these directions are followed, all will be well as far as the synthesis of ethyl bromide is concerned; but how about the student? The student ought to learn why more than twice the theoretical amount of alcohol is taken, why it is not necessary to cool the sulphuric acid while adding alcohol, why that amount of sulphuric acid is taken and not some other, why the water is added after the alcohol and sulphuric acid have been mixed and not before, why the potassium bromide is added last instead of the sulphuric acid, why the distillation must not be too slow, and what would be the effect of varying the relative proportions. These are all important points which the student ought to know and which will some day be included in every laboratory course. When that time comes it will be perceived that it is more important to incorporate the answers to these questions in the text than to include brief notes on the general theory of the reaction since these latter are to be found in any text-book on organic chemistry.

On p. 113, the translator writes: "For the preparation of ethyl benzene the ethyl bromide thus purified cannot be used." The German original reads: "For the preparation of ethyl benzene it is not necessary to purify the ethyl bromide in this way."

Wilder D. Bancroft

The Expansion of Gases by Heat. *Edited by W. W. Randall. (Scientific Memoirs, No. 14.) 13 × 20 cm; pp. x + 166. New York: The American Book Company, 1902. Price: bound, $1.00.* — There are given one article by Dalton, one by Gay-Lussac, one by Biot, two by Regnault, and an abstract of a paper by Chappuis. The selection has been well-made and the volume is worthy of its place in the series.

Wilder D. Bancroft

Strom- und Spannungsmessungen an Kathoden in Entladungsröhren. *Habilitationsschrift zur Erlangung der Venia docendi der hohen philosophischen Fakultät der Friedrich-Alexanders-Universität zu Erlangen. By Arthur Wehnelt. 15 × 23 cm; pp. 50. Leipzig: S. Hirzel, 1901. Price: paper, 1 mark.* — This is the author's "*Habilitationsschrift*" at the University of Erlangen. The chief conclusion reached is that the current flows only through that portion of the cathode which glows. It was also proved that the current density is less with curved cathodes at the inner portion than at the outer, though this difference disappears with increasing pressures.

Wilder D. Bancroft

REVIEWS

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

General

On the classification of the atomic weights of neon, argon, krypton, and xenon. *H. Wilde. Comptes rendus*, 134, *770* (*1902*). — The author believes that the group of inert gases belongs to his series H × $7n$, neon being the first, and nitrogen the second of this series. *W. D. B.*

Heat of reaction between substances as solids and as gases. *A. Ponsot. Comptes rendus*, 134, *651* (*1902*). — "The heat set free in the reaction of a substance in a solid state and under a pressure equal to the vapor pressure, and the heat set free in the reaction of the same substances in the gaseous state at constant volume tends toward the same value at the absolute zero." *W. D. B.*

Production and maintenance of low temperatures. *d'Arsonval. Comptes rendus*, 133, *980* (*1901*). — The author obtains temperatures down to −60° by placing methyl chloride in a porous earthenware vessel, the spontaneous evaporation being enough to lower the temperature without blowing air through the liquid. For temperatures down to −100° solid carbonic acid dissolved in acetone is used. With liquid air, the author uses a bath of petroleum ether which does not freeze at −194°. *W. D. B.*

A new method of handling liquefied gases in sealed tubes. *H. Moissan. Comptes rendus*, 133, *768* (*1901*). — To obtain temperatures down to −100° the author recommends the passage of air through a solution of solid carbonic acid in acetone; for lower temperatures he advises the use of liquid air or of liquid oxygen. When he has to study the action of liquefied gases on a solid in a sealed tube, he uses glass tubes of an internal diameter varying from 1 1/2 mm to 6 mm, and an external diameter varying from 6 mm to 10 mm. These tubes will stand pressures varying from 200 to 300 atmospheres. In order to seal them, the solid and liquefied gas are introduced into the tube and the liquefied gas solidified by cooling. It is then, of course, perfectly easy to seal the tube. Before opening the tube, the reaction products should again be converted into the solid state. This method is not possible when hydrogen is set free during the reaction because then the tubes invariably break. *W. D. B.*

Compounds of aluminum chloride with alkali chlorides. *E. Baud. Comptes rendus*, 133, *869* (*1901*). — Thermochemical data. *W. D. B.*

One-Component Systems

Formation of ice in the volcanoes of Auvergne during the summer. *P. Glanzeaud. Comptes rendus*, 133, *177* (*1901*). — In hot weather the rate of evaporation is so great in the porous lava beds in the Auvergne mountains that ice is formed even though the normal temperature is 35° in the shade. [It would seem as though a dry wind would be essential]. *W. D. B.*

On the boiling-point of selenium and on some other pyrometric constants. *D. Berthelot. Comptes rendus*, 134, *705* (*1902*). — The boiling-point of selenium is found to be 690° instead of the previously accepted value of 665°. A change of barometric pressure of 10 mm causes a change of 1° in the boiling-point. The author considers the following boiling-points as fairly well established : selenium 690°, cadmium 778°, zinc 918°. *W. D. B.*

Some physical properties of hydrogen selenide. *R. de Forcrand and Fonzes-Diacon. Comptes rendus*, 134, *171* (*1902*). — Hydrogen selenide boils at −42° and solidifies at −64°. Its density is about 2.12 at its boiling-point. *W. D. B.*

Vapor pressures of hydrogen selenide and the dissociation of its hydrate. *R. de Forcrand and Fonzes-Diacon. Comptes rendus*, 134, *229* (*1902*). — The authors have determined the vapor pressures of liquid hydrogen selenide at four temperatures, from which they calculate a molecular heat of vaporization of 4740 calories. This value agrees well with the requirements of Trouton's law for liquids which are not polymerized.

The change with the temperature of dissociation pressure of the hydrate of hydrogen selenide has also been determined and its heat of formation is calculated at 16,820 calories. *W. D. B.*

Comparison between the properties of hydrogen selenide and hydrogen sulphide. *R. de Forcrand and Fonzes-Diacon. Comptes rendus*, 134, *281* (*1902*). — The critical pressures of hydrogen sulphide and hydrogen selenide are almost identical; the heats of formation of the hydrates are nearly the same, and so are the molecular heats of vaporization. The vapor pressure curves are nearly parallel and both substances show values corresponding to normal molecular weights in the liquid. While the general data for hydrogen selenide and hydrogen sulphide are similar, both are very different from the corresponding values for water. *W. D. B.*

Preparation and properties of a new silicon hydride. *H. Moissan and S. Smiles. Comptes rendus*, 134, *569* (*1902*). — By acting on magnesium silicide with aqueous hydrochloric acid and condensing the gas evolved, there is formed a colorless mobile liquid boiling at + 52° and freezing at − 138°. It takes fire spontaneously in the presence of air at ordinary temperatures and burns with a brilliant flame, depositing amorphous silicon and silica. Its density is greater than that of water in which the liquid is but slightly soluble. At about 250° the vapor decomposes into silicon and hydrogen. The composition of this substance is represented by the formula Si_2H_6. *W. D. B.*

On the distillation of metals and the distilled metals. *G. W. A. Kahlbaum, K. Roth and P. Seidler. Zeit. anorg. Chem.* 29, *177* (*1902*). — By working under very low pressure the authors have succeeded in distilling copper, silver, gold, lead, zinc, cadmium, tellurium, antimony and bismuth. There was no satisfactory evidence of a real distillation of tin. The authors show that a fractional distillation in vacuo gives one a very pure metal indeed and they have therefore studied the densities, specific heats and optical properties of these distilled metals. They call attention to the very serious errors existing in most density determinations and special measurements of their own whereby copper was subjected to a pressure of 10,000 atmospheres in castor oil showed that a very marked increase of density took place under these circumstances. While a marked change in density was obtained for copper under pressure, the other metals did not show so definite an effect. The specific heat changed with the density, decreasing with increasing density; but the change is so slight as almost to lie within the limits of experimental error. *W. D. B.*

On the relation $\frac{L+S}{T} = \frac{Q}{T'} = K$. *R. de Forcrand. Comples rendus,* 134, *768* (*1902*). — From Regnault's experiments on vapor pressures of liquid ammonia, the author has calculated the molecular heat of vaporization for every 5°. The heats of vaporization decrease with increasing temperature, decreasing more rapidly the higher the temperature. The value for the boiling-point under 760 mm pressure corresponds very closely with the value calculated from the ammoniacal metallic chlorides. In the case of ammonia the author's law appears to hold in all physical or chemical phenomena the heat of solidification of a molecule of a gas is proportional to the absolute boiling-point under a pressure of 760 mm. *W. D. B.*

On the thermal equivalents, the dissociation, the vaporization and the heat of fusion of ammonia. *R. de Forcrand. Comples rendus,* 134, *708* (*1902*). — From the author's formula he deduces the relation that a substance which boils at *n*° absolute temperature under atmospheric pressure has a heat of vaporization at this temperature of $\frac{n}{33.33}$ cal. He checks this by comparison with the data for the ammoniacal metallic chlorides. *W. D. B.*

Heat of fusion of liquid ammonia. *R. de Forcrand and G. Massol. Comples rendus,* 134, *743* (*1902*). — The authors show that the heat of fusion of solid ammonia could have been calculated fairly accurately from de Forcrand's formula. They also point out that the difference between the molecular heats of vaporization of ammonia and of water is exactly what it should be when one takes into account the difference between the boiling-points of the two liquids. *W. D. B.*

On the molecular weight at the boiling-point. *R. de Forcrand. Comples rendus,* 133, *368* (*1901*). — Assuming the author's extension of Trouton's law to solids, it is possible to calculate the molecular weight. On this assumption he finds I_3 for iodine, $Hg_{1.18}$ for mercury, $S_{7.76}$ to $S_{8.64}$ for sulphur, and $(HNO_3)_{1.37}$ for nitric acid. *W. D. B.*

The molecular weight of chloral hydrate at the boiling-point. *R. de Forcrand. Comples rendus,* 133, *474* (*1901*). — The author concludes that liquid chloral hydrate at its boiling-point contains about four percent of undissociated chloral hydrate. This conclusion is deduced from an application of the author's formula (preceding review). *W. D. B.*

Calculation of the heat of sublimation and the heat of fusion of some elements. *R. de Forcrand. Comptes rendus*, 133, *513* (*1901*). — By means of the author's formula (preceding reviews) a heat of vaporization of 16,176 calories is calculated for P_4. On the assumption of As_4 a value of 20,550 calories is calculated for the sums of the heats of fusion and vaporization. The corresponding value for Se_2 is 29,190 calories, and for C_4 90,000 calories.
W. D. B.

A new volatile salt of beryllium. *G. Urbain and H. Lacombe. Comptes rendus*, 133, *874* (*1901*). — When beryllium hydroxide is evaporated with dilute acetic acid and the gummy mass dissolved in pure acetic acid, crystals of a basic salt are obtained readily soluble in chloroform. This new salt melts at 283° and distils without decomposition at 330. The vapor density determinations correspond to an atomic weight Be = 9. *W. D. B.*

Critical constants and molecular complexity of the higher hydrocarbons. *P. A. Guye and P. Mallett. Comptes rendus*, 133, *1287* (*1901*). — The authors have determined the ratio of the molecular refraction to critical coefficient, the ratio of the real critical density to the theoretical critical density, and the constant *f* for durene, diphenylmethane, diphenyl, and naphthalene. The results show that these substances have normal molecular weights in the liquid phase.
W. D. B.

Critical constants and molecular complexity of some organic compounds. *P. A. Guye and P. Mallett. Comptes rendus*, 134, *168* (*1902*). — Anisol, phenetol, *m*-cresol, aniline, dimethyl aniline, and dimethyl-*o*-toluidine show the characteristics of liquids which are not polymerized. On the other hand, five aliphatic nitriles showed very marked polymerization, the ratio of the actual density to the theoretical density being 5.93 for acetonitrile, which is the highest value yet observed. *W. D. B.*

Preparation and properties of metallic niobium. *H. Moissan. Comptes rendus*, 133, *20* (*1901*). — Niobite is mixed with sugar charcoal and heated in an electric furnace. An alloy of niobium, tantalum and carbon is thus obtained. This mass is converted into fluotantalates and fluoniobates, and separated by the method of Marignac. Niobic acid is mixed with charcoal and heated in an electric furnace. An ingot of niobium is thus obtained, containing two or three percent of carbon. This niobium scratches quartz and does not melt in the oxyhydrogen flame. It is readily attacked by fluorine and forms a volatile chloride when heated with chlorine to about 200°. Water vapor does not act on this niobium even at 600°. *W. D. B.*

Preparation of tantalum in the electric furnace. *H. Moissan. Comptes rendus*, 134, *211* (*1902*). —Tantalic acid was obtained from the mixture of columbium and tantalum, as described in the preceding review. Its purity was assured by determination of density and molecular weight. On heating the oxide with carbon in the electric furnace, a brilliant metallic mass was obtained containing small amounts of carbon. This tantalum scratches glass and rock crystal, is infusible in the oxyhydrogen blowpipe, which, however, changes it into oxide. It has a density of 12.79 as against the value of 10.78 found by Rose.
W. D. B.

Some properties of fused lime. *H. Moissan. Comptes rendus*, 134, *136* (*1902*). — Pure lime fuses in the oxyhydrogen blowpipe only when the gases are dry, intimately mixed and are exactly in the ratio of two parts of hydrogen to one of oxygen. On the other hand, it can be melted without difficulty and made to boil with an arc of 300 amperes and 50 to 70 volts. When a graphite cylinder is dipped into fused lime, there is first a formation of calcium carbide and then of calcium. Silicon is at once oxidized to silica, and a basic silicate is formed. *W. D. B.*

Two-Component Systems

Contribution to the study of aluminum-iron and aluminum-manganese alloys. *L. Guillet. Comples rendus*, 134, *236* (*1902*). — The author has prepared the following compounds: Fe_2Al_3, $FeAl_3$, Mn_2Al_3, $MnAl_3$, and $MnAl_4$. *W. D. B.*

Study of alloys of aluminum and molybdenum. *L. Guillet. Comples rendus*, 133, *291* (*1901*). — The author has reduced molybdic acid with aluminum powder. From a study of the alloys thus obtained, he deduces the existence of the following compounds: Al_7Mo, Al_3Mo, Al_4Mo, $AlMo$, $AlMO_4$, $AlMO_{20}$. *W. D. B.*

Contribution to the study of tin-aluminum alloys. *L. Guillet. Comples rendus*, 133, *935* (*1901*). — The author has reduced stannic acid by means of metallic aluminum and has succeeded in isolating the two compounds, $AlSn$ and Al_4Sn. *W. D. B.*

The alloys of aluminum and magnesium. *O. Boudouard. Comptes rendus*, 133, *1003* (*1901*). — By the action of ammonium chloride solution on magnesium-aluminum alloys the author has separated the compounds $AlMg_2$, $AlMg$, and Al_4Mg. *W. D. B.*

The chemical equilibrium in systems containing iron and carbon. *G. Charpy and L. Grenet. Comptes rendus*, 134, *103* (*1902*). — Some of the conclusions Roozeboom draws in regard to the formation of graphite in cast iron seemed to be in contradiction with some of the experimental facts. The authors show that the iron in the experiments in question contained silicon and that the presence of silicon has a marked effect on the separation of graphite. *W. D. B.*

On the expansion of steels at high temperatures. *G. Charpy and L. Grenet. Comptes rendus*, 134, *540* (*1902*). — For temperatures up to 650° the coefficients of expansion are practically the same, no matter what the percentage composition of carbon. Above this temperature the coefficients are nearly the same for steels containing less than 0.85 percent of carbon; but are different for those containing more carbon. *W. D. B.*

Study of the transformation of steels by means of the dilatometer. *G. Charpy and L. Grenet. Comptes rendus*, 134, *598* (*1902*). — All steels begin to change at 700° regardless of the carbon content. The amount of contraction at this temperature varies with the percent of carbon present, reaching a maximum when the steel contains 0.85 percent carbon and being less for any other concentration. On raising the temperature still further a second contraction takes place, which is a gradual one and can be observed only with steels containing more than 0.65 percent of carbon. *W. D. B.*

On the state of silicon in cast iron. *P. Lebeau.* *Comples rendus*, 133, *1008* (*1901*). — The authors who have studied the properties of silicon in iron and steel have hitherto decided that this silicon was present in a solid solution. The author decides that it is there as a compound $SiFe_2$, which, however, forms a solid solution with the excess of iron. The only proof for this assumption is that nitric acid or the double chloride of copper and potassium does not attack amorphous silicon while it does attack the silicon in iron. It is clear that this argument has little or no weight. *W. D. B.*

On the compounds of gold and chlorine. *F. Meyer.* *Comples rendus*, 133, *815* (*1901*). — By acting on finely powdered gold with liquid chlorine, the author has prepared auric chloride. He has then determined the dissociation pressures both for auric chloride and for aurous chloride at various temperatures. *W. D. B.*

Action of gaseous ammonia on the hydrochlorides of the fatty amines. *F. Bidet.* *Comptes rendus*, 133, *238* (*1901*). — At 0° a pressure of 340 mm was found as equilibrium pressure when gaseous ammonia in varying amounts is added to ethyl ammonium chloride. The author seems to believe that this pressure will be the same, no matter how much ammonia is added; but this can be true only so long as there are $n + 1$ phases present. With ammonia and diethyl ammonium chloride, the corresponding pressure is 891 mm.

W. D. B.

On the composition of the gas hydrates. *R. de Forcrand.* *Comptes rendus*, 134, *835*, *991* (*1902*). — The author points out that it is very difficult to analyze solid gas hydrates. Thus, Faraday obtained 10 of water for the water in chlorine hydrate, Rosebaum 8 of water, and Villard assumes that the value should be 6. The author attempts to solve the problem by means of his formula. He finds in this way a value of 7, differing therefore from those obtained by other people. *W. D. B.*

Heat of formation of chlorine hydrate. *R. de Forcrand.* *Comptes rendus*, 133, *1304* (*1901*). — Thermochemical measurements give 18.57 cal for the heat of formation of chlorine hydrate, while the value calculated from the dissociation pressures is 18.6 cal. *W. D. B.*

On the solubility of dicalcium phosphate in pure water. *A. Rindell.* *Comptes rendus*, 134, *112* (*1902*). — The author seems to believe that the concentration of the solution depends upon the time and on the ratio between the amounts of salt and the volume of water; but it is probable that these conclusions mean nothing more than that equilibrium is reached very slowly. Under such circumstances, the apparent solubility at the end of any given time would appear to be a function of the mass of the salt. *W. D. B.*

Compounds of alcohol with chlorides of manganese and cobalt. *F. Bourion.* *Comptes rendus*, 134, *555* (*1902*). — Manganese chloride crystallizes from absolute alcohol with three of alcohol; cobalt chloride with two and one-half of alcohol. Anhydrous nickel chloride, on the other hand, dissolves but slowly in boiling alcohol and is apparently decomposed by it to some extent.

W. D. B.

Crystallization of cerium oxide. *J. Sterba. Comptes rendus*, 133, *294* (*1901*). — The author has crystallized cerium oxide from fused sodium chloride, fused borax, and fused potassium sulphate. In each case the crystals are octahedric, isotropic, colorless, and transparent; but the density varies from 7.3 to 8.0, depending upon the temperature. A greenish olive color of the crystallized oxide is due to the presence of a ferrous salt. *W. D. B.*

Preparation and properties of potassium hydride. *H. Moissan. Comptes rendus*, 134, *18* (*1902*). — By the action of hydrogen on potassium at a temperature of 360° there is formed a white crystalline hydride having the formula KH. This is decomposed at once by water, takes fire when cooled in fluorine, chlorine and dry oxygen, and is a very energetic reducing agent. *W. D. B.*

Preparation and properties of sodium hydride. *H. Moissan. Comptes rendus*, 134, *71* (*1902*). — The hydride of sodium is made in the same way as the hydride of potassium (preceding review) and has similar properties.

W. D. B.

A new synthesis of formic acid. *H. Moissan. Comptes rendus*, 134, *261* (*1902*). — On treating potassium hydride at ordinary temperatures with carbon dioxide, there is formed potassium formate. On treating with carbon monoxide, there is formed potassium formate and carbon. *W. D. B.*

Vapor pressure of solutions. *A. Ponsot. Comptes rendus*, 133 *341* (*1901*). — "With a solvent which does not take part in the chemical reaction, if the substitution of a substance A for a substance B in the compound BC takes place with evolution of heat, the vapor pressure of the solvent is higher when there is in solution a given mass of AC than when there is present an equivalent mass of BC." *W. D. B.*

On inversion points for the heat of dilution. *A. Colson. Comptes rendus*, 133, *585* (*1901*). — An aqueous solution of sodium chloride at 52° has no heat of dilution. A normal solution of hydrochloric acid has a zero heat of dilution at 83°, a double normal solution at 100°. *W. D. B.*

On the dilution constants for salt solutions. *A. Colson. Comptes rendus*, 133, *1207* (*1901*). — The author finds that the temperature at which the heat of dilution is zero is independent of the concentration of any neutral salt. These temperatures are 52° for sodium chloride, 64.5° for potassium chloride, 116° for sodium nitrate, and 122° for potassium nitrate. These last two values were obtained by extrapolation. *W. D. B.*

Thermal study of solid hydrates of potassium hydroxide. *R. de Forcrand. Comptes rendus*, 133, *157* (*1901*). — From measurements of the thermochemical heats of solution, the author deduces the existence of KOH, $KOH.0.5H_2O$, $KOH.H_2O$, $KOH.2H_2O$. The author makes no reference to the freezing-point work of Pickering, though that work is conclusive while this is not.

W. D. B.

Thermal study of solid hydrates of sodium hydroxide. *R. de Forcrand. Comptes rendus*, 133, *223* (*1901*). — From a study of the thermochemical heats of solution, the author deduces the existence of the compounds $3NaOH.2H_2O$, $NaOH.H_2O$, $2NaOH.7H_2O$. *W. D. B.*

Heats of solution of solid and liquid ammonia at 75° and heat of fusion of solid ammonia. *G. Massol. Comptes rendus*, 134, *653* (*1902*). — The heat of solution of liquid ammonia at —75° and liquid water at + 10° is 1.77 cal. The heats of solution of solid ammonia is —0.068 cal and in consequence, the heat of fusion of solid ammonia is — 1.838 cal. These values referred to 17 grams of ammonia. *W. D. B.*

Specific heat and atomic mass of vanadium. *C. Matignon and E. Monnet. Comptes rendus*, 134, *542* (*1902*). — The authors have prepared a ferro-vanadium containing about 72 percent of iron. They have determined the specific heat of this alloy and have found the molecular and specific heats of vanadium from these data, assuming an additive relation. In this way they find an atomic heat of 6.4.

An alloy of aluminum and vanadium has been prepared which is believed to be a compound with a form AlVa. From the specific heat of this alloy they deduce an atomic heat for vanadium of 6.35. *W. D. B.*

On the preparation of barium. *A. Guntz. Comptes rendus*, 133, *872* (*1901*). —Barium amalgam was placed in a porcelain tube and heated gently and regularly by electricity. Under these circumstances 90 percent of the mercury is driven off by the time the temperature reaches 850°, and all of it at a temperature of 1000°. The barium melts below 1000° and appears to boil at about 1150°. The metal thus obtained is white and nearly as soft as lead.

W. D. B.

On metallic strontium and its hydride. *A. Guntz. Comptes rendus*, 133, *1209* (*1901*). — Metallic strontium has been obtained by driving off the mercury from strontium amalgam in the same way that the author obtained barium. Strontium is very like barium, but melts at a higher temperature and does not combine so readily with liquid ammonia. When strontium is heated with hydrogen there is formed a white hydride having the formula SrH_2.

W. D. B.

On the alloys of strontium with zinc and cadmium. *H. Gautier. Comptes rendus*, 133, *1005* (*1901*). — By heating dry strontium iodide with zinc and metallic sodium in a closed vessel, the author has obtained an alloy of zinc and strontium containing 18 percent strontium. By evaporating *in vacuo* this could be concentrated very considerably, but it was not possible to obtain pure strontium because this metal evaporated with the zinc. Pure strontium could not be obtained in this way from the cadmium alloy, though an alloy was prepared containing 45 percent strontium. *W. D. B.*

Investigations on calcium silicide. *H. Moissan and W. Dilthey. Comptes rendus*, 134, *503* (*1902*). — When lime is fused in presence of an excess of silicon, there is formed the compound $CaSi_2$. This substance is attacked but slowly by water, more rapidly by dilute hydrochloric acid. In both cases there is evolution of hydrogen but no formation of solid silicon hydride.

W. D. B.

On lithium antimonide and on some alloys of this metal. *P. Lebeau. Comptes rendus*, 134, *231* (*1902*). — The author has prepared an additional crystallized compound of antimony and lithium having the formula $SbLi_3$. This was obtained by electrolyzing a mixture of potassium and lithium chlorides with an antimony cathode. It was impossible to get any satisfactory results by the direct action of metallic lithium on antimony because the reaction was too violent.
W. D. B.

On the action of lithium ammonium on antimony and the properties of lithium antimonide. *P. Lebeau. Comptes rendus*, 134, *284* (*1902*). — Lithium ammonium reacts with antimony forming the compound $SbLi_3$, the same substance which is obtained by electrolysis. This compound is much less fusible than its components. It dissolves in liquid ammonia and crystallizes from it with one of ammonia. The compound is a powerful reducing agent.

W. D. B.

On a new sodium phosphate. *H. Joulie. Comptes rendus*, 134, *604* (*1902*). — With methyl orange as indicator, one equivalent of sodium hydroxide neutralizes one molecular weight of orthophosphoric acid. With phenolphthaleine as indicator, two equivalents of sodium hydroxide are necessary; with turmeric as indicator, about one and one-half equivalents of sodium hydroxide are necessary. With this as a starting point, the author has succeeded in preparing a crystallized salt having the formula $Na_3H_3(PO_4)_2$. It is believed that this salt will be of distinct advantage medicinally. *W. D. B.*

On the sesquisodic phosphate. *J. B. Senderens. Comptes rendus*, 134, *713* (*1902*). — The author points out that the salt described by Joulie (preceding review) has been known since 1882. *W. D. B.*

On monosodium acid orthophosphate. *H. Giran. Comptes rendus*, 134, *711* (*1902*). — The author has prepared a salt with the formula $NaH_5(PO_4)_2$. This is the monosodium salt corresponding to the trisodium salt described by Joulie (two reviews back). *W. D. B.*

Multi-Component Systems

On the solubility of mixtures of copper sulphate and sodium sulphate. *G. Massol and Maldes. Comptes rendus*, 133, *287* (*1901*). — At temperatures below 30° the same equilibrium is reached whether one adds sodium sulphate in excess to a saturated solution of copper sulphate or copper sulphate in excess to a saturated solution of sodium sulphate. Above 30° the equilibrium appears to depend upon the amount of salt added and the nature of the salt added. No explanation is offered, though it is perfectly evident that a double salt must be formed.
W. D. B.

The action of silver on hydrobromic acid and the reverse action. *Jouniaux. Comptes rendus*, 133, *228* (*1901*). — At 600° the ratio of hydrogen to hydrobromic acid is higher the higher is the initial pressure of hydrogen. This is as it should be, since there is an increase in pressure when hydrogen reduces silver bromide as shown by the equation

$$2AgBr + H_2 \rightleftarrows 2Ag + 2HBr.$$

From experiments on the displacement of equilibrium with the temperature, the author calculates a heat of reaction of 13,700 cal. From Berthelot's measurements the value is 14,800 cal. *W. D. B.*

On the chloride of neodymium. *C. Matignon. Comptes rendus*, 133, *289* (*1901*). — By heating $NdCl_3 6H_2O$ with hydrochloric acid gas at 105°, the author prepared the monohydrate. By heating above 160° also in dry hydrochloric acid gas, the anhydrous salt was obtained without any trace of oxychloride. Boiling-point measurements in absolute alcohol gave a value of 248, while the formula $NaCl_3$ calls for 50. *W. D. B.*

On praseodymium chloride. *C. Matignon. Comptes rendus*, 134, *427* (*1902*). — By successive dehydration of the heptahydrate of praseodymium chloride in a current of hydrochloric acid gas, the author has prepared a monohydrate and the anhydrous salt. He has determined the heat of solution of the heptahydrate and has studied qualitatively the solubility of the anhydrous chloride in various solvents. No difference between the chlorides of praseodymium and neodymium have been discovered which is sufficient to form an effective separation. *W. D. B.*

Preparation and properties of strontium hydride. *H. Gautier. Comptes rendus*, 134, *100* (*1902*). — The author treats a strontium cadmium alloy containing 45 percent strontium with heated hydrogen. Cadmium volatilizes and strontium hydride is formed. This hydride is a white solid having the formula SrH_2 and decomposes water with great readiness. *W. D. B.*

Decomposition of calcium ammonium and of lithium ammonium by ammonium chloride. *H. Moissan. Comptes rendus*, 133, *715* (*1901*). — It was hoped that ammonium could be prepared by allowing ammonium chloride to act on calcium ammonium $Ca(NH_3)_4$ at a temperature of — 100°; but the gas evolved proved to be a mixture of ammonia and hydrogen. Substituting lithium ammonium for calcium ammonium did not change the results. *W. D. B.*

Action of metal ammonias on hydrogen sulphide. *H. Moissan. Comptes rendus*, 133, *771* (*1901*). — At temperatures of −75° to −70° liquid hydrogen sulphide reacts with lithium ammonium, forming lithium sulphide, ammonia and hydrogen. The result is the same when calcium ammonium is substituted for the lithium compound. In neither case could the radical ammonium be obtained. *W. D. B.*

Study of ammonium amalgam. *H. Moissan. Comptes rendus*, 133, *803* (*1901*). — By acting on sodium amalgam at −35° with ammonium chloride dissolved in liquid ammonia, it was possible to obtain a solid ammonium amalgam. This was placed in a vacuum and allowed to decompose. Two volumes of ammonia were given off for each volume of hydrogen. The author does not, however, feel certain that this proves the existence of the radical ammonium in the amalgam. He considers it quite possible that we have present a hydride of sodium with ammonia of crystallization. If we write the formula of the compound $Na_2H.NH_3$, this would account for the effects. *W. D. B.*

Action of hydrogen on strontium amalgam. *A. Guntz. Comptes rendus,* 134, *838* (*1902*). — The author describes the precautions which have been taken in order to obtain strontium hydride free from mercury when acting on strontium amalgam with hydrogen. *W. D. B.*

Action of potassium hydride on ethyl iodide and methyl chloride. *H. Moissan. Comptes rendus,* 134, *389* (*1902*). — Ethyl iodide reacts at about 180° with potassium hydride, forming ethane and potassium iodide. The ethane thus formed is very pure. Methyl chloride reacts under the same conditions with potassium hydride, forming methane and potassium chloride. *W. D. B.*

New series of experiments on the action of hydrogen peroxide on silver oxide. *M. Berthelot. Comptes rendus,* 133, *555* (*1901*). — The author shows that very different thermal effects are obtained when silver nitrate is precipitated by sodium hydroxide and then redissolved at once by an acid and when silver nitrate is precipitated by sodium hydroxide, treated with hydrogen peroxide, and then dissolved in an acid. This proves that hydrogen peroxide has some action on silver oxide. *W. D. B.*

Phosphoric acid and the chlorides of the alkaline earths. *M. Berthelot. Comptes rendus,* 133, *5* (*1901*). — A study of chemical equilibrium in systems containing phosphoric acid and varying amounts both of the chlorides of the alkaline earths and of sodium hydroxide. The amount of alkaline earth in the precipitate varies from two to four equivalents and is a marked function of the time. *W. D. B.*

Action of hydrogen peroxide on zinc oxide. *R. de Forcrand. Comptes rendus,* 134, *601* (*1902*). — The author concludes that the action of hydrogen peroxide on zinc oxide causes the formation of Zn_3O_5, Zn_4O_7 and ZnO_2, the first of which is stable at 100°, and the last of which is very instable even in the cold. These three higher oxides are all hydrated. and it is possible to consider them as compounds of zinc oxide with hydrogen peroxide instead as of hydrated peroxides. *W. D. B.*

On some thallium salts. *V. Thomas. Comptes rendus,* 134, *545* (*1902*). — The author describes a number of acid salts of thallium chloride and bromide, and raises the question whether these are really compounds or are to be considered as mixtures of isomorphous compounds. *W. D. B.*

On the chlorobromides of thallium of the type Tl_4X_6. *V. Thomas. Comptes rendus,* 133, *735* (*1901*) — The author criticizes the statement of Cushman (5, 616) but states that he has been able to obtain the compound $Tl_4Cl_3Br_3$ in two crystalline forms depending upon whether he cooled the solution rapidly or slowly. *W. D. B.*

New method of preparing aniline and the analogous alkalies. *P. Sabatier and J. B. Senderens. Comptes rendus,* 133, *321* (*1901*). — When nitrobenzene and hydrogen in excess are passed over freshly reduced copper heated to 300° to 400° the nitrobenzene is reduced almost completely to aniline. When there is not enough hydrogen, some azobenzene is obtained. With freshly reduced nickel heated to 200° a very pure aniline can be obtained. When the nickel is heated to 250°-300° the chief products are benzene and ammonia. A similar reduction can be effected by means of water gas. *W. D. B.*

New synthesis of methane. *P. Sabatier and J. B. Senderens. Comptes rendus*, 134, *514* (*1902*). — At 250° methane is formed quantitatively by passing a mixture of hydrogen and carbon monoxide over freshly reduced nickel. The same reaction can be brought about with carbon dioxide if the temperature be raised to about 300°. In both cases the results are more satisfactory if an excess of hydrogen be taken. *W. D. B.*

Direct hydrogenization of the oxides of carbon in the presence of different metals. *P. Sabatier and J. B. Senderens. Comptes rendus*, 134, *689* (*1902*). — At 250° in the presence of finely divided nickel, hydrogen and carbon monoxide combine to form methane without precipitation of carbon and without formation of carbonic acid. Above 280° there is always a precipitation of carbon black of the nickel and a formation of carbon dioxide. With finely divided cobalt exactly the same reaction takes place, but at a somewhat higher temperature. Platinum, palladium and iron do not bring about the formation of methane at any temperature. Copper has no effect on the mixture of carbon monoxide and hydrogen. With carbon dioxide and hydrogen a reaction takes place at about 430°, but it consists in the reduction of carbon dioxide to carbon monoxide with the formation of water. *W. D. B.*

Preparation of pure cerium oxide. *J. Sterba. Comptes rendus*, 133, *221* (*1901*). — The author purified his cerium oxide by a modification of the Wyrouboff and Verneuil method, using electrolytic oxidation. The oxide when pure is perfectly white; but is colored by traces of nitrates. Zinc reduces the oxide CeO_2 to Ce_2O_3 and hydrogen does the same thing. *W. D. B.*

Action of cupric hydroxide on solutions of metallic salts. *A. Mailhe. Comptes rendus*, 133, *226* (*1901*); 134, *42*, *233* (*1902*). — The author has prepared a number of basic salts by bringing the black $Cu_4O_5H_2$ in contact with solutions of salts of the heavy metals. *W. D. B.*

On the crystallization of chromium sesquioxide. *A. Ditte. Comptes rendus*, 134, *336* (*1902*). — When a mixture of potassium bichromate and sodium chloride is heated to redness and the cool mass extracted with water there remain crystals of chromium sesquioxide. The author finds that this crystallization is due to the intermediate formation of chloro-chromate of sodium and is not due to the solubility of chromium oxide in fused alkali chlorides. *W. D. B.*

On the crystallization of ferric oxide. *A. Ditte. Comptes rendus*, 134, *507* (*1902*). — When ferrous sulphate and sodium chloride are heated together, a certain amount of crystallized ferric oxide is formed. The author shows that this takes place only when there is moisture present and when there is therefore a formation of hydrochloric acid. In other words, the necessary conditions are those worked out by H. Sainte Claire Deville for the formation of ferric oxide from ferric chloride. *W. D. B.*

Acid and basic sulphates of neodymium and of praseodymium. *C. Matignon. Comptes rendus,* 134, *657* (*1902*). — The author has prepared and studied the following new salts: $Nd(SO_4H)_3$, $Pr(SO_4H)_3$, $(NdO)_2SO_4$, $(PrO)_2SO_4$.

W. D. B.

On the polymerized state of ordinary indigotine and the isomeric transformation of indigotine into indirubine. *L. Maillard. Comptes rendus,* 134, *470* (*1902*). — The rapid oxidation of indoxyl in acid solution forms first indigotine which changes gradually into the stable form of bisindirubine; in alkaline solutions indirubine is first formed, which then changes into bisindigotine.

W. D. B.

Osmotic Pressure and Diffusion

Generalization on the fixation of metals by cell walls. *H. Devaux. Comptes rendus,* 133, *58* (*1901*). — The soft tissues of plants have the power of removing copper, lead, silver, iron, nickel, cobalt, and cadmium to a certain limited extent, from solutions of their salts. Gold, platinum, and chromium are not so fixed, and mercury only infinitesimally. The analytic methods for zinc, magnesium, and aluminum are not sufficiently delicate to make it certain that these metals are fixed. A metal thus fixed can be displaced by another metal, this displacement being reversible. *W. D. B.*

Germination of spores of Penicillium in moist air. *G. Bonnier. Comptes rendus,* 133, *174* (*1901*). — The author finds that the spores of *Penicillium* germinate when the percentage moisture is above 82. When the ratio of the partial pressure to the total pressure is less than 0.82, it seems probable that the spores cannot absorb moisture and therefore do not germinate. This lower limit is not to be looked upon as definitely fixed. *W. D. B.*

Velocities

Investigations of the law of action of sucrase. *V. Henri. Comptes rendus,* 133, *891* (*1901*). — The rate of inversion of saccharose by sucrase can be represented by the formula

$$2K = \frac{1}{T} \log \frac{a+x}{a-x}.$$

W. D. B.

On the inversion of saccharose. *P. Petit. Comptes rendus,* 134, *111* (*1902*). — The author has determined the heat of reaction for the inversion of saccharose at about 60° by means of hydrochloric acid. For a concentration of one molecular weight of saccharose in 140 molecular weights of water the heat of refraction is 2675 calories at 63°. This differs somewhat from the value of 3384 calories, at 18°, obtained by Brown and Pickering for the inversion of saccharose by sucrase. *W. D. B.*

Investigations on the mechanism of esterification in plants. *E. Charabot and A. Hébert. Comptes rendus.* 133, *390* (*1901*). — "Esterification in plants is caused by the direct action of acids on the alcohols and is accelerated by the presence of some substances acting as a dehydrating agent." "The substance which accelerates esterification is a diastase exerting a dehydrating action in a chlorophyll medium." *W. D. B.*

The formation of ozone. *A. Chassy. Comptes rendus,* 133, *789* (*1901*). — The author has determined the amount of ozone formed at 20° in a Berthelot apparatus. The amount of ozone thus formed increases asymptotically with the time, tending toward a limit which depends solely on the temperature and not on the current. *W. D. B.*

Distribution of acidity in the stalk and leaf of the flower. *A. Astruc. Comptes rendus,* 133, *491* (*1901*). — It is found that the portion of the plant which is growing the most rapidly is also most acid. There is therefore "a close relation between the formation of acid, the rate of growth and the activity of the plant cells." *W. D. B.*

Electromotive Forces

On oxidation and reduction cells. *C. Fredenhagen. Zeit. anorg. Chem.* 29, *296* (*1902*). — The author starts off with Ostwald's definition that oxidation is a process which increases the number of positive or decreases the number of negative charges. It would be interesting to know how this applies in the reaction between potassium chlorate and potassium sulphite. The author then distinguishes between oxidizing and reducing agents such as the metals and substances like permanganates.

The theory of oxidation cells made up of oxidizing agents is developed along the line of the theory of gas cells. The reason why platinum electrodes in some of these oxidizing agents give definite values at once and in other cases do not, is to be found in the different rates with which the ions of the oxidizing agents react with the gases always present in the platinum electrodes. It is shown that platinum electrodes in oxidizing agents always contain gas; and it is observed that the potential difference is always due to this charging with gas. It was shown that the results of Peters for potassium ferricyanide and ferrocyanide are accurate for a given constant total concentration, but that there are distinct variations from Peters' formula when acids or alkalies are present. It was shown that the results of Peters with regard to chromium and manganese solutions agree with the results to be expected *a priori*. It was further shown that the potential observed with platinum electrodes in hydrogen peroxide solutions does not correspond to the oxidizing action of hydrogen peroxide, but that secondary disturbances occur. It is believed to be better to consider hydrogen peroxide as a peracid of water. *W. D. B.*

On change of the electromotive force and of the temperature coefficient of the Daniell cell with the concentration of the zinc sulphate. *J. Chaudier. Comptes rendus,* 134, *277* (*1902*). — Starting with a 6 percent zinc sulphate the voltage of the Daniell cell increases with dilution until the concentration reaches one-half of one percent. With further dilution the voltage drops from about 1.127 to about 1.06. For concentrations above one-half of one percent the temperature coefficient is positive, while it is negative for the more dilute solutions.

The author writes the Nernst formula with a term added for the temperature coefficient. He writes the Helmholtz formula and attributes it to Lord Kelvin. *W. D. B.*

On the electro-capillary action of undissociated molecules. *A. Gouy. Comptes rendus*, 133, *284* (*1901*). — The author has made experiments on the maximum surface tension of mercury with one hundred and sixty different substances, each of which was added to a normal solution of sodium sulphate. In every case the addition of the organic substance produced a decrease in the maximum surface tension.
W. D. B.

On the electro-capillary maximum for some organic compounds. *A. Gouy. Comptes rendus*, 133, *1301* (*1901*). — The author has determined the maximum surface tension of mercury in a number of organic liquids and finds variations of 7 or 8 percent. Those substances which have the greatest effect in dilute aqueous solution have also the greatest effect when pure. *W. D. B.*

On the thermoelectricity of carbon and nickel steels. *G. Belloc. Comptes rendus*, 134, *105* (*1902*). — When the results for the carbon steels are plotted in the thermoelectric diagram there is a common minimum at about 380°, a maximum, and a second minimum about 120° from the maximum. Between 650° and 1000° the curves for steels with different amounts of carbon lie far enough apart so that thermoelectric force could be used as a method of analysis.

The nickel steels were measured against platinum and the general form of the electromotive force-temperature curve is parabolic except for the steel containing 5 percent nickel. All steels containing between 5 and 28 percent of nickel showed marked variations at about 400° to 500°, evidently due to molecular rearrangements. Slight changes in the amount of nickel are sufficient to cause large variations in the temperature of the neutral point and in the electromotive force.
W. D. B.

Investigation of electromotive forces. *M. Berthelot. Comptes rendus*, 134, *793* (*1902*). — After a discussion of the Helmholtz formula the author describes measurements made with platinum electrodes in acids and alkalies. He considers that the seat of the electromotive force is at the surface between the two solutions.
W. D. B.

On some phenomena of voltaic polarization. *M. Berthelot. Comptes rendus*, 134, *835* (*1902*). — A general discussion of polarization in which the author points out that formic acid, for instance, may act in two ways as a depolarizer depending upon whether it is oxidized or reduced. *W. D. B.*

On the processes giving rise to electrolytic action in the cell. *M. Berthelot. Comptes rendus*, 134, *873* (*1902*). — The author shows that such substances as sodium sulphate may be decomposed more readily if pyrogallol be added to the solution or if they are electrolyzed under diminished pressure so that the gases pass off more readily.
W. D. B.

Study of cells based on the reciprocal action of oxidizing and reducing agents. *M. Berthelot. Comptes rendus*, 134, *933* (*1902*). — The author has made measurements with a number of cells containing reducing and oxidizing agents and finds, among other things, that in ammoniacal solutions pyrogallol and formal behave very differently owing to different reactions taking place, while these two substances behave similarly in a sodium hydroxide solution.
W. D. B.

On a capillary electrometer. *P. Boley. Comptes rendus*, 134, *463* (*1902*). — In order to use liquid amalgams in a capillary electrometer, the author has devised a form whereby portions of the amalgam in the capillary can be forced over into the larger mass without difficulty. *W. D. B.*

On the use of the capillary electrometer for measuring true differences of potential between amalgam and electrolytes. *L. Poincaré. Comptes rendus*, 134, *527* (*1902*). — The author calls attention to the fact that in 1891 he had described a form of capillary electrometer suitable for the same purpose as that invented by Boley (preceding review). Attention is also called to the fact that a tin amalgam in presence of sulphuric acid has practically the maximum capillary constant and that it therefore gives direct single potential readings.
W. D. B.

On a form of electrical thermometer. *G. Meslin. Comptes rendus*, 134, *412* (*1902*). — The author uses the change with the temperature of the electromotive force of the Clark cell as a means of measuring the temperature.
W. D. B.

Electrolysis and Electrolytic Dissociation

Studies on the theory of electrolytic copper extraction. *J. Egli. Zeit. anorg. Chem.* 30, *18* (*1902*). — With a cuprous sulphide anode in sulphuric acid solution, copper goes into solution as cupric salt and sulphur precipitates on the anode, causing an increasing and variable resistance. With current densities running up to 30 amperes/dm^2, and sulphuric acid of a density 1.225, there is no appreciable oxidizing of the sulphur. Under these circumstances, the voltage varies very much.

With a cuprous sulphide anode in hydrochloric acid solution, copper goes into solution partly as cuprous salt and partly as cupric salt. The way in which this ratio varies with current density, temperature, and density of acid has not been carefully worked out. The sulphur is oxidized to sulphuric acid.

With cuprous sulphide as anode in alkaline solution, there is formed copper hydroxide and the sulphur is oxidized.

With cuprous sulphide as cathode in acid solution, hydrogen sulphide is formed and metallic copper remains on the electrode.

With cuprous sulphide as cathode in alkaline solution, sulphur dissolves as sulphide and metallic copper remains behind. The voltage under these circumstances remains very constant.

Experiments were also made on the precipitation of copper from cupric chloride solution, with the following results:

(1) The current efficiency decreases rapidly with increased stirring of the electrolyte and the electrolyte is therefore to be stirred only enough to keep its composition constant.

(2) Addition of hydrochloric acid has a favorable effect on the purity of the copper but decreases the current efficiency enormously. With very concentrated hydrochloric acid, however, the current efficiency increases somewhat.

(3) Addition of sodium chloride has a favorable effect on the purity of the copper, cutting down the formation of cuprous chloride under some circum-

stances to zero. The decrease in the current efficiency is not as great as with hydrochloric acid.

(4) A high concentration of cupric chloride is unfavorable both for the current yield and the purity of the copper, but the concentration of cupric chloride must not be too small or the copper does not separate in a coherent mass.

(5) Rise of temperature acts unfavorably on current efficiency and on the purity of the copper.

(6) Increasing the current density increases the current efficiency until such densities are reached that hydrogen begins to precipitate. From a solution containing 1/10 mol cupric chloride, 1/10 mol hydrochloric acid, and 4/10 mol sodium chloride, copper was precipitated which was over 99.9 pure.

W. D. B.

Electrolytic preparation of persulphates without a diaphragm. *E. Müller and O. Friedberger. Zeit. Elektrochemie*, 8, *230* (*1902*). — It was found that potassium persulphate can be made satisfactorily without using a diaphragm, the reduction being negligible. The reason for this is the sparing solubility of the potassium persulphate. When ammonium persulphate was prepared electrolytically, the reduction was a very disturbing factor. Addition of potassium chromate to the acid solution had no effect because metallic chromium is precipitated instead of a diaphragm of oxide or hydroxide. In neutral or alkaline solutions, addition of chromate is effective in cutting down the reduction.

W. D. B.

Electrolytic preparation of halide compounds of acetone. *A. Richard. Comptes rendus*, 133, *878* (*1901*). — Monochloracetone can readily be made by electrolyzing a solution of acetone in concentrated hydrochloric acid. No figures are given for the yield, but it is stated that low temperature and a low current density at the anode are advantageous and that there is practically no reduction at the cathode. By substituting hydrobromic acid for hydrochloric acid monobromacetone can be obtained. In this case, it is desirable to work at a temperature of 35°-40° and there is considerable reduction at the cathode.

W. D. B.

Electrolysis of ammonium chloride dissolved in liquid ammonia. *H. Moissan. Comptes rendus*, 133, *713* (*1901*). — When ammonium chloride dissolved in a solution of liquid ammonia is electrolyzed at a temperature of about −80°, there is evolved hydrogen and chlorine, but no nitrogen. When ammonium iodide is substituted for chloride, the products of electrolysis are hydrogen and iodine. The iodine does not react with the ammonia until the temperature rises well above −70°.

W. D. B.

New method of measuring and recording high temperatures. *A. Job. Comptes rendus*, 134, *39* (*1902*). — The author makes use of his voltameter with a capillary tube, keeping one capillary tube at the temperature to be measured and another capillary tube at ordinary temperature. From the ratio of the two pressures he determines the temperature. It appears that this ratio is a linear function of the temperature. By recording the variations of pressure one has therefore a record of all the changes of temperature.

W. D. B.

On the color of the ions. *G. Vaillant. Comples rendus*, 133, *366* (*1901*). — Measurement of the salts of potassium, barium and zinc permanganates show that the dilute solutions of these three substances have the same spectrum while this is not true for more concentrated solutions. *W. D. B.*

Acidimetry of arsenic acid. *A. Astruc and J. Tarbouriech. Comples rendus*, 133, *36* (*1902*). — With tenth-normal arsenic acid and methyl orange as indicator one equivalent of sodium, potassium, ammonium, barium, strontium or calcium hydroxide suffices to neutralize whether hot or cold. With phenolphthaleine, two equivalents are necessary in a cold solution and two equivalents of the alkalies in hot solutions, but three equivalents of the alkaline earths in hot solutions. The presence of salts complicates matters. *W. D. B.*

Dielectricity and Optics

Measures of wave-lengths in the solar spectrum. *A. Perot and C. Fabry. Comples rendus*, 133, *153* (*1901*). — The authors have compared thirty-three rays directly with the green cadmium ray by their method. On comparing their wave-lengths with those of Rowland, they find that the ratio between the two is not constant. They conclude that Rowland's scale is not absolutely correct even in relative values. *W. D. B.*

On the change of the optical rotation in the esters of the stable laevorotary borneol. *J. Minguin and E. Grégoire de Bellemont. Comples rendus*, 134, *608* (*1902*). — The authors have prepared a number of esters of borneol and find that the rotary power varies from about −19° to −49°. In some cases with the same homologous series, the rotary powers are approximately inversely proportional to the molecular weights. *W. D. B.*

Refractive indices of liquid mixtures. *J. de Kowalski and J. de Modzelewski. Comples rendus*, 133, *33* (*1901*). — The index of refraction of mixtures of ether and chloroform, of ethyl alcohol and benzene, and of ethyl alcohol and toluene can be calculated with fair accuracy from the values for the components on the assumption of the property being an additive one. Since the dielectric constants of these mixtures cannot be calculated from the values for the pure components, the authors conclude that it is only the absorption in the ultra-red which changes irregularly in these mixtures. *W. D. B.*

On the conservation of refractive energy in mixtures of alcohol and water. *A. Leduc. Comples rendus*, 134, *645* (*1902*). — Owing to the marked contraction, the index of refraction for aqueous alcohol passes through a maximum for a mixture containing 78 percent of alcohol by weight. The refractive energy seems to be as nearly additive in this case as in the case of mixtures of glycerol in water. *W. D. B.*

On the refractive indices in liquid mixtures. *E. van Aubel. Comples rendus*, 134, *985* (*1902*). — The observation by Leduc (preceding review) that the refractive index is an additive property for mixtures of alcohol and water has caused the author to investigate two other mixtures, acetone and water, and aniline and ethyl alcohol. In both these cases it is found that the refractive index is not an additive property. *W. D. B.*

On the radio-activity of salts of radium. *P. Curie and A. Debierne. Comptes rendus,* 133, *276* (*1901*).—If a solution of radium chloride be placed in a beaker under a bell-jar together with a second beaker containing pure water, the water in the second beaker will soon become active. If a similar solution be placed in a celluloid capsule and this dipped into pure water, the water will become active although no trace of salt passes through the celluloid walls.

If the capsule be suspended above the water, the water does not become active so long as the capsule is dry on the outside. When a salt of radium is dissolved in water, the water becomes active as can be shown by distillation. On the other hand, this transfer takes place slowly. If we distil off the water very soon after the solution has been made up, the activity of the distillate will be found to be very much less than if the distillation had been made ten days later.
W. D. B.

Some chemical reactions caused by radium. *M. Berthelot. Comptes rendus,* 133, *659* (*1901*).—Iodine pentoxide is decomposed by the light from radium chloride and a similar phenomenon was observed with HNO_3. On the other hand, no insoluble sulphur is precipitated from a solution of sulphur in carbon bisulphide and the oxidation of oxalic acid also is not affected by the action of the radium rays. It is, however, thought this lack of action may be due to the absorption of rays by the glass through which they had to pass. This is the more probable because it was noticed that the glass blackened.
W. D. B.

Some chemical reactions produced by radium rays. *H. Becquerel. Comptes rendus,* 133, *709* (*1901*).—Under the influence of radium rays white phosphorus changes to red and mercuric chloride reacts with oxalic acid. It was also found that seeds of white mustard which had been exposed to radiation from radium for a week had lost the power to germinate. *W. D. B.*

The effect of radio-active substances on the luminosity of gases. *A. de Hemptinne. Comptes rendus,* 133, *934*; *Zeit. phys. Chem.* 39, *345* (*1901*).—The author finds that the minimum pressure at which a gas becomes luminous under the influence of electrical vibrations is raised when the gas is exposed to radium rays. *W. D. B.*

On the radio-activity of uranium. *H. Becquerel. Comptes rendus,* 133, *977* (*1901*).—Crookes has found that it is possible to obtain an inactive uranium nitrate by fractional crystallization. By precipitating barium sulphate from a solution of barium chloride and uranium chloride, Debierne found that the barium sulphate was much more active than the uranium. The author has discovered that the inactive uranium regains its activity on standing, while the active barium sulphate loses its activity in time. He concludes in consequence that the radio-activity is not due to impurity in the uranium salt, but is really characteristic of uranium. *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

BY J. R. ROEBUCK

INTRODUCTION

The early researches on the rates at which chemical reactions take place in homogeneous systems at constant temperature, led to the enunciation of the simple law that "*the rate at any moment is proportional to the concentrations of the reacting substances at that moment.*"

$$dx/d\theta = k(A - x)(B - x)(C - x) \dots \qquad \text{Eq. 1.}$$

Considerations based on the relationship between the rates of inverse chemical reactions and the composition of the system at equilibrium (Guldberg and Waage's equation) made it seem probable that this law should be modified, and that the concentration of each reagent should appear as a factor on the right of Eq. 1, *once for each molecule of that substance entering into the reaction*; and the expression

$$dx/d\theta = k(A - x)^{\alpha}(B - x)^{\beta}(C - x)^{\gamma} \dots \qquad \text{Eq. 2.}$$

corresponding to the chemical equation for the reaction

$$\alpha A + \beta B + \gamma C + \dots = \delta D + \epsilon E + \dots$$

may be regarded as the fundamental equation of Chemical Kinetics. The mathematical consequences of this equation have been developed at length for a number of cases.

It is very difficult, however, to bring much of the recent work on Chemical Kinetics into line with the requirements of Eq. 2, although a great deal of ingenuity has been expended in the attempt, and no hesitation has been shown in writing formulas for and ascribing properties to hypothetical nonisolable "intermediate products," in order to help out the assumption of imaginary "initial reactions."

Under these circumstances, it is worth while to examine the fundaments of the theory somewhat critically. The introduction of the indices into Eq. 2 is based on the so-called "kinetic view of chemical equilibrium," viz.: that in a system at equilibrium the two opposite reactions are still taking place, but at equal rates. According to this view the concentration function of Guldberg and Waage's equation is to be regarded as the quotient of two other concentration functions belonging to the kinetic equations of the two opposite reactions.

The consequences of this assumption have been subjected to a strict test in one case only,[1] viz.: the Esterification-Saponification reaction, a reaction which in every respect behaves normally; the results were in accordance with the theory of kinetic equilibrium. The present research was undertaken with a view of ascertaining whether this theory may legitimately be extended to reactions whose rates can be accounted for only by assuming the existence of hypothetical "intermediate compounds."

The reaction selected for the trial was that between arsenious acid and iodine in acid solution. These substances react to form arsenic and hydriodic acids; the reaction is reversible, and under suitable conditions of temperature and dilution proceeds at a rate convenient for measurement.

The "ordinary" chemical equation representing this reaction is

$$H_3AsO_3 + I_2 + H_2O \rightleftarrows H_3AsO_4 + 2HI.$$

Adopting the notation of the ion theory, this equation may be written[2]

$$\overset{\prime\prime\prime}{AsO_3} + \overset{\prime}{I_3} + H_2O \rightleftarrows \overset{\prime\prime\prime}{AsO_4} + 3\overset{\prime}{I} + 2\overset{+}{H}, \qquad \text{Eq. 3.}$$

and the condition of equilibrium is:

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[1] Zeit. phys. Chem. 22, 268 (1897).

[2] Nothing certain is known as to the ions in a solution of arsenious acid. See page 391.

$$\text{Const.} = \frac{a.b}{x.y^3.z^2} \qquad \text{Eq. 4.}$$

(where a represents the concentration of the $\overset{'''}{\mathrm{AsO_3}}$, b that of the $\overset{'}{\mathrm{I_3}}$, and so forth in the order of Eq. 3. The "concentration of the water" is constant).

This equation is in agreement with the experiments on equilibrium of Table XXXIII.

Predictions of the theory

According to the theory of kinetic equilibrium, the expression $\frac{a.b}{x.y^3.z^2}$ must be regarded as the quotient of two others, for instance (i) $a.b$ and $x.y^3.z^2$, corresponding to the kinetic equations:

$$dx/d\theta = k.a.b, \text{ and } -dx/d\theta = k'.x.y^3.z^2, \qquad \text{Eqs. 5, 6.}$$

Should the experiments show that the rate of oxidation of arsenious acid was proportional to the first powers of the concentrations of the $\overset{'''}{\mathrm{AsO_3}}$ and $\overset{'}{\mathrm{I_3}}$, the theory would require that the rate of the reverse reaction (reduction of arsenic acid by hydrogen iodide) should be in accordance with Eq. 6; and the "explanation" would be furnished by assuming that "the reactions whose rates are really measured" are those represented in Eq. 3.

But this is obviously not the only way in which the fraction in question can be divided into two factors;[1] a number of other possibilities are enumerated in the following paragraphs.

(ii) $a.b/y$ and $1/x.y^2.z^2$; assuming the instantaneous reaction $\overset{'}{\mathrm{I_3}} \rightleftarrows \mathrm{I_2} + \overset{'}{\mathrm{I}}$, this may be explained by the chemical reaction:

$$\overset{'''}{\mathrm{AsO_3}} + \mathrm{I_2} + \mathrm{H_2O} = \overset{'''}{\mathrm{AsO_4}} + 2\overset{'}{\mathrm{I}} + 2\overset{+}{\mathrm{H}}.$$

(iii) $a.b/y^2.z$, and $1/x.y.z$; assuming the instantaneous reactions $\overset{'}{\mathrm{I_3}} \rightleftarrows \mathrm{I_2} + \overset{'}{\mathrm{I}}$, and $\mathrm{I_3} + \overset{'}{\mathrm{OH}} \rightleftarrows \mathrm{IOH} + 2\overset{'}{\mathrm{I}}$, this may be explained by the chemical equation:

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[1] Some of the possible factorings obviously cannot correspond to kinetic equations. To choose an extreme case, a, and $b/x.y^3.z^2$.

$$\overset{\prime\prime\prime}{\mathrm{AsO}_3} + \mathrm{HOI} = \overset{\prime\prime\prime}{\mathrm{AsO}_4} + \overset{+}{\mathrm{H}} + \overset{\prime}{\mathrm{I}}.$$

(iv) $a.b/y^2.z^2$ and $1/x.y$; adding to the assumptions of (iii) the following, viz: $\mathrm{HOI} \rightleftarrows \overset{+}{\mathrm{H}} + \overset{\prime}{\mathrm{OI}}$, this case may be explained by:

$$\overset{\prime\prime\prime}{\mathrm{AsO}_3} + \overset{\prime}{\mathrm{OI}} = \overset{\prime\prime\prime}{\mathrm{AsO}_4} + \overset{\prime}{\mathrm{I}}.$$

(v) Equation 4 may be changed into the form:

$$\text{Const.} = \frac{a^2.b^3}{x^3.y^6.z^4}$$

and this may be factored. For instance, into $\frac{a^2.b^3}{y^5.z^3}$ and $1/x^3.y.z$, which may be explained by the help of the reactions:

$$2\overset{\prime}{\mathrm{I}_3} + \mathrm{H_2O} \rightleftarrows \mathrm{IO_3H} + 5\overset{\prime}{\mathrm{I}} + 3\overset{+}{\mathrm{H}} \text{ (instantaneous)}$$

and

$$2\overset{\prime\prime\prime}{\mathrm{AsO}_3} + \mathrm{IO_3H} = 2\overset{\prime\prime\prime}{\mathrm{AsO}_4} + \overset{\prime}{\mathrm{I}} + \overset{+}{\mathrm{H}}.$$

(iv) Finally both numerator and denominator of the fraction of Eq. 4 may be multiplied by one and the same quantity (for instance by z), and the product may be factored. Under this head would come explanations based on "catalysis by hydrogen ions," etc., etc.

After reading the preceding paragraphs, the thought suggests itself, that, no matter what relation might be found to subsist between concentrations and rates, an "explanation" would be forthcoming. The object of this research, however, was not to seek such explanations, but to ascertain whether the connection between the forms of the rate and equilibrium functions postulated by the theory, exists in reality.

PART I.

THE RATE OF OXIDATION OF ARSENIOUS ACID BY IODINE IN ACID SOLUTION

EXPLANATION OF THE TABLES

Units

For the purposes of this paper, one unit of arsenious acid is defined as the quantity of arsenious acid represented by the symbol $\overset{\prime\prime\prime}{\mathrm{As}}\mathrm{O}_3$ in centigrammes; this corresponds to 0.99 grammes of white arsenic. Similarly, one unit of arsenic acid is 1.42 grammes of H_3AsO_4. One unit of "free iodine" is 3×1.269 grammes of I_3 ("triiodion"); it may be obtained by dissolving 2×1.269 grammes solid iodine in potassium iodide solution. One unit of "iodion" may be obtained by dissolving 3×1.66 grammes potassium iodide; and one unit of sulphuric acid (0.98 gramme H_2SO_4) is contained in 20 cc of "normal" sulphuric acid.

Representing by A, B, C, and D, the initial weights of the triiodion, arsenious acid, iodion, and acid, expressed in these units, and by x, the number of units of triiodion reduced at the time θ, the residual weights of the four constituents at this moment will be $A - x$, $B - x$, $C + x$, and $D + x$. In a solution whose initial composition is known, the quantities of all four components at any moment may, therefore, be ascertained by determining the "free iodine" by sodium thiosulphate.

The unit of volume is one litre. The unit of time is one minute.

Description of tables

At the head of each table is given the total volume of the solution in which the reaction was carried out, and also the number of units of each reagent present in that volume at the moment of mixing.

Under "Reading" is entered the number of cc of sodium thiosulphate used in the titration; this is proportional to the corresponding value of $A - x$. In the experiments of Series B, this entry has a different meaning, which is explained on page 372.

The "constants" k_1, k_2, k_3, and k_4 were calculated from the data of the tables by means of the following equations:

$$dx/d\theta = 2.30\,k_1(A - x),^{1}$$

$$dx/d\theta = k_2(A - x)^2$$

$$dx/d\theta = k_3 V \frac{(A - x)(B - x)}{(C + x)^2 D} = k_4 \frac{(A - x)(B - x)}{(C + x)^2},$$

$$\text{whence } k_3 V/D = k_4.$$

In calculating these constants, the time of the first reading (line 2 in the tables), and not the moment of mixing, was in general taken as the starting point. The labor of computation was much shortened by the use of an exponential method, which will shortly be published.

METHOD OF CARRYING OUT THE EXPERIMENTS

The reaction was carried on in a 600 cc flask kept at 0° C by immersion in a well stirred bath of snow and water. At intervals 50 cc were pipetted into a beaker in the bath; the time was noted and the triiodion determined.

The initial composition

The stock solutions from which the reacting mixtures were made up were (I.) white arsenic dissolved in a solution of sodium bicarbonate, (II.) iodine dissolved in a solution of potassium iodide, (III.) potassium iodide solution, (IV.) dilute sulphuric acid. They were made up and standardized in the usual manner.

In calculating the initial composition, the amount of acid necessary to neutralize the soda of the arsenite solution was deducted from the total amount of acid added. Similarly with the iodine; from the potassium iodide used in making up solution (II.) was subtracted the part which united with the iodine to form triiodion, and the difference was added to the potassium iodide supplied from stock solution (III.) in calculating the

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[1] In the tables of *Series B*, A in this formula was replaced by B.

initial amount of the iodion. For example, in making up the solution for the experiments of Table I., I used sodium arsenite solution 50 cc, containing 50 × 49.4/1000 units $\overset{'''}{AsO_3}$, and soda sufficient to neutralize 50 × 0.0396 = 1.98 units of sulphuric acid; iodine solution 5 cc, containing 5 × 49.2/1000 = 0.246 units triiodion, and 5 × 17.6/1000 = 0.088 units iodion; potassium iodide solution 50 cc, containing 50 × 29.3/1000 = 1.47 units iodion; sulphuric acid, 10 cc 9.43 *n*.acid = 4.715 units; water, 485 cc.

Hence the initial composition of the solution was:

$\overset{'''}{AsO_3}$, 2.47 units = B.
Triiodion, 0.246 unit = A.
Iodion, 1.47 + 0.088 = 1.56 units = C.
Acid, 4.715 − 1.98 = 2.735 units = D.
Volume, 600 cc = 0.6 unit = V.

Determination of the residual free iodine

Preliminary experiments showed that sodium thiosulphate is oxidized by acid solutions of arsenic acid, the rate of oxidation increasing with increased concentration of the thiosulphate and of the acid. As dilution, or removal of the acid (by acetates or carbonates) accelerates the rate of the reaction between arsenious acid and iodine, these obvious methods of overcoming the difficulty were excluded.

A special investigation, however, showed that if care were taken to avoid excess of thiosulphate during the titration, the error due to the oxidation could be neglected in solutions containing less than 50 grammes of H_2SO_4 per liter. I accordingly restricted[1] my measurements to solutions which were normal or less than normal with respect to the acid. The greater part of the thiosulphate solution was run in quickly, the contents of the beaker being well stirred meanwhile, and the titration was

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[1] A litre of a strong solution of an alkaline carbonate readily dissolves 100 grammes of arsenious oxide; but if such a solution be acidified the greater part of the arsenic will crystallize out. This set a limit to the concentration of the arsenious acid in my experiments.

completed without excess of thiosulphate. I endeavored to determine the residual arsenious acid directly by Penot's method, after removing the triiodion by sodium thiosulphate. The end point however was very unsatisfactory (no doubt owing to the large quantity of potassium iodide present) and the attempt was given up.

In the experiments of Series B, where triiodion was in excess, the titration was begun by adding approximately normal sodium thiosulphate solution from a pipette in quantity sufficient to react with all the triiodion initially present *minus* an amount equivalent to the arsenious acid initially present. The readings were then finished with a more dilute solution from a burette. The burette readings were thus proportional to the amount of arsenious acid unoxidized, and are entered in the tables under the heading "Reading." The experimental error is comparatively large in cases of this nature, where the value of x is obtained in the form of a small difference between two large numbers.

All pipettes used were calibrated at the outset by weighing the water discharged; both in the calibration and in subsequent use 30 seconds was allowed for draining.

RESULTS OF THE EXPERIMENTS

Series A

With a view to determining the effect exercised by each component on the rate of the reaction, I carried out a set of experiments, Series A, whose results are summarized in Tables I. to VII. In all these the quantity of triiodion present initially was very much less than that of the acid, the iodion, or the arsenious acid. The concentrations of these latter, and consequently their effect on the rate remained approximately constant during the progress of the reaction, while the concentration of the triiodion fell to less than 1/10 of its initial value.

In Table I. the constancy of k_1 as compared with k_2, shows that the rate is proportional to the first power of the concentration of the triiodion.

In Table II. the initial concentrations of triiodion, potassium iodide, and acid are the same as in Table I., but that of the

TABLE I.

A, 0.246; B, 2.47; C, 1.56; D, 2.735; V, 0.6

No.	Reading	θ	$A-x$	$k_1 \times 10^3$	$k_4 \times 10^3$	$k_2 \times 10$
1	42.6	0.0	0.246	—	—	—
2	30.8	5.0	0.178	—	—	—
3	25.5	8.67	0.147	2.23	5.95	3.23
4	22.0	11.8	0.127	2.15	6.48	3.41
5	18.6	15.8	0.1074	2.03	5.52	3.40
6	15.35	19.7	0.0886	2.06	5.71	3.84
7	13.15	23.3	0.0759	2.02	5.68	4.14
8	11.5	26.7	0.0664	1.97	5.57	4.56
9	9.1	31.8	0.0526	1.97	5.76	5.00
10	7.33	37.2	0.0423	1.93	5.67	5.69
11	5.35	45.3	0.0309	1.89	5.67	6.63
12	2.83	60.0	0.0163	1.89	—	10.1
				Average	5.7	

TABLE II.

A, 0.246; B, 4.95; C, 1.56; D, 2.735; V, 0.6

No.	Reading	θ	$A-x$	$k_1 \times 10^3$	$k_4 \times 10^3$
1	42.7	0.0	0.246	—	—
2	23.2	3.8	0.134	—	—
3	18.65	6.3	0.1074	3.40	5.33
4	14.35	8.67	0.0827	4.25	6.08
5	10.4	11.7	0.0599	4.40	6.40
6	8.15	14.2	0.0470	4.37	6.48
7	6.55	16.3	0.0377	4.39	6.59
8	4.4	20.8	0.0254	4.25	6.45
9	3.5	23.0	0.0202	3.86	6.55
10	1.85	30.0	0.0107	4.20	—
				Average	6.4

arsenious acid is doubled. The value of k_1, calculated from the readings in this table, is double that of k_1 in Table I. It follows that the rate of the reaction is proportional to the first power of the concentration of the arsenious acid.

In Table III. the concentration of the iodion is approximately four times as great as in Table I., and k_1 has fallen to about one-fourteenth of its value in Table I.; that is, the rate is

TABLE III.

A, 0.246 ; B, 2.47 ; C, 5.95 ; D, 2.735 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	42.5	0.0	0.000	—	—
2	41.55	6.7	0.006	—	—
3	39.2	22.8	0.019	0.16	5.42
4	36.6	42.8	0.034	0.15	5.35
5	34.1	63.3	0.048	0.15	5.24
6	29.2	100.0	0.077	0.16	5.81
7	26.7	137.0	0.091	0.15	5.27
8	23.2	183.0	0.112	0.14	5.23
				Average	5.38

TABLE IV.

A, 0.246 ; B, 2.47 ; C, 1.56 ; D, 5.47 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	42.0	0.0	0.000	—	—
2	38.2	2.5	0.022	—	—
3	35.4	5.0	0.039	1.32	2.87
4	31.3	8.9	0.063	1.25	2.49
5	26.3	15.1	0.092	1.29	3.21
6	21.6	22.0	0.119	1.27	3.16
7	17.8	29.7	0.142	1.22	3.19
8	13.9	40.0	0.165	1.18	3.09
9	9.55	56.5	0.190	1.30	3.09
10	4.95	88.5	0.217	1.03	2.96
11	1.70	139.0	0.236	0.99	2.98
				Average	3.02

inversely proportional to the square of the concentration of the iodion.

Now as to the acid. In the experiments summarized in Table IV. the concentration of the acid is twice that in Table I.; the value of k_1 has fallen from 2.15 to 1.25, or in the ratio of 1 to 0.58. In Table V. the concentration of the acid is 3/2 that in Table IV., and the ratios of the constants are:

$$k_1(\text{Table IV.}) : k_1(\text{Table V.}) = 1.0 : 0.7.$$

From this it appears that when the quantity of acid present in the 600 cc is not less than 5 units, the rate is inversely proportional to the concentration of the acid. This conclusion is supported by subsequent experiments (see Table XVII.), and the deviation observed in the case of Table I. must be attributed to the effect of the relatively large quantity of neutral salt on the dissociation of the acid.

TABLE V.

A, 0.246 ; B, 2.47 ; C, 1.56 ; D, 4.1 ; V, 0.6

No.	Reading	θ	$A-x$	$k_1 \times 10^3$	$k_4 \times 10^2$
1	41.1	0.0	0.246	—	—
2	40.2	2.0	0.241	—	—
3	36.1	7.33	0.216	8.76	2.08
4	30.95	15.0	0.185	8.77	2.11
5	23.65	29.0	0.141	8.52	2.18
6	20.35	37.3	0.122	8.43	1.86
7	17.45	46.7	0.104	8.10	2.14
8	14.15	58.7	0.0847	7.99	2.18
9	11.35	72.2	0.0680	7.82	2.06
10	7.25	116.0	0.0434	7.17	1.86
11	3.75	143.0	0.0224	7.29	2.16
12	2.30	179.0	0.0138	7.01	—
				Average	2.07

TABLE VI.

A, 0.492 ; B, 4.95 ; C, 3.11 ; D, 2.735 ; V, 0.6

No.	Reading	θ	$A-x$	$k_1 \times 10^2$	$k_4 \times 10^3$
1	41.1	0.0	0.492	—	—
2	40.4	3.16	0.484	—	—
3	38.05	6.83	0.456	0.71	3.15
4	34.25	13.66	0.410	0.68	3.24
5	30.35	21.66	0.363	0.67	3.25
6	26.33	31.83	0.315	0.65	3.29
7	22.63	43.5	0.271	0.62	3.11
8	19.4	57.5	0.232	0.59	2.99
9	14.7	84.3	0.176	0.54	2.85
10	9.5	118.3	0.114	0.56	3.01
11	8.03	134.2	0.0961	0.54	2.99
12	5.82	165.5	0.0697	0.47	3.73
				Average	3.16

Finally the experiments of Table I. were repeated, with the same quantities of the four reacting substances, but dissolved in half the volume (in other words all four concentrations doubled). The value of k_4 (Table VI.) is in accordance with the conclusions of the preceding paragraphs.

Table VII. resembles Table VI., except that the concentration of the triiodion is halved. In conformity with the conclusion reached by comparing k_1 and k_2 in Table I., this change has not affected the value of the constant.

TABLE VII.

A, 0.246 ; B, 4.95 ; C, 3.02 ; D, 5.47 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	41.0	0.0	0.000	—	—
2	39.1	2.08	0.012	—	—
3	35.6	6.8	0.032	0.85	3.68
4	31.2	14.8	0.059	0.76	3.43
5	26.0	24.3	0.090	0.80	3.64
6	21.0	36.3	0.120	0.78	3.66
7	18.3	46.7	0.136	0.74	3.45
8	12.7	68.0	0.156	0.73	3.41
9	10.1	81.7	0.185	0.73	3.45
10	8.75	92.7	0.193	0.72	3.53
11	6.65	110.0	0.206	0.71	3.55
12	5.0	129.5	0.216	0.70	3.51
				Average	3.51

Employing the notation of page 369, the results of the series of experiments just described may be condensed in the following expression, which connects the rate of the reaction with the concentrations of the reacting substances :

$$dx/d\theta = k_4 \frac{(\mathrm{A}-x)/\mathrm{V}.(\mathrm{B}-x)/\mathrm{V}}{(\mathrm{C}+x)^2/\mathrm{V}^2.(\mathrm{D}+x)/\mathrm{V}}. \qquad \text{Eq. 7.}$$

Series B

For the purpose of ascertaining whether the effect of the various concentrations on the rate of the reaction was independent of wide variations in the quantities of the reagents present, a similar set of experiments (Tables VIII. to XII.) were carried out, in which the arsenious acid was present in much

Table VIII.

A, 2.46 ; B, 0.247 ; C, 2.99 ; D, 8.2 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	41.2	0.0	0.000	—	—
2	38.7	11.0	0.015	—	—
3	36.0	25.0	0.031	2.04	2.13
4	31.6	46.5	0.057	2.32	2.17
5	27.5	71.5	0.082	2.30	2.23
6	24.0	96.6	0.103	2.25	2.22
7	19.6	136.0	0.129	2.15	2.17
				Average	2.20

Table IX.

A, 4.92 ; B, 0.247 ; C, 2.99 ; D, 8.2 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	20.6	0.0	0.000	—	—
2	19.8	2.16	0.009	—	—
3	17.0	13.7	0.043	5.9	2.7
4	15.9	26.5	0.061	4.4	1.9
5	12.6	46.3	0.091	4.4	1.8
6	10.4	69.3	0.122	4.2	1.9
7	8.7	89.5	0.143	4.1	1.9
8	7.3	104.0	0.159	4.2	1.9
9	6.1	118.0	0.174	4.4	2.0
10	5.0	136.0	0.187	4.5	2.1
11	3.0	176.0	0.211	4.7	2.2
				Average	2.0

Table X.

A, 2.46 ; B, 0.247 ; C, 2.99 ; D, 3.865 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	20.6	0.0	0.000	—	—
2	19.6	2.5	0.012	—	—
3	18.3	6.7	0.028	7.3	5.7
4	17.5	11.0	0.037	5.8	4.6
5	15.6	23.3	0.060	4.8	4.1
6	14.7	28.5	0.071	4.9	4.2
7	13.8	34.0	0.082	4.9	4.4
8	12.5	43.2	0.097	4.8	4.2
9	12.0	48.3	0.103	4.7	4.2
10	10.9	58.5	0.116	4.5	4.0
				Average	4.2

TABLE XI.

A, 1.22 ; B, 0.124 ; C, 1.50 ; D, 4.10 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	10.3	0.0	0.000	—	—
2	9.8	3.3	0.006	—	—
3	9.0	7.3	0.016	9.6	4.3
4	8.4	12.0	0.023	7.8	3.3
5	7.25	19.6	0.037	8.1	3.0
6	5.85	30.0	0.054	8.5	4.0
7	4.4	45.9	0.071	8.2	3.9
8	3.35	64.0	0.084	7.7	3.7
9	2.6	79.5	0.093	7.5	3.7
10	1.9	100.0	0.101	7.4	3.6
				Average	3.6

TABLE XII.

A, 2.46 ; B, 0.247 ; C, 2.01 ; D, 8.2 ; V, 0.6

No.	Reading	θ	$B - x$	$k_1 \times 10^3$	$k_4 \times 10^3$
1	20.6	0.0	0.247	—	—
2	19.7	2.66	0.236	—	—
3	18.8	7.0	0.225	4.5	1.93
4	16.2	16.7	0.194	6.1	2.46
5	14.9	25.3	0.179	5.3	2.09
6	13.1	39.5	0.157	4.8	1.99
7	11.9	50.0	0.143	4.6	1.93
8	9.3	72.0	0.112	4.7	1.96
9	7.2	95.0	0.086	4.8	2.08
10	5.1	129.0	0.061	4.7	2.07
11	2.6	194.0	0.031	4.6	2.18
				Average	2.09

smaller quantity than the other three. The results are presented in a condensed form in Table XVII. and, as will be seen, are in full accordance with the requirements of equation 7.

Series C

In order to have a series of measurements where the concentration of the acid was about the same as in the experiments on equilibrium of Table XXXIII., and in those on reduction of arsenic acid of Series D, I carried out a third series, whose results are contained of Tables XIII. and XIV.

TABLE XIII.

A, 0.256 ; B, 4.89 ; C, 1.69; D, 27.9; V, 0.6

No.	Reading	θ	$A-x$	$k_1 \times 10^3$	$k_4 \times 10^3$
1	43.1	0.0	0.256	—	—
2	33.7	2.5	0.200	—	—
3	32.8	7.5	0.195	2.35	3.12
4	28.5	20.25	0.169	3.55	5.39
5	24.1	35.0	0.143	4.46	5.76
6	21.6	48.5	0.126	4.37	5.89
7	18.4	63.0	0.109	4.35	5.93
8	15.5	79.7	0.092	4.37	5.80
9	13.7	94.5	0.0813	4.25	5.95
10	10.5	121.0	0.0647	4.15	5.92
11	4.4	271.0	0.0261	3.92	4.93
				Average	5.69

TABLE XIV.

A, 0.277 ; B, 4.89 ; C, 1.69 ; D, 62.3; V, 0.6

No.	Reading	θ	$A-x$	$k_1 \times 10^3$	$k_4 \times 10^3$
1	46.7	0.0	0.277	—	—
2	42.8	2.33	0.254	—	—
3	41.6	10.67	0.247	1.18	1.99
4	38.9	24.67	0.231	1.85	1.81
5	37.2	39.5	0.220	1.64	2.19
6	34.5	69.0	0.210	1.38	1.66
7	30.7	111.0	0.182	1.31	1.84
8	22.5	262.0	0.134	1.07	1.54
				Average	1.81

In the experiments of Table XIV. the concentration of the acid was 2¼ times as great as in those of Table XIII. ; if the rate is inversely proportional to the concentration of the acid then

$$k_1(\text{Table XIV.}) = 4/9 \text{ of } k_1(\text{Table XIII.}) = 20 \times 10^{-4}.$$

If, on the other hand, the rate vary as the inverse square of the concentration, then

$$k_1(\text{Table XIV.}) = (4/9)^2 \text{ of } k_1(\text{Table XIII.}) = 9 \times 10^{-4}$$

The results of the trial were marred by slow deposition of arsenious oxide during the measurements; to this is due the steady fall of k_1 in Table XIV.; but its value at the beginning of the experiment (line 4, Table XIV., $k_1 = 18.5 \times 10^{-4}$) leaves no doubt that the rate is inversely proportional to the first power, and not to the second power, of the concentration of the acid.

Other experiments

As it is not possible to prepare a solution in which the concentration of the triiodion is greatly in excess of that of the iodion, it was not possible to parallel Series A and B by a fourth in which the concentration of the iodion was small.

With regard to the acid, the experiments of Table I. made it seem very unlikely that simple results would be obtained from solutions in which the acid was present in small quantity; the more so, because in order to keep the rate within measureable limits, the concentration of the salts would have to be increased in proportion as that of the acid was lowered.

TABLE XV.

A, 0.500 ; B, 0.499 ; C, 0.500 ; D, 22.75 ; V, 0.6

No.	Reading	θ	x	$k_4 \times 10^3$
1	41.6	0.0	0.0	—
2	41.0	1.83	0.007	4.92
3	39.25	4.83	0.029	7.04
4	37.1	9.5	0.054	6.95
5	34.9	15.16	0.081	7.37
6	31.65	26.7	0.120	7.49
7	29.0	39.0	0.152	7.64
8	25.45	62.5	0.194	7.58
9	23.55	79.5	0.217	7.61
10	20.55	113.0	0.253	7.79
11	19.1	140.0	0.271	7.64
			Average	7.45

Finally, Table XV. gives the results of an experiment with equivalent quantities of arsenious acid, triiodion and iodion in presence of a large excess of acid. The constancy of k_4 may be regarded as further confirmation of the truth of equation 7.

Temperature coefficient

The experiments of Table XVI. were carried out at 10° C, all the others at 0° C. By comparing the values of k_3 from Tables XVI. and XVII., it will be seen that a rise in temperature of 10° C multiplies the rate by 3.5.

TABLE XVI.

A, 0.271; B, 0.979; C, 1.254; D, 22.75; V, 0.6
Temperature 10° C

No.	Reading	θ	$A-x$	$k_4 \times 10^4$
1	25.0	0.0	0.271	—
2	23.1	2.5	0.250	—
3	20.6	6.0	0.223	1.74
4	17.2	12.0	0.186	1.96
5	13.8	17.8	0.149	2.51
6	11.9	21.2	0.129	2.87
7	9.9	33.5	0.107	2.39
8	7.7	47.3	0.0835	2.41
9	5.85	59.3	0.0634	2.62
10	3.9	78.5	0.0423	2.84
11	3.0	95.3	0.0325	2.82
12	2.9	123.0	0.0314	2.20
			Average	2.51

Résumé of Tables I-XVI.

In order to facilitate comparison, the initial compositions and the values of k_1, k_3, and k_4 from Tables I. to XVI. have been collected in Table XVII.

k_1 has been taken from line 4 of each table. k_4 is the average of all the values (except the first) in each table, and k_3 has been calculated from k_4 by the formula given on page 370.

The fact that k_3 does not vary in any regular manner with D is proof that the rate of the reaction remains proportional to the first power of the concentration of the acid up to the highest concentrations; while the constancy of k_3 from table to table is evidence of the accuracy of Equation 7.

TABLE XVII.

Table	A	B	C	D	V	$k_1 \times 10^2$	$k_4 \times 10^3$	k_3
I.	0.246	2.47	1.56	2.74	0.6	2.15	5.7	0.26
II.	0.246	4.95	1.56	2.74	0.6	4.25	6.4	0.29
III.	0.246	2.47	5.95	2.74	0.6	0.15	5.4	0.25
IV.	0.246	2.47	1.56	5.47	0.6	1.25	3.0	0.28
V.	0.246	2.47	1.56	8.20	0.6	0.88	2.1	0.29
VI.	0.490	4.95	3.11	5.47	0.6	0.68	3.2	0.29
VII.	0.246	4.95	3.02	5.47	0.6	0.76	3.5	0.32
VIII.	2.35	0.247	3.01	8.20	0.6	2.32	2.2	0.30
IX.	4.92	0.247	2.99	8.20	0.6	4.4	2.0	0.28
X.	2.46	0.247	2.99	3.87	0.6	5.8	4.2	0.27
XI.	1.22	0.124	1.50	4.10	0.6	7.8	3.6	0.25
XII.	2.46	0.247	2.01	8.20	0.6	6.1	2.1	0.29
XIII.	0.256	4.89	1.69	27.9	0.6	0.35	0.57	0.27
XIV.	0.277	4.89	1.69	62.3	0.6	—	—	—
XV.	0.500	0.499	0.500	22.75	0.6	—	0.75	0.28
XVI.[1]	0 271	0.979	1.254	22.75	0.6	—	2.51	0.95
				Average (omitting XVI.)				0.28

PART II.

THE RATE OF REDUCTION OF ARSENIC ACID BY HYDROGEN IODIDE

The plan of these experiments is the same as that of Part I., my object being to determine the effect of changing the concentration of each reagent singly. Except in the experiments of Tables XVIII. and XIX. arsenic acid was chosen as the reagent to be present in small quantity, in order to avoid oxidation of the sodium thiosulphate during the titration.

The units and symbols defined on page 369 are employed in this part also, with the addition of the letter E to represent the number of units of arsenic acid initially present in any experiment. The sign of x has been changed, so that in Part II. x represents the number of units of arsenious acid formed by the reduction of arsenic acid.

To the constants there has been added k_5, defined as follows:

$$dx/d\theta = k_5 V^{-3}(C - x)(D - x)(E - x).$$

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[1] Temperature 10° C. All the others, 0° C.

METHOD OF CARRYING OUT THE EXPERIMENTS

The reaction was carried out in flasks kept at 0° C by a 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 half the sulphuric acid was added to the potassium iodide and part of the water; in the other flask the arsenic acid was mixed with the remainder of the sulphuric acid and water. By thus dividing the acid I avoided a rise in temperature when the contents of the flasks were mixed and the reaction commenced. Any iodine liberated in the first flask (owing to the action of the air on the acid solution of potassium iodide) was determined and allowed for. Owing to the short duration of most of the experiments no more elaborate precautions against the action of air seemed necessary; but to make sure, the experiments in Table XXIV*a*. were carried out with solutions freed from air and kept under carbon dioxide. The constants calculated from these experiments are almost identical with those of Table XXIV., where no such precautions were taken.

The experiments of Tables XXVIII. and XXIX., where the rate of reaction was measured over an interval of 50 hours, were carried out in test-tubes filled with carbon dioxide and sealed.

The progress of the reaction was determined at intervals by measuring out 10 cc of the reacting mixture, diluting it to 10 or 20 times its volume, in order to stop the reaction and reduce the concentration of the acid; and then quickly titrating with sodium thiosulphate. For the reasons given on page 371 excess of sodium thiosulphate was avoided.

RESULTS OF THE MEASUREMENTS

Series D

The constancy of k_1 in each of the tables (in Table XXI. k_2 is calculated for comparison) shows that the rate is proportional to the first power of the concentration of the arsenic acid. Evidence that this law holds for higher concentrations as well, is afforded by the experiments of Tables XVIII. and XIX, (where the reagent present in small quantity is iodion); in one of these the quantity of arsenic acid present is twice that in the other, and the values of k_1 stand in the same proportion.

TABLE XVIII.

C, 0.1385; D, 22.85; E, 1.16; V, 0.12

No.	Reading	θ	x	$C-x$	$k_1 \times 10^3$	$k_5 \times 10^6$
1	0.0	0.0	0.0	0.1385	—	—
2	4.0	1.2	0.0095	0.129	—	—
3	7.25	3.7	0.0172	0.121	9.2	1.70
4	10.7	6.2	0.0255	0.113	15.9	1.47
5	15.2	10.5	0.0361	0.102	10.8	1.65
6	21.7	17.5	0.0515	0.087	10.5	1.65
7	25.0	28.2	0.0594	0.079	7.8	1.21
8	27.3	38.0	0.0648	0.0737	6.6	1.30

58.3 cc sodium thiosulphate solution is equivalent to 0.1385 units I_2.

TABLE XIX

C, 0.1385; D, 22.85; E, 0.580; V, 0.12

No.	Reading	θ	x	$C-x$	$k_1 \times 10^3$	$k_5 \times 10^6$
1	0.0	0.0	0.0	0.1385	—	—
2	2.8	1.0	0.00665	0.132	—	—
3	5.3	4.2	0.0125	0.126	6.24	1.84
4	9.5	10.7	0.0226	0.116	5.75	1.68
5	15.2	20.0	0.0361	0.102	5.79	1.83
6	18.0	27.0	0.0427	0.096	5.35	1.65
7	22.0	37.7	0.0523	0.0862	5.02	1.61
8	24.2	46.7	0.0575	0.0810	4.64	1.48
9	25.8	58.7	0.0613	0.0772	4.02	1.30

58.3 cc sodium thiosulphate solution is equivalent to 0.1385 units I_2.

TABLE XX.

C, 5.64; D, 9.4; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	3.45	2 7	0.0224	0.268	—
3	11.65	10.8	0.0602	0.230	8.2
4	16.3	17.0	0.106	0.184	11.4
5	19.8	22.5	0.1288	0.161	11.2
6	23.6	29.0	0 153	0.137	11.1
7	27.3	37.2	0.177	0.113	10.9
8	29.9	43.8	0.194	0.096	10.9
9	31.9	50.5	0.207	0 083	10.7
10	34.3	59.3	0.223	0.067	10.6
11	37.2	73.0	0.242	0.048	10.6
12	39.2	87.5	0.255	0.035	10.4
13	41.4	108.0	0.269	0.021	10.5

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3.

TABLE XXI.

C, 3.76; D, 9.4; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$	$k_2 \times 10^3$
1	0.0	0.0	0.0	0.290	—	—
2	1.7	2.2	0.0109	0.279	—	—
3	7.55	12.8	0.0486	0.241	6.0	5.33
4	9.3	16.5	0.0598	0.230	5.87	5.34
5	13.9	27.0	0.0894	0.201	5.72	5.56
6	17.95	37.3	0.115	0.175	5.78	6.07
7	22.75	52.5	0.146	0.144	5.71	6.68
8	28.5	76.5	0.184	0.106	5.65	7.87
9	33.2	103.0	0.213	0.077	5.54	9.31
10	37.0	134.0	0.238	0.052	5.53	11.9
11	39.8	167.0	0.256	0.034	5.54	15.6
12	42.5	218.0	0.273	0 017	5.65	25.5

45.1 cc sodium thiosulphate solution is equivalent to 0.290 units I_3.

TABLE XXII.

C, 1.288; D, 22.85; E, 0.136; V, 0.12

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.136	—
2	1.8	1.33	0.0066	0.129	—
3	3.8	5.3	0.0140	0.122	6.3
4	12.5	10.3	0.0460	0.090	17.4
5	18.1	17.0	0.0666	0.069	17.2
6	25.1	28.5	0.0923	0.044	17.3
7	30.3	42.2	0.1114	0.025	17.5
8	32.8	53.2	0.1206	0.015	17.7

37.0 cc sodium thiosulphate solution is equivalent to 0.136 units I_2.

TABLE XXIII.

C, 0.644; D, 22.85; E, 0.136; V, 0.12

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.136	—
2	1.05	1.66	0.00386	0.132	—
3	8.85	15.5	0.0326	0.103	7.68
4	12.5	25.5	0.0460	0.090	7.77
5	16.7	35.7	0.0614	0.075	7.32
6	20.4	48.3	0.0751	0.061	7.21
7	23.7	64.0	0.0871	0.049	6.94
8	26.9	87.0	0.0989	0.037	6.47
9	29.8	116.0	0.1095	0.026	6.13
10	31.9	161.0	0.1173	0.019	5.83
11	32.8	198.0	0.1206	0.015	3.84

37.0 cc sodium thiosulphate solution is equivalent to 0.136 units I_2.

In Tables XX., XXI., XXII., and XXIII. are given the results obtained by varying the concentration of the iodion. In the first pair, where the concentrations are highest, adding fifty percent to the iodion doubles the rate; in the second pair, doubling the iodion multiplies the rate by about two and a quarter. Thus the "order of the reaction with respect to iodion" decreases with decrease in the concentration of that reagent. Even in Tables XVIII. and XIX. the rate seems to fall

TABLE XXIV.

C, 1.88; D, 18.25; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	2.85	2.5	0.0185	0.271	—
3	8.1	8.3	0.0527	0.237	10.0
4	12.9	14.5	0.0838	0.206	9.92
5	17.8	22.2	0.116	0.174	9.77
6	21.8	29.3	0.142	0.148	9.81
7	25.2	37.0	0.164	0.126	9.65
8	29.9	47.3	0.194	0.096	10.0
9	32.2	59.0	0.209	0.081	9 27
10	36.3	76.3	0.236	0.064	8.50
11	40.7	111.0	0.265	0.025	9.63

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXIV*a*.

C, 1.88; D, 18.25; E, 0.290; V, 0.13

All solutions were free of air and the experiment was carried out under an atmosphere of carbon dioxide.

No.	Reading	θ	$k_1 \times 10^3$
1	0.0	0.0	—
2	3.35	2.3	—
3	7.05	6.7	9.4
4	12.0	12.5	10.0
5	15.5	17.3	10.1
6	19.0	22.7	10.1
7	22.1	28.5	10.0
8	25.3	35.0	10.1
9	28.9	44.3	10.0
10	32.0	54.3	9.9
11	34.9	67.0	9.7

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXV.

C, 1.88; D, 13.7; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	1.5	1.5	0.00975	0.280	—
3	4.7	8.0	0.0307	0.259	5.22
4	7.7	14.8	0.0501	0.240	5.03
5	10.4	21.7	0.0677	0.222	4.99
6	12.5	27.3	0.0813	0.209	4.92
7	16.5	39.7	0.1073	0.183	4.84
8	20.8	55.0	0.135	0.155	4.80
9	24.2	70.3	0.157	0.133	4.70
10	28.0	89.8	0.182	0.108	4.69
11	32.1	119.0	0.208	0.082	4.50
12	36.2	160.0	0.235	0.055	4.47

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXVI.

C, 1.88; D, 9.15; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	1.3	3.0	0.0085	0.281	—
3	2.15	7.5	0.0140	0.276	1.73
4	4.75	20.3	0.0309	0.259	2.04
5	7.95	37.5	0.0517	0.238	2.09
6	10.6	52.7	0.0689	0.221	2.09
7	14.9	83.0	0.0967	0.193	2.04
8	18.9	112.0	0.123	0.167	2.07
9	21.7	137.0	0.141	0.149	2.05
10	25.6	179.0	0.166	0.124	2.02
11	29.3	223.0	0.191	0.099	2.06
12	32.7	279.0	0.212	0.078	2.02

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXVII.

C, 3.76 ; D, 4.70 ; E, 0.290 ; V, 0.13

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	0.85	2.0	0.00553	0.284	—
3	3.9	19.0	0.0252	0.265	1.85
4	7.4	41.5	0.0482	0.242	1.78
5	11.05	68.0	0.0719	0.218	1.76
6	15.5	104.5	0.1007	0.189	1.72
7	19.1	139.0	0.124	0.166	1.71
8	22.4	175.0	0.146	0.144	1.71
9	29.2	262.0	0.190	0.100	1.74
10	31.2	302.0	0.203	0.087	1.71
11	33.3	351.0	0.217	0.073	1.69
12	35.8	414.0	0.233	0.057	1.69
13	38.3	490.0	0.249	0.041	1.70

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXVIII.

C, 2.270 ; D, 2.293 ; E, 0.310 ; V, 0.155

No.	Reading	θ	x	$E - x$	$k_3 + 10^7$	$k_1 \times 10^4$
1	0.0	0.0	0.0	0.310	—	—
2	0.35	10.0	0.00161	0.308	—	—
3	2.3	66.0	0.0107	0.299	3.84	2.30
4	2.65	74.0	0.0122	0.298	4.22	2.51
5	9.45	296.0	0.0434	0.267	3.62	2.17
6	24.6	994.0	0.113	0.197	3.22	1.97
7	26.6	1177.0	0.122	0.188	3.17	1.83
8	29.7	1432.0	0.137	0.173	3.07	1.77
9	35.8	2480.0	0.164	0.137	2.61	1.43
10	37.3	2880.0	0.171	0.130	2.34	1.31
				Average	3.26	

67.5 cc sodium thiosulphate solution is equivalent to 0.310 units I_2.

Table XXIX.

C, 2.270; D, 1.147; E, 0.310; V, 0.155

No.	Reading	θ	x	$E-x$	$k_6 \times 10^7$	$k_1 \times 10^4$
1	0.0	0.0	0.0	0.310	—	—
2	0.2	9.5	0.00092	0.309	—	—
3	1.2	70.0	0.00551	0.304	3.54	1.17
4	3.7	292.0	0.0170	0.293	2.72	0.819
5	13.1	991.0	0.0602	0.250	3.19	0.938
6	14.8	1175.0	0.0680	0.242	3.04	0.906
7	16.9	1430.0	0.0776	0.232	3.05	0.873
8	21.6	2470.0	0.0989	0.211	2.38	0.675
9	22.4	2880.0	0.102	0.208	2.13	0.599
				Average	2.88	

67.5 cc sodium thiosulphate solution is equivalent to 0.310 units I_2.

Table XXX.

C, 1.88; D, 18.75; E, 0.290; V, 0.26

No.	Reading	θ	x	$E-x$	$k_1 \times 10^4$
1	0.0	0.0	0.000	0.290	—
2	0.9	2.5	0.006	0.284	—
3	2.35	18.7	0.0153	0.275	8.64
4	4.15	38.0	0.0269	0.263	9.38
5	6.55	66.8	0.0426	0.247	9.42
6	9.4	99.8	0.0611	0.229	9.61
7	11.6	131.0	0.0745	0.215	9.45
8	14.4	176.0	0.0936	0.196	9.31
9	15.9	197.0	0.1034	0.187	9.33

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

off more rapidly than the concentration of the iodion — at least, the "constant" k_5, calculated on the assumption that the rate is proportional to the concentrations of the iodion and of the arsenic acid, certainly diminishes as the reaction progresses.

In the case of the acid the effect of concentration on the order is even more marked. Comparing Tables XXIV., XXV., and XXVI.; XXI. and XXVII; and XXVIII. and XXIX., it is apparent that the order falls from well over the second, to almost the first, while the concentration of the acid decreases in the ratio 16 : 1. That this is not due to changes in the dissociation of the sulphuric acid, is evidenced by the fact that nothing analogous was found in the reaction between arsenious acid and triiodion; it may, however, be ascribed to a change in the dissociation of the arsenious acid as the concentration of the sulphuric acid is increased. The reactions would then take place according to the equation

$$H\overset{\prime\prime}{AsO_3} + IOH \rightleftarrows \overset{\prime\prime\prime}{AsO_4} + \overset{\prime}{I} + 2\overset{+}{H}.$$

This explanation does not necessarily assume that the ions of arsenious and arsenic acids which I have selected for use in the chemical equations are those "actually present and reacting," but only that when the concentration of the hydrogen ions is below a certain limit the ions of the arsenious and arsenic acids contain an equal number of hydrogen atoms, while above that limit hydrogen is taken up more rapidly by the arsenious ion than by the arsenic ion. This is in full accord with what we know of the relative strengths of the two acids; the polymeric formulas of the acids however receive no support from these results.

TABLE XXXI.

C, 0.941; D, 11.7; E, 1.16; V, 0.12

Temperature 10° C

No.	Reading	θ	x	$k_6 \times 10^7$
1	0.0	0.0	0.0	—
2	2.9	1.7	0.0316	—
3	6.2	4.2	0.0676	4.9
4	8.5	6.5	0.0926	8.8
5	13.3	11.5	0.145	5.9
6	17.7	16.7	0.193	8.0
7	20.5	22.0	0.224	6.8
8	22.3	27.5	0.243	6.0
9	25.9	33.5	0.282	6.2
10	30.6	40.3	0.334	6.6
11	34.8	48.5	0.377	6.5
12	36.5	56.0	0.398	6.3
			Average	6.8

1 cc sodium thiosulphate solution is equivalent to 0.0109 units $\overset{\prime}{I}_3$.

Table XXXII.

C, 0.842 ; D, 11.8 ; E, 1.16 ; V, 0.12

No.	Reading	θ	x	$k_6 \times 10^7$
1	0.0	0.0	0.0	—
2	2.85	8.5	0.0408	—
3	4.6	15.8	0.0658	1.5
4	6.3	23.0	0.0905	3.6
5	8.9	35.0	0.127	3.2
6	10.8	48.3	0.155	2.9
7	12.7	63.8	0.182	3.0
8	14.7	81.8	0.210	2.8
9	18.8	111.0	0.269	2.9
			Average	3.1

1 cc sodium thiosulphate solution is equivalent to 0.0143 units I_3.

Temperature coefficient

Comparing Tables XXXI. and XXXII., it appears that a rise of 10° C multiplies the rate by 2.2.

PART III.

EQUILIBRIUM

A priori considerations, and the results of some preliminary experiments made it seem probable that at equilibrium the relation[1]

$$K_8V^4 = \frac{(E+x)(D+x)^3(C+x)^2}{(A-x)(B-x)} \qquad \text{Eq. 8.}$$

would subsist between the concentrations of the reagents.

The change in the concentration of triiodion needed to balance given changes in the concentrations of each of the other con-

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[1] A, B, C, D, E, x, V have the meanings assigned on page 382. The signs + and — must be interchanged if the reaction leading to equilibrium involves the formation instead of the disappearance of triiodion.

stituents was determined quite sharply by keeping the quantity of that reagent in the mixture small, in comparison with those of the others; the concentrations of the latter being thus almost unaffected by reactions taking place in the solution.

The interpretation of the results was still further simplified by making up the mixtures according to a plan described under "Series E."

METHOD OF CARRYING OUT THE EXPERIMENTS°

As a criterion that the solutions had actually reached a state of equilibrium, it was obviously not sufficient to make sure that their compositions remained unaltered for a longer or shorter period of time; such evidence would not exclude cases of "false equilibrium." It was necessary therefore to make up solutions containing the same total weights of arsenic, potassium iodide, iodine, sulphuric acid, and water; in one of which the components were originally present as arsenious acid, triiodion, iodion and acid, and in the other as arsenic acid, iodion and acid.

To avoid loss of iodine by evaporation, the experiments were carried out in stoppered bottles. In each case two bottles were prepared, using the same volumes of the various stock solutions (page 370), but in one of them the order of mixing was: Sodium arsenite, sulphuric acid, iodide, iodine, and water to make up the volume; and in the other: Sodium arsenite, iodine, iodide, sulphuric acid, and water to make up the same volume.

So that in the first case the arsenious acid was slowly oxidized by the triiodion, and in the second the arsenic acid formed by the instantaneous reaction between sodium arsenite and triiodion was slowly reduced by the hydriodic acid.

Final analyses were carried out only when the quantity of triiodion was the same in the two mixtures within one percent; a period of less than twenty-four hours was quite sufficient for the purpose.

Direct titration of the triiodion in the solution by sodium thiosulphate was not feasible; as in the absence of triiodion the reaction between arsenic acid and hydriodic acid was rapid enough to affect the result. It was found, however, that by pouring into the solution to be analyzed a solution of thiosulphate in quantity sufficient to remove almost all the triiodion, mixed with water to slow the rate of reduction of the arsenic acid, the titration could be brought to a satisfactory conclusion. For the reasons given on page 371, excess of thiosulphate was avoided. If after the conclusion of the analysis at least one minute elapsed before reappearance of the blue color of iodide of starch, it was evident that the water had been added in sufficient quantity.

Two analyses were made of the solution in each bottle; and consequently four determinations of each equilibrium point.

RESULTS OF THE MEASUREMENTS

Series E

Having found by trial the proportions in which the stock solutions might be mixed so that only a very slight reaction was necessary to bring the system to equilibrium ("standard" mixture), I prepared a set of bottles[1] in which the concentration of the triiodion was twice that of the standard, while the concentration of the iodion was $\sqrt{2}$, $\sqrt[3]{2}$, and $\sqrt[4]{2}$ times the standard respectively. In the first, the amount of triiodion increased, and in the third decreased, while in the second it remained stationary. From this it is obvious without further calculation that the third power of the concentration of the iodion must appear in the equilibrium constant.

The same method was employed with the other reagents and with the volume; finally the value of K_6 (Eq. 8) was calculated from each experiment.

A glance at Table XXXIII. shows that the requirements of Equation 8 are satisfied. The greatest deviation is in the case of the iodion, for which the third power of the concentration seems, if anything, a trifle high. This is in line with the observation made in discussing Series A (page 373), that multiplying the

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[1] Nos. 4, 5, and 6 of Table XXXIII. No. 1 is standard.

concentration of the iodion by four divided k_1 by fourteen instead of by sixteen.

TABLE XXXIII.[1]

No.	$A-x$	$B-x$	$C+x$	$D+x$	$E+x$	V	$K_6 \times 10^{-4}$
1	0.01857	0.3424	0.5689	1.140	0.4016	0.1	15.1
2	0 03607	0.3432	0.5750	1.612	0.4008	0.1	16.1
3	0.03098	0.3381	0.5801	1 446	0.4059	0.1	15 8
4	0.04792	0.3260	0.7958	1.127	0.3890	0.1	14.2
5	0.0381	0.3452	0.7198	1.137	0.3988	0.1	14.6
6	0.03346	0.3411	0.6856	1.141	0.4029	0.1	14.8
7	0.03941	0.3465	0.5717	1.136	0.801	0.1	14.1
8	0.03509	0.1720	0.5760	1.138	0.4018	0.1	16 5
9	0.01635	0.1699	0.5712	1.139	0.4039	0.1189	17.7
10	0.0198	0.1734	0.5677	1.136	0.4004	0.1149	16.1
11	0.0212	0.1748	0.5663	1.135	0.3990	0.1123	15.8
12	0.01903	0.3428	0.5685	1.139	0.4012	0.1	14.6
13[2]	0.01113	0.3349	0 5652	1.147	0.4091	0.1	26.1
14	0.01787	0.3412	0.5596	1.130	0.4023	0.1	14.8
15	0.01646	0.1701	0.5678	1.135	0.4037	0.1189	17.0
16	0.01354	0.1698	0.5644	1.132	0.4003	0.1260	15.9

TABLE XXXIV.

No.	A	$A-x$	$B-x$	$C+x$	$D+x$	$E+x$	V
1	0.0384	0.0384	0.4836	0.1991	10.80	0.0985	0.1
2	0.0768	0.0909	0.5036	0.1801	14.49	0 0785	0.1
3	0.0768	0.0844	0.4971	0.1866	13.72	0.0850	0.1

Series F

On finding that the effect which doubling the concentration of the sulphuric acid produced on the rate of reduction of arsenic

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[1] No. 1 is the standard. In Nos. 9 to 16, A was the same as in No. 1; in Nos. 2 to 8, A was twice as great as in No. 1.

[2] Temperature 20° C. All other experiments of Part III, temp. 0°C.

acid was dependent on the concentration of the sulphuric acid (Series D), I undertook the experiments of Table XXXIV. in order to determine whether the conditions of equilibrium were affected by the same circumstance. The measurements show clearly that when the acid is present in large quantity, the third or a higher power of its concentration and not the second power must be introduced into the equation of equilibrium.

Temperature coefficient

Experiments Nos. 12 and 13 of Table XXXIII. were carried out with different portions of the same solutions, No. 13 at 20° C, and No. 12 (like all the others of the table) at 0° C. A rise of 20° C thus almost doubles the constant. From the experiments of Parts I. and II. a rise of 10° multiplies the quotient k_3/k_5 by 1.6, which is not far from 1.4, the square root of 2.

Relation between k_3, k_5, and K_6

According to the theory explained in the Introduction, the constants of the two rates and that of equilibrium should be connected by the relation

$$K_6 = \frac{k_3}{k_6}.$$

Introducing the values $k_3 = 0.28$ (Table XVII.), and $k_5 = 3.26 \times 10^{-7}$ (Table XXVIII.) gives 8.6×10^5 as the "calculated" value of K_6; while direct experiment (Table XXXIII.) gives $K_6 = 1.5 \times 10^5$. The two numbers are thus of the same order of magnitude.

In selecting k_5 I was forced to use the data of Table XXXIII., as it is only when the concentration of the acid is low that the rate obeys the law of paragraph iii of the introduction. The large amount of salt present in this experiment (three molecules of potassium iodide to one of sulphuric acid) was introduced in order to make the rate quick enough to measure. Perhaps the considerable numerical discrepancy between k_3/k_5 and K_6 is due in part to this circumstance.

CONCLUSION

The results of my experiments can only be regarded as a very striking confirmation of the Theory of Kinetic Equilibrium.

In Part I. it is shown that the reaction between arsenious acid and iodine in acid solution proceeds according to the scheme[1]

$$dx/d\theta = k.a.b/.x.y.^2z$$

The "order" of the rate of the reverse reaction, however (Part II.), depends on the concentrations of the reagents; in comparatively dilute solutions it is of the third order,

$$-dx/d\theta = k'..x.y.z,$$

but if the concentration of the iodide or of the acid be increased, higher powers of y and z must be introduced into the equation.

Finally, in Part III. it is shown that the condition of equilibrium of Eq. 4

$$K = \frac{a.b}{x.y^3.z^2}$$

holds only for the dilute solutions, where the reverse reaction is of the third order,[2] and that in the case of solutions containing a greater proportion of acid a higher power of z must be introduced.

Thus for dilute solutions my experiments on the rates of the two reactions and on the equilibrium between them are in full accord with the theory developed in paragraph iii of the Introduction. For solutions containing larger quantities of acid, the expression for the rate of oxidation of arsenious acid remains the same, while the change in the form of the equilibrium function is parallel to that in the expression for the rate of reduction of arsenic acid; on page 391 I have suggested a plausible explanation of the changes in question.

The quotient of the two rate constants is of the same order of magnitude as the equilibrium constant (page 396); and the few experiments carried out at higher temperatures show that the temperature coefficient of the equilibrium constant accords, both

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[1] Using the symbols of page 367.

[2] In the experiments of Table XX. it is of the fifth order.

in sign and in magnitude, with the quotient of the temperature coefficients of the two rates (page 396). Owing to the conditions under which the measurements were carried out, a closer agreement could hardly be expected.

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

University of Toronto,
July, 1902.

TABLE OF CONTENTS

ON THE TRIPLE POINT

BY PAUL SAUREL

Bakhuis Roozeboom has recently given[1] a complete classification of the various possible kinds of triple point. Although there is nothing to be added to his results, it may be of interest to indicate two other methods of obtaining them. One of these methods is due to Gibbs, but up to the present it does not seem to have received the attention it deserves.

The fundamental equations of the triple point are well known. They are

$$(v_2 - v_3)\frac{d\Pi_1}{dT_1} + (v_3 - v_1)\frac{d\Pi_2}{dT_2} + (v_1 - v_2)\frac{d\Pi_3}{dT_3} = 0, \qquad (1)$$

$$(\eta_2 - \eta_3)\frac{dT_1}{d\Pi_1} + (\eta_3 - \eta_1)\frac{dT_2}{d\Pi_2} + (\eta_1 - \eta_2)\frac{dT_3}{d\Pi_3} = 0. \qquad (2)$$

In these equations η_i, v_i denote the entropy and the volume of the unit of mass of the i-th phase, and $d\Pi_i/dT_i$ denotes the slope of the pressure-temperature curve of the i-th univariant system, that is to say, of the system which is formed by suppressing the i-th phase of the invariant system.

Let us suppose that the phases are so numbered that

$$v_1 > v_2 > v_3, \qquad (3)$$

and let us write equation 1 in the form

$$\frac{d\Pi_2}{dT_2} = \frac{(v_2 - v_3)\frac{d\Pi_1}{dT_1} + (v_1 - v_2)\frac{d\Pi_3}{dT_3}}{v_1 - v_3}. \qquad (4)$$

If we observe that, in virtue of 3, the coefficients $(v_2 - v_3)$, $(v_1 - v_2)$ are positive, and also that

$$v_1 - v_3 = (v_2 - v_3) + (v_1 - v_2),$$

it follows from 4, by a well-known theorem in algebra, that

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[1] Die heterogenen Gleichgewichte, 1, 189 (1901).

$d\Pi_2/dT_2$ is intermediate in value between $d\Pi_1/dT_1$ and $d\Pi_3/dT_3$. We thus obtain the following theorem of Duhem :[1]

THEOREM I. — *At a temperature slightly higher or slightly lower than that of the triple point, the univariant curve which corresponds to the transformation that is accompanied by the greatest change in volume lies between the other two curves.*

In like manner, let us imagine for a moment that the phases are so numbered that

$$\eta_1 > \eta_2 > \eta_3, \tag{5}$$

and let us write equation 2 in the form

$$\frac{dT_2}{d\Pi_2} = \frac{(\eta_2 - \eta_3)\frac{dT_1}{d\Pi_1} + (\eta_1 - \eta_2)\frac{dT_3}{d\Pi_3}}{\eta_1 - \eta_3}. \tag{6}$$

From this equation we obtain at once the following theorem of Roozeboom :[2]

THEOREM II. — *Under a pressure slightly greater or slightly less than that of the triple point, the univariant curve which corresponds to the transformation that is accompanied by the greatest change in entropy lies between the other two curves.*

The univariant system can be grouped into two classes. The systems of one class can exist in stable equilibrium only at temperatures higher than that of the triple point; the systems of the other class can exist in stable equilibrium only at temperatures lower than that of the triple point. We have shown[3] that the coefficients $(v_2 - v_3)$, $(v_3 - v_1)$, $(v_1 - v_2)$ in equation 1 enable us to form these two classes without, however, enabling us to say which class corresponds to the higher temperatures and which to the lower. The univariant systems which correspond to positive coefficients form one class while the univariant systems which correspond to negative coefficients form the other. If we suppose that the phases are so numbered that

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[1] Zeit. phys. Chem. 8, 367 (1891). Traité élémentaire de Mécanique chimique, 2, 98.

[2] Die heterogenen Gleichgewichte, 1, 98 (1901).

[3] Jour. Phys. Chem. 6, 257 (1902).

conditions 3 are satisfied, then the univariant systems 1 and 3 form one class while the univariant system 2 forms the other. We may accordingly state the following theorem :[1]

THEOREM III. — *The univariant system which corresponds to the transformation that involves the greatest change in volume is in stable equilibrium at temperatures which lie on one side of the triple point while the two other univariant systems are in stable equilibrium at temperatures which lie on the other side of the triple point.*

We can also group the univariant systems into two classes by putting into one class the systems which can exist in stable equilibrium only under pressures greater than that of the triple point and into the other class the systems which can exist in stable equilibrium only under pressures less than that of the triple point. We have shown[2] that the coefficients $(\eta_2 - \eta_3)$, $(\eta_3 - \eta_1)$, $(\eta_1 - \eta_2)$ in equation 2 enable us to form these two classes. The systems corresponding to positive coefficients form one class, while the systems corresponding to negative coefficients form the other. If we suppose that the phases are so numbered that conditions 5 are satisfied, then the univariant systems 1 and 3 form one class while the univariant system 2 forms the other. We may accordingly state the following theorem :[3]

THEOREM IV. — *The univariant system which corresponds to the transformation that involves the greatest change in entropy is in stable equilibrium under pressures which lie on one side of the triple point while the two other univariant systems are in stable equilibrium under pressures which lie on the other side of the triple point.*

By combining theorems I. and III. or theorems II. and IV. we get at once the following theorem of Gibbs :[4]

THEOREM V. — *If we describe a small closed curve about*

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[1] Duhem. Zeit. phys. Chem. 8, 379 (1891). Traité élémentaire de Mécanique chimique, 2, 123.

[2] Jour. Phys. Chem. 6, 257 (1902).

[3] Roozeboom. Die heterogenen Gleichgewichte, 1, 98 (1901).

[4] "On the Equilibrium of Heterogeneous Substances," p. 174.

the triple point, this curve alternately cuts stable and unstable branches of the three univariant curves.

Roozeboom has shown[1] that the five theorems which we have just given suffice, when taken in connection with the well-known equations

$$\frac{d\Pi_1}{dT_1} = \frac{\eta_2 - \eta_3}{v_2 - v_3}, \quad \frac{d\Pi_2}{dT_2} = \frac{\eta_3 - \eta_1}{v_3 - v_1}, \quad \frac{d\Pi_3}{dT_3} = \frac{\eta_1 - \eta_2}{v_1 - v_2}, \qquad (7)$$

to completely classify the various types of triple point that can occur.

The classification of the various types of triple point can be obtained in a slightly different way. In the first place, if we take a pair of v, η axes respectively parallel to the T, Π axes and if, in the $v\,\eta$ plane, we construct the triangle whose vertices are the points (v_i, η_i), it follows at once from equations 7 that the sides of this triangle are parallel to the tangents to the three univariant curves at the triple point.

Moreover, we have shown previously[2] that if each term of equation 1 be divided by the determinant

$$\begin{vmatrix} v_1, & \eta_1, & 1 \\ v_2, & \eta_2, & 1 \\ v_3, & \eta_3, & 1 \end{vmatrix}, \qquad (8)$$

the sign of the coefficient of $d\Pi_i/dT_i$ enables us to tell on which side of the triple point the corresponding univariant system is stable. If the coefficient $d\Pi_i/dT_i$ is positive the i-th univariant system is stable at temperatures higher than that of the triple point, while if this coefficient is negative the corresponding system is stable at temperatures lower than that of the triple point.

The determinant 8 is positive or negative according as the arrangement of the vertices 1, 2, 3 of the triangle is counter-clockwise or clockwise. If the phases are so numbered that conditions 3 are satisfied, it follows that when the determinant is positive the sides 12 and 23 lie above the side 13, and when the

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[1] Die heterogenen Gleichgewichte, 1, 189 (1901).

[2] Jour. Phys. Chem. 6, 261 (1902).

determinant is negative the sides 12 and 23 lie below the side 13. We thus have the following theorem:

THEOREM VI. — *If a pair of v, η axes be drawn parallel respectively to the* T, Π *axes and if the three points* (v_i, η_i) *be constructed, we can obtain the directions of the stable portions of the univariant curves by drawing, through the triple point, lines parallel to the sides of the triangle. If the side corresponding to the greatest change in volume lies below the other two, the corresponding curve extends in the direction of lower temperatures while the other two extend in the direction of higher temperatures. If, on the other hand, the side corresponding to the greatest change in volume lies above the other two, the corresponding curve extends in the direction of higher temperatures while the other two curves extend in the direction of lower temperatures.*

We can get an analogous theorem by making use of the fact[1] that if each term of equation 2 be divided by the determinant

$$\begin{vmatrix} \eta_1, & v_1, & 1 \\ \eta_2, & v_2, & 1 \\ \eta_3, & v_3, & 1 \end{vmatrix}, \qquad (9)$$

the sign of the coefficient of $dT_i/d\Pi_i$ enables us to tell on which side of the triple point the corresponding univariant system is stable. If the coefficient of $dT_i/d\Pi_i$ is positive the i-th univariant system is stable under pressures lower than that of the triple point, while if this coefficient is negative the corresponding system is stable under pressures higher than that of the triple point. From this we obtain without difficulty the following theorem:

THEOREM VII. — *If the side of the triangle which corresponds to the greatest change in entropy lies to the right of the other two sides, the corresponding univariant curve extends in the direction of lower pressures. If, on the other hand, this side lies to the left of the other two, the corresponding curve extends in the direction of higher pressures.*

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[1] Jour. Phys. Chem. 6, 261 (1902).

If we turn the $v\eta$ plane through a right angle so that the η axis becomes parallel to the T axis, and the v axis parallel to the negative direction of the Π axis, we can restate theorems VI. and VII. as follows:

THEOREM VIII. — *If the $v\eta$ plane is so placed that the η axis is parallel to the* T *axis and the v axis parallel to the negative direction of the* Π *axis and if, from a point within the triangle whose vertices are (v_i, η_i) we drop perpendiculars to the three sides of the triangle, these three lines are respectively parallel to the directions at the triple point of the stable portions of the three univariant curves.*

This theorem is due to Tammann,[1] who has stated it without adequate demonstration.

By means of the last theorem we can at once enumerate the various types of triple point. The results are given in the accompanying diagram (Fig. 1). The eight figures correspond respectively to the following eight sets of conditions:

$$\eta_1 > \eta_2 > \eta_3.$$

$\begin{vmatrix} \eta_1, & v_1, & 1 \\ \eta_2, & v_2, & 1 \\ \eta_3, & v_3, & 1 \end{vmatrix} < 0.$	$\begin{vmatrix} \eta_1, & v_1, & 1 \\ \eta_2, & v_2, & 1 \\ \eta_3, & v_3, & 1 \end{vmatrix} > 0.$
(1) $v_1 > v_2 > v_3$;	(5) $v_1 > v_2 > v_3$; (10)
(2) $v_1 > v_3 > v_2$;	(6) $v_2 > v_1 > v_3$;
(3) $v_3 > v_1 > v_2$;	(7) $v_2 > v_3 > v_1$;
(4) $v_3 > v_2 > v_1$;	(8) $v_3 > v_2 > v_1$.

It now remains to show that the above classification can be very easily obtained by carrying out in detail a course of reasoning outlined by Gibbs.[2]

Consider a system consisting of three phases formed by means of a single component. If we denote by Φ_i the total thermodynamic potential of the unit of mass of the i-th phase, the well-known conditions of equilibrium of the invariant system are

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[1] Drude's Ann. 6, 65 (1901).

[2] "On the Equilibrium of Heterogeneous Substances," p. 174.

$$\Phi_1 = \Phi_2 = \Phi_3. \tag{11}$$

For the three univariant systems that can be obtained by taking the phases in pairs the well-known conditions of equilibrium are

$$\begin{aligned} \Phi_2 &= \Phi_3, \\ \Phi_3 &= \Phi_1, \\ \Phi_1 &= \Phi_2. \end{aligned} \tag{12}$$

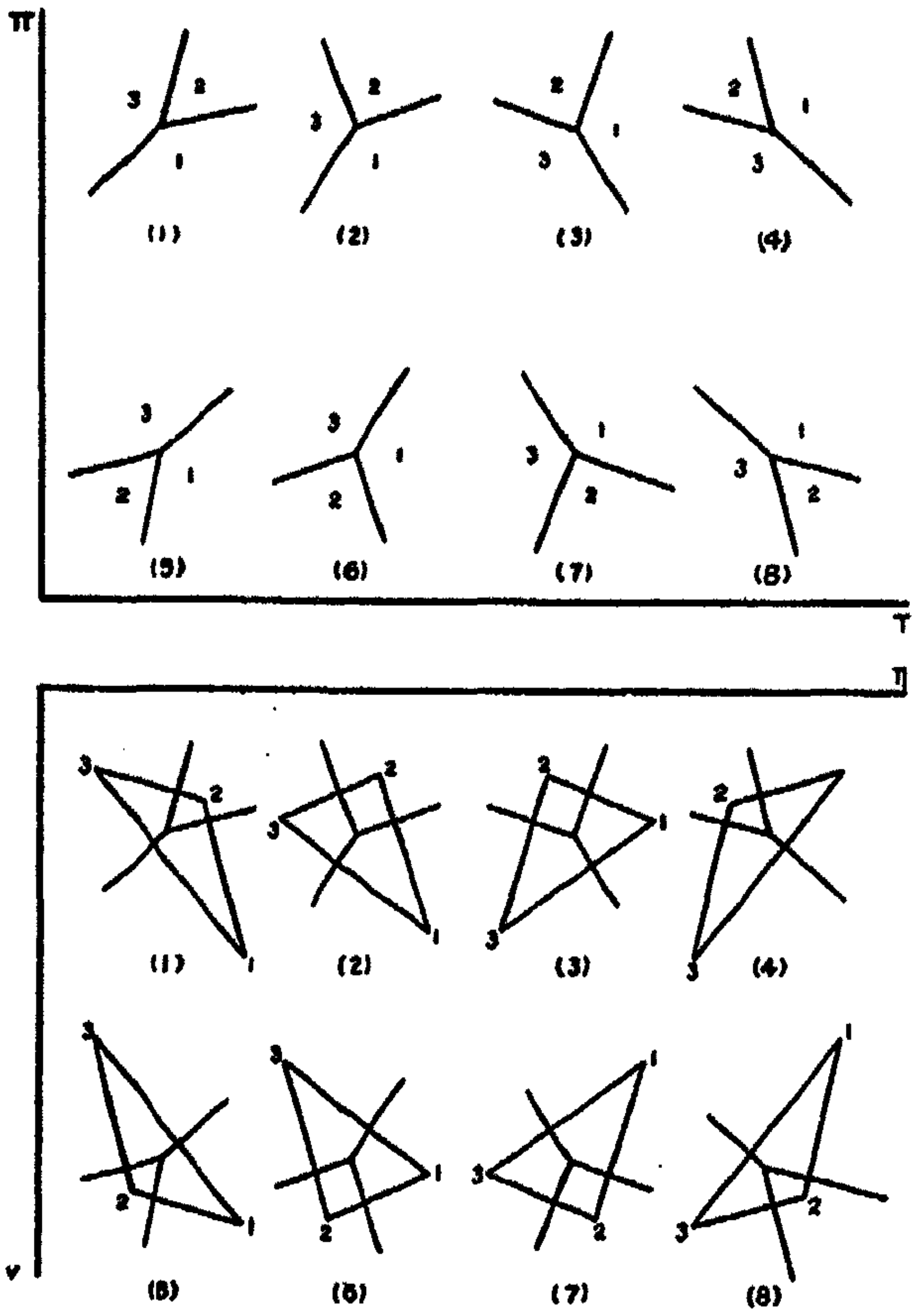

Fig. 1

Let us take in space a system of rectangular axes along which we shall measure the temperature T, the pressure Π, and the thermodynamic potential Φ. At a given temperature T and under a given pressure Π we shall have three values Φ_1, Φ_2, Φ_3 for the thermodynamic potential, corresponding to the three phases. We thus obtain three surfaces or rather three sheets of the same surface.

The three sheets of our potential surface taken in pairs intersect in three lines which, by equations 12, represent the states of equilibrium of the three univariant systems; and the point in which these three lines intersect represents the state of equilibrium of the invariant system. The projections, upon the temperature-pressure plane, of these lines and this point are respectively the pressure-temperature curves of the univariant systems and the triple point of the invariant system.

At a given temperature and under a given pressure the most stable state of equilibrium of a system is that for which the thermodynamic potential has the smallest value. Accordingly, at a given temperature and under a given pressure, the lowest of the three sheets in our diagram will represent the most stable state of equilibrium of our one-component system.

The three univariant curves divide the space about the triple point into six regions. By considering a small closed curve surrounding the triple point we shall be able to determine, in each of the six regions, which sheet of our thermodynamic surface is the lowest and consequently which phase is the stable phase. For this purpose we shall need the equation which connects the change in the thermodynamic potential with the changes of temperature and pressure, viz:

$$d\Phi_i = -\eta_i dT + v_i d\Pi. \tag{13}$$

Through the triple point M (Fig. 2) draw two lines MT′, MΠ′ parallel respectively to the positive directions of the temperature and pressure axes. If we move from the triple point a short distance along the line MT′ to a point M_1, we shall have, from equation 13, for the corresponding changes in the thermodynamic potential

$$\begin{aligned} d\Phi_1 &= -\eta_1 dT, \\ d\Phi_2 &= -\eta_2 dT, \\ d\Phi_3 &= -\eta_3 dT. \end{aligned} \tag{14}$$

The relative positions of the three sheets above the point M_1 depend upon the relative values of η_1, η_2, η_3. Thus, for example, if

$$\eta_1 > \eta_2 > \eta_3,$$

we shall have

$$d\Phi_1 < d\Phi_2 < d\Phi_3,$$

and the three sheets, beginning with the lowest, are arranged in the order 1, 2, 3. At the temperature and under the pressure corresponding to the point M_1, the phase 1 is the stable phase.

In like manner, if we move from the triple point a short distance along the line $M\Pi'$ to a point M_2, we shall have, from equation 13, for the corresponding changes in the thermodynamic potential

$$\begin{aligned} d\Phi_1 &= v_1 d\Pi, \\ d\Phi_2 &= v_2 d\Pi, \\ d\Phi_3 &= v_3 d\Pi. \end{aligned} \tag{15}$$

The relative positions of the three sheets above the point M_2 depend upon the relative values of v_1, v_2, v_3. Thus, for example, if

$$v_1 > v_2 > v_3,$$

we shall have

$$d\Phi_1 > d\Phi_2 > d\Phi_3,$$

and the three sheets, beginning with the lowest, are arranged in the order 3, 2, 1. At the temperature and under the pressure corresponding to the point M_2, the phase 3 is the stable phase.

In our discussion there are the following four cases to be considered corresponding to four different arrangements of the univariant curves at the triple point:

Case I. The three slopes $d\Pi_i/dT_i$ are positive ;

Case II. Two of the slopes are positive and one negative ;

Case III. One of the slopes is positive and two negative ;

Case IV. The three slopes are negative.

Throughout the discussion we shall suppose that the phases are so numbered that

$$\eta_1 > \eta_2 > \eta_3. \tag{16}$$

Let us suppose that, at the triple point, the slopes of the three univariant curves are positive. Thus

$$\frac{d\Pi_1}{dT_1} > 0, \qquad \frac{d\Pi_2}{dT_2} > 0, \qquad \frac{d\Pi_3}{dT_3} > 0. \tag{17}$$

Conditions 7, 16 and 17 yield at once

$$v_1 > v_2 > v_3. \tag{18}$$

From 14 and 16 we find that, above the point M_1 (Fig. 2), the sheets beginning with the lowest, are arranged in the order 1, 2, 3. It follows that, as we move along the closed circuit from M_1 towards M_2, the first univariant curve encountered is either the curve that corresponds to the intersection of the sheets 1, 2 or the curve that corresponds to the intersection of the sheets 2, 3. In like manner, from 15 and 18 we find that, above the point M_2, the sheets, beginning with the lowest, are arranged in the order 3, 2, 1. It follows that, as we move along the circuit from M_2 towards M_1, the first univariant curve encountered is either the curve that corresponds to the intersection of the sheets 3, 2 or the curve that corresponds to the intersection of the sheets 2, 1. There are thus two sub-cases to be considered corresponding respectively to Figs. 2 and 3.

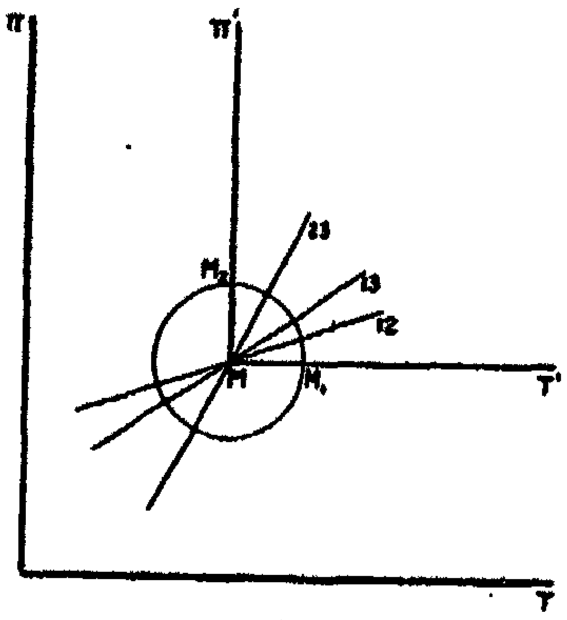

Fig. 2

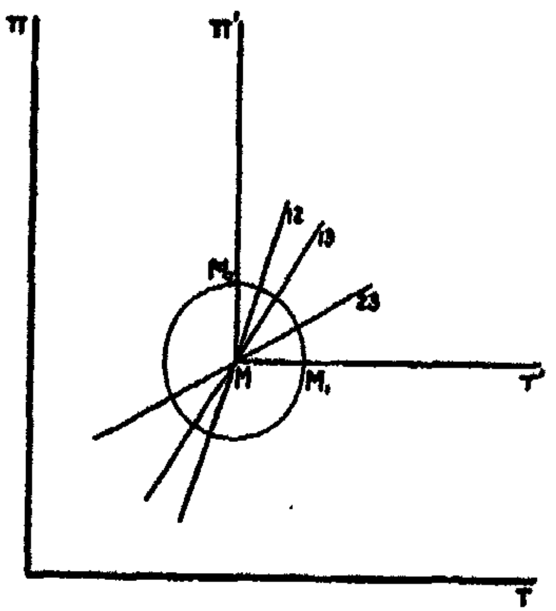

Fig. 3

If, in the first of these cases, we describe, from M_1, a small circuit counter-clockwise about M, we shall find that the relative positions of the three sheets in each of the six regions of the plane are given by the following table:

3	3	1	1	2	2
2	1	3	2	1	3
1	2	2	3	3	1

In this table the numbers in the same vertical column refer to the same region and indicate by their relative positions the relative positions of the corresponding sheets. If we erase the portions of the univariant curves which correspond to unstable states of equilibrium we obtain the first of the eight diagrams given in *Fig. 1*.

If, in Fig. 3, we describe a small circuit counter-clockwise about M, we shall find that the relative positions of the three sheets are given by the table:

3	2	2	1	1	3
2	3	1	2	3	1
1	1	3	3	2	2

If we erase the portions of the univariant curves which correspond to unstable states of equilibrium we obtain the fifth diagram in Fig. 1.

An analogous discussion of the remaining cases yields the remaining diagrams in Fig. 1. Case II. corresponds to the diagrams 2 and 6, Case III. to 3 and 7, and Case IV. to 4 and 8.

The method yields not only the stable portions of the univariant curves, but also the regions of the plane in which the different phases are stable. The numbers in Fig. 1 have been placed so as to indicate these regions.

New York, May 15, 1902.

ON A THEOREM OF TAMMANN

BY PAUL SAUREL

We have recently given[1] a demonstration of the following theorem of Tammann[2] relative to the triple point of a one-component system: Construct in the volume-entropy plane a triangle whose vertices have for coordinates the specific volume and specific entropy of each of the three phases of an invariant one-component system, and from a point within the triangle drop perpendiculars to the three sides. If the temperature-pressure plane be so placed that the temperature axis is parallel to the entropy axis and the pressure axis parallel to the negative direction of the volume axis, then the perpendiculars just drawn are respectively parallel to the directions at the triple point of the stable portions of the three univariant curves.

The object of the present note is to show that this theorem can be extended to the multiple point of an n-component system.

Consider a two-component system and denote by η_i, v_i the entropy and the volume of the unit of mass of the i-th phase and by m_{ij} the mass of the j-th component which is present in the unit of mass of the i-th phase. At the quadruple point four phases can exist in equilibrium; along each of the four univariant curves that meet in the quadruple point three phases can coexist. If we denote by $d\Pi_i/dT_i$ the slope of the pressure-temperature curve of the i-th univariant system, that is to say of the system which is formed by suppressing the i-th phase of the invariant system, we have the following relations:[3]

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[1] Jour. Phys. Chem. 6, 399 (1902).

[2] Drude's Ann. 6, 65 (1901).

[3] Gibbs. "On the Equilibrium of Heterogeneous Substances," p. 154. Cf. Jour. Phys. Chem. 5, 50 (1901).

$$\frac{d\Pi_1}{dT_1} = \frac{\begin{vmatrix} \eta_2, & m_{21}, & m_{22} \\ \eta_3, & m_{31}, & m_{32} \\ \eta_4, & m_{41}, & m_{42} \end{vmatrix}}{\begin{vmatrix} v_2, & m_{21}, & m_{22} \\ v_3, & m_{31}, & m_{32} \\ v_4, & m_{41}, & m_{42} \end{vmatrix}}, \qquad \frac{d\Pi_2}{dT_2} = \frac{\begin{vmatrix} \eta_3, & m_{31}, & m_{32} \\ \eta_4, & m_{41}, & m_{42} \\ \eta_1, & m_{11}, & m_{12} \end{vmatrix}}{\begin{vmatrix} v_3, & m_{31}, & m_{32} \\ v_4, & m_{41}, & m_{42} \\ v_1, & m_{11}, & m_{12} \end{vmatrix}},$$

$$\frac{d\Pi_3}{dT_3} = \frac{\begin{vmatrix} \eta_4, & m_{41}, & m_{42} \\ \eta_1, & m_{11}, & m_{12} \\ \eta_2, & m_{21}, & m_{22} \end{vmatrix}}{\begin{vmatrix} v_4, & m_{41}, & m_{42} \\ v_1, & m_{11}, & m_{12} \\ v_2, & m_{21}, & m_{22} \end{vmatrix}}, \qquad \frac{d\Pi_4}{dT_4} = \frac{\begin{vmatrix} \eta_1, & m_{11}, & m_{12} \\ \eta_2, & m_{21}, & m_{22} \\ \eta_3, & m_{31}, & m_{32} \end{vmatrix}}{\begin{vmatrix} v_1, & m_{11}, & m_{12} \\ v_2, & m_{21}, & m_{22} \\ v_3, & m_{31}, & m_{32} \end{vmatrix}}. \qquad (1)$$

At the quadruple point the slopes of the four univariant curves are connected by the so-called fundamental equations of the point,[1] viz:

$$\begin{vmatrix} \frac{d\Pi_1}{dT_1}, & v_1, & m_{11}, & m_{12} \\ \frac{d\Pi_2}{dT_2}, & v_2, & m_{21}, & m_{22} \\ \frac{d\Pi_3}{dT_3}, & v_3, & m_{31}, & m_{32} \\ \frac{d\Pi_4}{dT_4}, & v_4, & m_{41}, & m_{42} \end{vmatrix} = 0, \qquad \begin{vmatrix} \frac{dT_1}{d\Pi_1}, & \eta_1, & m_{11}, & m_{12} \\ \frac{dT_2}{d\Pi_2}, & \eta_2, & m_{21}, & m_{22} \\ \frac{dT_3}{d\Pi_3}, & \eta_3, & m_{31}, & m_{32} \\ \frac{dT_4}{d\Pi_4}, & \eta_4, & m_{41}, & m_{42} \end{vmatrix} = 0. \qquad (2)$$

It should be observed that since

$$m_{i1} + m_{i2} = 1$$

the letters in the last column of each of the determinants in equations 1 and 2 can be replaced by unity.

Let us take in space a system of rectangular axes along which we shall measure the specific volumes v_i, the specific entropies η_i and the concentrations m_{i1}. If we construct the points which correspond to the four phases that coexist at the

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[1] Riecke. Göttinger Nachrichten, p. 223 (1890). Zeit. phys. Chem. 6, 268 (1890). Cf. Jour. Phys. Chem. 5, 170 (1901).

quadruple point we shall obtain a tetrahedron. From a point within the tetrahedron drop perpendiculars to the four faces. Let us take also a pair of temperature-pressure axes parallel respectively to the entropy axis and to the negative direction of the volume axis. Then it can be shown that if we project upon the $v\ \eta$ plane the four perpendiculars which we have just drawn, the projections will be respectively parallel to the tangents to the four univariant curves at the quadruple point.

For this purpose consider the plane passing through the points 2, 3, 4. The equation of this plane is

$$\begin{vmatrix} v, & \eta, & m, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \end{vmatrix} = 0, \tag{3}$$

and the direction cosines of the perpendicular to this plane are proportional to the coefficients of v, η and m in this equation. Thus the cosines of the angles which the perpendicular makes with the v and η axes are respectively proportional to

$$\begin{vmatrix} \eta_2, & m_{21}, & 1 \\ \eta_3, & m_{31}, & 1 \\ \eta_4, & m_{41}, & 1 \end{vmatrix}, \qquad - \begin{vmatrix} v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \end{vmatrix}, \tag{4}$$

and consequently the cosines of the angles which the projection of this line upon the $v\ \eta$ plane makes with the same axes are also proportional to these determinants. From this it follows that the cosines of the angles which this projection makes with the pressure and temperature axes are proportional to

$$- \begin{vmatrix} \eta_2, & m_{21}, & 1 \\ \eta_3, & m_{31}, & 1 \\ \eta_4, & m_{41}, & 1 \end{vmatrix}, \qquad - \begin{vmatrix} v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \end{vmatrix}. \tag{5}$$

Accordingly the slope of this line with reference to the T axis is the ratio of these two determinants; and the first of equations 1 shows at once that this ratio is equal to the slope of the first univariant curve at the quadruple point.

In like manner we can show that the projection upon the $v\,\eta$ plane of each of the remaining perpendiculars is parallel to the tangent at the quadruple point to one of the remaining univariant curves.

But we can go further; we can show that the direction of each projected perpendicular indicates the direction of the stable portion of the corresponding univariant curve.

For this purpose consider again the plane passing through the points 2, 3, 4. The perpendicular to this plane from a point within the tetrahedron has the same direction as the perpendicular to this plane drawn from the point 1; and the perpendicular from the point 1 extends in the direction of smaller or of larger entropies according as the point 1 and the point at infinity on the positive end of the η axis lie on the same or on opposite sides of the plane 2 3 4. It is well known that if we substitute for v, η, m in the determinant of equation 3 the coordinates of various points, the result is positive for all the points that lie on one side of the plane and negative for all points that lie on the other side. Therefore the point 1 and the point at infinity on the η axis lie on the same or on opposite sides of the plane 2 3 4, according as the fraction

$$\frac{\begin{vmatrix} 0, & \eta, & 0, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \end{vmatrix}}{\begin{vmatrix} v_1, & \eta_1, & m_{11}, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \end{vmatrix}}$$

is positive or negative. If we remember that η is positive and very large in comparison with unity, we may say that the point at infinity on the positive end of the η axis and the point 1 lie on the same or on opposite sides of the plane 2 3 4 according as the fraction

$$-\frac{\begin{vmatrix} v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \end{vmatrix}}{\begin{vmatrix} v_1, & \eta_1, & m_{11}, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \end{vmatrix}}$$

is positive or negative. Thus the perpendicular from a point within the tetrahedron to the plane 2 3 4 extends in the direction of smaller values of η or in the direction of larger values of η according as

$$\frac{\begin{vmatrix} v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \end{vmatrix}}{\begin{vmatrix} v_1, & \eta_1, & m_{11}, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \end{vmatrix}} \qquad (6)$$

is negative or positive.

In like manner it can be shown that each of the remaining perpendiculars extends in the direction of smaller or of larger values of η according as the fraction

$$\frac{\begin{vmatrix} v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \\ v_1, & m_{11}, & 1 \end{vmatrix}}{\begin{vmatrix} v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \\ v_1, & \eta_1, & m_{11}, & 1 \end{vmatrix}}, \quad \frac{\begin{vmatrix} v_4, & m_{41}, & 1 \\ v_1, & m_{11}, & 1 \\ v_2, & m_{21}, & 1 \end{vmatrix}}{\begin{vmatrix} v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \\ v_1, & \eta_1, & m_{11}, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \end{vmatrix}} \text{ or } \frac{\begin{vmatrix} v_1, & m_{11}, & 1 \\ v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \end{vmatrix}}{\begin{vmatrix} v_4, & \eta_4, & m_{41}, & 1 \\ v_1, & \eta_1, & m_{11}, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \end{vmatrix}} \quad (7)$$

which corresponds to it is negative or positive.

On the other hand, we have shown[1] that if each term of the first of equations 2 be divided by the determinant

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[1] Jour. Phys. Chem. 6, 261 (1902).

$$\begin{vmatrix} v_1, & \eta_1, & m_{11}, & 1 \\ v_2, & \eta_2, & m_{21}, & 1 \\ v_3, & \eta_3, & m_{31}, & 1 \\ v_4, & \eta_4, & m_{41}, & 1 \end{vmatrix}, \qquad (8)$$

the coefficient of $d\Pi_i/dT_i$ in the result enables us to tell the direction at the quadruple point of the stable portion of the *i*-th univariant curve. The *i*-th univariant curve extends in the direction of lower or of higher temperatures according as the coefficient of $d\Pi_i/dT_i$ is negative or positive. The first of equations 2 when expanded becomes

$$\begin{vmatrix} v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \end{vmatrix} \frac{d\Pi_1}{dT_1} - \begin{vmatrix} v_3, & m_{31}, & 1 \\ v_4, & m_{41}, & 1 \\ v_1, & m_{11}, & 1 \end{vmatrix} \frac{d\Pi_2}{dT_2} + \begin{vmatrix} v_4, & m_{41}, & 1 \\ v_1, & m_{11}, & 1 \\ v_2, & m_{21}, & 1 \end{vmatrix} \frac{d\Pi_3}{dT_3} - \begin{vmatrix} v_1, & m_{11}, & 1 \\ v_2, & m_{21}, & 1 \\ v_3, & m_{31}, & 1 \end{vmatrix} \frac{d\Pi_4}{dT_4} = 0, \qquad (9)$$

and it is easy to see that after dividing by the determinant 8 the coefficients of the different terms are respectively equal to the fractions 6 and 7.

If we remember that the temperature axis has been taken parallel to the entropy axis, it follows immediately that the projections upon the $v\,\eta$ plane of the perpendiculars drawn from a point within the tetrahedron to its faces are respectively parallel to the directions at the quadruple point of the stable portions of the four univariant curves.

The demonstration which we have just given applies without change not only to the triple point of a one-component system but also to the multiple point of an *n*-component system. The theorem in its general form may be stated as follows: Construct in a flat space of $n + 1$ dimensions the $n + 2$ points whose coordinates are the specific volume, the specific entropy and the concentrations of the $n + 2$ phases of the invariant *n*-component system. These points form a figure which is bounded by $n + 2$ flat *n*-dimensional spaces. From a point within this figure drop perpendiculars to the $n+2$ faces and project this set of lines upon the volume-entropy plane. Take a temperature axis parallel to the entropy axis and a pressure axis parallel to the negative direction of the volume axis. Then the lines drawn in the volume-entropy plane are respectively parallel to the tangents drawn at the multiple point to the stable portions of the $n+2$ univariant curves.

New York, May 19, 1902.

EXPERIMENTS ON THE ELECTROLYTIC REDUCTION OF POTASSIUM CHLORATE

BY G. H. BURROWS

When a solution of potassium chlorate is subjected to electrolysis with use of copper electrodes a remarkably high electrical reduction efficiency is gained. At the suggestion of Professor Bancroft I have made a study of the conditions best suited to this reduction, at the same time attempting to obtain insight into its character.

The problem is of especial interest in that a principle is involved which, it seems probable, will prove of general application in the carrying out of useful reduction processes.

By varying singly the different factors involved, a series of results are obtained from which the conditions for maximum reduction are readily deduced. After a general description of experimental details these results will be taken up.

Except in the experiments intended to test the effect of change of concentration, the chlorate solution used contained 50 g of $KClO_3$ to the liter. The chlorate used contained the faintest trace only of chloride. For each experiment 450 cc of the solution was measured into a beaker of 500 cc capacity. The beaker was supported in a water-bath.

The electrodes were cut from sheet copper. One of these, usually the anode, was rotated. This mode of stirring proved very convenient, saving the space of separate apparatus and being quite efficient. In this way also both surfaces of the anode shared equally in the action. On account of the presence of additional resistance in the circuit the rotation did not cause appreciable fluctuation in the current. A mercury cup on the stem of the rotating electrode furnished means of contact.

The current used was taken from a 110 volt circuit. In the earlier experiments this was measured by an ammeter, reading to tenths of amperes, or by a voltmeter used as an ammeter, all runs being timed. Later a copper voltameter was also placed in series. Error due to its previous absence is within that resulting from other uncontrolled factors.

The amount of reduction was estimated by gravimetric determination of the chloride formed, this being the sole product of the reduction of the chlorate. In the electrolysis of an undivided solution of potassium chlorate using copper electrodes, a dark brown precipitate, essentially copper oxide, forms; this is mixed with particles of lighter color which are probably an oxychloride. The cathodes are slightly blackened, while the anodes are rapidly consumed, what remains of them being coated with oxide and peculiarly pitted; the pits are filled with cuprous chloride. The precipitates were dissolved and the anodes cleaned by dilute nitric acid, the solutions gained being added to the main solution and the whole filtered and made up to a definite volume. From this portions were taken for analysis.

Usually two reductions were carried out at the same time, those experiments being made in series, the results of which were to be directly compared or contrasted.

The "percentage efficiencies" used are electrical efficiencies on the basis that for 100 percent one molecule of $KClO_3$ will be reduced by 3 × 26.8 ampere hours.

The variables that are considered as determining the yield are anode and cathode densities, temperature, concentration and ampere hours. A compact tabulation of results may be of service in their discussion:

With anodes of 5 × 10 cm and 2 × 10 cm, other conditions being the same, the cathodes in each case 5 × 10 cm, the average reduction efficiencies are 140 pct and 176 pct respectively. In a shorter run anodes of 2 × 10 cm and 0.41 cm diameter (latter a copper wire, the solution was stirred by attached glass rods) gave efficiencies of 200 pct and 175 pct. The efficiency, then, increases markedly with increase of anode current density, a maximum being reached when the density is very high.

Using cathodes of 5 × 10 cm, 2 × 10 cm, and 1 × 10 cm, the percentages are 140 pct, 144 pct, and 139 pct respectively. Within a wide range the extent of reduction appears independent of the current density at the cathode.

The temperature usually chosen was that reached through a bath of boiling water, slightly elevated, about 2°, by the heating effect of the current, that is 94°–96°. An experiment of which the efficiency at this temperature was 189 pct, duplicated

No.	Anode	Cathode	Amperes	Hours	Temp.	Conc.	Series with	Efficiency
1*a*	5×10 cm	5×10 cm	4	2	94°–96°	50	2*a*	136.2
b	"	"	"	"	"	"	3*a*	147
c	"	"	"	"	"	"	4	137.8
								av. 140.3
2*a*	2×10 cm	"	"	"	"	"	1*a*	173.3
b	"	"	"	"	"	"	3*b*	179.4
								av. 176
3*a*	5×10 cm	2×10 cm	"	"	"	"	1*b*	132
b	"	"	"	"	"	"	2*b*	155.5
								av. 143.8
4	"	1×10 cm	"	"	"	"	1*c*	138.7
5*a*	"	5×10 cm	"	3	"	"	5*b*	85.1
b	"	"	"	"	"	"	5*a*	78.7
								av. 81.9
6*a*	"	"	"	1.5	"	"	6*b*	95.9
b	"	"	"	"	"	"	6*a*	96.6
								av. 96.3
7*a*	2×10 cm	"	"	0.5	"	"	7*b*	196
b	"	"	"	"	"	"	7*a*	204
								av. 200
8*a*	0.41 cm dia	"	"	"	"	"	8*b*	174.4
b	"	"	"	"	"	"	8*a*	175.4
								av. 174.9
9	2×10 cm	"	"	1	"	"	10	189.1
10	"	"	"	"	"	100	9	189.7
11*a*	"	"	"	"	62°–63°	50	11*b*	184.6
b	"	"	"	"	"	"	11*a*	189.7
								av. 187
12*a*	"	"	"	"	37°–39°	"	12*b*	149.2
b	"	"	"	"	"	"	12*a*	135
								av. 142

at 62°–63° gave 187 pct, and at 37°–39°, 142 pct. Between about 62° and 96°, an unexpectedly wide range, the efficiency is constant, while that for 37°–39° shows a marked falling off. At this lower temperature the blue hydrated copper oxide at first separates and gradually darkens, changing to brown.

The efficiency is, within the limits tried, independent of the concentration of the chlorate solution. Solutions of 50 g and 100 g $KClO_3$ to the liter gave efficiencies of 189 pct and 190 pct.

With constant current the yield decreases as the length of the run increases. Runs of one-half, one, and two hours duration, other factors being constant, gave 200 pct, 189 pct, and 176 pct. On account of the formation of cuprous chloride and of copper oxychloride (?) the solution gradually becomes alkaline. The decreasing rate of reduction is in part due to the free alkali formed. On initially adding 10 cc of sodium hydroxide solution, containing approximately 1 g NaOH to 15 cc of its solution, to the chlorate solution, the yield was decreased from 171 pct to 112 pct. Using a greater amount of the caustic soda solution, 20 cc and 30 cc respectively, there was practically no reduction of chlorate. The anodes were but slightly attacked and there was a vigorous evolution of gas at each electrode, which is not the case without free alkali initially added.

Summary of the foregoing results:

In the electrolytic reduction of potassium chlorate in solution, using copper electrodes, the anode not being placed in a separate compartment, a yield approaching 200 pct is readily gained, and this percentage appears to be the maximum. This efficiency can be obtained over a wide range of temperature and of concentration. It is favored by a high current density at the anode and is independent of the cathode current density. The efficiency is rapidly cut down by the presence of free alkali and this is slowly formed during the course of the electrolysis.

The explanation that first suggests itself for this extraordinary efficiency is that a large fraction of the yield of chloride is simply the result of spontaneous decomposition of the chlorate itself, or of one of its reduction products. The temperature of the water-bath and the presence of finely divided copper oxide and of certain amounts of copper salts in solution would favor such action.

As a result of spontaneous decomposition there must be either evolution of oxygen or simultaneous formation of a higher oxidation product, that is, of a perchlorate. In the experiments tabulated above there is little or no gas evolved from the anodes, none from the main body of the liquid and a momentary evolution only, of hydrogen from the cathodes, this seeming to cease when the copper oxide begins to separate. Tests made for perchlorate yield negative results. Moreover neither boiling a solution of chlorate of the strength used with copper sulphate nor heating it on the water-bath with finely divided copper oxide, causes it to break down to chloride. These facts show plainly that the hypothesis of direct spontaneous decomposition is untenable.

It is conceivable that our high efficiency rests upon a change in valence of the copper which dissolves from the anode. If the copper goes into solution in cuprous form subsequently becoming further oxidized, an efficiency of 200 pct might be realized. This, however, would necessitate a loss in weight at the anode equal to twice the increase in weight of the copper voltameter cathode. In runs one-half hour in length the loss is, indeed, 1.6 times the weight of copper deposited in the voltameter. But when the time is extended to two hours the two weight differences are approximately equal, and this without great falling off of efficiency. This, then, as an explanation, must also be set aside.

The rapid destruction of the copper anode and the initial, but momentary, evolution of hydrogen at the cathode would be in accord with the formation of intermediate reduction products at the anode, which are further reduced by the hydrogen, absorbing it. The assumption of reduction taking place at the anode is unusual, its validity is, however, readily tested.

If such an action takes place we would expect that on separating the anode and cathode liquids by a membrane or porous cup, hydrogen would be continuously evolved from the cathode and the anode electrolyte would give evidence of the intermediate products of reduction, probably through the giving off of oxygen with formation of a chloride. A trial of this was made through two experiments carried out in series, each being arranged as follows: An unglazed clay cell was placed in a 500 ccm beaker. 450 ccm of the chlorate solution was distributed between the two compartments. A copper anode, 2 × 10 cm, was inserted in the cell. A cathode of like dimensions was rotated in the outer compartment. A current of four amperes was allowed to pass for half an hour. The temperature was 94°-96°.

From the outset, and continuing through the experiments, there is a vigorous evolution of hydrogen from the cathodes, but no bubbles of gas rise from the anode liquid. About the cathode the liquid remains almost colorless, being slightly brown at the close. Here there is no, or at most very slight, formation of chloride. In the anode compartments, on the other hand, the reduction is marked, giving a heavy precipitate of cuprous chloride as the chief product. The anode liquids become blue, showing the presence in solution of some copper salt. There is, however, no trace of chlorites or of hypochlorites to be found in this liquid and these cannot have spontaneously decomposed, giving rise to the chloride, for as above noted, no oxygen is set free. The chlorate that undergoes reduction here must, therefore, pass directly to chloride. The hydrogen cannot play the rôle tentatively assigned to it. Determinations of the chloride formed in the cathode compartments show efficiencies of 73 pct and 76 pct respectively.

In these last experiments the anode liquids differed from those in which no cell was used in becoming acid instead of faintly alkaline. To eliminate this difference and so make more positive the proof of anode reduction under the conditions of the first series, other experiments were carried out in which caustic soda solution, made by the action of sodium on water and free from chloride, was added in small portions to keep the liquid as nearly as possible neutral. Otherwise the detail of arrangement was as described above.

Here too the reduction was noteworthy, though instead of cuprous chloride copper oxide was precipitated, the chief amount of chloride formed remaining in solution. There was no evidence of the chlorate being reduced in steps. Each of two trials gave an efficiency of 58 pct.

The acid or alkaline reaction of the solution was determined by litmus paper. In order to prevent great increase of volume it was necessary to use a rather strong solution of sodium hydroxide. On this account it was possible only to approach neutrality, the solution being much of the time slightly alkaline, and as previously shown the presence of free alkali in sufficient amount completely prevents reduction. It is probable that with more perfect means of neutralization the efficiency would be considerably higher than found.

The marked difference in the action at the cathode according to whether or not this electrode is contained in a porous cell, not being readily explicable through any change which takes place in the chlorate, appears to be connected with the copper which goes into solution from the anode. This points to an analogy with the results obtained by Binz[1] in the electrolytic reduction of indigo.

Binz finds that with use of a zinc anode in caustic soda solution reduction of suspended indigo to indigo white takes place at the anode by direct action of the metal. And further that by dissolving zinc in an alkaline cathode electrolyte in which indigo is suspended, the reduction is about 15 times as great as takes place without the zinc, the trials being made in series. Repeating with use of soluble coloring matters Binz and Hagenbach[2] obtained like results and conclude that reductions attributed to nascent hydrogen are frequently better explained

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

[2] Ibid. 6, 261 (1899).

as direct reductions by metals. The same principle underlies the process patented by the firm of C. F. Boehringer and Son[1] for the reduction of nitrobenzene to aniline. This is effected through use of a tin cathode, or of an indifferent cathode and addition of a tin salt to the cathode compartment, from which the anode is separated by a membrane. Later they find that the tin may be replaced by certain other metals, as copper, lead and iron. By this method is gained an almost quantitative reduction of nitrobenzene to aniline hydrochloride.

A. Chilesotti[2] has recently extended these results and has called attention to the importance of the methods of Boehringer and Son. He regards the spongy metal which is deposited on the cathode during the reduction as the active agent, but states that the reduction cannot be ascribed to the catalytic action of this metal, since when the reduction of a portion of nitrobenzene with tin is complete all of the tin is precipitated, but on adding a fresh portion of nitrobenzene tin again passes into solution.

To test whether this theory of Binz would apply to the case in hand, an experiment was devised in which 10 g of crystals of pure copper sulphate were initially added to the chlorate solution about the cathode. Reduction at the anode was prevented by inserting the latter in a porous cell containing a solution of potassium sulphate. The electrodes were of sheet copper, the size being 2 × 10 cm. The cathode was rotated. The temperature was that of the water-bath and a current of four amperes was passed for half an hour. At the outset no bubbles rise from either electrode. The anode liquid assumes a deep blue color and the anode is split into a number of layers between which a white substance is deposited. The cathode liquid, originally blue in color, from the copper salt added, becomes almost colorless. A heavy deposit of cuprous chloride forms mixed with a yellow substance which also coats the electrode.

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[1] German Patent, 116942, 117007 (1900).

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

Analysis shows an efficiency of 91 pct, and this confined to the cathode compartment where under like conditions, but in absence of the copper salt, no reduction takes place. The result, therefore, is in harmony with the experiments of Binz.

When the reduction was confined to the anode the efficiency was 58 pct. This added to that just obtained for the cathode gives 149 pct as a total. It seems probable that this sum with greater accuracy in securing comparable conditions would approach the maximum of 200 pct, found for the corresponding case in which simultaneous reduction is allowed to take place, no cell being used. Assuming that under like conditions the sum of the separate efficiencies would equal the joint efficiency, the most apparent cause of discrepancy lies in the free acid and alkali respectively present when the electrodes are separated.

The substance reduced in the above experiments is an electrolyte, while the investigations of Binz and the processes of Boehringer and Son deal immediately with non-electrolytes.

In the reduction of nitrobenzene it was seen that there is a choice between using a cathode of a particular metal or of using an indifferent cathode and a salt of the metal dissolved in the cathode electrolyte. At the temperatures employed with potassium chlorate in solution the simple use of a copper cathode is not sufficient to cause reduction.

Previous use has not been made, as far as the writer has discovered, of simultaneous reduction at anode and cathode. And the only instance of anode reduction noted is that in which Binz effects the change of indigo to indigo white in alkaline solution by the direct action of a zinc anode. In his subsequent work, however, Binz makes use of a porous cell.

Disregarding the higher efficiency attainable, the doing away with the necessity of two liquids in many, particularly organic, reductions would in itself make possible a decided saving in time and material.

The fact that spontaneous decomposition of the chlorate is not one of the factors and that the passage from chlorate to chloride seems to be direct, renders it highly probable that the result is general. This will be determined by further experiments.

The work described in this paper was carried on under the direction of Professor Bancroft, to whom the writer takes pleasure in expressing his sincere thanks.

Cornell University.

NEW BOOKS

Department of Agriculture: Field Operations of the Division of Soils, 1900. *By Milton Whitney. Government Printing Office, Washington, 1901.* — The volume contains a general review of the work, with special reference to the purpose, progress and cost of soil surveys. There are also the following special reports: —

A Soil Survey around Lancaster, Pa., by C. W. Dorsey.

Soil Survey of Montgomery County, Ohio, by C. W. Dorsey and G. M. Coffey.

Soil Survey of Cecil County, Md., by C. W. Dorsey and J. A. Bonsteel.

Soil Survey of St. Mary County, Md., by J. A. Bonsteel.

Soil Survey of Calvert County, Md., by J. A. Bonsteel and R. T. Avon Burke.

Soil Survey of Calvert County, Md., by J. A. Bonsteel.

Soil Survey from Raleigh to Newbern, N. C., by W. G. Smith.

Soil Survey in Weber County, Utah, by F. D. Gardner and C. A. Jensen.

Soil Survey in Sevier County, Utah, by F. D. Gardner and C. A. Jensen.

Soil Survey in Salt River Valley, Arizona, by T. H. Means.

Soil Survey around Fresno, Cal., by T. H. Means and J. G. Holmes.

Soil Survey around Santa Ana., Cal., by J. G. Holmes.

Investigations on the Physical Properties of Soils, by L. J. Briggs.

Application of the Theory of Solutions to the Study of Soils, by F. K. Cameron.

Results of Tobacco Experiments Conducted in Various Parts of the United States, by M. L. Floyd.

In addition there are twenty-four most excellent soil maps.

In the paper by Mr. Briggs, it is shown that the capillary rise in moist soils may be four to five times that in dry soils; that solutions of sodium chloride and sodium sulphate in concentrations up to half-normal differ very little in their capillary rise from pure water; that the capillary rise for saturated solutions of these salts is only about two-thirds of that for pure water; and that the capillary rise for sodium carbonate solutions is greater than that for pure water. This last phenomenon is attributed by the author to the action of sodium carbonate in removing grease. Attention is also drawn to the fact that the amount of carbon dioxide absorbed on the surface of a pure quartz sand in equilibrium with the partial pressure of carbon dioxide in the atmosphere is 200 times the amount of carbon dioxide contained in the interstitial spaces of the sand."

In the paper by Dr. Cameron we find a discussion of the following points: nature and function of soil solutions; equilibrium between carbonates and bicarbonates in aqueous solutions; solubility of calcium carbonate in aqueous solutions of various electrolytes; solubility of sodium chloride in contact with calcium carbonate and calcium sulphate simultaneously; a classification of alkali soils; occasional occurrence of alkali in humid regions; estimation of carbonates, bicarbonates, and chlorides; chemical phenomena presented by some alkali vegetation.

The volume is a worthy successor to the 1899 report (5, 264). If one is to judge from the reviewer's copy, more care on the part of the government book binders would be very desirable. *Wilder D. Bancroft*

Elementary Illustrations of the Differential and Integral Calculus. *By Augustus de Morgan. 13 × 19 cm; pp. viii + 144. Chicago: The Open Court Publishing Co., 1899. Price: cloth, $1.00.*—The Open Court Publishing Company deserves thanks for reprinting and thus rendering generally accessible De Morgan's little book. To any one who is interested in the principles as distinguished from the processes of the infinitesimal calculus—and every educated person is or at any rate ought to be—this little book is invaluable. Any one who reads through the one hundred and thirty pages which constitute this unique book will acquire a clear comprehension of the two facts that a differential coefficient is the limit of a certain ratio and that a definite integral is the limit of a certain sum. These two ideas are of fundamental importance in all applications of the calculus and should be familiar to every physicist and to every chemist. If one were asked to name the most interesting and useful portions of the book one would be tempted to cite the entire table of contents. If, however, one were obliged to limit the list to a dozen topics, the following selection would perhaps be justified: Taylor's Theorem, Derived Functions, Differential Coefficients, Rational Explanation of the Language of Leibnitz, Approximations, Solution of Equations, Calculus of Finite Differences, Successive Differentiation, The Integral Calculus, Connection of the Integral with the Differential Calculus, Nature of Integration. *Paul Saurel*

Census Bulletin, No. 210: *Chemicals and Allied Products. By Charles E. Munroe and Thomas M. Chatard. 23 × 29 cm; 306 pp. Washington, 1902.*—This is the report on chemicals and allied products prepared for the twelfth census. The matter is classified under the following groups: acids; sodas; potashes; alums; coal-tar products; cyanides; wood distillation; fertilizers; bleaching materials; chemicals produced by the aid of electricity; dye-stuffs; tanning materials; paints, pigments, and varnishes; explosives; plastics; essential oils; compressed and liquefied gases; fine chemicals; general chemicals. In addition to the general report there are sixty pages of tables giving statistics in regard to these nineteen groups, and there is also an appendix in which are given the chemical patents of the decade. It is a most valuable bulletin and it is very interesting to notice the importance given in it to physical chemistry. *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

Ammonium bromide and the atomic weight of nitrogen. *A. Scott. Jour. Chem. Soc.* **79**, *147* (*1901*). — The author's samples of ammonium bromide were brilliantly white and showed no grayness when heated in air to 180°. No difficulty was experienced in subliming the salt, either in a vacuum, in a mixture of ammonium and hydrogen, or in pure ammonia itself, and no trace of yellow coloration was observed in any instance, the condensed salt being a somewhat horny, translucent mass. The salt therefore differed from that of Stas, which became grayish when heated in air to temperatures above 100°, and which became yellow when heated in the presence of dry ammonia.

The author finds for the equivalents of ammonium bromide and chloride when referred to silver, 97.995 and 53.516 respectively, instead of 98.032 and 53.532 as found by Stas. While it is not certain that the discrepancy is due to an error on the part of Stas, it seems probable that the ammonium bromide of Stas contained some platinum. *W. D. B.*

The calculation of atomic weights. *F. W. Clarke. Am. Chem. Jour.* **27**, *321* (*1902*). — The author points out that the usual tendency in the present method of calculating atomic weights is to accumulate all errors, accidental or systematic, upon the constant which is last determined. He further shows that a more satisfactory method would be to obtain a group of normal equations involving the atomic weights of a number of elements and to solve these equations all at once. In this way the errors would be distributed and the result would be more accurate. At present the data are insufficient for carrying out this method. *W. D. B.*

A new determination of the atomic weight of calcium. *T. W. Richards. Jour. Am. Chem. Soc.* **24**, *374*; *Zeit. anorg. Chem.* **30**, *271* (*1902*). — The author has prepared pure calcium chloride from an Italian marble and from a Rutland marble. The two are apparently identical and when the ratio of chlorine to calcium is determined by precipitation of silver chloride a value for the atomic weight of calcium of 40.126 is obtained, differing but slightly from the value of 40.142 recently obtained independently by Hinrichsen.

W. D. B.

A new investigation concerning the atomic weight of uranium. *T. W. Richards and B. S. Merigold. Zeit. anorg. Chem.* **31**, *271* (*1902*). — Reviewed (**6**, 146) from. Proc. Am. Acad. **37**, 365 (1902).

Specific heats at the absolute zero. *A. Ponsot. Comptes rendus*, **134**, *703*

(*1902*).—The author deduces the following conclusions:—"At the absolute zero two systems of solids containing the same elements have the same specific heat. The specific heat of a solid and of its saturated vapor tend toward the same value for $T = 0$. The specific heat of a solid and that of its saturated vapor tend toward the value zero as the absolute temperature approaches zero. The specific heat of a saturated vapor is less than that of the solid or the liquid from which it is formed. The specific heat under constant pressure has a limiting value of $2\frac{fv}{T}$.

W. D. B.

Contribution to the calculation of atomic weights. *J. Schmidt. Zeit. anorg. Chem.* 31, *146* (*1902*).—The author assumes that a part of the atomic weight of each element except hydrogen is due to a chemically active portion, while the balance is chemically inactive. Starting with this assumption, he deduces a series of formulas and compares them with the accepted atomic weights.

W. D. B.

The heat of formation, and constitution of iron nitride. *G. J. Fowler and R. J. Hartog. Jour. Chem. Soc.* 79, *299* (*1901*).—The authors find 81.56 cal for the heat of decomposition of iron nitride by sulphuric acid. The heat of formation of iron nitride is probably about 3 Cal, but this is not certain until some of Thomsen's values have been gone over again. The authors believe it impossible that the formula Fe_2N should be accurate and hold it more probable that the molecular formula is Fe_4N_2.

W. D. B.

A system of corrections for the heat losses in calorimeter experiments. *J. W. Richards. Jour. Franklin Inst.* 152, *81* (*1901*).—The author determines experimentally the water values of his calorimeter for 1, 2, 3, etc., minutes after standing. Water at a known temperature is poured into the empty calorimeter, and the change of the temperature with the time noted. The author claims that it is now possible to measure the heat evolved in the calorimeter with an accuracy equal to the precision with which the thermometer can be read.

W. D. B.

An automatic temperature regulator. *C. T. Knipp. Phys. Rev.* 12, *47* (*1901*).—The regulation was made by means of two copper-iron bars which moved a system of levers and these made or broke the electrical circuit. It was possible to hold the bath constant to within a degree at 376°.

W. D. B.

A chemical method for obtaining vacuo. *F. G. Benedict and C. R. Manning. Am. Chem. Jour.* 27, *340* (*1902*).—The authors displace the air in a desiccator by ether and then let the ether be absorbed by hydrochloric acid. In this way there is no difficulty in obtaining a vacuum of 1-4 mm in a very few minutes.

W. D. B.

Recommendations in regard to the use of modified equality signs in chemical equations. *H. Marshall. Zeit. phys. Chem.* 41, *103* (*1902*).—The author objects to the use of the double arrow signs to represent equilibrium because these are already in use in organic chemistry for other purposes. He therefore suggests modifications of these.

W. D. B.

Modification of Hempel's gas apparatus. *T. W. Richards. Zeit. anorg.*

Chem. 29, *359* (*1902*). — Reviewed (6, 149) from Proc. Am. Acad. 37, 273 (1901).

One-Component Systems

The boiling-point of liquid hydrogen determined by hydrogen and helium gas thermometers. *J. Dewar. Am. Jour. Sci.* (*4*) 11, *290* (*1901*). — A platinum resistance thermometer gives − 238.4° for the boiling-point of hydrogen. Since the readings of the platinum thermometer are not accurate at this temperature, the author has checked these results on a hydrogen and a helium thermometer. It now seems probable that the boiling-point of hydrogen is − 252.5°, of neon − 239°, and of oxygen − 182.5°. *W. D. B.*

Melting-point of gold. *L. Holborn and A. L. Day. Am. Jour. Sci.* (*4*) 10, *145* (*1901*). — Reviewed (6, 66) from Drude's Ann. 4, 99 (1901).

Preliminary communication on the method for calculating solubilities and equilibrium constants of chemical reactions, and on a formula for heats of vaporization. *A. Findlay. Zeit. phys. Chem.* 41, *28* (*1902*). — The author has applied the formula of Ramsay and Young for the calculation of the vapor pressure of one substance from the vapor pressure of another to the solubility. He writes the formula

$$R = R' + c(t' - t).$$

In this equation R and R′ are the ratios of the temperatures at which the substances have the same solubilities; *c* is a constant; *t′* and *t* are the temperatures at which one of the two substances has the two solubilities in question. This equation holds whether the substances are dissociated or not, and whether the heat of solution is positive or negative. The author has tested this formula for zinc bromide and zinc chloride, for potassium bromide and potassium chloride, and for cadmium bromide and potassium nitrate.

This same formula can also be applied to the calculation of equilibrium constants, and has been tested for the reaction between acetone and di-acetone alcohol. The author finds further that the heat of vaporization for two substances is given approximately by the formula

$$L_1 = L_2 T_1^x .$$

In this equation, L_1 is the heat of vaporization of the first substance at the absolute temperature T_1; L_2 is the heat of vaporization of the second substance at the temperature T_2 at which the vapor pressure of the second substance is equal to that of the first substance at the temperature T_1. *W. D. B.*

On the expansion of certain metals at high temperatures. *L. Holborn and A. L. Day. Am. Jour. Sci.* (*4*) 11, *374* (*1901*). — Reviewed (5, 613) from Sitzungsber. Akad. Wiss. Berlin, 1900, 1009.

On the density of ice. *H. T. Barnes. Phys. Rev.* 13, *55* (*1901*). — Measurements were made on the density of ice which had been formed that year, a year preceding, and two years earlier. According to these determinations the density of old and new river ice is the same and may be taken as 0.91661 ± 0.00007. This agrees to two parts in 10,000 with the value of 0.91644 given by Nichols for river ice not newly cut. *W. D. B.*

On the gas law between 75 and 150 mm pressure. *Lord Rayleigh. Zeit. phys. Chem.* 41, *71* (*1902*). — At temperatures of 10°-15° and between the pressure limits of 75 and 150 mm, Boyle's law holds for air, hydrogen, oxygen, and argon, at any rate, within a limit of one in fifty thousand. *W. D. B.*

The two specific heats of gases. *W. D. Boynton. Phys. Rev.* 12, *353* (*1901*). — The author discusses the ratio of the specific heats of gases, assuming the van der Waals formula. He finds that there is a correction term which is of the same order and magnitude, and the same sign, as the variations of the observed values of the ratios from the simple values 1.4, and 1.825.

W. D. B.

Gas thermometer at high temperatures. *L. Holborn and A. L. Day. Am. Jour. Sci.* (*4*) 10, *171* (*1900*). — Reviewed (5, 613) from Drude's Ann. 2, 505 (1500).

On germanium hydride. *E. Voegelen. Zeit. anorg. Chem.* 30, *325* (*1902*). — The author has succeeded in preparing a germanium hydride which probably has the formula GeH_4. As he was not successful in preparing the hydride of tin, the author concludes that the division between metalloids and metal should be made between germanium and tin. *W. D. B.*

Two-Component Systems

Note on the application of the phase rule to the fusing point of copper, silver, and gold. *T. W. Richards. Am. Jour. Sci.* (*4*) 13, *377* (*1902*). — Holborn and Day find that the fusing point of gold is 1064° whether determined in presence or absence of air. The author points out that this is as one would expect because the tendency of gold to dissolve air, oxygen, or nitrogen is very slight.

Holborn and Day find further that the fusing point of silver is very variable in presence of air and the author shows that this would necessarily be the case if we assume a variable absorption of oxygen. Holborn and Day find a constant melting-point for copper of 1065° in presence of air and 1084° in absence of air. This is easily explained. The higher melting-point is the true melting-point for pure copper. The lower melting-point is the value for the quadruple point, solid copper, a solution of cuprous oxide in liquid copper, a solution of copper in liquid cuprous oxide, and vapor. *W. D. B.*

On the constitution of binary alloys. *J. A. Mathews. Jour. Franklin Inst.* 153, *1* (*1902*). — This is a paper on the general properties of binary alloys and the author shows how the freezing-point curves and cooling curves are obtained and discusses the conclusions to be drawn from these and from a study of the microscopical structure of the cooled alloy. The value of the paper would be greater were the statements more accurate. The author seems to believe that the freezing-point always falls when a solid solution separates, and always rises when a pure component separates. The truth of the matter is that the freezing-point always falls when a pure component separates and may rise or fall when a solid solution separates. *W. D. B.*

On thallium alloys. *W. S. Kurnakow and N. A. Puschin. Zeit. anorg.*

Chem. 30, *86* (*1902*). — Addition of thallium to sodium causes a lowering of the freezing-point and there is a eutectic point at 64°. The temperature then rises to a quadruple point at 78°, to another at 159°, then passes through a maximum at 305.8°, and falls to a eutectic point at 238°. Further addition of thallium causes a rise to the freezing-point of pure thallium. Judging from the lowering of the freezing-point, pure thallium does not separate from any solution. The maximum melting-point corresponds to a compound NaTl. *It is not known* what are the solid phases at the quadruple point at 78°.

When thallium is added to potassium there is no evidence of any lowering of the freezing-point and it is therefore probable that a solid solution separates. There is a quadruple point at a temperature of 242.2°; the freezing-point curve passes through a maximum at a temperature of 335° and falls to a eutectic point at 172.5°. From this point it rises normally to the melting-point of pure thallium. The position of the maximum corresponds to a compound having the formula KTl.

The freezing-point curves for cadmium and thallium and for tin and thallium consist of two branches only. In both cases, the lowering of the freezing-point by thallium is normal and in both cases the lowering of the freezing-point of the thallium is abnormal. The freezing-point curve for mercury and thallium shows the existence of a compound Hg_2Tl stable at its melting-point.

W. D. B.

On the melting-point of alloys of sodium and potassium. *N. S. Kurnakow and N. A. Puschin. Zeit. anorg. Chem.* 30, *109* (*1902*). — The freezing-point curve for sodium and potassium consists of three branches. The eutectic point comes at − 12.5° and the solution contains 66.6 atomic percent of potassium. There is a quadruple point at 6.9° where the solution contains 40 atomic percent of potassium. The general form of the curve makes it possible, though by no means certain, that there is a compound having the formula Na_2K. This investigation is very valuable in that it disposes once for all of the myth in regard to the compound NaK. *W. D. B.*

The alloys of lead and tellurium. *H. Fay and C. B. Gillson. Am. Chem. Jour.* 27, *81* (*1902*). — When tellurium is added to lead, the freezing-point rises, passes through a maximum at a composition corresponding to PbTe, then falls to the eutectic point at a concentration of about 80 atomic percents of tellurium. From this point the curve rises to the freezing-point of pure tellurium. The authors conclude from this curve that there is such a compound as PbTe.

While this conclusion may be right, it is not justified by the experiments. All that the experiments show is that a series of solid solutions separate until the eutectic point is reached, and that there is a point at which the concentration of the liquid and solid solutions are the same. *W. D. B.*

The alloys of antimony and tellurium. *H. Fay and H. E. Ashley. Am. Chem. Jour.* 27, *95* (*1902*). — When tellurium is added to antimony the freezing-point falls, passes through a minimum at about 30 atomic percents of tellurium and through a maximum at about 60 atomic percents of tellurium, and reaches the eutectic point at a composition of about 87 atomic percents of tellurium. The authors conclude that there is a compound Sb_2Te_3; but this conclusion is as unjustifiable as the conclusion in regard to the lead telluride (preceding review). *W. D. B.*

The formula for the depression of the freezing temperature of solutions. *W. F. Magie. Phys. Rev.* 12, *240* (*1901*). — The author deduces a formula which is somewhat more complicated than that of van 't Hoff's, but the difference between the two is in most cases too small to be detected by the present methods of measurement. *W. D. B.*

On the freezing-point of aqueous solutions of non-electrolytes, II. *E. H. Loomis. Phys. Rev.* 12, *220; Zeit. phys. Chem.* 37, *467* (*1901*). — The value of the molecular depression is found to be 1.85–1.86 in extreme dilution for all the non-electrolytes studied except three, and is found to remain constant for all the various concentrations of the non-electrolytes, levulose, dextrose, mannite, dulcite, glycerol, and chloral hydrate. The value of the molecular depression increases with increasing concentration, for cane-sugar, milk sugar, and maltose. With a number of benzene derivatives it was found that the molecular depression decreases at a rapid rate with increase of concentration. Not one of the twenty-six non-electrolytes that have been studied shows any evidence of dissociation in extreme dilution. *W. D. B.*

The molecular weights of certain salts in acetone. *H. C. Jones. Am. Chem. Jour.* 27, *16* (*1902*). — Dutoit and Friderich stated that ammonium sulphocyanate, mercuric chloride, sodium iodide, lithium chloride, and cadmium iodide have normal molecular weights in acetone. Since these substances also conduct, it seemed worth while to repeat these measurements. The author finds that cadmium iodide and ammonium sulphocyanate have values higher than the normal, which decrease with dilution. Sodium iodide gives values lower than the normal, while mercuric chloride gives values which are practically normal and its conductivity is exceedingly small. Lithium chloride is so insoluble in acetone that no determinations could be made. The author regards these results as entirely satisfactory, assuming both polymerization and dissociation for cadmium iodide and ammonium sulphocyanate. *W. D. B.*

The solubility of manganous sulphate. *T. W. Richards and F. R. Fraprie. Am. Chem. Jour.* 26, *75* (*1901*). — Reviewed (6, 150) from Proc. Am. Acad. 36, 509 (1901).

On the heat evolved when liquids are brought in contact with powders. *C. E. Linebarger. Phys. Rev.* 13, *48* (*1901*). — The author has determined the heat effect when finely divided silica is moistened by different liquids. "The relative amount of liquid does not seem to influence the heat effect. A certain minimum quantity is necessary to produce the maximum heat change, but any excess of that amount has no appreciable influence. The heat effect per unit mass of the powder is the same for the same liquid at the same temperature provided this minimum amount be present."

"The finer the powder the greater the heat effect seems in general to be true. In the case of water, toluidine, pyridine, and nitrobenzene, the heat effect with silica I. is twice that of silica II., and the granules of the second powder are about double the size of those of the first. But in the case of benzene, no such differences are apparent. Here about the same heat effect is produced with either powder. While qualitatively it undoubtedly holds that the finer the powder the greater the heat effect, it has not been shown quantitatively that such is the case. It is noteworthy that the different liquids do not vary much in their heat effects; water gives the largest and benzene the smallest. But pyridine and nitrobenzene, although very similar to benzene chemically, give heat effects which near that of water." *W. D. B.*

Heat of solution of resorcinol in ethyl alcohol. *C. L. Speyers and C. R. Rosell. Am. Jour. Sci.* (*4*) 10, *449* (*1900*).—Resorcinol dissolves in a large excess of ethyl alcohol with evolution of heat. The authors show that it dissolves in a saturated solution with absorption of heat and that the heat of dilution is large enough to reverse the sign. *W. D. B.*

Remarks on a paper of Mr. Caubet: On the liquefaction of gas mixtures. *J. P. Kuenen. Zeit. phys. Chem.* 41, *43* (*1902*). —The author gives reasons for believing that the van der Waals theory is a more perfect working hypothesis than the Duhem theory. He also criticizes some of Caubet's statements and experiments (5, 411). *W. D. B.*

Some physical properties of nitric acid solutions. *V. H. Veley and J. J. Manley. Proc. Roy. Soc.* 69, *86* (*1901*). —The authors believe that the changes of the densities and of the refractive indices with the composition are discontinuous for mixtures of nitric acid and water. The points of discontinuity for the densities correspond to mixtures of nitric acid with 14, 7, 4, 3, 1.5, and 1 molecular proportions of water. The points of discontinuity as shown by the refractive indices correspond to mixtures of nitric acid with 14, 7, and 1.5 molecular proportions of water. *W. D. B.*

The specific heat of solutions which are not electrolytes, II. *W. F. Magie. Phys. Rev.* 13, *91* (*1901*). —The substances studied were cane-sugar, dextrose, maltose, milk sugar, levulose, mannite, dulcite, resorcin, hydroquinone, and pyrocatechin in water. The last three solutions were also studied in aqueous alcohol. Milk sugar showed a specific heat which varied with the time, finally reaching a constant value. The general result is that the molecular heats are constant for different concentrations when the solutions are so dilute that the assumptions of the theory apply to them. Molecular heats of isomers in solution in the same solvent are not always the same. The apparent molecular heats of the same solute differ in different solvents. The author states that the heat capacity C of an electrolytic solution may be given accurately by the formula

$$C = H + A - pB.$$

Here H is the original heat capacity of the solvent, p is the dissociation factor, or the ratio of the mass of the solute which is dissociated to the whole mass of the solute, A and B are constants to be determined from the observed heat capacities. *W. D. B.*

On the union of hydrogen and chlorine, I.-III. *J. W. Mellor. Jour. Chem.*

Soc. *79*, *216* (*1901*). — The author finds that oxygen is present among the gaseous products of the electrolysis of hydrochloric acid and that even though traces of the lower chlorine oxides may be formed during electrolysis it is unlikely that any escape a preliminary washing of the gases. The solubility curve for chlorine in hydrochloric acid at 21° falls off rapidly from pure water to a solution containing about 0.99 hydrochloric acid per 100 cc. With increasing concentration of hydrochloric acid, the solubility of chlorine increases very nearly lineally. *W. D. B.*

Multi-Component Systems

Solubility of mixtures of sodium sulphate and sodium chloride. *A. Seidell. Am. Chem. Jour.* 27, *52* (*1902*). — A number of isotherms have been determined for the system sodium sulphate, sodium chloride, and water. These results are useful in themselves, but the author's interpretation of them is erroneous and he has overlooked the fact that most of the points which he believes to be new were pointed out more clearly a number of years ago. *W. D. B.*

On the mixed crystals of silver chloride and sodium chlorate, and their solutions. *H. W. Foote. Am. Chem. Jour.* 27, *345* (*1902*). — The author has determined isotherms for silver chlorate, sodium chlorate, and water at 25° and at 50°. At both temperatures the salts form two series of solid solutions and the ratio of sodium chlorate to silver chlorate in the solution is always greater than in the crystals. *W. D. B.*

The lowering of the freezing-point of aqueous hydrogen dioxide. *H. C. Jones, J. Barnes, and E. P. Hyde. Am. Chem. Jour.* 27, *22* (*1902*). — The presence of hydrogen peroxide in water decreases the lowering of the freezing-point produced by a dissolved salt. The authors incline to the belief that the hydrogen peroxide decreases the dissociation which would otherwise be caused by the water. *W. D. B.*

The solubility of barium sulphate in ferric chloride, aluminium chloride, and magnesium chloride. *G. S. Fraps. Am. Chem. Jour.* 27, *288* (*1902*). — The author finds that magnesium chloride increases the solubility of barium sulphate slightly and that aluminium chloride and ferric chloride increase the solubility quite markedly, though less so than an equal concentration of hydrochloric acid. *W. D. B.*

Influence of sodium sulphate on the vapor pressure of aqueous ammonia solutions. *E. P. Perman. Jour. Chem. Soc.* 79, *725* (*1901*). — The vapor pressure of ammonia solution is much increased by addition of sodium sulphate and is higher than it would become supposing the hydrate $Na_2SO_4 10H_2O$ to be formed and so increase the concentration of the ammonia solution. The vapor pressure curve shows no trace of a break at 33°, and the author therefore concludes that there is no change in the state of hydration of the dissolved sodium sulphate. *W. D. B.*

The decomposition of mercurous chloride by dissolved chlorides. *T. W. Richards and E. H. Archibald. Zeit. phys. Chem.* 40, *385* (*1902*). — Reviewed (6, 152) from Proc. Am. Acad. 37, 347 (1902).

On the nature of polyiodides and their dissociation in aqueous solution. *H. M. Dawson. Jour. Chem. Soc.* 79, *238* (*1901*).—The author finds that the molecular conductivity of potassium iodide solutions is considerably diminished by the addition of iodine. His experiments lead to the view that the electrolytic dissociation constant of HI_3 is of the same order of magnitude as that of the hydriodic acid and that the complex ion has a smaller migration velocity than the simple ion.
W. D. B.

Metal-ammonia compounds in aqueous solutions, I. *H. M. Dawson and J. McCrae. Jour. Chem. Soc.* 79, *493* (*1901*).—The authors have studied the specific action exerted by various salts of the alkali metals, and the influence of the concentration of the salt solutions on the distribution of ammonia between water and chloroform. They find that the solvent power of aqueous solutions of the alkali salts is, in general, less than that of pure water, lithium chloride, ammonium bromide, sodium iodide being exceptions. In most cases the authors find that the decrease in the distribution coefficient is proportional to the concentration, but this is not always the case.
W. D. B.

On the hydroxides of zinc and lead. *W. Herz. Zeit. anorg. Chem.* 28, *474* (*1901*).—Freshly precipitated zinc hydroxide required six equivalents of 0.8 *n* caustic potash to dissolve it. After drying at 60°–70°, thirty-six equivalents were necessary. In the case of lead hydroxide, eight and one-half equivalents of alkali were necessary to dissolve freshly precipitated lead hydroxide and 8.8 to dissolve dried lead hydroxide. No change, therefore, takes place in lead hydroxide on drying, whereas zinc hydroxide appears to change into a more stable and less soluble form.
W. D. B.

On the interpretation of certain modifications of metallic hydroxides. *A. Hantzsch. Zeit. anorg. Chem.* 30, *338* (*1902*).—The author believes that the difference in behavior between some freshly precipitated substances and the same substances after drying is due to a physical difference, analogous to the difference between yellow and red mercuric oxide, and is not due to the formation of an isomer as has been assumed by Herz.
W. D. B.

On the solubility of zinc hydroxide in ammonia and ammonia bases. *W. Herz. Zeit. anorg. Chem.* 30, *280* (*1902*).—The author has made experiments with ammonia, methyl amine, and ethyl amine, dimethyl amine and diethyl amine. Zinc hydroxide is insoluble in the last two. With the others it was found that more of the base was required to dissolve the dried zinc hydroxide, the more dilute the base. The substituted ammonias dissolve zinc hydroxide less readily than ammonia, this difference being greater the higher the molecular weight of the substituted radical.
W. D. B.

On the reaction between ethyl alcohol and hydrochloric acid. *T. S. Price. Jour. Chem. Soc.* 79, *303* (*1901*).—The author nas studied the reaction between ethyl alcohol and hydrochloric acid at 99° and finds that the results can be divided into two groups, in one of which an average constant of 0.176 is obtained, while the constant in the other group is 0.230. It seems certain that the value of the constant decreases with increasing concentration of the hydrochloric acid. While there are many disturbing factors which might affect the equilibrium constant, it is not possible to determine whether the discrepancy was to be referred to any one or to all of them.

Experiments on reaction velocity show that the constants are very satisfactory when no water is present at the beginning, but that the constant diminishes with the time when water takes part in the reaction from the beginning.
W. D. B.

The preparation of esters from other esters of the same acid. *T. S. Patterson and C. Dickinson. Jour. Chem. Soc. 79, 280 (1901).* — The authors find that pure ethyl tartrate may be made from methyl tartrate by heating this substance with an excess of ethyl alcohol, using hydrochloric acid as a catalytic agent. Conversely, pure methyl tartrate can be obtained by heating ethyl tartrate with an excess of methyl alcohol, using hydrochloric acid as a catalytic agent. The authors have also determined the rotation of methyl tartrate at various temperatures.
W. D. B.

The effect of temperature, of colloidal ferric hydrate, and of a magnetic field on the hydrolysis of ferric chloride. *H. M. Goodwin and F. W. Grover. Phys. Rev. 11, 193 (1900).* — "The effect of lowering the temperature is very greatly to diminish the rate of formation of colloidal ferric hydrate and to increase the initial lag in the reaction. The presence of colloidal hydrate exerts a very marked catalytic action, causing the reaction to be accelerated by an amount approximately proportional to the amount of colloidal hydrate present in the solution. No effect of the magnetic field could be detected on the course of the reaction."
W. D. B.

On the formation of calcium carbide. *V. Rothmund. Zeit. anorg. Chem. 31, 136 (1902).* — We write the equation for the formation of calcium carbide

$$CaO + 3C = CaC_2 + CO.$$

This reaction is endothermic and the question arose as to the necessary temperature and whether the reaction was reversible. The author obtained distinct formation of calcium carbide at a temperature of 1620°. If the reaction is a dissociation reaction as would appear from these results, it should be possible to lower the temperature by lowering the partial pressure of carbon monoxide. The author did this by passing an indifferent gas over the mass and found that under these circumstances carbide was certainly formed at 1575°. At this temperature, the dissociation pressure is apparently so low that it is practically impossible to reduce the partial pressure of carbon monoxide further by passing an indifferent gas over the mass.
W. D. B.

Contributions to our knowledge of cuprous compounds, I. *G. Bodländer and O. Storbeck. Zeit. anorg. Chem. 31, 1 (1902).* — Cuprous chloride is decomposed to a certain extent by water with formation of cuprous oxide and hydrochloric acid; but to a greater extent into cupric chloride and metallic copper. This latter decomposition is decreased by addition of chlorides. In potassium chloride solutions stronger than 0.05 normal, cuprous chloride dissolves without decomposition. The authors conclude that cuprous chloride goes into solution partly as such, and partly in the form of complex ions. From solubility determinations and from measurements of electromotive force they conclude that there is one atom of copper in the complex salt but that the nature of the salt varies, being $KCuCl_2$ in dilute solutions of potassium chloride and K_2CuCl_3 in more concentrated solutions. They were unable to decide whether free cuprous ions are monatomic or diatomic. *W. D. B.*

The decomposition of chlorates, III. *W. H. Sodeau. Jour. Chem. Soc.* 79, *247* (*1901*). — In the slow decomposition of calcium chlorate there is about one hundred and eighty times as much chloride formed as oxide, and the free chlorine has no appreciable action on the oxide or oxychloride. With silver chlorate, chloride is formed at about twice the rate of the oxide, but the free chlorine reacts with the oxide so that all but about 0.2 percent of the total chlorine recombines at atmospheric pressure. *W. D. B.*

Pyrite and marcasite. *H. N. Stokes. Am. Jour. Sci.* (*4*) 12, *414* (*1901*). — It is not always possible to distinguish pyrite from marcasite, either by the color or by the density. The author finds, however, that under uniform and easily controllable conditions the percentage of the total sulphur oxidized by ferric salts is very constant for each mineral but differs greatly in the two. The oxidation coefficient is about 60 for pyrite, and about 17 for marcasite. The oxidation coefficient in any given mixture of pyrite and marcasite is not an additive function. The author has determined these coefficients experimentally and finds that one can analyze a mixture of pyrite and marcasite by means of the curve to within one percent when the mixture is quite rich in pyrite, and to two or three percent when it consists mainly of marcasite. *W. D. B.*

On the decomposition of hydrogen peroxide by various substances at high temperatures. *J. H. Kastle and M. E. Clark. Am. Chem. Jour.* 26, *518* (*1901*). — The authors have studied the action of a number of substances on aqueous hydrogen peroxide at 100°. Some of these substances catalyzed the peroxide rapidly, while others were apparently without action upon it at this temperature. It is not possible to draw any general conclusions as yet concerning the cause of this decomposition, but it seems possible that the substances capable of bringing about the decomposition of hydrogen peroxide first combines with it to produce an even more instable derivative than the hydrogen peroxide itself, and that this then decomposes into oxygen, water, and the substance originally causing the catalysis. *W. D. B.*

Velocities

On the saponification of carbonic and sulphuric esters. *R. Wegscheider. Zeit. phys. Chem.* 41, *52* (*1902*). — The author finds that the saponification of sulphonic esters by water is not accelerated by the presence of hydrogen as ion. Acids exert an influence only when they bring about a side reaction having a measurable velocity. The accelerating action of alkalis can be considered as a saponification by hydroxyl as ion, in which case it is a side reaction, or as a catalytic action due to hydroxyl as ion. *W. D. B.*

On chemical dynamics and the chemical equilibrium under the influence of light. *M. Wilderman. Zeil. phys. Chem.* 41, *87* (*1902*). — The author has studied the reaction between carbon monoxide and chlorine under the influence

of light. He finds that the reaction is of the second order and that there is no law corresponding to Faraday's law by which the reaction velocity is directly proportional to the amount of radiant energy supplied during the unit of time.
W. D. B.

Velocity of chemical reaction. *W. Duane. Am. Jour. Sci.* (*4*) 11, *346* (*1901*). — The author proposes following reaction velocities by making a photographic record of the change in the index of refraction. One experiment of this sort on the rate of inversion of cane-sugar is given. The constant is not satisfactory; but the author does not seem to look upon this as militating against his method.
W. D. B.

Note on the rate of hydration of metaphosphoric acid. *J. C. and F. C. Blake. Am. Chem. Jour.* 27, *68* (*1902*). — The authors have made a qualitative study of the rate of hydration of metaphosphoric acid, using Duane's optical method (preceding review).
W. D. B.

Catalysis of hydrazine. *S. Tanatar. Zeit. phys. Chem.* 40, *475*; 41, *37* (*1902*). — The author finds that the catalysis of hydrazine sulphate in hot aqueous solution by means of platinum is given by the equation

$$3N_2H_4 = 4NH_3 + N_2.$$

The catalysis of free hydrazine in hot aqueous solution by platinum can be described by the equation

$$2N_2H_4 = 2NH_3 + N_2 + H_2.$$

The catalysis of hydrazine in alkaline solution can be represented by the equation

$$3N_2H_4 = 2NH_3 + 2N_2 + 3H_2.$$

W. D. B.

A study of growing crystals by instantaneous photomicrography. *T. W. Richards and E. H. Archibald. Am. Chem. Jour.* 26, *61* (*1901*). — The authors have made photographs of solutions of sodium nitrate, barium chloride, copper sulphate, ferrous ammonium sulphate, and potassium iodide while these solutions are crystallizing. In none of these cases was there any evidence that a second liquid phase separates just before crystallization. The authors believe that they could have detected such a second liquid phase if the globule had had a diameter of 0.001 mm. They studied the rate at which the crystal grows and find that increments of time correspond to equal increments of volume and not to equal increments of surface, as might have been expected.

While the authors' experiments seem to be conclusive in regard to the non-appearance of a second liquid phase in these cases, it would have been much more satisfactory if they had also studied a case in which a second liquid phase does appear. While they are certain that they could have recognized a liquid phase, they never have done so.
W. D. B.

Electromotive Forces

Thermodynamics of the voltaic cell. *H. S. Carhart. Phys. Rev.* 11, *1* (*1900*). — The author shows that the temperature coefficient of the cell must be the sum of the temperature coefficients at the junctions. He has measured the temperature coefficient at the junctions between metal and liquid in the Daniell cell and finds that the sum of these is approximately equal to the temperature coefficient of the cell. *W. D. B.*

Various determinations of the electromotive force of the Clark cell. *H. S. Carhart. Phys. Rev.* 12, *129* (*1901*). — The author tabulates all the determinations of the electromotive force of the Clark cell and shows that the mean, omitting Clark's determinations, of the absolute determinations, three in number, is 1.4333 volts at 15°. *W. D. B.*

The electromotive force of metals in solutions of cyanide. *S. B. Christy. Am. Chem. Jour.* 27, *354* (*1902*). — Reviewed (6, 140) from a Bulletin of the Department of Mining and Metallurgy of the University of California.

The effect of gravity and pressure on electrolytic action. *R. R. Ramsey. Phys. Rev.* 13, *1* (*1901*). — With zinc amalgam and zinc sulphate the current flows up through the tube opposite to gravity. With a nearly saturated solution of cadmium sulphate, the current flows down through the tube. Experiments have been made on the change of the electromotive force of a number of cells with the pressure, running up to 300 atmospheres. *W. D. B.*

On the graduation of thermopiles. *D. Berthelot. Comples rendus*, 134, *983* (*1902*). — Since the curve for *log E* and *log t* is represented by a straight line between 400° and 1100°, only two fixed points are necessary in order to graduate a thermopile between 400° and 1100°. The author recommends the melting-point of zinc, 419°, and the melting-point of gold, 1064°, as these two points. The boiling-point of sulphur, 445°, is not suitable, owing to the great precautions necessary to get an accurate reading. *W. D. B.*

Study of cells in which a salt reaction is re-enforced by oxidizing and reducing agents. *M. Berthelot. Comptes rendus*, 134, *1009* (*1902*). — The author describes a number of experiments with two liquid cells, containing salts, bases, or acids, and to which either pyrogallol or hydrogen peroxide, or both, have been added. *W. D. B.*

Polarization and internal resistance of electrolytic cells. *M. D. Atkins. Phys. Rev.* 13, *102*, *182* (*1901*). —

1. Electrodes of copper in $CuSO_4$ and zinc amalgam (both plates and liquid amalgam) in $ZnSO_4$, when freshly placed in their respective solutions, give with varying currents, curves completely satisfied by a formula of the Bartoli-Wiedeburg form, and its derived equations.

2. With such electrodes, therefore, the internal resistance *r* is, according to our assumption, constant.

3. Electrodes of silver in $AgNO_3$ and zinc in $ZnSO_4$, in the main, give curves satisfied by such a formula.

4. Electrodes of platinum (polished) in H_2SO_4, do not conform as far as investigated, to the formulas. The maximum value for the depolarization, however, is in agreement with that found by other methods.

5. Electrodes of all these metals in their respective solutions show, upon standing, a marked increase in apparent resistance. All results obtained concur in their testimony that this is not an increase in the real resistance of the cell. *W. D. B.*

On the decomposition voltages of fused sodium hydroxide and lead chloride. *J. F. Sacher. Zeit. anorg. Chem.* 28, *385* (*1901*). — Fused sodium hydroxide shows two cathodic breaks and two anodic breaks, the lower one of the anodic breaks being very slight and irregular. The cathodic break at 1.16 volts at 390° is due to hydrogen and the break at 2.06 volts at 389° to sodium. The anodic break at 1.31 volts at 393° is attributed to hydroxyl as ion and the value of 0.11 volt at 395° points to oxygen as ion. With fused lead chloride, two cathodic and two anodic breaks were found, but the lower one in each case tends to disappear the more completely the anode and cathode are separated. Consequently these breaks are due to depolarization and the explanation of Garrard is incorrect. *W. D. B.*

Electro-affinity as a basis for the systematization of inorganic compounds. *J. Locke. Am. Chem. Jour.* 27, *105* (*1902*). — The author gives a brief discussion of the electro-affinity hypothesis of Abegg and Bodländer and then shows that there are a large number of cases in which this hypothesis does not hold. The final paragraph of the paper is worth quoting in full.

"The physical chemist is not the only one who regrets the more or less tardy acceptance of the newer theories by the teachers of inorganic subjects. There are many of us whose line of study lies wholly in inorganic fields, who are willing and anxious to do such missionary work as we can for the extension of these theories, but the publication of such a speculation as the above by men prominent in the physical-chemical world does not materially assist toward that end, for it naturally raises doubts as to the accuracy and range of our colleague's knowledge of practical chemistry. It is as a protest in the name of that practical, experimental chemistry that the above criticisms are submitted."

The author is entirely right in this. The hypothesis of Abegg and Bodländer was an interesting speculation, but it has never advanced beyond that stage, and it is a great pity that many people have looked upon it as being a fairly trustworthy guide. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Manufacture and use of metallic sodium. *J. D. Darling. Jour. Franklin Inst.* 153, *65* (*1902*). — The author prepares metallic sodium in a two-compartment cell with fused sodium hydroxide at the cathode and fused sodium nitrate at the anode. The diaphragm is a mixture of magnesite and Portland cement, contained between walls of perforated sheet steel. In order to prevent these steel walls from being eaten away, they are also made electrodes and about 5 percent current is wasted here. This is profitable because it increases the life of the diaphragm about ten times. The nitrogen dioxide and the oxygen evolved at the anode are carried into water and converted into nitric acid. A current of 400 amp is used at an average electromotive force of 15 volts. External heat is used only when starting out and when changing the cups.

W. D. B.

On the rate of the electrolytic decomposition of oxalic acid in the presence of sulphuric acid. *T. Åkenberg. Zeit. anorg. Chem.* 31, *161* (*1902*). — When oxalic acid in sulphuric acid solution is electrolyzed with smooth platinum electrodes there is practically no decomposition, but decomposition takes place when platinized anodes are used. From these facts, the author concludes that the decomposition is a secondary process due to the chemical action of the electrolytic oxygen. When the concentration of the oxalic acid is high the decomposition follows Faraday's law very closely. In dilute solutions the decomposition follows the law for a monomolecular reaction. The reaction velocity constant is independent of the current density and changes approximately proportionally to the temperature between 15° and 55°. Since the reaction is monomolecular, the author concludes that oxygen reacts as O and not as O_2.

W. D. B.

On the preparation of bromoform by electrolysis. *P. Coughlin. Am. Chem. Jour.* 27, *63* (*1902*). — The author has studied the effect of varying conditions in the electrolytic preparation of bromoform from acetone. By working at about 25° with an anode density of 3 amp/sq dm, taking twice the theoretical amount of potassium bromide and adding sodium carbonate so as to keep the solution faintly yellow, he gets 100 percent efficiency. This is a most gratifying result, though it must be admitted that the author's method of analysis would cause him to overestimate the yield very much. With alcohol instead of acetone the current yield was never greater than 10 percent. *W. D. B.*

A new solution for the copper voltameter. *W. K. Shepherd. Amer. Jour. Sci.* (*4*) 12, *49* (*1901*). — A saturated solution of copper sulphate was boiled for a short time to expel the air, and then kept at 100° for about one hour in contact with metallic copper, in order to neutralize the solution. The density was then about 1.20. A very small amount of ammonium chloride was added, about 0.05 percent. This solution gives satisfactory results at temperatures between 20° and 40°, and can be used with a current density as high as 0.07 amp/cm^2.

W. D. B.

Remarks on the determinations of transference numbers of ions during the electrolysis of their solutions. *W. Hittorf. Zeit. phys. Chem.* 39, *612* (*1902*). — The author has repeated some of the measurements made forty years ago and finds that an animal membrane changes the transference number in the case of salts of bivalent metals. It has no effect on the salts of the alkali metals. In the earlier experiments, the author obtained no change for copper sulphate and for the salts of the alkali metals, and he therefore concluded that the animal membrane had no effect. The results for the salts of the alkali metals have been confirmed but a mistake must have been made in the measurement with copper sulphate. *W. D. B.*

A new apparatus for determining the relative velocities of ions, with some results for silver ions. *W. T. Mather. Am. Chem. Jour.* 26, *473* (*1901*). — The author's apparatus for determining migration velocities consists essentially of two tubes connected by a U-tube in which there is a glass stop-cock. He has made measurements of silver nitrate at different temperatures, both in water, absolute alcohol, and aqueous alcohol. He finds that the transference number tends toward unity with rising temperature, that the effect of decrease in concentration is in the same direction as that of the increase in temperature, and that the migration velocities vary with the nature of the solvent.

W. D. B.

A new method for the measurement of ionic velocities in aqueous solutions. *B. D. Steele. Jour. Chem. Soc.* 79, *414* (*1901*); *Zeit. phys. Chem.* 40, *689* (*1902*). — The method is a modification of that of Masson, but differs as to two essential respects. The measurements are made in water and not in gelatine, and the employment of a colored ion as indicator is not necessary, all that is required being that a solution of the indicator contains about the same number of gram-molecules per liter as the measured salt solution, but differs from the latter in density and in refractive power. The essential features of the method consist in the imprisonment of aqueoussolution to be measured between two partitions of gelatine containing the indicator ions in solution, thus preventing displacement of the liquid during the course of an experiment. The values for potassium bromide and potassium chloride thus obtained are somewhat lower than those previously adopted, but the reason for this is to be found in a forcing of the liquid through the gelatine. The author had himself noticed that a porous cell cannot be substituted for gelatine.

W. D. B.

Liquid sulphur dioxide as solvent. *P. Walden and M. Centnerszwer. Zeit. phys. Chem.* 39, *513*; *Zeit. anorg. Chem.* 30, *145* (*1902*). — This is a general summing up of the authors' work on liquid sulphur dioxide as solvent. The experiments on the molecular weight of electrolytes in liquid sulphur dioxide show that tetramethyl ammonium iodide and tetraethyl ammonium iodide are the only salts whose molecular weights are smaller than the normal; that the chlorides and bromides of the quarternary ammonium bases and chlorides of the tertiary bases give normal molecular weights and that most of the other salts give molecular weights higher than the normal. There is therefore no relation between the dissociation as calculated from the molecular weight determinations and as calculated from the conductivity. The authors consider this difficulty and come to the conclusion that the discrepancy is to be explained partly by the change of the heat of vaporization and partly by the assumption of a polymerization of the undissociated portion of the salt. In no case does Ostwald's dilution law hold; but a fairly good approximation may be obtained in some cases by means of Rudolphi's formula, or the formula of van 't Hoff. Experiments on the change of the conductivity with the temperature show that the conductivity passes through a maximum with rising temperature and becomes zero at the critical temperature. In view of the fact that the conductivity, so far as is known, always becomes zero at the critical temperature, the authors decide that it must be intimately connected with the liquid state. Since surface tension is one property which disappears at the critical point, it is therefore believed that it is an important factor in determining the question of conductivity. This assumption receives confirmation in the fact that solutions which conduct well have a high surface tension. [This would seem to be merely another way of stating the exploded doctrine that polymerized liquids were necessarily the ones in which conductivity took place.] *W. D. B.*

On inorganic solvents and ionizing media. *P. Walden. Zeit. anorg. Chem.* 29, *371* (*1902*). —Arsenic tribromide has a freezing-point constant 189. While some inorganic substances show an abnormally high molecular weight, most binary salts give molecular weights distinctly lower than the normal, although the variation is less than with arsenic trichloride. Chlor-sulphuric acid, sulphuric acid, and dimethyl sulphate are solvents which have a marked ionizing tendency. *W. D. B.*

The influence of cane-sugar on the conductivities of solution of potassium chloride, hydrogen chloride, and potassium hydroxide, with evidence of salt formation in the last case. *C. J. Martin and O. Masson. Jour. Chem. Soc.* 79, *707* (*1901*). —The addition of sugar to a potassium chloride solution causes a decrease in conductivity which the authors believe may be ascribed wholly to increased viscosity. When sugar is added to hydrogen chloride solutions, a similar result is obtained. With sugar and potassium hydroxide solutions an entirely different result is obtained, which points to the formation of potassium sucrate. The authors conclude that sugar is really to be looked upon as a very weak acid. *W. D. B.*

Dielectricity and Optics

Dielectric constant of paraffin. *W. G. Hormell. Amer. Jour. Sci.* (*4*) 12, *433* (*1901*). —1. For reversals as high as 800,000,000 per second the velocity of electrical disturbances in magnetic and non-magnetic wires of different diameters is the same, thus showing that the magnetic properties of iron are not able to follow such rapid changes.

2. The effective field run of Lecher wires, as far as it can be deduced by means of an argon tube, does not extend more than 3 cm from the wires and the effect of the heavy wave within this region varies approximately inversely as the square of the distance from the wires.

3. The dielectric constant of a given paraffin increases with the density of the paraffin. It increases rapidly from a temperature 20° above the melting-point to a temperature 30° below the melting-point, Among different paraffins the dielectric constant increases as the melting-point of the paraffin increases.

4. The dielectric constant increases as the wave-length decreases. It is greater for short light waves than it is for short electrical waves. Cauchy's formula as a means of obtaining the index of refraction for indefinitely long waves does not meet the experimental facts. *W. D. B.*

Optical activity of certain ethers and esters. *P. A. Guye. Jour. Chem. Soc.* 79, *475* (*1901*). —The author shows that the conclusions reached by McCrae and Patterson in regard to the properties of the acetyl and phenacetyl derivatives of diethyl *d*-tartrate are merely one case of the much more general statement already made by Guye that: "When substitutions of chains or groups of elements are effected in an asymmetric carbon compound in a position sufficiently far removed from the asymmetric carbon atom, the rotatory power is only slightly affected." *W. D. B.*

A spectrophotometric study of the hydrolysis of dilute ferric chloride solu-

tions. *B. E. Moore. Phys. Rev.* 12, *151* (*1901*).—The author draws the following conclusions:—

1. A study of the absorption spectra has proven to be a good method for following the progressive changes in the colloidal formation and will be serviceable whenever any color changes take place.

2. The presence of ionization is detected and the fact that the ions are not completely transparent are shown.

3. Quantitative determinations of the rate of ionization is impossible in the present case, but it is indicated that it is quite possible with some solutions.

4. There is slight direct evidence for the presence of two iron ions so clearly shown by the electrical method. However, the general agreement of the optical with the electrical methods of finding the rate of formation of the final products gives us further, though indirect, reason for accepting Goodwin's theory of the reaction.

5. There is some, but rather slight, evidence for thinking that the molecules of the final product are not all of the same magnitude, i. e., x in the formula

$$(FeO_3H_3)_x$$

may have more than one value for different molecules.

6. The clearing of the solutions and the displacement of the absorption bands toward the violet upon dilution; and the subsequent formation of a much greater absorption band displaced toward the red upon the formation of a more complex molecule, confirm the dynamic considerations. *W. D. B.*

The absorption spectrum of colloidal ferric hydrate. *B. E. Moore. Phys. Rev.* 13, *246* (*1901*).—The absorption curve for Graham's colloidal ferric hydrate lies between the hydrolyzed ferric hydrate and the ferric chloride spectra. The author assumes that Graham's colloidal ferric hydrate contains appreciable quantities of inactive crystalloid hydrate. *W. D. B.*

On the continuous spark spectrum. *B. Eginitis. Comptes rendus,* 134, *1106* (*1902*).—When the spark passes between two metal electrodes there is always a continuous spectrum in addition to the spark spectrum. It seems probable that this continuous spectrum is due to incandescent particles set free at the poles and this is confirmed by the fact that those metals, iron, nickel, cobalt, manganese, which give a large number of incandescent particles are those which give the most intense continuous spectrum. The increase of self-induction decreases the intensity of this continuous spectrum and it also decreases the number of incandescent particles. *W. D. B.*

Spectra of hydrogen and the spectrum of aqueous vapor. *J. Trowbridge. Am. Jour. Sci.* (*4*) 10, *222* (*1900*).—Reviewed (5, 89) from Phil. Mag. [5] 50, 338 (1900).

The spectra of hydrogen and some of its compounds. *J. Trowbridge. Am Jour. Sci.* (*4*) 12, *310* (*1901*).—Reviewed (6, 284) from Phil. Mag. [6] 2, 370 (1901).

SOLUBILITY, ELECTROLYTIC CONDUCTIVITY AND CHEMICAL ACTION IN LIQUID HYDROCYANIC ACID

BY LOUIS KAHLENBERG AND HERMAN SCHLUNDT

The properties of solutions in which liquid hydrocyanic acid is the solvent are of importance in investigating the general problem of nature of solutions. Special interest attaches to the electrical conductivity of solutions in liquid hydrocyanic acid because of the high dielectric constant of this solvent.[1] Some time ago we made preliminary tests[2] of the electrical conductivity of solutions in liquid hydrocyanic acid; but before we could collect a sufficient number of quantitative measurements to warrant a publication of them, M. Centnerszwer,[3] at the request of P. Walden, measured the electrical conductivity of two substances, KI and $S(CH_3)_3I$ in liquid HCN.[4] These solutions

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[1] H. Schlundt, Jour. Phys. Chem. 5, 191 (1901), found the dielectric constant of liquid HCN to be 95.

[2] Jour. Phys. Chem. 5, 162 and 384 (1901).

[3] Zeit. phys. Chem. 39, 220 (1901).

[4] These determinations of M. Centnerszwer were clearly made after the work on the same subject had been begun in this laboratory, and after the article in Jour. Phys. Chem. 5, 159 (1901) had appeared; for in speaking of the desirability of measuring the conductivity of solutions in liquid HCN, M. Centnerszwer (l. c.) mentions Jour. Phys. Chem. 5, 159 (1901) and says:—"Es schien dies um so mehr lohnenswert, als die vor kurzem veröffentlichten Versuche von Schlundt diesem Korper eine Dielektrizitätskonstante von 95 zuschreiben ——." We therefore wish to call attention to the fact on p. 162, Vol. 5, Jour. Phys. Chem., is the statement: "—— an investigation of the conductivity and other properties of salts dissolved in hydrocyanic acid is now in progress in this laboratory," and that the priority claim with which Centnerszwer closes his article: "Da inzwischen die Ausführung ähnlicher Messungen von anderer Seite (L. Kahlenberg, Jour. Phys. Chem. 5, 384 (1901)) angekündigt wurde, so hielt ich es für angemessen, das vorläufig von mir in dieser Frage gesammelte Material hier mitzuteilen" is not justifiable, since announcement of the progress of our measurements was made in the earlier article, Jour. Phys. Chem. 5, 162 (1901). It is of course immaterial for the progress of the science as to who makes the investigations; but in justice to

he found to be better conductors than the corresponding aqueous solutions.

The hydrocyanic acid used was prepared by gradually adding a strong solution of Kahlbaum's best potassium cyanide to a solution of pure sulphuric acid of 1.25 sp gr, which was contained in a retort connected with a reflux condenser, whose temperature was kept at 30° C. The gas was dried by passing it through a series of three large U-tubes filled with fused calcium chloride, and finally through two such tubes containing dry pumice covered with phosphorus pentoxide. These drying tubes were also kept at 30° C. The thoroughly dried gas was then conducted into two glass bottles immersed in an ice-bath. The liquid obtained by thus condensing the gas was colorless and left no residue upon evaporation. Its specific electrical conductivity varied somewhat in the case of different samples that were prepared. The results of these conductivity measurements are given in the tables below. In this connection we desire simply to emphasize that the sample of lowest conducting power had a specific conductivity of 0.473×10^{-5} reciprocal ohms at 0°. This figure is lower than the one (0.496×10^{-5} reciprocal Siemen's units) that M. Centnerszwer[1] obtained in the

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ourselves, we feel that attention should be called to the facts here presented.

It should further be stated, that work on the so-called dissociative power of solvents was published from this laboratory in the Jour. Phys. Chem. 3, 12 (1899), and that the research included a number of inorganic solvents (notably PCl_3, $AsCl_3$, $SnCl_4$) as well as a large number of organic solvents. In that article it was made evident that it was desirable to subject to further investigation the dielectric constants of many solvents. This work was consequently done by H. Schlundt, Jour. Phys. Chem. 5, pp. 157 and 503 (1901). After the publication of the first article on dissociative power of solvents from this laboratory in 1899, Walden took up admirable, extensive researches on the dissociative power of inorganic solvents. He did not measure the dielectric constants of these solvents, nor did he even announce his attention to make such measurements. In view of this and the additional fact that work on the dissociative power of solvents, both inorganic and organic, was done here before Walden began his researches on inorganic solvents, the insinuation of the latter that the studies of H. Schlundt on the dielectric constants of (both organic and inorganic) solvents constitute a continuation of his (Walden's) work is clearly unjust.

[1] l. c.

case of his most carefully prepared sample.

The resistance cell consisted of a graduated and calibrated tube of about 20 cc capacity, closed at one end into which the electrodes were fused. The latter consisted of two rectangular pieces of heavy platinum foil to which were welded, short pieces of platinum rod, the joints being further carefully secured by means of soldering with gold. The electrodes were placed in a vertical position in the tube. To the end of the platinum rods, which projected slightly beyond the glass tube, copper wires about 1 mm in diameter were carefully soldered. These were covered with an excellent rubber insulation, and the soldered joints and the projecting platinum rods were carefully coated with wax. The insulation thus secured was tested and was found to be entirely satisfactory. The copper wires were conducted upward parallel to the glass tube of the cell, being held close to the outer wall of the latter by means of small rubber bands. These copper wires were long enough to allow the cell to be immersed in an ice-bath and at the same time to be connected conveniently with the rheostat and the bridge of the Wheatstone combination. The electrodes were coated with platinum black. The volume of the liquid in the tube could be read to 0.02 cc. The so-called resistance capacity of the cell was determined by means of a *n*/50 KCl solution (whose specific conductivity was taken to be 0.002765 in reciprocal ohms at 25° C) and was found to be 0.4264. The upper end of the resistance cell was securely closed by means of an excellent rubber stopper.

All the conductivity measurements were made at 0° C by means of the well-known method devised by Kohlrausch. In making a series of determinations, the liquid hydrocyanic acid was first run into the cell. And after the conductivity of the pure solvent had been determined, very carefully weighed quantities of the solute were successively introduced into the cell, the volume of the liquid and the conductivity being noted in each case.

The substances employed were all of a high degree of purity, and special care was taken to guard against the presence of moisture.

Besides the quantitative measurements of electrical conductivity of solutions in liquid hydrocyanic acid given in Tables 1 to 24 below, a large number of qualitative solubility and conductivity tests were made, the results of which will now be presented. In this work it was sought to select representative substances of various kinds.

The following substances are readily soluble in liquid hydrocyanic acid, but the resulting solutions are non-electrolytes, their conductivity being no greater than that of the solvent itself, and commonly less: Iodine, water, methyl alcohol, ethyl alcohol, glycerine, ethyl ether, phenol, picric acid, resorcine, menthol, acetic aldehyde, chloral, benzaldehyde, acetone, benzophenone, ethyl iodide, chloroform, propyl nitrate, aceto-acetic ester, benzene, benzil, urea, urethane, aniline, *p*-toluidine, xylidine, camphor, borneol, ethylene cyanide, α-naphthonitrile, β-naphthonitrile, amyl sulphydrate, benzoic acid, cinnamic acid, tin tetrachloride, tin tetrabromide, tin tetraiodide, sulphur monochloride, nicotine, theobromine, caffeine, papaverine, narcotine, cyanine, Hoffmann's violet.

The following are soluble in liquid hydrocyanic acid, but the resulting solutions are very poor[1] conductors of electricity: Acetic acid, cyanacetic acid, trichloracetic acid, trichlorlactic acid, crotonic acid, *o*-nitrobenzoic acid, amidobenzoic acid, pyridine, quinoline, phenylhydrazine, benzamide, acetanilide, diphenyl amine, aconitine, coniine, delphine, arsenic trichloride, antimony trichloride.

The following are soluble in liquid hydrocyanic acid and yield solutions of fair conducting power: Bismuth trichloride, silver nitrate,[2] strychnine, morphine, brucine, atropine, cocaine,

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[1] A fair idea of the extent of the conduction of these substances may be formed from the quantitative measurements that were made in a number of cases — see tables below.

[2] This salt is only sparingly soluble in liquid HCN.

veratrine, acetyl chloride, phosphorus oxychloride, thionyl chloride,[1] sulphuryl chloride.[1]

The following dissolve in liquid hydrocyanic acid and the resulting solutions are good electrolytes: Potassium iodide, potassium sulphocyanate, potassium permanganate, potassium cyanate, platinum potassium cyanide, ferric chloride, antimony pentachloride, hydrochloric acid, sulphur trioxide, sulphuric acid (H_2SO_4), amyl amine, and $NH(C_5H_{11})CS.SNH_3(C_5H_{11})$.[2]

The following substances are sparingly soluble in liquid hydrocyanic acid, the solubility being detected in the case of the salts by the increase of the electrical conductivity of the saturated solution above that of the pure solvent: Sodium chloride, potassium chloride, ammonium chloride, sodium bromide, potassium nitrate, sodium nitrate, potassium sulphate, potassium chromate, borax glass, sodium oleate, potassium platinic chloride, potassium phthalimide, cobaltous chloride, cadmium iodide, mercuric chloride, mercuric bromide, cupric arsenite, cupric arsenate, silver sulphate, silver cyanide, silver cyanate, arsenic triiodide, tartaric acid, camphoric acid, boric acid, biuret, thiourea, quinine, sulphate, brucine chloride.

The substances that were found to be insoluble in liquid hydrocyanic acid are: Calcium chloride, barium chloride, calcium nitrate, strontium nitrate, barium nitrate, lead fluoride, lead bromide, lead iodide, lead chromate, mercurous chloride, mercuric iodide, mercuric oxide, cadmium nitrate, cadmium sulphate, cupric sulphate, cuprous cyanide, cupric oleate, aluminum chloride, stannous chloride, silver chloride, silver cyanide, silver cyanacetate, chromium trioxide, phosphorus pentoxide, iodic acid, oxalic acid anhydride, phthalic acid anhydride, petroleum ether, paraffine, naphthalene, carbon disulphide, iodoform, oleic acid, palmitic acid, stearic acid, cane-sugar, levulose, erythrite, asparagine, phenol-phthaleine, fluoresceine, naphthol green, alloxan, alloxantine.

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[1] The solutions of these substances showed an increase of conductivity with lapse of time. Furthermore, the solutes may have contained traces of moisture in these two cases.

[2] Prepared by treating carbon disulphide with amyl amine.

In the following tables giving the results of quantitative measurements of electrical conductivity of solutions in liquid hydrocyanic acid, *v* represents the volume in liters in which one gram-molecule of solute is contained, and Λ the molecular conductivity of the solutions in reciprocal ohms at 0° C. The specific conductivity of the solvent is given at the head of each table. In computing the values of Λ the conductivity of the solvent has *not* been subtracted. Any one desiring to deduct the conductivity of the pure solvent[1] will find all necessary data for that purpose in the tables.

TABLE 1

$FeCl_3$

(Sp. cond. HCN = 4.07×10^{-5})

v	Λ	*v*	Λ
4.17	111.7	75.5	174.7
7.24	135.5	119.1	181.5
10.78	145.8	431.1	213.7
22.87	152.4	1042.0	259.9
33.12	154.0		

TABLE 2

$SbCl_3$

(Sp. cond. HCN = 1.42×10^{-5})

v	Λ
0.709	0.77
2.269	0.41
3.123	0.40
6.188	0.45
28.08	1.19

TABLE 3

$BiCl_3$

(Sp. cond. HCN = 3.5×10^{-5})

v	Λ
4.526[2]	6.67
7.273	4.89
20.24	3.13
81.31	4.32

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[1] The practice of deducting the conductivity of the pure solvent from that of the solution is, to say the least, open to serious question.

[2] Solution probably slightly supersaturated.

TABLE 4

$AgNO_3$[1]

(Sp. cond. HCN = 1.4×10^{-5})

v	Λ
31.08	16.01
104.8	17.49
392.0	24.71

TABLE 5

Ag_2SO_4[2]

(Sp. cond. HCN = 3.6×10^{-5})

v	Λ
160.7	259.6

TABLE 6

$NH(C_6H_{11})CS.SNH_3(C_6H_{11})$

(Sp. cond. HCN = 4.07×10^{-5})

v	Λ
5.559	83.7
12.70	127.4
23.58	160.3
53.17	194.1
91.37	208.3
163.9	223.3
244.9	227.5
600.0	238.7

TABLE 7

KI

(Sp. cond. HCN = 4.07×10^{-5})

v	Λ
12.04	254.1
27.07	278.0
81.57	300.4
212.6	308.2
452.5	324.8

TABLE 8

KCNO[3]

(Sp. cond. HCN = 1.0×10^{-5})

v	Λ
1262	284.0

TABLE 9

KCNS

(Sp. cond. HCN = 1.0×10^{-5})

v	Λ
1.679	132.1
2.799	169.3
5.826	214.1
22.20	275.1

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[1] The saturated solution of this salt has a sp. cond. of 0.00384. It contains less than 40 grams of $AgNO_3$ per liter.

[2] The sp. cond. of the saturated solution is 0.00797.

[3] The saturated solution has a sp. cond. of 0.00233.

TABLE 10

KNO_3

(Sp. cond. HCN = 0.89×10^{-5})

v	Λ
18.58[1]	236.1
109.6	285.3

TABLE 11

K_2CrO_4[2]

(Sp. cond. HCN = 3.6×10^{-5})

v	Λ
141.0	367.8
1226	670.9

TABLE 12

$KMnO_4$

(Sp. cond. HCN = 1.4×10^{-6})

v	Λ
5.534[3]	142.1
9.890	214.1
23.40	263.5
104.5	310.5
195.0	340.2
1329	511.0

TABLE 13

NH_4Cl

(Sp. cond. HCN = 1.4×10^{-5})

v	Λ
66.15[4]	191.3

TABLE 14

Amyl amine, $(C_5H_{11})NH_2$

(Sp. cond. HCN = 1.4×10^{-5})

(Sp. cond. $C_5H_{11}NH_2 < 1.9 \times 10^{-6}$)

v	Λ
0.2698	8.86
0.4977	24.5
0.954	36.8
2.203	55.1
5.733	78.2
15.80	109.4

TABLE 15

Pyridine, C_5H_5N

(Sp. cond. HCN = 0.752×10^{-5})

(Sp. cond. $C_5H_5N < 2 \times 10^{-6}$)

v	Λ
0.1370	0.038
0.1906	0.106
0.3026	0.190
0.5070	0.320
0.7798	0.344
1.858	0.500
7.455	0.792

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[1] This solution was nearly saturated. A saturated solution was found to have a sp. cond. of 0.1754.

[2] The saturated solution has a sp. cond. of 0.0084.

[3] This solution was nearly saturated. The sp. cond. of the saturated solution is 0.026.

[4] This solution was very nearly saturated.

TABLE 16
Strychnine[1]
(Sp. cond. HCN = 0.473×10^{-5})

v	Λ
33.3	57.6
88.0	87.4
290.2	130.9

TABLE 17
Morphine[2]
(Sp. cond. HCN = 0.665×10^{-5})

v	Λ
155.2	84.2
592.5	99.9

TABLE 18
Acetic acid
(Sp. cond. HCN = 4.07×10^{-6})
(Sp. cond. acetic acid $< 2 \times 10^{-8}$)

v	Λ
0.0883	0.0016
0.1208	0.0045
0.4325	0.0233
1.371	0.0798
10.52	0.623

TABLE 19
Cyanacetic acid[3]
(Sp. cond. HCN = 2.13×10^{-6})

v	Λ
0.2378	0.146
0.4231	0.221
20.14	0.812

TABLE 20
Trichloracetic acid
(Sp. cond. HCN = 1.4×10^{-6})

v	Λ
0.3990	0.068
0.5588	0.087
1.062	0.128
2.402	0.210
6.068	0.359
36.59	1.809

TABLE 21
Trichlorlactic acid[4]
(Sp. cond. HCN = 1.8×10^{-4})

v	Λ
4.617	0.367
48.72	2.42

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[1] The saturated solution has a sp. cond. of 0.00273.

[2] A saturated solution contains nearly 1 gram-molecule in 26 liters and has a sp. cond. of 0.00131.

[3] The sp. cond. of the saturated solution is 6.12×10^{-4}.

[4] The saturated solution has a sp. cond. of 1.31×10^{-4}.

TABLE 22

Crotonic acid[1]

(Sp. cond. HCN = 1.4×10^{-6})

v	Λ
0.8066	0.021
1.567	0.041
2.708	0.071
19.33	0.495

TABLE 23

Hydrochloric acid. (Series 1)

(Sp. cond. 1.05×10^{-5}

v	Λ
5.70[2]	64.4 (after two hours)
8.55	75.8 (initially)[3]
8.55	89.1 (after 75 minutes)
17.10	113.9 (after 2 hours)

Hydrochloric acid. (Series 2)

(Sp. cond. HCN = $0.54 \times 10.^{-5}$)

v	Λ
16.67	14.56 (initially)[3]
16.67	74.3 (after two hours)

Hydrochloric acid. (Series 3)

(Sp. cond. HCN = 0.83×10^{-5})

v	Λ
19.32	39.8 (initially)[3]
19.32	44.9 (after 15 minutes)
19.32	71.9 (after 30 minutes)
19.32	91.6 (after several hours)

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[1] The saturated solution has a sp. cond. of 2.6×10^{-4}.

[2] This solution had a sp. cond. of 0.0113, while a saturated solution showed a sp. cond. of 0.128. This will serve to give an approximate idea as to the extent to which HCl is soluble in HCN.

[3] The determinations marked "initially" were made as soon as the gas was completely absorbed. As the absorption was not performed in the same length of time in the different series the figures are, of course, not really comarable.

TABLE 24

Sulphuric acid

(Sp. cond. HCN = 0.8×10^{-6}

The sulphuric acid used had a sp. gr. of 1.840 at 20° and therefore, according to Winkler's tables, it contained 94.79 percent H_2SO_4, or 77.38 percent SO_3.

Grams of this acid in 100 cc. solution	Sp. cond. $\times 10^3$
0.520	5.75
1.688	9.98
4.584	13.06
10.086	15.03
17.158	16.18
34.459	15.85
62.044	11.60
The sulphuric acid itself	6.37

Sulphuric acid

(Sp. cond. HCN = 1.4×10^{-6}

The sulphuric acid used had a sp. gr. of 1.898 at 20° and therefore, according to Winkler's tables, it contained 90.08 percent H_2SO_4 plus 9.92 percent SO_3, or 83.46 percent SO_3.

Grams of this acid in 100 cc. solution	Sp. cond. $\times 10^3$
1.226	11.53
4.855	18.62
The sulphuric acid itself	15.60

The solutions of known strength of hydrochloric acid in liquid hydrocyanic acid were obtained by filling a gas burette with hydrochloric acid gas thoroughly dried with concentrated sulphuric acid and finally with phosphorus pentoxide, and causing a measured volume of the gas to be absorbed in the liquid hydrocyanic acid contained in the resistance cell above described at 0°. The graduation on the cell permitted the volume of the solution to be read. The gas was forced out of the burette by means of dry mercury, a very fine capillary tube running from the burette to the bottom of the column of liquid hydrocyanic acid in the cell. The gas was displaced very slowly and the absorption was quite complete. Exposure to the air was avoided as much as possible, but it is not claimed that the solution was absolutely free from traces of moisture. Presence of moisture would elevate the conductivity, and therefore the results in Table 23 are probably a trifle too high. It will further be noted that in Series 2 of Table 23, where the HCN had the lowest sp. cond., the solutions also had the lowest conductivity; and furthermore, the solutions in Series 1 had the highest conductivity, and the HCN used in this series also had the highest conductivity. The conductivity of solutions of HCl in liquid HCN moreover increases with lapse of time, showing that the speed of the reaction which goes on can readily be measured. It was not our purpose to investigate the rate of this reaction. We simply desired to ascertain approximately how well solutions of HCl in liquid HCN conduct as compared with corresponding aqueous solutions. The results are entirely sufficient to show at a glance that HCl in liquid HCN is a much poorer conductor than HCl in water.

No attempt was made to prepare a sulphuric acid corresponding exactly to the formula H_2SO_4, that is to say one that contained 81.63 percent SO_3. In the one case (Table 24) the sulphuric acid dissolved in liquid HCN contained 77.38 percent SO_3, in the other case 83.46 percent SO_3. To compute molecular conductivities in these cases was not attempted. The specific conductivities given in the table are sufficient to indicate that sulphuric acid in liquid HCN is a much poorer electrolyte than comparable solutions of sulphuric acid in water.

An inspection of Tables 1 to 24 shows that the potassium salts investigated, namely, KI, KNO_3, KCNS, $KMnO_4$, K_2CrO_4, KCNO, (Tables 7 to 12) are most excellent electrolytes when dissolved in liquid HCN. KI and KNO_3 have a molecular conductivity in liquid HCN which is over 3.5 times as great as that of the corresponding aqueous solutions at the same temperature.[1] The conductivity of aqueous solutions of KCNS, $KMnO_4$, K_2CrO_4, and KCNO have apparently not been investigated at 0°; but the conductivity of these salts in liquid HCN even at 0° exceeds

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[1] For comparison see the mol. con. of these salts in aqueous solutions at 0° in Jour. Phys. Chem. 5, 348 (1901).

their conductivity in aqueous solutions at 25°.[1] The conductivity of NH_4Cl (Table 13) also exceeds that of corresponding aqueous solutions at 18°; and the same is true of Ag_2SO_4.[2] $NH(C_5H_{11})CS.SNH_3(C_5H_{11})$, Table 6, also has a high conductivity in liquid HCN; though the conductivity of aqueous solutions of this salt has apparently not been determined, it would seem that the figures would probably not reach the magnitude of those in Table 6.

The high conductivity of the solutions mentioned in the preceding paragraph, as compared with the conductivity of the corresponding aqueous solutions, might tempt one to draw the conclusion that the Nernst-Thomson rule is indeed verified in case of the solvent, liquid HCN, inasmuch as its high dielectric constant would lead one to expect a conductivity exceeding that of comparable aqueous solutions.[3] But all such ideas are at once dispelled by a further consideration of the remaining substances in the foregoing tables. So it appears at a glance that acids (Tables 18 to 24) dissolved in liquid HCN are incomparably poorer electrolytes than the corresponding aqueous solutions.[4] Silver nitrate (Table 4) in liquid HCN conducts only about one-fourth as well as in aqueous solutions of the same strength at 0°.[5] Ferric chloride in liquid HCN (Table 1) conducts less than half as well as the corresponding aqueous solutions of this salt at 25°;[6] so that it seems likely that the aqueous solutions of this salt at 0° will conduct better than those in liquid HCN. Again $SbCl_3$ and $BiCl_3$ (Tables 2 and 3) are poor electrolytes in HCN; a comparison with aqueous solutions is of course impossible in these cases as the salts are decomposed

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[1] Compare Kohlrausch and Holborn. Leitvermögen d. Elektrolyte.

[2] Compare tables in Ostwald's Lehrbuch d. allgem. Chem. 2, 756, 771.

[3] M. Centnerszwer (l. c.) found KI and $S(CH_3)_3I$ to conduct better in liquid HCN than in water and drew such a conclusion.

[4] While the conductivity of these acids in aqueous solutions at 0° has apparently not been determined, the values in liquid HCN are so very low as to admit of this conclusion. In fact, if the conductivity of the pure HCN were subtracted from that of the acetic acid solutions the remainders would in several cases be negative in sign.

[5] Compare Jour. Phys. Chem. 5, 348 (1901).

[6] Compare Goodwin. Zeit. phys. Chem. 21, 3 (1896).

into oxychlorides by water. The relatively high conductivity of amyl amine, strychnine and morphine in liquid HCN (Tables 14, 16, 17) is worthy of note. These bases undoubtedly react with the liquid HCN, forming salts that dissolve in excess of the solvent;[1] the action in the case of amyl amine is violent in character, being accompanied with liberation of much heat. Pyridine (Table 15) forms very poorly conducting solutions, though it probably also unites chemically with the solvent.

The facts are then, that while some salts dissolved in liquid HCN conduct electricity better than in water, many others conduct much poorer than in their corresponding aqueous solutions. The acids as a class illustrate this in an especially striking manner; for while their aqueous solutions are most excellent electrolytes, their solutions in liquid HCN are only moderately good electrolytes in the case of HCl and H_2SO_4, while the solutions of the organic acids are exceedingly poor conductors of electricity. In the face of these facts, the Nernst-Thomson rule can clearly not be considered as substantiated by the conductivity of solutions in liquid HCN.

A comparison with the conductivity of liquid ammonia solutions shows that KNO_3, NH_4Cl, and KI are better electrolytes in liquid HCN than in liquid ammonia;[2] on the other hand, $AgNO_3$ is a much better conductor in the latter solvent than in the former. Solutions of KI and KCNS in liquid HCN are much better electrolytes than the corresponding solutions in liquid SO_2.[3]

While in some cases, like KI and KNO_3 (Tables 7 and 10), the molecular conductivity increases but slightly with the dilution, as it does in the corresponding aqueous solutions, in other cases like KCNS, $KMnO_4$ and K_2CrO_4 (Tables 9, 12 and 11) this increase is very considerable, exceeding by far that in the aqueous solutions. These statements hold even if the conduc-

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[1] This is the secret of the solubility of so many of the alkaloids in liquid HCN.

[2] Compare Cady. Jour. Phys. Chem. 1, 712 (1897); also Franklin and Kraus. Amer. Chem. Jour. 24, 87 (1900).

[3] Compare Walden and Centnerszwer. Zeit. anorg. Chem. 30, 168 (1902).

tivity of the liquid HCN used as solvent be deducted from the conductivity of the solutions, as is commonly done in the case of aqueous solutions. Again, the molecular conductivity of $AgNO_3$ (Table 4) changes but slightly with the dilution, which is also true of aqueous solutions of this salt; although as has been remarked, the latter are much better conductors than the HCN solutions. In the case of $BiCl_3$ (Table 3) the molecular conductivity passes through a minimum; or, if the conductivity of the solvent be deducted, the molecular conductivity would decrease as the concentration decreases.

When the results of the conductivity measurements of the solutions in liquid hydrocyanic acid are regarded in connection with the conductivity of aqueous solutions, liquid ammonia solutions, solutions in liquid sulphur dioxide, etc., it becomes evident that the conductivity of a solution is not determined by the dielectric constant of the solvent, its state of polymerization or its spare valences, but rather by the specific nature of the compound formed when solute and solvent act on each other to form the solution.

Only a very limited number of tests of chemical action in solutions in liquid HCN were made. Metallic sodium and metallic potassium act upon thoroughly dry liquid HCN, forming hydrogen and the cyanides of the metals; the latter are soon coated over with the white salts which are practically insoluble in liquid HCN. Metallic magnesium and sodium carbonate are not attacked by liquid HCN. A solution of SO_3 in HCN, though it conducted well (having a sp. cond. of 0.0066), nevertheless did *not* act in the least on dry magnesium, zinc, calcium carbonate or potassium carbonate. Fuming sulphuric acid of sp gr 1.898 at 20°, when dissolved in liquid HCN[1] attacks magnesium, zinc (amalgamated as well as plain), and potassium carbonate, but does not act on aluminum, cadmium, iron, copper, silver, lead, platinum, or calcium carbonate. But when cadmium is placed in the solution in contact with platinum, hydrogen is evolved on the platinum. On the other hand, iron, aluminum,

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[1] The solutions used were those in Table 24.

copper, lead and silver are not attacked by the solution even when in contact with platinum.

Hydrochloric acid solutions in liquid HCN attack magnesium and also zinc (amalgamated as well as plain). Cadmium is also attacked, but very slowly. Zinc or cadmium when placed in contact with platinum in the solution, cause hydrogen to be evolved mainly on the platinum — as in the corresponding aqueous solution. Hydrochloric acid dissolved in liquid HCN does *not* attack aluminum, iron, lead, copper, silver, platinum, sodium carbonate, sodium bicarbonate, calcium carbonate or barium carbonate.

Solutions of trichloracetic acid in liquid HCN attack metallic magnesium and sodium carbonate, but *not* calcium carbonate or zinc, even when the latter is in contact with platinum. Yet Table 20 above shows that trichloracetic acid in liquid HCN is an electrolyte, though to be sure not a very good one. Trichlorlactic acid dissolved in liquid HCN does not attack magnesium of zinc, while cyanacetic acid in solution in liquid HCN does act on magnesium. Phosphorus trichloride, thionyl chloride, sulphuryl chloride and amyl amine react violently with liquid HCN.

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Madison, Wis.,
July, 1902.

THE EXPANSION OF A GAS INTO A VACUUM AND THE KINETIC THEORY OF GASES[1]

BY PETER FIREMAN

It is a fundamental fact that when a gas expands into a vacuum there is, roughly speaking, no evolution or absorption of heat in the whole body of the gas. But while the passing of a gas into an empty vessel is not accompanied by any change in the total quantity of heat in the gas, a change in the distribution of the heat takes place. If the experiment is carried out[2] with the aid of two metallic vessels of equal capacity communicating by means of a tube provided with a stop-cock, and if one vessel is filled with a gas under considerable pressure while the other is vacuous, then on opening the stop-cock and allowing the gas to pass into the empty vessel until equilibrium is established, we observe a considerable rise of temperature in the vessel which was vacuous and a nearly equal fall in the other.

What is the cause of this simultaneous rise and fall of temperature, a rise and fall which seem to compensate one another? An attempt to give a clear answer to this question is the object of the present paper.

Let us dwell for a little while on the important theoretical bearings of the experiment described. In the first place, it at once leads to the thermodynamical principle that the energy of a gas is independent of its volume. In the second place, the fact that there is no change in the total energy when a gas expands into a vacuum clearly shows that there is no repulsive force between its molecules. For if there were a repulsive force the expansion would involve a decrease of potential energy, which decrease would have to be made good by the increase of kinetic energy, by an absolute increase of the temperature of the entire mass of the gas. Since this is not the case, it follows that there

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[1] Read before the Chemical Section of the American Association for the Advancement of Science, Pittsburg, July 2, 1902.

[2] J. P. Joule. Phil. Mag. May, 1845, p. 377.

is no repulsive force between the molecules of the gases. The proof of the absence of a repulsive force in the gases is an indirect support of the kinetic theory of gases, the only other doctrine regarding the nature of the gaseous state. According to this theory, the tendency of a gas to expand and to fill any space that is assigned to it is not due to a repulsive force between the molecules of the gas, but to the kinetic energy of the moving molecules under the influence of heat.

In the third place, a most accurate study of the energy changes when a gas expands without doing work supplies the experimental basis for one of the corrections made in the gas equation by van der Waals and embodied in the so-called van der Waals equation. Joule and Thomson[1] on causing gases to expand "from a high pressure vessel through a porous plug" found a slight loss of heat. This loss leads to the assumption that there is an attractive force between the molecules and that the loss of heat is due to the work done in overcoming this attraction. This attraction is taken into account in the van der Waals equation.

I have dwelt at some length on the theoretical bearings of the phenomenon under consideration in order to emphasize more the importance of finding an adequate interpretation of it.

The phenomenon is this: When a gas passes from one vessel into another which is vacuous, there results an increase of heat in the empty vessel and a decrease in the other. Why? A plausible explanation would appear to be this: As soon as some of the gas has entered the vacuous vessel the rest of the gas does work on it, causing the rise of temperature in one vessel and the lowering in the other. But this explanation is very vague, and if not properly qualified, can be refuted as follows: You start with the molecules at a given temperature, i. e., with a certain mean kinetic energy; you start with the molecules which are perfectly elastic bodies. Now what can be the result of collisions of that portion of the molecules which first entered the empty vessel and the remaining portion which is pressing after and on

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[1] William Thomson's Mathematical and Physical Papers, Vol. I., Article 49, p. 333.

the former? The molecules of both portions have the same average velocity. Nothing else can result than an exchange of a certain mean kinetic energy with the same mean kinetic energy. Hence in consequence of the increase of volume, only the free mean path of the molecules will increase, which has nothing to do with the magnitude of the kinetic energy, with the magnitude of the heat.

The proper explanation, without bringing in any notions which themselves require elucidation, can be, in my opinion, found as follows: Consider the molecules of the gas as they are ready to pass into the vacuous vessel. They arrive with various degrees of velocity. Consider, first, a swift molecule. In the empty vessel it will evidently retain its high velocity. Next, consider a slow molecule. Before it will have made much progress it will be overtaken by a fast one and exchange velocities with the latter, according to the law of impacts of elastic bodies; it will continue on its way, but with a high velocity. And so with all the molecules or, at least, with the greatest part of the molecules which enter the empty vessel; they will either have possessed a high velocity and retain it or acquire it as explained. The result will be a congregation of swift molecules in the vessel which was vacuous and a lagging behind of the slow ones in the vessel which was filled with the gas at the beginning.

We have here as it were a separation of molecules with high velocities from those with low velocities. Hence a rise of temperature in one vessel and a fall in the other.

But this result is only possible owing to the fact that in the body of a gas at a given temperature there are molecules with widely different velocities. If the gas molecules in a given vessel at a constant temperature moved all with the same velocity then the expansion of a gas into a vacuum could not bring about a new distribution of the heat in the body of the gas.

Thus the experiment of the expansion of a gas into a vacuum throws further light on the kinetic theory of gases, corroborating the view that the molecules in a closed vessel at a constant temperature move with various degrees of velocity.

Further, in the light of the above reasoning, the cold produced by the escaping of a gas from under a high pressure into the atmosphere is due to the swift molecules rushing away far into space and the slow ones lagging behind.

ON THE DISPLACEMENT OF EQUILIBRIUM

BY PAUL SAUREL

It is well known that among the consequences of the phase rule are the following theorems: The state of equilibrium of an invariant system is completely determined if its entropy and its volume be given; the state of equilibrium of a univariant system is completely determined if any one of the three pairs of variables: entropy and volume, temperature and volume, entropy and pressure be given; and, finally, the state of equilibrium of a bivariant or multivariant system is completely determined if any one of the four pairs of variables: entropy and volume, temperature and volume, entropy and pressure, temperature and pressure be given. The object of the present note is to show that to each of the above pairs of variables there correspond two theorems relating to the displacement of equilibrium.

As is well known, the two fundamental principles of thermodynamics may be expressed by the following relations:

$$dE = dQ - \Pi dV, \qquad (1)$$

$$dQ \leqq T dH, \qquad (2)$$

in which E, H, V, T, Π denote respectively the energy, entropy, volume, temperature, and pressure of the system, and dQ denotes the heat absorbed during a small change. In the second of the above relations the sign of equality applies to reversible changes while the sign of inequality applies to real changes. As a consequence of the above relations we obtain at once

$$dE \leqq T dH - \Pi dV. \qquad (3)$$

If we define the three functions: F, the free energy, G, the heat function, and Φ, the thermodynamic potential, by means of the equations

$$F = E - TH,$$

$$G = E + \Pi V,$$

$$\Phi = E - TH + \Pi V,$$

we obtain from 3 without difficulty

$$dF \leqq -HdT - \Pi dV, \tag{4}$$

$$dG \leqq \quad TdH + Vd\Pi, \tag{5}$$

$$d\Phi \leqq -HdT + Vd\Pi. \tag{6}$$

From 3, 4, 5, 6 it follows that the condition of stable equilibrium can be expressed in any one of the four forms:

$$(\Delta E)_{H,V} > 0, \tag{7}$$

$$(\Delta F)_{T,V} > 0, \tag{8}$$

$$(\Delta G)_{H,\Pi} > 0, \tag{9}$$

$$(\Delta \Phi)_{T,\Pi} > 0. \tag{10}$$

In each of these inequalities the quantity in parenthesis denotes the variation due to a virtual change during which the mass of the system and the variables written as subscripts are kept constant.

Let us denote by M_{ij} the mass of the j-th component which is present in the i-th phase, and let us denote by r the number of phases and by n the number of independent components. Then inequality 7 can be written in the form

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial E}{\partial M_{ij}}\delta M_{ij} + \tfrac{1}{2}\sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 E}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}\delta M_{ik} > 0. \tag{11}$$

If all the virtual changes are reversible we may replace each variation δM_{ij} by its negative; we thus obtain

$$-\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial E}{\partial M_{ij}}\delta M_{ij} + \tfrac{1}{2}\sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 E}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}\delta M_{ik} > 0. \tag{12}$$

From 11 and 12 it follows without difficulty that

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial E}{\partial M_{ij}}\delta M_{ij} = 0, \quad \sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 E}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}\delta M_{ik} > 0. \tag{13}$$

In like manner we can replace 8, 9 and 10 by the following pairs of conditions:

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial F}{\partial M_{ij}}\delta M_{ij}=0, \quad \sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 F}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}\delta M_{ik}>0; \quad (14)$$

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial G}{\partial M_{ij}}\delta M_{ij}=0, \quad \sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 G}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}\delta M_{ik}>0; \quad (15)$$

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial \Phi}{\partial M_{ij}}\delta M_{ij}=0, \quad \sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 \Phi}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}\delta M_{ik}>0. \quad (16)$$

The first relation in each of the four pairs of relations 13, 14, 15 and 16 may be called the condition of equilibrium; the condition of equilibrium serves to establish the various theorems included in the phase rule. The second relation in each of the above pairs of relations may be called the condition of stability. Corresponding to each form of the condition of stability there are two theorems relating to the displacement of equilibrium. These theorems we shall now deduce.

Consider a system which is in stable equilibrium under a volume V and with an entropy H. Conditions 13 are satisfied. If we increase the entropy and the volume by dH and dV, a new state of equilibrium establishes itself. In passing from the first state of equilibrium to the second the mass M_{ij} receives an increment dM_{ij}. The first of conditions 13 must be satisfied when we replace H, V, M_{ij} by $H + dH$, $V + dV$, $M_{ij} + dM_{ij}$. Making these substitutions we obtain without difficulty

$$dH\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial^2 E}{\partial H\partial M_{ij}}\delta M_{ij}+dV\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial^2 E}{\partial V\partial M_{ij}}\delta M_{ij}$$
$$+\sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 E}{\partial M_{ij}\partial M_{ik}}\delta M_{ij}dM_{ik}=0. \quad (17)$$

If we refer to equation 3 we find that when the system is in equilibrium

$$\frac{\partial E}{\partial H}=T, \qquad \frac{\partial E}{\partial V}=-\Pi. \qquad (18)$$

From these equations it follows that

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\partial^2 E}{\partial H \partial M_{ij}}\delta M_{ij} = \delta T, \quad \sum_{i=1}^{r}\sum_{j=1}^{n}\frac{\delta^2 E}{\partial V \partial M_{ij}}\delta M_{ij} = -\delta \Pi, \qquad (19)$$

in which δT and $\delta \Pi$ denote the changes which would have occurred in the temperature and the pressure, if, with constant entropy and under constant volume, the masses M_{ij} alone had varied. If we suppose that $\delta M_{ij} = dM_{ij}$, in other words, if we suppose that the virtual changes in the masses are the same as the actual changes which occur when the system passes from one state of equilibrium to an adjoining state of equilibrium, it follows from the second of conditions 13 that the third term in equation 17 is positive. Equation 17 can accordingly be written in the form

$$\delta T . dH - \delta \Pi . dV < 0. \qquad (I.)$$

Similar reasoning applied to conditions 14, 15 and 16 yields without difficulty the following inequalities:

$$-\delta H . dT - \delta \Pi . \delta V < 0, \qquad (II.)$$

$$\delta T . dH + \delta V . d\Pi < 0, \qquad (III.)$$

$$-\delta H . dT + \delta V . d\Pi < 0. \qquad (IV.)$$

Inequality I. applies to all systems which are in stable equilibrium under a given volume and with a given entropy; it therefore applies to all systems whose variance is equal to or greater than zero. Inequality II. applies to all systems which are in stable equilibrium at a given temperature and under a given volume; it therefore applies to all systems whose variance is equal to or greater than one. Inequality III. applies to all systems which are in stable equilibrium under a given pressure and with a given entropy; it therefore applies to all systems whose variance is equal to or greater than one. Finally, inequality IV. applies to all systems which are in stable equilibrium at a given temperature and under a given pressure; it therefore applies to all systems whose variance is equal to or greater than two.

From each of the inequalities I., II., III. and IV. we can obtain without difficulty two theorems relating to the displacement of equilibrium. Thus from I. we get the two pairs of conditions:

$$\begin{array}{lll} dV = 0, & \delta T \cdot dH < 0\,; & \text{I.}(a) \\ dH = 0, & \delta \Pi \cdot dV > 0. & \text{I.}(b) \end{array}$$

In like manner from II., III. and IV. we get the pairs of conditions

$$\begin{array}{lll} dV = 0, & \delta H \cdot dT > 0\,; & \text{II.}(a) \\ dT = 0, & \delta \Pi \cdot dV > 0\,; & \text{II.}(b) \\[1ex] d\Pi = 0, & \delta T \cdot dH < 0\,; & \text{III.}(a) \\ dH = 0, & \delta V \cdot d\Pi < 0\,; & \text{III.}(b) \\[1ex] d\Pi = 0, & \delta H \cdot dT > 0\,; & \text{IV.}(a) \\ dT = 0, & \delta V \cdot d\Pi < 0. & \text{IV.}(b) \end{array}$$

These eight pairs of inequalities fall naturally into the four following groups:

$$\begin{array}{llll} & dV = 0, & & \\ \text{or} & & \delta H \cdot dT > 0\,; & \text{V.} \\ & d\Pi = 0, & & \\[1ex] & dV = 0, & & \\ \text{or} & & \delta T \cdot dH < 0\,; & \text{VI.} \\ & d\Pi = 0, & & \\[1ex] & dH = 0, & & \\ \text{or} & & \delta V \cdot d\Pi < 0\,; & \text{VII.} \\ & dT = 0, & & \\[1ex] & dH = 0, & & \\ \text{or} & & \delta \Pi \cdot dV > 0. & \text{VIII.} \\ & dT = 0, & & \end{array}$$

Conditions V. stated in words give us van 't Hoff's theorem: If, under constant volume (or under constant pressure) the temperature of a system in equilibrium be increased, there results a change in the masses M_{ij}, or as we shall say, a change in the state of the system, which, if it were to take place under constant volume (or under constant pressure) and at constant temperature, would have for effect an increase of entropy. Similarly, if the temperature be lowered the resulting change in the state of the system would correspond to a decrease of entropy.

Conditions VII. stated in words give us Le Chatelier's theorem: If, with constant entropy (or at constant temperature) the pressure of a system in equilibrium be increased, there results a change in the state of the system which, if it were to take place with constant entropy (or at constant temperature) and under constant pressure, would have for effect a decrease in volume. Similarly, if the pressure be decreased the resulting change in the state of the system would correspond to an increase in volume.

Conditions VI. give us the following theorem which is analogous to van't Hoff's theorem: If, under constant volume (or under constant pressure) the entropy of a system in equilibrium be increased, there results a change in the state of the system which, if it were to take place under constant volume (or under constant pressure) and with constant entropy, would have for effect a decrease in temperature. Similarly, if the entropy be decreased the resulting change in the state of the system would correspond to an increase in temperature.

Conditions VIII. give us the following theorem which is analogous to Le Chatelier's theorem: If, with constant entropy (or at constant temperature) the volume of a system in equilibrium be increased, there results a change in the state of the system which, if it were to take place with constant entropy (or at constant temperature) and under constant volume, would have for effect an increase in pressure. Similarly, if the volume be decreased the resulting change in the state of the system would correspond to a decrease in pressure.

It may not be out of place to recall briefly the principal dates in the history of the above theorems. In 1884 van't Hoff gave[1] the theorem which is expressed by conditions II.(*a*), and in the same year Le Chatelier gave,[2] without demonstration, a theorem which was avowedly a generalization of van't Hoff's theorem and which in fact is equivalent to the theorems expressed by conditions IV.(*a*) and IV.(*b*). A few years later

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[1] Études de Dynamique, p. 161 (1884).

[2] Compt. rend. 99, 786 (1884).

Le Chatelier[1] gave to the theorems enunciated by him a somewhat more definite form and asserted[2] that the theorems concerning the displacement of equilibrium are consequences of the stability of the equilibrium of a system. In 1890 Duhem made good this assertion by showing[3] that the theorems corresponding to conditions II.(*a*), IV.(*a*) and IV.(*b*) are consequences of the following theorems of Gibbs:[4] when a system is in stable equilibrium at a given temperature and under a given volume the free energy has a minimum value; when a system is in stable equilibrium at a given temperature and under a given pressure the thermodynamic potential has a minimum value. In 1891 Le Chatelier and Mouret gave a demonstration[5] of inequality IV. and deduced from it the two theorems IV.(*a*) and IV.(*b*). In 1897 Duhem gave[6] the theorem which corresponds to conditions II.(*b*). Finally, in 1897, Planck gave[7] an equation analogous to equation 17 without, however, deducing the theorems IV.(*a*) and IV.(*b*) which are consequences of it. The demonstration which we have just given of inequalities I., II., III. and IV. is identical with the demonstration which we have previously given[8] of inequality IV.

Since the above was written there has appeared a note by Jouguet (Comptes rendus, 134, 1418 (1902)) in which is given a demonstration of theorems I.(*a*), I.(*b*), III.(*a*) and III(*b*). This demonstration is in all essentials the same as the one given above.

New York, June 14, 1902.

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[1] Recherches expérimentales et théoriques sur les Equilibres chimiques, pp. 48, 210 (1888).

[2] Recherches expérimentales et théoriques sur les Equilibres chimiques, p. 58 (1888).

[3] Annales de la Faculté de Toulouse, 4, N; (1890). Cf. Traité élémentaire de Mécanique chimique, 1, 145, 184 (1897).

[4] On the Equilibrium of Heterogeneous Substances, pp. 145, 147.

[5] Les Equilibres chimiques, p. 29 (1891). Extrait de la Revue Générale des Sciences, 28 février et 15 mars, 1891.

[6] Traité élémentaire de Mécanique chimique, 1, 153 (1897).

[7] Thermodynamik, p. 176 (1897).

[8] Jour. Phys. Chem. 5, 61 (1901).

ON THE CRITICAL STATE OF A ONE-COMPONENT SYSTEM

BY PAUL SAUREL

It does not seem to be generally known that Gibbs, in his memoir on the energy surface,[1] has given in outline a very elegant theory of the critical state of a one-component system and of the continuity of the liquid and gaseous states. In particular, he has deduced four pairs of conditions which are satisfied at the critical point. One of these pairs of conditions when interpreted geometrically shows that the critical isotherm has a point of inflexion at the critical point. This theorem had previously been given by van der Waals[2] as a consequence of the equation of state to which he had been led by molecular considerations.

The conditions given by Gibbs in this first memoir do not readily lend themselves to further developments. But in the great memoir, published a few years later, Gibbs gives a general discussion of the critical state of a two-phase system from which he deduces the general conditions which must be satisfied by a critical phase.[3] These conditions lend themselves more readily to analytical treatment than those first given.

In the present article we give a demonstration of the conditions which are satisfied by a one-component system in a critical state, and from them we deduce the most important of the theorems relating to the critical state. In particular, it will be found that most of the theorems which Duhem, in his very complete discussion of the critical state,[4] has found it necessary

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[1] A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. Transactions of the Connecticut Academy of Arts and Sciences, 2, (2) 382 (1873).

[2] Over de Continuiteit van den Gas-en Vloeistoftoestand, p. 84. Leiden (1873).

[3] On the Equilibrium of Heterogeneous Substances, p. 191.

[4] Traité élémentaire de Mécanique chimique, 2, 147-157 (1898).

to assume as hypotheses, are consequences of the fundamental assumptions of Gibbs.

The assumption which lies at the basis of Gibbs' discussion is that, for a given substance, there exists a one-valued analytic function ϵ of the two variables η and v such that if η and v denote the entropy and the volume of the unit of mass of a homogeneous phase of the substance in equilibrium, ϵ is equal to the energy of the unit of mass of the homogeneous phase. This hypothesis is one form, and perhaps the simplest, of the so-called principle of continuity. If we measure η, v and ϵ along three rectangular axes in space, the surface determined by the simultaneous values of η, v and ϵ is Gibbs' energy surface.

From the definition of the function ϵ, it follows that, in passing from one point of the energy surface to an adjacent point on the surface, we have

$$d\epsilon = \frac{\partial\epsilon}{\partial\eta}\, d\eta + \frac{\partial\epsilon}{\partial v}\, dv. \tag{1}$$

If we compare this equation with the thermodynamic equation which applies to an infinitely small reversible change, viz.:

$$d\epsilon = \mathrm{T}d\eta - \Pi dv, \tag{2}$$

in which T and Π denote the temperature and the pressure, it follows that when a homogeneous phase is in equilibrium

$$\begin{aligned} \mathrm{T} &= \frac{\partial\epsilon}{\partial\eta}, \\ -\Pi &= \frac{\partial\epsilon}{\partial v}. \end{aligned} \tag{3}$$

The condition that the equilibrium be stable requires that, in any virtual change from a state of a stable equilibrium, we should have

$$\delta\epsilon > \mathrm{T}\delta\eta - \Pi\delta v, \tag{4}$$

in which the variations are to be construed strictly. On the other hand, the definition of the function ϵ requires that, in passing from one point of the energy surface to an adjacent point of the surface, we should have

$$\delta\epsilon = \frac{\partial\epsilon}{\partial\eta}\delta\eta + \frac{\partial\epsilon}{\partial v}\delta v$$
$$+ \tfrac{1}{2}\left\{ \frac{\partial^2\epsilon}{\partial\eta^2}\delta\eta^2 + 2\frac{\partial^2\epsilon}{\partial\eta\partial v}\delta\eta\delta v + \frac{\partial^2\epsilon}{\partial v^2}\delta v^2 \right\} + \ldots. \qquad (5)$$

From 3, 4 and 5 it follows without difficulty that when a homogeneous phase is in stable equilibrium, the quantity

$$\frac{\partial^2\epsilon}{\partial\eta^2}\delta\eta^2 + 2\frac{\partial^2\epsilon}{\partial\eta\partial v}\delta\eta\delta v + \frac{\partial^2\epsilon}{\partial v^2}\delta v^2$$

is positive for all values of $\delta\eta$ and δv. The well-known conditions that this be so, are that

$$\begin{vmatrix} \dfrac{\partial^2\epsilon}{\partial\eta^2}, & \dfrac{\partial^2\epsilon}{\partial\eta\partial v} \\ \dfrac{\partial^2\epsilon}{\partial\eta\partial v}, & \dfrac{\partial^2\epsilon}{\partial v^2} \end{vmatrix} > 0, \qquad (6)$$

$$\frac{\partial^2\epsilon}{\partial\eta^2} > 0. \qquad (7)$$

As a consequence of 6 and 7 we obtain without difficulty

$$\frac{\partial^2\epsilon}{\partial v^2} > 0. \qquad (8)$$

Equations 3 may be called the conditions of equilibrium while inequalities 6, 7, 8 may be called the conditions of stability. If we suppose the ϵ-axis to be drawn upward, conditions 6 and 7 may be expressed geometrically by saying that at a point of the energy surface which corresponds to a homogeneous phase in stable equilibrium the surface is convex in every direction and this convexity is turned downward.

Let us consider next the equilibrium of a system of two phases formed from a single component. To each phase in equilibrium there corresponds a point of the energy surface whose coordinates are respectively the specific energy, the specific entropy and the specific volume of the phase. If we denote quantities referring to these two points by the subscripts 1 and 2 respectively, it can be shown that when the system of two phases is in equilibrium, the following conditions are satisfied:

$$\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 = \left(\frac{\partial\epsilon}{\partial\eta}\right)_2, \tag{9}$$

$$\left(\frac{\partial\epsilon}{\partial v}\right)_1 = \left(\frac{\partial\epsilon}{\partial v}\right)_2, \tag{10}$$

$$\epsilon_1 - \eta_1\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 - v_1\left(\frac{\partial\epsilon}{\partial v}\right)_1 = \epsilon_2 - \eta_2\left(\frac{\partial\epsilon}{\partial\eta}\right)_2 - v_2\left(\frac{\partial\epsilon}{\partial v}\right)_2. \tag{11}$$

These conditions may be expressed geometrically by saying that the tangent planes at the points 1 and 2 of the energy surface coincide. To show this we observe that the equation of the tangent plane at the point 1 can be obtained by writing the subscript 1 after each of the quantities in equation 1 and then replacing $d\epsilon_1$, $d\eta_1$, dv_1 by $\epsilon - \epsilon_1$, $\eta - \eta_1$, $v - v_1$. The equation of the tangent plane at the point 1 is accordingly

$$\epsilon - \epsilon_1 = \left(\frac{\partial\epsilon}{\partial\eta}\right)_1(\eta - \eta_1) + \left(\frac{\partial\epsilon}{\partial v}\right)_1(v - v_1) \tag{12}$$

or

$$\epsilon - \eta\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 - v\left(\frac{\partial\epsilon}{\partial v}\right)_1 = \epsilon_1 - \eta_1\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 - v_1\left(\frac{\partial\epsilon}{\partial v}\right)_1. \tag{13}$$

From equations 9, 10, 11 and 13 it follows at once that the tangent planes at the points 1 and 2 coincide.

If we denote by ϵ, η and v the specific energy, the specific entropy and the specific volume of the system, by M_1 and M_2 the masses of the two phases and by M the mass of the system, we have the following relations

$$M = M_1 + M_2,$$
$$M\epsilon = M_1\epsilon_1 + M_2\epsilon_2,$$
$$M\eta = M_1\eta_1 + M_2\eta_2,$$
$$Mv = M_1v_1 + M_2v_2,$$

from which we get

$$\epsilon = \frac{M_1\epsilon_1 + M_2\epsilon_2}{M_1 + M_2},$$

$$\eta = \frac{M_1\eta_1 + M_2\eta_2}{M_1 + M_2},$$

$$v = \frac{M_1v_1 + M_2v_2}{M_1 + M_2}.$$

From these equations it follows at once that the point which represents the specific energy, entropy and volume of the system of two phases lies on the straight line which joins the points 1 and 2 and divides this line into two segments which are to each other inversely as the masses of the two phases. From this it follows further that if the two-phase system is in equilibrium at a given temperature and under a given pressure, it admits of a continuous series of states of equilibrium at that temperature and under that pressure; throughout this series of states of equilibrium the specific entropy and the specific volume of each phase remains unchanged, while the masses of the phases, and the specific energy, entropy and volume of the system change.

Let us suppose that the system undergoes a reversible change such that the representative point moves from the point 1 to the point 2 along the straight line joining them. Throughout this change the temperature and the pressure remain constant; the thermodynamic equation 2 accordingly gives us

$$\epsilon_2 - \epsilon_1 = T(\eta_2 - \eta_1) - \Pi(v_2 - v_1). \qquad (14)$$

Instead of moving from the point 1 to the point 2 along the straight line joining them let us move from one point to the other along some curve of the energy surface. Then, by equation 1 we have

$$\epsilon_2 - \epsilon_1 = \int_1^2 \left(\frac{\partial \epsilon}{\partial \eta} d\eta + \frac{\partial \epsilon}{\partial v} dv \right). \qquad (15)$$

If, in particular, we move along a curve on the energy surface such that constantly

$$\frac{\partial \epsilon}{\partial \eta} = \left(\frac{\partial \epsilon}{\partial \eta} \right)_1 = \left(\frac{\partial \epsilon}{\partial \eta} \right)_2 = T, \qquad (16)$$

(such a curve is called an isothermal curve), equation 15 becomes

$$\epsilon_2 - \epsilon_1 = T(\eta_2 - \eta_1) + \int_1^2 \frac{\partial \epsilon}{\partial v} dv. \qquad (17)$$

If, on the other hand, we move along a curve on the energy surface such that constantly

$$\frac{\partial \epsilon}{\partial v} = \left(\frac{\partial \epsilon}{\partial v}\right)_1 = \left(\frac{\partial \epsilon}{\partial v}\right)_2 = -\Pi, \tag{18}$$

(such a curve is called an isopiestic curve), equation 15 becomes

$$\epsilon_2 - \epsilon_1 = \int_1^2 \frac{\partial \epsilon}{\partial \eta}\, d\eta - \Pi(v_2 - v_1). \tag{19}$$

Comparing equations 14, 17 and 19, we obtain the following equations

$$\Pi(v_2 - v_1) = -\int_1^2 \frac{\partial \epsilon}{\partial v}\, dv, \tag{20}$$

$$\mathrm{T}(\eta_2 - \eta_1) = \int_1^2 \frac{\partial \epsilon}{\partial \eta}\, d\eta. \tag{21}$$

Equations 20 and 21 admit of a simple geometrical interpretation. Let us take in a plane a pair of rectangular axes along which we shall measure the specific volume and the pressure of a one-component system. If the system is kept at the constant temperature T the representative point in the pressure-volume plane describes a curve which may be called the actual isotherm corresponding to the temperature T. If, on the other hand, we construct in the same plane the curve whose equation is obtained by eliminating η between the equations

$$-\Pi = \frac{\partial \epsilon}{\partial v},$$

$$\mathrm{T} = \frac{\partial \epsilon}{\partial \eta},$$

in which T is supposed to be constant, we obtain a curve which may be called the theoretical isotherm corresponding to the temperature T. Equation 20 then gives us Maxwell's theorem:[1] If we agree that areas lying on opposite sides of a curve shall be given opposite signs, then the area included between the actual isotherm and the theoretical isotherm is equal to zero. Equation 21 yields in like manner the following theorem analogous to Maxwell's: The area included between the actual isopiestic and the theoretical isopiestic is equal to zero.

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[1] Maxwell. Nature, 11, 358 (1875). Clausius. Wied. Ann. 9, 337 (1880). Planck. Gleichgewichtszustände isotroper Körper, p. 39 (1880).

Let us now return to the consideration of the conditions of equilibrium 9, 10 and 11. If we remember that ϵ_1 is a function of η_1 and v_1 and that ϵ_2 is a function of η_2 and v_2, it follows that equations 9, 10 and 11 furnish three relations between the four quantities η_1, v_1, η_2, v_2; one of the four being chosen arbitrarily the others are accordingly determinate. Thus the point 1 must lie on a certain curve of the energy surface and the point 2 must lie on a certain other curve of the surface; moreover to each point of either of these curves there corresponds one and only one point of the other. These two curves together constitute the so-called connodal curve, the locus of the points of contact of a doubly tangent plane.

Since the temperature and the pressure of the two-phase system in equilibrium are determined by the position of the tangent plane at the points 1 and 2, it follows that for a two-phase system in equilibrium the temperature and pressure cannot both be chosen arbitrarily; they are functions one of the other. We can go further and determine the relation that exists between the simultaneous increments in the temperature and equilibrium pressure. For this purpose let us consider equations 9, 10 and 11. As we pass from a pair of corresponding points 1 and 2 to an adjacent pair, the following relations, obtained by differentiating equations 9, 10 and 11, must hold:

$$d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 = d\left(\frac{\partial\epsilon}{\partial\eta}\right)_2, \qquad (22)$$

$$d\left(\frac{\partial\epsilon}{\partial v}\right)_1 = d\left(\frac{\partial\epsilon}{\partial v}\right)_2, \qquad (23)$$

$$d\epsilon_1 - \left(\frac{\partial\epsilon}{\partial\eta}\right)_1 d\eta_1 - \left(\frac{\partial\epsilon}{\partial v}\right)_1 dv_1 - \eta_1 d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 - v_1 d\left(\frac{\partial\epsilon}{\partial v}\right)_1$$
$$= d\epsilon_2 - \left(\frac{\partial\epsilon}{\partial\eta}\right)_2 d\eta_2 - \left(\frac{\partial\epsilon}{\partial v}\right)_2 dv_2 - \eta_2 d\left(\frac{\partial\epsilon}{\partial\eta}\right)_2 - v_2 d\left(\frac{\partial\epsilon}{\partial v}\right)_2. \qquad (24)$$

If we make use of equations 1, 22 and 23, equation 24 reduces to

$$(\eta_2 - \eta_1) d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 + (v_2 - v_1) d\left(\frac{\partial\epsilon}{\partial v}\right)_1 = 0, \qquad (25)$$

or

$$\frac{\eta_2-\eta_1}{v_2-v_1} = -\frac{d\left(\frac{\partial\epsilon}{\partial v}\right)_1}{d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1} = -\frac{d\left(\frac{\partial\epsilon}{\partial v}\right)_2}{d\left(\frac{\partial\epsilon}{\partial\eta}\right)_2}\,; \tag{26}$$

and if we remember that when a homogeneous phase is in equilibrium equations 3 are satisfied, we obtain Clapeyron's equation

$$\frac{\eta_2-\eta_1}{v_2-v_1} = \frac{d\Pi}{dT}\,. \tag{27}$$

The straight lines which join pairs of corresponding points of the connodal curve form a ruled surface, the various points of which represent the specific energy, entropy and volume of the various states of equilibrium of the two-phase system. We shall show that this ruled surface is a developable surface and that it is the envelope of the doubly tangent plane. To show this we observe that the equation of the tangent plane at the point 1 can be written in either of the forms

$$\epsilon-\epsilon_1 = \left(\frac{\partial\epsilon}{\partial\eta}\right)_1(\eta-\eta_1) + \left(\frac{\partial\epsilon}{\partial v}\right)_1(v-v_1) \tag{28}$$

or

$$\epsilon-\eta\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 - v\left(\frac{\partial\epsilon}{\partial v}\right)_1 = \epsilon_1-\eta_1\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 - v_1\left(\frac{\partial\epsilon}{\partial v}\right)_1. \tag{29}$$

In virtue of conditions 9, 10, and 11 this tangent plane is also tangent to the surface at the point 2. Moreover, in virtue of the same conditions, the coefficients in equation 29 are, as we have already shown, functions of a single arbitrary parameter. Consequently, the doubly tangent plane, in its motion, remains tangent to a developable surface. To find the characteristic of this surface, that is to say to find the intersection of two consecutive doubly tangent planes, we must differentiate equation 28 with reference to the arbitrary parameter. We thus obtain

$$-d\epsilon_1 = -\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 d\eta_1 - \left(\frac{\partial\epsilon}{\partial v}\right)_1 dv_1 + (\eta-\eta_1)\,d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1 + (v-v_1)\,d\left(\frac{\partial\epsilon}{\partial v}\right)_1$$

or

$$(\eta-\eta_1)d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1+(v-v_1)d\left(\frac{\partial\epsilon}{\partial v}\right)_1=0. \tag{30}$$

Equations 28 and 30 are the equations of the characteristic. The plane 30 passes through the point 1 as is at once evident by substituting η_1 and v_1 for η and v. Moreover, it passes through the point 2 for, replacing η and v by η_2 and v_2, we obtain

$$(\eta_2-\eta_1)d\left(\frac{\partial\epsilon}{\partial\eta}\right)_1+(v_2-v_1)d\left(\frac{\partial\epsilon}{\partial v}\right)_1=0. \tag{31}$$

Equation 25 shows that when the points 1 and 2 are on the connodal curve the condition 31 is satisfied. Thus the line joining the points 1 and 2 is the characteristic of the developable surface to which the doubly tangent plane remains tangent. This developable surface is therefore the same as the ruled surface formed by joining corresponding points of the connodal curve.

To complete the discussion of the equilibrium of the two-phase system it is necessary to add that it can be shown that the conditions of stability require that at each of the points 1 and 2 we should have

$$\begin{vmatrix} \dfrac{\partial^2\epsilon}{\partial\eta^2}, & \dfrac{\partial^2\epsilon}{\partial\eta\partial v} \\ \dfrac{\partial^2\epsilon}{\partial\eta\partial v}, & \dfrac{\partial^2\epsilon}{\partial v^2} \end{vmatrix} > 0, \tag{32}$$

$$\frac{\partial^2\epsilon}{\partial\eta^2} > 0, \quad \frac{\partial^2\epsilon}{\partial v^2} > 0.$$

To simplify we shall represent the determinant written above by the symbol Δ, so that, by definition,

$$\Delta \equiv \begin{vmatrix} \dfrac{\partial^2\epsilon}{\partial\eta^2}, & \dfrac{\partial^2\epsilon}{\partial\eta\partial v} \\ \dfrac{\partial^2\epsilon}{\partial\eta\partial v}, & \dfrac{\partial^2\epsilon}{\partial\eta^2} \end{vmatrix}. \tag{33}$$

We shall next deduce the conditions which are satisfied when a pair of corresponding points of the connodal curve coincide. Such a point of the energy surface is called a plait point and the corresponding state of the one-component system is called a critical state of the system.

If we expand by Taylor's theorem the expressions which appear on the right-hand side of equations 9 and 10, we obtain

$$\left(\frac{\partial \epsilon}{d\eta}\right)_1 = \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 + \left(\frac{\partial^2 \epsilon}{\partial \eta^2}\right)_1 (\eta_2 - \eta_1) + \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 (v_2 - v_1) + \cdots, \quad (34)$$

$$\left(\frac{\partial \epsilon}{\partial v}\right)_1 = \left(\frac{\partial \epsilon}{\partial v}\right)_1 + \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 (\eta_2 - \eta_1) + \left(\frac{\partial^2 \epsilon}{\partial v^2}\right)_1 (v_2 - v_1) + \cdots, \quad (35)$$

the terms which are omitted being of the second and higher degrees in the differences $\eta_2 - \eta_1$, $v_2 - v_1$. If we suppose that $\eta_2 - \eta_1$, $v_2 - v_1$ are very small, that is to say, if we consider a pair of corresponding points very near the plait point, we may write the following equations which are approximately correct

$$(\eta_2 - \eta_1)\left(\frac{\partial^2 \epsilon}{\partial \eta^2}\right)_1 + (v_2 - v_1)\left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 = 0, \quad (36)$$

$$(\eta_2 - \eta_1)\left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 + (v_2 - v_1)\left(\frac{\partial^2 \epsilon}{\partial v^2}\right)_1 = 0. \quad (37)$$

Thus at the plait point we have

$$\text{limit} \frac{\eta_2 - \eta_1}{v_2 - v_1} = -\frac{\dfrac{\partial^2 \epsilon}{\partial \eta \partial v}}{\dfrac{\partial^2 \epsilon}{\partial \eta^2}} = -\frac{\dfrac{\partial^2 \epsilon}{\partial v^2}}{\dfrac{\partial^2 \epsilon}{\partial \eta \partial v}}. \quad (38)$$

From equations 38 it follows that at the plait point

$$\Delta = 0. \quad (39)$$

The plait point is accordingly a point on the spinodal curve, that is to say, on the curve which divides the portions of the surface which are convex in all directions from those which are concavo-convex. For, as is well-known, equation 39 is the equation of the spinodal curve.

We shall assume that the line joining corresponding points of the connodal curve becomes in the limit the tangent to the connodal curve at the plait point. From this assumption and from equations 38 it follows that the direction of the tangent to the connodal line at the plait point is given by either of the equations

$$\frac{\partial^2 \epsilon}{\partial \eta^2} d\eta + \frac{\partial^2 \epsilon}{\partial \eta \partial v} dv = 0, \qquad (40)$$

$$\frac{\partial^2 \epsilon}{\partial \eta \partial v} d\eta + \frac{\partial^2 \epsilon}{\partial v^2} dv = 0. \qquad (41)$$

Furthermore, at the plait point the connodal curve is tangent to the spinodal curve. For, in the first place, the plait point is on the spinodal curve and, in the second place, two corresponding points of the connodal curve adjacent to the plait point lie on the portion of the surface which is convex in every direction and for which therefore

$$\Delta > 0.$$

It follows that the spinodal curve does not cut the connodal curve at the plait point, and the simplest assumption that we can make is that the two curves are tangent at the plait point. The equation of the spinodal curve being

$$\Delta = 0,$$

it follows that the direction of the tangent at any point of the spinodal curve is given by the equation

$$\frac{\partial \Delta}{\partial \eta} d\eta + \frac{\partial \Delta}{\partial v} dv = 0. \qquad (42)$$

At the plait point this equation must give the same value for the fraction $d\eta/dv$ as equations 40 and 41. Accordingly, at the plait point the three determinants of the second order which can be formed from the matrix

$$\begin{array}{cc} \frac{\partial^2 \epsilon}{\partial \eta^2}, & \frac{\partial^2 \epsilon}{\partial \eta \partial v} \\ \frac{\partial^2 \epsilon}{\partial \eta \partial v}, & \frac{\partial^2 \epsilon}{\partial v^2} \\ \frac{\partial \Delta}{\partial \eta}, & \frac{\partial \Delta}{\partial v} \end{array} \qquad (43)$$

are equal to zero. Moreover, the limiting position of the line joining corresponding points of the connodal curve and the direction of the common tangent to the connodal and spinodal curves at the plait point are given by the equations

$$\text{limit}\ \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{d\eta}{dv} = -\frac{\dfrac{\partial^2\epsilon}{\partial\eta\partial v}}{\dfrac{\partial^2\epsilon}{\partial\eta^2}} = -\frac{\dfrac{\partial^2\epsilon}{\partial v^2}}{\dfrac{\partial^2\epsilon}{\partial\eta\partial v}} = -\frac{\dfrac{\partial\Delta}{\partial v}}{\dfrac{\partial\Delta}{\partial\eta}}\,. \qquad (44)$$

Conditions 43 and 44 suffice to establish the principal properties of the critical state of a one-component system. As the only case in which a critical state of a one-component system has been realized is when the coexistent phases are liquid and vapor, we shall, in what follows, suppose that the phases denoted by the subscripts 1 and 2 are respectively liquid and vapor.

As we move along the connodal curve towards the plait point the quantities ϵ_1 and ϵ_2, η_1 and η_2, v_1 and v_2 approach limits which we may call the specific energy, entropy and volume of the critical state. The temperature and the pressure also approach limits which we may call the critical temperature and the critical pressure. It follows that the change in volume during the vaporization of unit mass, $v_2 - v_1$, the corresponding change in entropy, $\eta_2 - \eta_1$, the external work during vaporization, $\Pi(v_2 - v_1)$, and the heat of vaporization, $T(\eta_2 - \eta_1)$, all approach zero as the system approaches the critical state.

Although $\eta_2 - \eta_1$ and $v_2 - v_1$ approach zero as a limit, the ratio of these two quantities, in general, will approach a finite limit. This follows from the fact that there is nothing in equations 44 which obliges us to assume that the limit in question is either zero or infinity. Equation 27 taken in connection with the result just obtained shows that as we approach the critical state the slope of the temperature-pressure curve of the two-phase system approaches a finite limit.

We have stated above that the system under consideration is supposed to consist of the two phases liquid and vapor. This assumption is expressed analytically by the inequalities

$$\eta_2 > \eta_1, \qquad v_2 > v_1. \qquad (45)$$

It follows from these inequalities that the limit of the ratio $(\eta_2 - \eta_1)/(v_2 - v_1)$ is positive, from which it follows at once that at the critical point the slope of the temperature-pressure curve of the two-phase system is positive. Moreover, since the plait point is an ordinary point on the connodal curve it follows that the specific entropy and volume of the critical state lie respectively between the specific entropies and the specific volumes of the two phases in equilibrium in the immediate neighborhood of the critical state.

Since, by conditions 45, the different fractions in equations 44 are positive and since, by conditions 32,

$$\frac{\partial^2\epsilon}{\partial\eta^2} > 0, \quad \frac{\partial^2\epsilon}{\partial v^2} > 0, \tag{46}$$

it follows that, at the plait point,

$$\frac{\partial^2\epsilon}{\partial\eta\partial v} < 0. \tag{47}$$

Equations 3, 9 and 10 give the temperature and the pressure of the two-phase system in equilibrium. As we move along the connodal curve the changes in temperature and pressure are accordingly given by the equations

$$dT = \left(\frac{\partial^2\epsilon}{\partial\eta^2}\right)_1 d\eta_1 + \left(\frac{\partial^2\epsilon}{\partial\eta\partial v}\right)_1 dv_1 = \left(\frac{\partial^2\epsilon}{\partial\eta^2}\right)_2 d\eta_2 + \left(\frac{\partial^2\epsilon}{\partial\eta\partial v}\right)_2 dv_2, \tag{48}$$

$$-d\Pi = \left(\frac{\partial^2\epsilon}{\partial\eta\partial v}\right)_1 d\eta_1 + \left(\frac{\partial^2\epsilon}{\partial v^2}\right)_1 dv_1 = \left(\frac{\partial^2\epsilon}{\partial\eta\partial v}\right)_2 d\eta_2 + \left(\frac{\partial^2\epsilon}{\partial v^2}\right)_2 dv_2. \tag{49}$$

From equations 44 it follows that at the plait point the right-hand members of equations 48 and 49 are equal to zero. We have accordingly at that point

$$\frac{dT}{d\eta_1} = 0, \quad \frac{dT}{d\eta_2} = 0; \tag{50}$$

$$\frac{dT}{dv_1} = 0, \quad \frac{dT}{dv_2} = 0; \tag{51}$$

$$\frac{d\Pi}{d\eta_1} = 0, \quad \frac{d\Pi}{d\eta_2} = 0; \tag{52}$$

$$\frac{d\Pi}{dv_1} = 0, \quad \frac{d\Pi}{dv_2} = 0. \tag{53}$$

Let us consider equations 50. These equations show that if in the temperature-entropy plane we draw the two curves which show the relation between the temperature and the specific entropies of the two phases in equilibrium, these two curves meet at the point corresponding to the critical state and have at that point a common tangent parallel to the entropy axis. Moreover, since the specific entropy of the critical state is intermediate between η_1 and η_2, it follows that the critical temperature is a maximum or a minimum of the temperatures at which the two-phase system can exist in equilibrium. If we assume that the critical temperature is a maximum, and if we remember that η_1 is less than η_2 it follows that in the neighborhood of the critical state

$$\frac{dT}{d\eta_1} > 0, \quad \frac{dT}{d\eta_2} < 0. \tag{54}$$

Similar reasoning enables us to deduce the following pairs of inequalities which correspond respectively to equations 51, 52 and 53.

$$\frac{dT}{dv_1} > 0, \quad \frac{dT}{dv_2} < 0; \tag{55}$$

$$\frac{d\Pi}{d\eta_1} > 0, \quad \frac{d\Pi}{d\eta_2} < 0; \tag{56}$$

$$\frac{d\Pi}{dv_1} > 0, \quad \frac{d\Pi}{dv_2} < 0. \tag{57}$$

Corresponding to each of the three sets of conditions 51 and 55, 52 and 56, 53 and 57, there is a theorem analogous to the theorem stated above for conditions 50 and 54. Of these theorems the best known are those corresponding to conditions 51 and 55, 53 and 57.

Let us denote by L the heat of vaporization. We have

$$L = T(\eta_2 - \eta_1). \tag{58}$$

As we pass along the connodal curve the change in the heat of vaporization is given by the equation

$$dL = (\eta_2 - \eta_1)dT + T(d\eta_2 - d\eta_1)$$

or by

$$\frac{dL}{dT} = \eta_2 - \eta_1 + T\left(\frac{d\eta_2}{dT} - \frac{d\eta_1}{dT}\right). \tag{59}$$

If we make use of conditions 50 and 54 we find that as we approach the critical state dL/dT approaches negative infinity. From equation 59 it can also be shown that $dL/d\Pi$ also approaches negative infinity.

In like manner if we denote by W the external work during vaporization, we have

$$W = \Pi(v_2 - v_1), \tag{60}$$

and it can be shown without difficulty that $dW/d\Pi$ and dW/dT approach negative infinity as we approach the critical state.

Let us suppose that T and Π are always defined by equations 3, remembering, however, that only those points of the energy surface for which conditions 6, 7 and 8 are satisfied correspond to stable states of equilibrium. As we move from one point of the energy surface to an adjacent point, we have, from equations 3

$$dT = \frac{d^2\epsilon}{\partial\eta^2}\,d\eta + \frac{\partial^2\epsilon}{\partial\eta\partial v}\,dv, \tag{61}$$

$$-d\Pi = \frac{\partial^2\epsilon}{\partial\eta\partial v}\,d\eta + \frac{\partial^2\epsilon}{\partial v^2}\,dv. \tag{62}$$

By solving these equations for $d\eta$ and dv we obtain

$$\Delta d\eta = \begin{vmatrix} dT, & \dfrac{\partial^2\epsilon}{\partial\eta\partial v} \\ -d\Pi, & \dfrac{\partial^2\epsilon}{\partial v^2} \end{vmatrix}, \tag{63}$$

$$\Delta dv = \begin{vmatrix} \dfrac{\partial^2\epsilon}{\partial\eta^2}, & dT \\ \dfrac{\partial^2\epsilon}{d\eta\partial v}, & -d\Pi \end{vmatrix}. \tag{64}$$

If we suppose the point to move on the energy surface along an isopiestic curve we must have constantly

$$d\Pi = 0.$$

We thus obtain from equations 63 and 64

$$\left(\frac{dT}{d\eta}\right)_\Pi = \frac{\Delta}{\dfrac{\partial^2\epsilon}{\partial\eta^2}}, \tag{65}$$

$$\left(\frac{dT}{dv}\right)_{\Pi} = -\frac{\Delta}{\dfrac{\partial^2 \epsilon}{\partial \eta \partial v}}. \tag{66}$$

The subscript Π in the left-hand members of these equations denotes that Π is supposed to remain constant during the change considered.

If we suppose the point on the energy surface to move along an isothermal curve we must have constantly

$$dT = 0.$$

Equations 63 and 64 then give us

$$\left(\frac{d\Pi}{d\eta}\right)_{T} = \frac{\Delta}{\dfrac{\partial^2 \epsilon}{\partial \eta \partial v}}, \tag{67}$$

$$\left(\frac{d\Pi}{dv}\right)_{T} = -\frac{\Delta}{\dfrac{\partial^2 \epsilon}{\partial \eta^2}}. \tag{68}$$

At the plait point of the energy surface Δ is equal to zero. Accordingly for the critical state of a one-component system the following conditions hold

$$\left(\frac{dT}{d\eta}\right)_{\Pi} = 0, \quad \left(\frac{dT}{dv}\right)_{\Pi} = 0, \quad \left(\frac{d\Pi}{d\eta}\right)_{T} = 0, \quad \left(\frac{d\Pi}{dv}\right)_{T} = 0. \tag{69}$$

Moreover, if we consider a point on the energy surface in the immediate neighborhood of the plait point, conditions 46 and 47 are satisfied. If, in addition, we suppose that for the point considered Δ is positive, we obtain from equations 65, 66, 67 and 68 the following inequalities:

$$\left(\frac{dT}{d\eta}\right)_{\Pi} > 0, \quad \left(\frac{dT}{dv}\right)_{\Pi} > 0, \quad \left(\frac{d\Pi}{d\eta}\right)_{T} < 0, \quad \left(\frac{d\Pi}{dv}\right)_{T} < 0. \tag{70}$$

These inequalities apply to a one-component system consisting of a single homogeneous phase in stable equilibrium in the immediate neighborhood of the critical state. Since the quantities on the right-hand sides of equations 65 and 68 are positive for any homogeneous phase in stable equilibrium it follows that the first and fourth of inequalities 70 are verified for any homogeneous phase in stable equilibrium. But we are not justified in asserting that the second and third of these inequalities are verified elsewhere than in the immediate neighborhood of the critical state.

We shall next calculate the value of

$$\left(\frac{d^2\mathrm{T}}{d\eta^2}\right)_\Pi$$

at the plait point. From equation 65 we get

$$d\left(\frac{d\mathrm{T}}{d\eta}\right)_\Pi = \frac{\dfrac{\partial\Delta}{\partial\eta}d\eta + \dfrac{\partial\Delta}{\partial v}dv}{\dfrac{\partial^2\epsilon}{\partial\eta^2}} - \frac{\Delta . d\dfrac{\partial^2\epsilon}{\partial\eta^2}}{\left(\dfrac{\partial^2\epsilon}{\partial\eta^2}\right)^2}. \qquad (71)$$

At the plait point Δ is equal to zero and the right-hand member of the above equation reduces to its first term. Since Π is to remain constant, equation 62 gives us

$$0 = \frac{\partial^2\epsilon}{\partial\eta\partial v}d\eta + \frac{\partial^2\epsilon}{\partial v^2}dv. \qquad (72)$$

If we eliminate *dv* between equation 72 and the simplied form of equation 71, we obtain

$$\left(\frac{d^2\mathrm{T}}{d\eta^2}\right)_\Pi = \frac{\begin{vmatrix} \dfrac{\partial\Delta}{\partial\eta}, & \dfrac{\partial}{\partial v} \\ \dfrac{\partial^2\epsilon}{\partial\eta\partial v}, & \dfrac{\partial^2\epsilon}{\partial v^2} \end{vmatrix}}{\dfrac{\partial^2\epsilon}{\partial\eta^2} \cdot \dfrac{\partial^2\epsilon}{\partial v^2}}. \qquad (73)$$

From conditions 43 we know that the determinant which appears in this equation is equal to zero at the plait point. We thus obtain the first of the following equations:

$$\left(\frac{d^2\mathrm{T}}{d\eta^2}\right)_\Pi = 0, \quad \left(\frac{d^2\mathrm{T}}{dv^2}\right)_\Pi = 0, \quad \left(\frac{d^2\Pi}{d\eta^2}\right)_\mathrm{T} = 0, \quad \left(\frac{d^2\Pi}{dv^2}\right)_\mathrm{T} = 0. \qquad (74)$$

The others can be established in the same manner.

The corresponding relations in 69, 70 and 74 give us four theorems. For the sake of brevity we shall state only the last of these:[1] If in the pressure volume plane, we construct the isothermal corresponding to the critical temperature, this curve will have a point of inflexion at the critical point. The tangent at the point of inflexion is parallel to the volume axis; at any other point of the curve the tangent makes an obtuse angle with the volume axis.

Equations 69 and 74 were given by Gibbs in his memoir on the energy surface.[2] Conditions 43, which we have taken as the starting point of our discussion, were given a few years later in the great memoir "On the Equilibrium of Heterogeneous Substances."[3]

It is hoped that the foregoing discussion will help to draw attention to the fact that Gibbs' memoir on the energy surface contains a general theory of the critical state of a one-component system and of the continuity of the liquid and gaseous states which is not only extremely simple but which, at the same time, is entirely independent of molecular hypotheses.

The memoir in question is important in the history of thermodynamics for another reason. In it Gibbs shows that the condition that a system be in stable equilibrium at a given temperature and under a given pressure is that the thermodynamic potential, $\epsilon - T\eta + \Pi v$, be a minimum.[4] A few months previously Horstman had stated the condition of equilibrium in terms of the entropy.[5]

New York, June 30, 1902.

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[1] van der Waals. Over de Continuiteit, p. 84.

[2] p. 396.

[3] p. 191.

[4] p. 393.

[5] Liebig's Annalen, 170, 197 (1873).

NEW BOOKS

The Principles of Inorganic Chemistry. *By Wilhelm Ostwald. Translated with the author's sanction by Alexander Findlay. 14 × 22 cm; pp. xxvii + 785. New York: Macmillan and Co., 1902. Price, $6.00 net.*—It is distinctly a matter for congratulation that Ostwald's *Grundlinien der anorganischen Chemie* has appeared in an adequate English translation. The translator is unquestionably justified in his expressed hope that he is contributing to a more wide-spread knowledge of the application of the more recent developments of general chemistry, and consequently to a juster appreciation of their importance in the study of the other branches of the science. The book is too bulky to serve as a text for the most of our introductory college courses; but it ought to be widely used by beginning students as a reference book. An interesting element of the translation is the introduction of Walker's nomenclature of the ions. The book is clearly printed, and has a proper index. *J. E. Trevor*

Die Begriffe und Theorien der modernen Physik. *By J. B. Stallo. Nach der 3. Auflage des englishen Originals, übersetzt und herausgegeben von Dr. Hans Kleinpeter. Mit einem Vorwort von Ernst Mach. 13 × 19 cm; pp. xx + 332. Liepzig: Johann Ambrosius Barth, 1901. Price: 7 marks; bound, 8.50 marks.* — Further gratifying evidence that the world really does move is afforded by the belated appearance of a German version of Judge Stallo's Concepts and Theories of Modern Physics (first edition, 1881). It is strange that the philosophically inclined Germans, of all peoples, should have overlooked this important work for so long a time. When Mach's attention was attracted by the book, he interested himself in it with enthusiasm and inspired the present translation, for which he has provided a most interesting eleven page preface. With this introduction to the German public the work will now continue on a broadened career of usefulness, in contributing to the spread of sounder and clearer views in regard to physics and chemistry. In the light of all the newly awakened interest in Stallo's ideas, we have little occasion to regret that the book appeared a decade or two before its time. The German edition is prefaced by a fair portrait of the author, and the index has been reproduced. *J. E. Trevor*

The Science of Mechanics. *A Critical and Historical Account of its Development. By Ernst Mach. Translated from the German by Thomas J. McCormack. Second revised and enlarged edition. 13 × 19 cm; pp. xix + 605. Chicago: Open Court Publishing Co., 1902. Price: bound, $2.00 net.* — In signalizing the appearance of a revised English edition of Mach's famous *Mechanics*, we cannot do better than to quote the introductory paragraph of the Translator's preface.

"Since the appearance of the first edition of the present translation of Mach's Mechanics the views which Professor Mach has advanced on the philosophy of science have found wide and steadily increasing acceptance. Many fruitful and elucidative controversies have sprung from his discussions of the historical, logical, and psychological foundations of physical science, and in consideration of the great ideal success which his works have latterly met with in Continental Europe, the time seems ripe for a still wider dissemination of his views in English-speaking countries. The study of the history and theory of science is finding fuller and fuller recognition in our universities, and it is to be hoped that the present exemplary treatment of the simplest and most typical branch of physics will stimulate further progress in this direction."

The fourth German edition of this work appeared in 1901. The author's additions are presented in a long series of appendices. The text of the present edition has been thoroughly revised by the translator, and is wholly admirable. The typographic dress of the English version is distinctly better than that of the German. *J. E. Trevor*

The Theory of Optics. *By Paul Drude. Translated from the German by C. Riborg Mann and Robert A. Millikan. 14 × 21 cm; pp. xxi + 546. New York: Longmans, Green and Co., 1902. Price: $4.00.* — When Drude's treatise appeared in 1900, it was announced that its purpose was to introduce the reader who is familiar with the differential and integral calculus into the domain of optics in such a way that he might be able to understand the aims and results of the most recent investigation, and to follow the original papers in detail. In his preface to the present translation, Prof. A. A. Michelson writes that there is in English no general advanced text on optics that embodies the important advances of the last decade in both theory and experiment. He points out that the only general text in English, Preston's Theory of Light, contains no fundamental development of some fundamentally important theories, in particular of the theory of optical instruments, the electromagnetic theory of light, or the application of thermodynamics to the study of radiation. Such matters being exceptionally well treated in Drude's book, Prof. Michelson concludes that, "No one who desires to gain an insight into the most modern aspects of optical research can afford to be unfamiliar with this remarkably original and consecutive presentation of the subject of optics."

J. E. Trevor

Anwendung der Differential- und Integral-rechnung auf Geometrie. *By Georg Scheffers. Zweiter Band: Einführung in die Theorie der Flächen. 15 × 23 cm; pp. viii + 518. Leipzig: Veit und Comp., 1902. Price: paper, 13 marks.* — An important feature of chemical thermodynamics is the use of surfaces for graphical representation of the thermodynamic behavior of bodies and systems of bodies. These surfaces were first studied by Gibbs, and have recently been extensively employed by van der Waals and other workers in the equilibrium theory of two and three component systems. In order to keep in touch with such work, some knowledge of the theory of surfaces is requisite; and it is this fact that makes of interest to the physical chemist the appearance of a new introductory treatise on this theory. Scheffers's book is the second volume of a work, Application of the Differential and Integral Calculus to Geometry, the first volume being an Introduction to the Theory of Curves in the Plane and in Space.

In plan and in detail the work deserves high praise. The theorems are developed from the analytical standpoint, and everything discussed is treated thoroughly and is well illustrated by examples. Many well-drawn figures add to the intelligibility of the treatment. Being intended for beginners, the author has avoided presenting the subject as the theory of invariance of two quadratic differential forms. The text is divided into four sections: The Arc Element of the Surface, Curvature, the Fundamental Equations of the Theory of Surfaces, Surface Curves. The typography of the book is wholly admirable.

J. E. Trevor

Leichtfassliche Vorlesungen über Elektrizität und Licht. *By G. Jaumann. 13 × 19 cm; pp. xii + 375. Leipzig: Johann Ambrosius Barth, 1902. Price: paper, 6; bound, 7.20 marks.* — This book is the development of a series of university extension lectures delivered at Prague in 1899–1900. It aims to supply an outline of the Faraday-Maxwell theory of electricity and of the relation of light to electric phenomena, for the benefit of teachers in the schools and of beginners in the university. The method is a visualizing of the geometrical drawing of lines of force, by considering magnetic and electric flux in analogy with stream lines in water. It is introduced by a chapter on the flow of water. The first lecture deals with the magnetism of iron, under the title of The Magnetic Flux, the second with electrostatics under the title of The Electric Flux. The voltaic current is treated as a flux in which the lines are closed curves; and the whole subject is carried through on this plan. Electromagnetic waves and light come into consideration in the concluding chapters. No attention is given to any of the current corpuscular theories.

J. E. Trevor

Cryoscopie. *By F. M. Raoult. Scientia, No. 13. 106 pp.* (*1901*).

Franges d'Interférence et leurs Applications métrologiques. *By J. Macé de Lépinay. Scientia, No. 14. 101 pp.* (*1902*).

La Géométrie non euclidienne. *By P. Barbarin. Scientia, No. 15. 79 pp.* (*1902*).

Le Phénomène de Kerr et les Phénomènes électro-optiques. *By E. Néculcéa. Scientia, No. 16. 91 pp.* (*1902*).

Théorie de la Lune. *By H. Andoyer. Scientia, No. 17. 86 pp.* (*1902*).

Géométrographie ou Art des Constructions géométriques. *By Emile Lemoine. Scientia, No. 18. 85 pp.* (*1902*).

L'Electricité, *deduite de l'Expérience et ramenée au principe des Travaux virtuels. By M. E. Carvallo. Scientia, No. 19. 91 pp.* (*1902*).

Sur les Principes fondamentaux de la Théorie des Nombres et de la Géométrie. *By H. Laurent. Scientia, No. 20. 68 pp.* (*1902*).

Limp boards; 13 × 20 cm. Paris: C. Naud. Price: 2 francs each. —

It will be recalled that each volume of the Scientia series is intended to present an account of the present state of development of some scientific topic. In the numbers already issued this work has been admirably done, partly as a consequence of entrusting it to competent authorities, and in part because the authors have not been required to write down to the level of a popular audience.

Three of the present volumes are concerned with pure mathematics: non-

Euclidean geometry, geometrography or the art of geometric construction, and the fundamental principles of the theory of numbers and of geometry. One volume treats a topic of mathematical physics, the theory of the moon, by which is meant the analytical determination of the motion of the center of gravity of the moon relative to the center of gravity of the earth. Three volumes deal with physical topics: interference fringes, electro-optic phenomena, and electricity; the last of these developing the Maxwellian theory in a consistent and clear way. The remaining volume is a treatise on cryoscopy, by Raoult. The matter is discussed under the successive heads: general principles, methods of observation, cryoscopy of non-electrolytes, cryoscopy of electrolytes. Every one interested in physical chemistry will be attracted by this book. A list of Raoult's scientific publications, eighty-seven in number, is appended. *J. E. Trevor*

A Laboratory Manual of Physics, for Use in High Schools. *By Henry Crew and Robert R. Tatnall. 12 X 18 cm; pp. xi + 234. New York: The Macmillan Company, 1902. Price: bound, $0.90.*—This manual of laboratory work in physics may naturally be regarded as a companion volume to Crew's Physics, but it might be used to supplement any good text. The aim of the authors is not to describe classical experiments but rather to illustrate the principles of physics, and to do this with simple means. They have succeeded in producing a well balanced and homogeneous course, which if carefully worked through should prove very instructive. Ninety-four experiments are described. *J. E. Trevor*

The Foundations of Geometry. *By David Hilbert. Authorized translation by E. J. Townsend. 13 X 19 cm; pp. viii + 132. Chicago: Open Court Publishing Co., 1902. Price: bound, $1.00 net.*—Hilbert's widely known essay (1889) on The Foundations of Geometry is put into English in the present edition. At this date it is hardly necessary to say anything of the contents of the book; the title moreover is sufficiently self-explanatory. The translation has been subjected to severe criticism. *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

On the atomic weight of calcium. *F. W. Hinrichsen. Zeit. phys. Chem.* 39, *311* (*1901*); 40, *746* (*1902*). — The author has analyzed calcium carbonate obtained from the purest Iceland spar and finds an atomic weight for calcium of 40.142. He has also analyzed a calcium carbonate coming from Russia, and this gives him an atomic weight for calcium of 40.136. He points out that this is in good agreement with the value found by Richards of 40.126, and that the method used by Richards would be likely to give values which are a trifle low.
W. D. B.

On the atomic weight of arsenic. *W. C. Ebaugh. Jour. Am. Chem. Soc.* 24, *489* (*1902*). — The author has converted silver arsenate into silver chloride, silver arsenate into silver bromide, lead arsenate into lead chloride, and lead arsenate into lead bromide. He finds 75.008 for the atomic weight of arsenic.
W. D. B.

Ninth annual report of the Committee on Atomic Weights. *F. W. Clarke. Jour. Am. Chem. Soc.* 24, *201* (*1902*). — This is the report on the determinations published in 1901. The elements which have been studied during the past year are nitrogen, calcium, arsenic, antimony, tellurium, tungsten, uranium, lanthanum, praseodymium, neodymium, and thorium. *W. D. B.*

The significance of changing atomic volume, II. *T. W. Richards. Zeit. phys. Chem.* 40, *597* (*1902*). — Reviewed (6, 147) from Proc. Amer. Acad. 37, 399 (1902).

On the theory of unsaturated compounds. *F. W. Hinrichsen. Zeit. phys. Chem.* 39, *304* (*1901*). — This is an argument in favor of the assumption of free valences as against the assumption of a double bond. *W. D. B.*

The classification of the elements. *H. E. Armstrong. Proc. Roy. Soc.* 70, *86* (*1902*). — The author outlines and discusses a new arrangement of the elements in the periodic table. *W. D. B.*

The effective temperature of the sun. *W. E. Wilson. Proc. Roy. Soc.* 69, *312* (*1902*). — From a comparison between the heat radiated from the sun and a uniformly heated iron tube, the author concludes that the temperature of the sun is 6590° C. *W. D. B.*

One-Component Systems

Correction of the boiling-points of liquids from observed to normal pressure.

S. Young. Jour. Chem. Soc. 81, *777* (*1902*). — The results bearing on the relation

$$C = \frac{dt}{dp}\,\frac{1}{T}$$

at 760 mm have been carefully revised and tabulated and the connection with other constants, as well as with the constitution of the substance indicated.

H. R. C.

Vapor pressures and specific volumes of isopropyl isobutyrate. *S. Young. Jour. Chem. Soc.* 81, *783* (*1902*). — Determination of these physical constants.

H. R. C.

The density and surface tension of liquid air. *C. T. Knipp. Phys. Rev.* 14, *75* (*1902*). — The density of liquid air varies with the time from a value 0.932 asymptotically to the value 1,131, the density of liquid oxygen. The surface tension of liquid air when first made is between 9 and 10 dynes per centimeter.

W. D. B.

Density determinations of gaseous sulphur by Dumas's method. *H. Biltz and G. Prenner. Zeit. phys. Chem.* 39, *323* (*1901*). — The authors have determined the vapor density of sulphur under varying pressures at a temperature of about 449°. For pressures above 150 mm the values are approximately constant, and point to a value slightly higher than S_7. With decreasing pressure the values dropped so that a value not much above S_4 is reached for a pressure of 20 mm. The authors conclude that there is therefore a sulphur corresponding to S_8 and one corresponding to S_2, but they are not yet certain whether the form of the dissociation curve calls for a sulphur with an intermediate value or not.

W. D. B.

Specific volumes of oxygen and nitrogen vapor at the boiling-point of oxygen. *J. Dewar. Proc. Roy. Soc.* 69, *360* (*1902*). — The mean weight of one liter of oxygen vapor at 760 mm and 90.5° abs is 4.420 g and the specific volume is 226.25 cc. The specific volume of nitrogen at its boiling-point of 78° abs is believed by the author to be 221.3 cc.

W. D. B.

On an extension of the conception of the critical constants. *A. Batschinski. Zeit. phys. Chem.* 40, *629* (*1902*). — The author defines as orthomeric those substances in which the molecular weight of the liquid is the same as that of the saturated vapor; allomeric substances are those in which these two values are different. The author further concludes that we may consider an orthomeric polymerized substance as following the law of the corresponding states provided we substitute the variable or "meta critical" values of temperature, pressure and volume for the critical temperature, pressure, and volume.

W. D. B.

The polymerization of cyanic acid. *A. Senier and T. Walsh. Jour. Chem. Soc.* 81, *290* (*1902*). — The solid obtained when liquid cyanic acid is allowed to polymerize at about 0° C is a mixture of cyamelid and cyanuric acid, and is not pure cyamelid as is generally supposed. This was shown by treating the solid with an excess of hot water when about 30 percent of the mass remained insoluble. The solution yielded crystals of cyanuric acid on evaporation.

W. D. B.

Two-Component Systems

On the constitution of copper-tin alloys. *C. T. Heycock and F. H. Neville. Proc. Roy. Soc.* 68, *171* (*1901*); 69, *320* (*1902*).—The authors point out that a microscopic study of slowly cooled copper-tin alloys may be entirely misleading unless confirmed by examination of samples suddenly chilled at specified temperatures. From the freezing-point curve of copper and tin and from a microscopic study of the cooled alloys, the authors conclude that there can exist in stable equilibrium with the melt three types of mixed crystals, the compound Cu_3Sn, the compound CuSn, and pure tin. In addition, there is a substance which is stable at lower temperatures and which is probably the compound Cu_4Sn.
W. D. B.

On the melting of dissociating compounds. *F. A. Lidbury. Zeit. phys. Chem.* 39, *453* (*1902*). — Owing to the slow crystallization of $CaCl_26H_2O$ it was necessary to provide for almost complete insulation of the freezing vessel if any accuracy was to be attained. Experiments with calcium chloride hexahydrate as solid phase and with aniline phenolate showed that in each case the freezing-point curve was continuous through the melting-point of the compound. In each case also the rate of crystallization varied continuously on adding either of the components. Addition of H_2O or SO_3 to H_2SO_4 caused a sudden very large change in the rate of crystallization, and the author therefore concludes that H_2SO_4 is not appreciably dissociated into its components at its melting-point, while the single components are present more or less in the calcium chloride-water or the aniline-phenol melt. *W. D. B.*

On the alloys of aluminum. *W. Campbell and J. A. Mathews. Jour. Am. Chem. Soc.* 24, *253* (*1902*). — A general discussion of the alloys of aluminum with lead, bismuth, cadmium, platinum, tungsten, nickel, tin, antimony, and copper. The authors believe in the existence of the following compounds: AlSb, Al_6Cu_7, and $AlCu_3$. *W. D. B.*

On the alloys of cadmium with barium and calcium. *H. Gautier. Comptes rendus*, 134, *1054* (*1902*).—The alloys of barium and of calcium with cadmium have been prepared in the same way as the alloys of cadmium with strontium. By distillation it was possible to obtain an alloy containing 45 percent of barium and one containing 55 percent of calcium. *W. D. B.*

On selenium. *J. Meyer. Zeit. anorg. Chem.* 30, *258* (*1902*). — The author has melted together phosphorus and selenium in various proportions and comes to the conclusion that P_4Se_3 and P_2Se_6 are to be considered as compounds. His definition of a compound under these circumstances appears to be a solid which will melt and distil without change, a definition which is satisfactory so far as it goes, but which would exclude large numbers of compounds. Since the author has not determined the freezing-point curve with any degree of accuracy, it is impossible to tell much of anything from his results. *W. D. B.*

The solubility of gypsum. *G. A. Hulett and L. E. Allen. Jour. Am. Chem. Soc.* 24, *667* (*1902*). — The authors have determined the solubility curve for calcium sulphate between 0° and 107°, reaching equilibrium from both sides and paying special attention to the size of the particles of solid gypsum.

They find a maximum solubility of about 45° and they find also that this is not due to the appearance of a new solid phase. *W. D. B.*

Solubility of the calcium salts of the acids of the acetic series. *J. S. Lumsden. Jour. Chem. Soc.* 81, *350* (*1902*). — The author has determined the solubility curves for the calcium salts of a number of acids of the acetic series. All except calcium isobutyrate and calcium formate show a minimum solubility at some temperature. With the exception of calcium formate all the salts crystallize with one of water at 100°. *W. D. B.*

The equilibrium between the solid and its saturated solution at various temperatures. *J. S. Lumsden. Jour. Chem. Soc.* 81, *363* (*1902*). — The author decides that there are three factors which affect the solubility: thermal energy, affinity, and osmotic pressure. The first tends to cause a solubility increasing with increase of temperature, while the other two work in the opposite direction. The author believes that the theoretical resultant of these three forces is always a solubility curve passing through a minimum. *W. D. B.*

On the solubility of analogous salts. *W. O. Rabe. Zeit. anorg. Chem.* 31, *154* (*1902*). — The author finds that in many cases the ratio of the molecular solubilities of two analogous salts at the same temperature is approximately a whole number and decreases with rising temperature. *W. D. B.*

Theoretical heat of solution of $CdSO_4{}^8/_3H_2O$. *H. B. Holsboer. Zeit. phys Chem.* 39, *691* (*1901*). — The author has determined the thermochemical heat of solution of cadmium sulphate and the heat of dilution from a number of concentrations. He calculates the thermodynamical heat of solution of the salt, and shows that this is positive at low temperatures, negative at high temperatures, and passes through zero at about 15°. This is in agreement with the solubility relations for cadmium sulphate. Incidentally the author states his belief that the methods of Roozeboom and of van Deventer for determining the thermodynamical heat of solution are better than that of Stackelberg. *W. D. B.*

On methods of determining heats of solutions at the saturation point. *E. von Stackelberg. Zeit. phys. Chem.* 41, *96* (*1902*). — A reply to Holsboer (preceding review). *W. D. B.*

Study of lithium silicide. *H. Moissan. Comptes rendus*, 134, *1083* (*1902*). — By heating together silicon and an excess of lithium, the author has prepared the compound Si_2Li_6 corresponding to the new hydride of silicon previously obtained. Lithium silicide forms indigo-blue crystals, has a density of about 1.12 and decomposes in vacuo above 600° forming lithium vapor and amorphous silicon. When treated with a small amount of water, there is formed hydrogen and hydrogen silicide containing some Si_2H_6 which renders the mixture spontaneously inflammable. When water acts slowly on this silicide the hydrides are destroyed by lithium hydroxide and pure hydrogen alone is evolved. *W. D. B.*

Absorption, VII.; on action of high temperatures and the structure of silicic acid hydrogel. *J. M. van Bemmelen. Zeit. anorg. Chem.* 30, *265* (*1902*). — The specific gravity of the substance which forms the walls of the cells in the silicic acid hydrogel is about 2.5–3.0 after the sudden change in dehydration has taken place. This corresponds probably to the contraction of the substance when it is saturated with water. After the gel has been ignited, the specific gravity of this substance is 2.2. It therefore does not contract further when saturated with water, but the hollow spaces fill up. When ignited, the cell substance gradually loses the power of absorption whereby it forms a solid solution with water. In addition, the whole mass contracts in such a way that the hollow spaces gradually disappear and therefore there is a gradual disappearance of that absorption power by which these hollow spaces contain water vapor. In some cases it is probable that a few hollow spaces remain for a time, and that the absorption of water is prevented by the walls of the cell having become impermeable. *W. D. B.*

The properties of mixtures of the lower alcohols with benzene and with benzene and water. *S. Young and E. C. Fortey. Jour. Chem. Soc.* 81, *739* (*1902*). — By distillation the authors have found that with benzene the following alcohols give mixtures of minimum boiling-point — methyl, ethyl, isopropyl, tertiary butyl, *n*-propyl, and isobutyl. Isoamyl and benzene show a normal curve. With water and benzene present, ternary mixtures of constant boiling-point were obtained with ethyl, isopropyl, tertiary butyl, and *n*-propyl alcohol. The fact that solubility relations have a very important bearing in the explanation of these results seems to have been overlooked; for example, benzene added to an alcohol-water mixture must increase the relative proportion of water to alcohol in the vapor because the benzene is less soluble in the water than in the alcohol. The results given in this paper give frequent confirmation of this theory. *H. R. C.*

Fractional distillation as a method of quantitative analysis. *S. Young and E. C. Fortey. Jour. Chem. Soc.* 81 *752* (*1902*). — Defining "middle point" as the temperature midway between the boiling-points of the two liquids into which the original solution tends to separate, the authors find that the weight of the distillate which comes over before the middle point is reached is almost exactly equal to the weight of the more volatile component or mixture. The fractionation is effected by means of a Young evaporator still-head. Excellent results were obtained for the normal fluid pairs, methyl alcohol and water, isoamyl alcohol and benzene. In other cases where a mixture of constant boiling-point is the first distillate, the method has been confirmed, e. g., with the higher alcohols and water, and mixtures of benzene with methyl, ethyl, and propyl alcohols. Success has also attended the work in the ternary systems.

Exceptions were met in the cases of benzene and hexane, ethyl alcohol and water, which the authors ascribe to the fact that the curve representing the relation between boiling-point and molecular composition is very flat at either end. It would be more rational to refer all results directly back to vapor compositions. This must be done before the limitations of the method are understood. *H. R. C.*

The vapor pressure and boiling-points of mixed liquids, I. *S. Young. Jour. Chem. Soc.* 81, *768* (*1902*). — Guthrie has shown that, if two liquids when mixed show neither volume nor heat change, the relation between vapor pressure and percentage composition by weight should be a straight line. Young has tested this for the fluid pair chlorbenzene and brombenzene and found Guthrie's formula verified. *H. R. C.*

The properties of mixtures of the lower alcohols with water. *S. Young and E. C. Forley. Jour. Chem. Soc.* 81, *717* (*1902*).—The boiling-points, specific gravity and dp/dt values for the lower alcohols have here been very carefully determined. In the cases where minimum boiling-points have been observed with water as the other component, these constants have also been determined for the constant boiling mixtures. There is also given a table showing the percentage contraction found when the alcohols are mixed with water.
H. R. C.

Liquid mixtures and minimum boiling-points. *C. D. Holley. Jour. Am. Chem. Soc.* 24, *448* (*1902*).—The author finds minimum boiling-points for amyl bromide and amyl alcohol, amyl bromide and isobutyl alcohol, amyl bromide and propyl alcohol, amyl iodide and amyl alcohol, amyl alcohol and amyl acetate. With amyl iodide and isobutyl alcohol and with amyl iodide and propyl alcohol, there is an apparent lowering of the boiling-point of 0.1°, but the author does not feel certain that these are really cases of minimum boiling-points. *W. D. B.*

Vapor pressures of aqueous solutions. *E. P. Perman. Jour. Chem. Soc.* 79, *718* (*1901*).—The author has determined the pressure-concentration curves for aqueous ammonia at five temperatures, and proposes to determine the composition of the vapor phase. *W. D. B.*

The molecular weights of some carbon compounds in concentrated solutions with carbon compounds as solvents. *C. L. Speyers. Am. Jour. Sci.* (*4*) 13, *213* (*1902*).—The author has studied the behavior of a number of organic compounds in organic solvent, using the Ostwald-Walker method. He decides that the equation

$$\log\left(\frac{n}{N}+1\right)=\frac{Q'}{R}\,\frac{T_1-T_0}{T_1T_0}$$

will answer for all purposes to which van 't Hoff's formula is put and that it is altogether independent of the osmotic theory. In this equation Q' is the heat of vaporization of one gram-molecule of solvent from the solution, the quantity of the solution being so great that no change in concentration is produced when the gram-molecule is removed; T_1 is the boiling-point of the solution, T_0 that of the pure solvent, and R is the gas constant. *W. D. B.*

The union of hydrogen and oxygen. *H. B. Baker. Jour. Chem. Soc.* 81, *400* (*1902*).—

1. The gases produced by the electrolysis of purified barium hydroxide do not explode on heating to redness after drying with distilled phosphoric oxide.

2. The gases can be heated to the melting-point of silver without combination.

3. If only partially dried, the gases unite slowly on heating, and although visible water is present, no explosion takes place.

4. The undried gases unite slowly in sunlight at ordinary temperatures; the dried gases do not.

5. There is no contraction observable during thorough drying of gases, so that the dissociation of gases in the undried condition, if it exists, cannot be proved by volume measurements. *W. D. B.*

The direct union of carbon and hydrogen, II. *W. A. Bone and D. S. Jerdan. Jour. Chem. Soc.* 79, *1042* (*1901*). — Methane begins to be formed from carbon and hydrogen at the temperature of 1200°. At some temperature, at present unknown, between 1200° and 3500° acetylene and ethane begin to be formed. In the arc the formation of all these hydrocarbons continues until a certain equilibrium between them and carbon vapor and hydrogen is established. Since methane and ethane are produced simultaneously and at rates which bear a constant ratio to each other during the whole time the arc is maintained, the authors believe that ethane is formed directly from its elements and not by decomposition of either methane or acetylene. The authors also believe that acetylene is formed direct from its elements. *W. D. B.*

The specific heat of solutions, III. *W. F. Magie. Phys. Rev.* 14, *193* (*1902*). — This is a description of a modified Pfaundler calorimeter.

W. D. B.

Multi-Component Systems

Equilibria in the system, sodium carbonate, ethyl alcohol, and water. *C. H. Ketner. Zeit. phys. Chem.* 39, *641* (*1902*). — The author has made a very complete study of the system, sodium carbonate, ethyl alcohol, and water. This is one in which two liquid layers occur. As a preliminary, the author found that there is another stable hydrated sodium carbonate, the β-modification, $Na_2CO_3 7H_2O$. This hydrate crystallizes between 31.9° and 35.1°. In addition to determining isotherms and boundary curves, the author has made some measurements of vapor pressures. He confirms the results of other observers, that the addition of a salt to aqueous alcohol may cause a rise or a fall of the boiling-point, depending upon the relative masses of water and alcohol.

W. D. B.

Contribution to our knowledge of equilibria in systems of three components, in which two liquid phases can occur. *R. A. Meerburg. Zeit. phys. Chem.* 40, *641* (*1902*). — This is a study of the systems, di-ethyl amine, alcohol, and water, and di-ethyl amine, ether, and water. These systems differ from those which have previously been considered in that di-ethyl amine and water have a minimum consolute point. This, of course, reverses the general relations.

W. D. B.

On the system bismuth oxide nitric acid, and water. *G. M. Rutten. Zeit. anorg. Chem.* 30, *342* (*1902*). — The author has made a careful study of the basic bismuth nitrates and finds the following salts. To simplify the formulas, we will let B stand for Bi_2O_3, N for N_2O_5, and W for H_2O. The neutral salts are then BN_3W_{10}, BN_3W_4, and BN_3W_3. The basic salts have the formulas BN_2W_2, BNW_2, BNW, $B_6N_5W_8$, $B_{10}N_9W_7$, and B_2NW. A number of other basic salts which have been described by Becker, Janssen, and others, could not be obtained, and it is probable that their formulas were based on analytical errors, due to too long washing or to too intense drying. The neutral salt, BN_3W_{10}, and the basic salt, BNW_3, show a continuous change of vapor pressure on dehydrating at 15°. *W. D. B.*

On the mixed crystals of copper sulphate and zinc sulphate. *H. W. Foote. Am. Chem. Jour.* 26, *418* (*1901*). — Between 12° and 56° copper sulphate and zinc sulphate form two sets of mix crystals. The author shows that the limiting compositions for the two series change with the temperature. *W. D. B.*

Decomposition of hydrated mix crystals. *R. Hollmann. Zeit. phys. Chem.* 40, *561* (*1902*). — The author has given an extended discussion of the possible decomposition of hydrated mix crystals, and finds that there are three possible types of decomposition curves for systems where complete miscibility occurs. For the composition of mix crystals with different amounts of water separating from a common solution, the rule is stated that the mix crystal of the higher hydrate is always richer in comparison with the lower hydrate in the component, addition of which raises the decomposition temperature. *W. D. B.*

The double salts of magnesium sulphate and zinc sulphate. *R. Hollmann. Zeit. phys. Chem.* 40, *577* (*1902*). — A study of the decomposition temperatures for mix crystals of zinc and magnesium sulphates shows maxima at the points where magnesium and zinc are present in equivalent quantities and where there are two equivalents of magnesium to one of zinc. *W. D. B.*

The reciprocal nature of solubility changes. *V. Rothmund and N. T. M. Wilsmore. Zeit. phys. Chem.* 40, *611* (*1902*). — By means of a thermodynamic cycle the authors conclude that if substance A decreases the solubility of substance C in substance B, substance C will decrease the solubility of substance A in substance B. They conclude, further, which is probably wrong, that these two changes of solubility will be approximately equal. Instead of testing this directly, they get at their results indirectly by measuring the change in the distribution of phenol between water and benzene when potassium sulphate and other salts are added to the water. They also study the effect of different salts on the distribution of acetic acid between water and chloroform. Under conditions like these, it is impossible to test any theory, and it is therefore not surprising that the authors decide that the agreement between theory and experiment is as good as could be expected. *W. D. B.*

On the solubility of the heavy metal hydroxides in sodium hydroxide. *J. Rabenbauer. Zeit. anorg. Chem.* 30, *331* (*1902*). — Solutions of the hydroxides of beryllium, zinc, tin, and lead in alkalies show a concentration varying with the concentration of the alkali. The author concludes from this that no compound exists according to definite proportions; but this conclusion is not justified by the facts, which merely show that no non-dissociating compound exists. With zinc hydroxide, more hydroxide goes into solution at first than corresponds to the stable state and zinc hydroxide reprecipitates spontaneously. This phenomenon was not observed with the hydroxides of tin and lead, but probably occurs with beryllium hydroxide. The change of solubility with the concentration of the alkali is relatively small with beryllium and tin hydroxides,

very appreciable with lead hydroxides, and very large indeed with zinc hydroxides.
W. D. B.

On the nature of alkaline solutions of metallic hydroxides. *A. Hantzsch. Zeit. anorg. Chem.* 30, *289* (*1902*).—The hydroxides of beryllium, zinc, germanium, tin, and lead are very weak acids since their alkali salts are strongly hydrolyzed in aqueous solutions and these solutions are only stable in presence of a large excess of alkali. These hydroxides behave only as monobasic acids. Zinc and beryllium hydroxides are very weak acids, and it is even doubtful whether alkali zincates exist to any appreciable extent in aqueous solutions. The hydroxides of lead, tin, and germanium are distinctly acid, lead being the weakest and germanium the strongest acid of the three.

Lead hydroxide is a stronger base than beryllium hydroxide and also a stronger acid. The author accounts for this discrepancy by assuming that there is a change of constitution in the case of the lead hydroxide, the plumbites belonging really to the formic acid type.
W. D. B.

The behavior of molecular compounds when dissolving, II. *G. Bodländer and R. Fittig. Zeit. phys. Chem.* 39, *597* (*1902*).—The authors have determined the solubility of silver chloride in ammoniacal solutions of varying concentrations, to which potassium chloride was also added. In addition they have measured the electromotive force of a number of concentrated salts. They conclude that the complex salt, $AgCl2NH_3$, exists in solution and that the cation is $Ag2NH_3$. In a 1/10 normal solution they decide that only 0.068 percent of the silver is present in the form of silver as ion.
W. D. B.

On the solubility of carbon monoxide in binary organic mixtures. *F. W. Skirrow. Zeit. phys. Chem.* 41, *139* (*1902*).—The solubility curve for carbon monoxide in mixtures of two organic liquids may show a maximum, a minimum, or neither. In the cases of maximum solubility, the author shows that there is a minimum surface tension very close to the point of maximum solubility.
W. D. B.

On the action of organic acids on metallic antimony, I. *B. Moritz and C. Schneider. Zeit. phys. Chem.* 41, *129* (*1902*).—While the aliphatic acids have but little action on antimony in the presence of air, the oxyacids dissolve antimony readily under these circumstances. No definite relation seems to hold in the aromatic series because phenol, benzoic acid and salicylic acid do not act on antimony while gallic acid and tannic acid do.
W. D. B.

The preparation of absolute alcohol from strong spirit. *S. Young. Jour. Chem. Soc.* 81, *707* (*1902*).—In 1893 Squibb expressed the belief that absolute alcohol had not been prepared, although he obtained a product of sp. gr. 0.80581 at 0°/4°. The author, noting that the ternary mixture of alcohol, benzene and water gave a boiling-point lying lower than any of the minima for the three binary mixtures, decided that on careful fractional distillation it should be possible to obtain three well-marked fractions—first the ternary mixture of minimum boiling-point, then a binary mixture also of constant composition, while the last fraction should be the pure component. Working with alcohol containing 7.4 percent and less of water, he has, by distilling with an amount of benzene approximately equal to his alcohol solution, obtained distillates of sp gr 0.80635 at 0°/4°; with hexane in place of the benzene 0.80627. This use of benzene as a dehydrating agent for alcohol is of great interest to all who are concerned in the study of phase separations. *H. R. C.*

The nature of metal-ammonia compounds in aqueous solutions. *H. M. Dawson and J. McCrae. Jour. Chem. Soc. 77, 1239 (1900).* — The authors have determined the distribution ratio for ammonia in chloroform and water at 20° and have then studied the effect of adding salts to the aqueous solutions. Copper sulphate, zinc sulphate, copper chloride, and cadmium iodide all increase the concentration of ammonia in the aqueous solution and this increase is the same for equivalent quantities for each salt. The authors conclude that this increase can be accounted for on the assumption of a dissociating ammonia compound containing up to four of ammonia to one of the salt. *W. D. B.*

Metal-ammonia compounds in aqueous solutions, III.-IV. *H. M. Dawson. and J. McCrae. Jour. Chem. Soc. 79, 1069, 1072 (1901).* — The authors find little or no evidence that calcium chloride forms a complex salt with ammonia in aqueous solution. In Part IV. the authors describe experiments showing the influence of temperature on the dissociation of copper ammonia sulphate. While the results point to a slight increase in dissociation with rising temperature, the amount of the change is too small to permit of any accurate conclusions being drawn. *W. D. B.*

Generalizations on double halogen salts. *H. L. Wells. Am. Chem. Jour.* 26, *389 (1901).* — These generalizations refer to the salts of the alkali metals, ammonium and univalent thallium, and do not include the double halides of the organic bases or the salts in which bivalent metals form the more positive halides. The valency of inactive halides has little or no influence upon the types of double halides that they formed. The binding power of negative halides, whatever their valency may be, is nearly the same as that of alkaline halides. A very large proportion of these double salts belong to simple types. It is probable that the ease of formation and variety of double halides increases from the iodides to the fluorides. The other gradations, and energies existing in some cases are probably not general.

The author advocates the classification of double halides under three groups, based upon their behavior in solutions: —

1. Salts that form complex ions.
2. Other salts that can be recrystallized from water or dilute acids.
3. Salts that require the presence of an excess of one of their components for their formation. *W. D. B.*

Contact hydrogenization of ethylene hydrocarbons. *P. Sabatier and J. B. Senderens. Comptes rendus, 134, 1127 (1902).* — The authors find that hydrogenization by means of copper can only be effected with a mono-substituted ethylene. Thus, propylene can be reduced but not trimethylene. The authors have utilized this fact to determine the structure formula of menthene.

W. D. B.

Lead silicates in relation to pottery manufacture. *T. E. Thorpe and C.*

Simmonds. Jour. Chem. Soc. 79, *791* (*1901*). — The authors have studied the conditions for the production of nearly insoluble lead silicates and find that the following conditions are essential:

"The preservation of the proper relation between the acidic and basic constituents; the fusion of the materials for such a time and in so thorough a manner as to allow of the chemical reactions being completed. In certain cases it is also desirable to dry the silicate with acid in order to extract small quantities of admixed or loosely combined lead compounds from the bulk of the product.

"Provided that the foregoing conditions are satisfied, then, without prejudice to the non-solubility in the standard solvent of the lead in the silicate:

"1. The quantity of lead oxide in the silicate may have any value up to 50–55 percent or even higher.

"2. The other bases (lime, aluminum, the alkalies) may vary considerably, replacing one another and also the lead oxide within very wide limits.

"3. The influence of boric oxide, irrespective of that of the silicate with which it may be associated, still remains to be ascertained, but it has been pointed out that boric oxide up to 6 percent, the highest amount met with in the specimens examined, may in certain cases be present without apparently exercising any special influence in promoting the solubility of the lead."

The silicates which yield lead in quantity to the standard solvent are referable to meta-silicic acid, H_2SiO_3; while all those of slight solubility are derived from meta-polysilicic acid, $H_4Si_3O_8$, and from meta-di-silicic acid, $H_2Si_2O_5$.

W. D. B.

Osmotic Pressure and Diffusion

On the permeability of animal membranes. *A. Galeotti. Zeit. phys. Chem.* 40, *481* (*1902*). — The author has studied the behavior of a number of animal membranes and finds that these behave very differently. Some are permeable to all the salts taken, while others are more or less impervious. In some cases the impermeability seems to be a specific property of the living cell, and disappears with its death. *W. D. B.*

The preparation of osmotic membranes by electrolysis. *H. N. Morse and D. W. Horn. Amer. Chem. Jour.* 26, *80* (*1901*). — The authors precipitated a membrane of copper ferrocyanide in the walls of a porous cup by placing the usual solutions inside and out, and passing an electric current through the walls of the cell, until a resistance of 1500–3000 ohms has been reached. Cells made in this way stood pressures of four and one-half atmospheres without difficulty and the failure above this pressure was due to the connections and not to the membrane. *W. D. B.*

Retrograde diffusion of electrolytes. *J. Thovert. Comptes rendus*, 134, *826* (*1902*). — When a solution of hydrochloric acid is placed above a solution of sodium chloride the hydrochloric acid diffuses into the upper layer of the sodium chloride and, at first, there is a retrograde diffusion of sodium chloride into the lower portion of the sodium chloride solution. The author shows that this result can be accounted for by means of the Nernst theory of diffusion.

W. D. B.

Velocities

On the decomposition of organic halogen compounds in alcoholic solutions by sodium amalgam. *R. Löwenherz. Zeit. phys. Chem.* 40, *399* (*1902*). — While a very simple formula was found for the action of metallic sodium on halogen compounds in alcoholic solutions, it was not possible to write any formula for the action of sodium amalgam. With bromine compounds, the decomposition varied with the rate of stirring. The addition of water has little or no effect on the decomposition of iodbenzene by sodium amalgam, while water has a great effect when metallic sodium is used. The amount of decomposition of the iodine compounds is much greater when sodium amalgam is used than with metallic sodium. The concentration of the sodium amalgam has no appreciable effect upon the decomposition of iodbenzene, but a very marked effect on the decomposition of brombenzene. Lithium, potassium, and sodium amalgam are very similar in their action on iodbenzene, but the three metals, when taken pure, act differently. *W. D. B.*

Contribution to the kinetics of photochemical reactions. *E. Goldberg. Zeit. phys. Chem.* 41, *1* (*1902*). — The author has studied the oxidation of quinine by chromic acid under the influence of light. It was shown that Vogel's absorption law and the photochemical law of Bunsen and Roscoe both hold. While the reaction is apparently of the first order, it is really of the second order when one takes into account the change in the strength of the light due to the change of concentration. In this as in other photochemical processes, the reaction velocity changes but slowly with the temperature. *W. D. B.*

Note on cerium peroxide. *E. Bauer. Zeit. anorg. Chem.* 30, *251* (*1902*). — When a cerous salt is dissolved in potassium carbonate solution and treated with arsenious acid, both the cerium salt and the arsenious acid are oxidized by the oxygen of the air. *W. D. B.*

Glucose and cerium carbonates. *A. Job. Comptes rendus*, 134, *1052* (*1902*). — When potassium arsenite is oxidized by cerous carbonate there is a limit to the reaction because the cerous salt is converted into ceric salt, which latter cannot take up oxygen from the air. On the other hand it has been found that a concentrated solution of glucose and of potassium carbonate will reduce perceric salts to cerous salts. The cerous salt will then take up oxygen from the air, oxidizing the glucose and changing the perceric salt. Under these circumstances, the cerium salt is a true catalytic agent, and the existence of an intermediate compound can easily be shown. *W. D. B.*

The decomposition of chlorates. *W. H. Sodeau. Jour. Chem. Soc.* 79, *939* (*1901*). — This paper deals with the supposed mechanical facilitation of the decomposition of potassium chlorate.

"The author is of the opinion that the supposed ability of chemically inert solid particles to facilitate the decomposition of potassium chlorate is unsupported by chemical evidence, and, if existing, is inadequate to explain even a small fraction of the great facilitation produced by the oxides of manganese, iron, nickel, cobalt, and copper. The action of the latter substances now engaging his attention would, therefore, appear to be entirely chemical.

"Veley had observed that the addition of one percent of barium sulphate increases the rate of decomposition of potassium chlorate about 100 percent. The author has repeated this experiment and finds an average increase of rate of only 16 percent. This can easily be accounted for by the formation of barium chlorate, a substance less stable than potassium chlorate. *W. D. B.*

Electromotive Forces

Some measurements of gas cells. *V. Czepinski. Zeit. anorg. Chem.* 30, *1* (*1902*). — The author has worked with gas cells under different pressures and finds that methane is a completely indifferent gas electrolytically, and that therefore it affects the potential of electrically active gases with which it does not react chemically, only in so far as it dilutes them. With hydrogen electrodes under different partial pressures, the final equilibrium is reached fairly rapidly and the electromotive force corresponds very closely to that required by the theory. The presence of traces of oxygen produce a marked effect as was to be effected, and the effect is the more marked the more dilute the hydrogen. *W. D. B.*

Remarks on the paper by Mr. V. Czepinski. *E. Bose. Zeit. anorg. Chem.* 30, *406* (*1902*). — The author calls attention to the fact that he himself had supposed that the high value of the gas cell was due to the direct formation of water and not to secondary reaction as seemed to be implied in the reference made by Czepinski. *W. D. B.*

On gas cells. *R. Lorenz. Zeit. anorg. Chem.* 30, *275* (*1902*). — The author expresses his regret that Czepinski should have misinterpreted Bose (preceding review). He discusses the four types of gas potentials which can be deduced from the Nernst theory. *W. D. B.*

On the absolute potential of hydrogen at a mercury cathode. *A. Coehn and E. Neumann. Zeit. phys. Chem.* 39, *353* (*1901*). — Caspari had found that a greater excess voltage was necessary to precipitate hydrogen on mercury than on platinum. This difference might be due to the fact that mercury is a liquid, and might be due to a specific property of the metal. In order to decide between these two hypotheses, the authors have made experiments with platinum and mercury at —85°. At this temperature, mercury is solid, but the same differences in behavior between mercury and platinum are found. *W. D. B.*

On the potential of ozone. *L. Gräfenberg. Zeit. Elektrochemie,* 8, *297* (*1902*). — The author finds 1.66 volts for the hydrogen-ozone gas cell. *W. D. B.*

Addition to the paper: "On the effect of a salt with a common ion on the electromotive force of concentration cells." *O. Sackur. Zeit. phys. Chem.* 39, *364* (*1901*). — Planck has called the author's attention to the fact that certain assumptions made in his paper (6, 157) are inaccurate. The result of the correction is that the Abegg-Bose formula is only an approximation formula, while

Planck's formula is exact. The authors had previously come to the reverse conclusion. *W. D. B.*

Electromotive behavior of hypochloric acid and chloric acid. *E. Müller. Zeit. Elektrochemie*, 8, *425* (*1902*). — A higher voltage is necessary to produce a current with a smooth platinum anode than with a platinized anode. The author is inclined to believe that this is due to the formation of a metastable chemical compound at the smooth electrode but recognizes the other possibility that the formation of O_2 from 2O may take place more rapidly at a platinized anode than at a smooth one. *W. D. B.*

On the depolarization of the hydrogen electrode by substances of the aromatic series. *A. Panchaud de Bottens. Zeit. Elektrochemie*, 8, *305*, *332* (*1902*). — The author has determined the effect of adding a large number of organic substances to the hydrogen electrode. The amount of depolarization is 0.64–0.41 for the nitroso group, 0.33–0.22 for the nitro group, and 0.16–0.05 for the nitrosamines. Substances with analogous constituents give analogous depolarization values, but no regularities could be found between isomers in a given group. In the case of nitro bi-substitution products, however, the ortho compound is the strongest depolarizing agent. *W. D. B.*

Measurement of the internal resistance of galvanic cells. *C. H. Ayres, Jr. Phys. Rev.* 14, *17* (*1902*).—The method used is a modification of Kohlrausch's method and is called by the author the "capacity bridge". For three cells that were studied, it was found that the resistance was the same, whether the cell was on open or closed circuit. *W. D. B.*

On the decomposition of carbon dioxide when submitted to electric discharge at low pressures. *J. N. Collie. Jour. Chem. Soc.* 79, *1063* (*1901*). — When carbon dioxide under low pressures is submitted to the action of the electric spark, it is rapidly decomposed into carbon monoxide and oxygen. In one case in which dry gas under 5 mm pressure was sparked for one minute, a decomposition of 65 percent was found. In another case, under 1 mm pressure, there was 63 percent decomposition in ten seconds. Carbon monoxide is far more stable. The authors believe it possible that the absorption of carbon dioxide by plants and the subsequent liberation of oxygen when the plant is exposed to sunlight may be due to the excessive stability of carbon dioxide when submitted to electrical strain. *W. D. B.*

Magnetization of steel at liquid air temperatures. *C. C. Trowbridge. Phys. Rev.* 14, *181* (*1902*). —

1. Approximately the same magnetic moment is obtained whether tungsten steel or carbon steel is magnetized at normal, or liquid air temperatures, other conditions being the same.

2. The initial loss in the magnetic moment due to the change of temperature of a bar of steel magnetized at −185° and then heated to 20°, is much greater than when the bar is magnetized at 20° and then cooled to −185°, a considerable loss occurring in both cases.

3. There is a certain amount of instable magnetism in a newly-made steel magnet which tends to pass off at the first change of temperature in either

direction from that at which magnetization takes place, much more instable magnetism passing off by heating than by cooling.

4. Tungsten steel magnets give a much higher magnetic moment than carbon steel and have much less of the instable magnetism just referred to.

W. D. B.

Crystallization under electrostatic stress. *P. R. Heyl. Phys. Rev.* 14, *83* (*1902*). — The author has studied the crystallization of sulphur from carbon bisulphide and mercury iodide from alcohol under electrostatic stress. In no case could any influence be detected due to this cause. *W. D. B.*

Electrolysis and Electrolytic Dissociation

The electrolytic reduction of nitric acid in the presence of hydrochloric acid and sulphuric acid. *J. Tafel. Zeit. anorg. Chem.* 31, *289* (*1902*). — The author finds that, with a mercury cathode and under suitable conditions, nitric acid can be converted almost completely into hydroxylamine without formation of ammonia. With a lead cathode, about 40 percent yield can be obtained, and with copper only 15 percent. When using a copper cathode covered with finely divided copper only a small amount of hydroxylamine is formed, while the nitric acid is reduced almost completely to ammonia. The author believes that the reduction to ammonia with copper cathodes does not pass through the hydroxylamine stage.

Experiments have been made on the quantitative reduction of nitric acid with cathodes of different metals. With platinum cathodes no certain reduction was obtained. When the electrolyte was a mixture of nitric acid and sulphuric acid the total reduction varied from 76 percent with nickel to 100 percent with lead, while the yield of hydroxylamine varied from 15 percent with silver to 45 percent with tin. When a little less nitric acid was taken, a yield of hydroxylamine of 52 percent was obtained with tin, and 59 percent with bismuth, while the yield dropped to 1 percent with pulverulent copper. With amalgamated cathodes, a hydroxylamine yield of about 67 percent was obtained, which varied only slightly with the nature of the amalgam. Increase of concentration of sulphuric acid decreases the total current yield but increases the percentage yield of hydroxylamine.

The author deduces the following conditions as favorable for obtaining a high yield of hydroxylamine: amalgamated lead cathodes, low temperature, moderate concentration of nitric acid at the cathode, and a high concentration of sulphuric acid at the cathode. *W. D. B.*

On the reducing action of lead and mercury cathodes in sulphuric acid solutions. *J. Tafel and K. Schmitz. Zeit. Elektrochemie*, 8, *281* (*1902*). — With lead cathodes the reduction of caffeine is much less than with mercury cathodes. Amalgamating the lead electrode improves it. Cathodes of tin amalgam are very effective. The reduction of acetone takes place more readily with mercury cathodes than with lead cathodes, and the reaction goes further, the reduction product being almost exclusively isopropyl alcohol, practically no pinacone being formed. *W. D. B.*

The electrolytic reduction of nitro-urea. *G. W. F. Holroyd. Jour. Chem. Soc.* 79, *1326* (*1901*). — The author has reduced nitro-urea in ammonium chloride solution using iron or zinc electrodes. The solution is kept cold and as high as 70 percent efficiency was obtained. The reduction product is semicarbazide and was precipitated as the benzylidene derivative. *W. D. B.*

Electrolytic refining of tin scrap with caustic soda solution. *H. Minnicke. Zeit. Elektrochemie*, 8, *315*, *357*, *381* (*1902*). — This is a very able account of the electrolytic process of the working up of tin scrap, and the author discusses the difficulties in much detail. The best solution contains 8–10 percent sodium hydroxide and no chloride. The solution is electrolyzed hot and the tin is removed as hydrated stannic oxide by treating first with carbonic acid, and then with lime. *W. D. B.*

On the formation of difficultly soluble precipitates during electrolysis with soluble anodes. *M. Le Blanc and D. Bindschedler. Zeit. Elektrochemie*, 8, *255* (*1902*). — The authors have repeated Luckow's process for making lead chromate where he used lead anodes and a solution containing a small amount of sodium chromate and a large amount of sodium chlorate. The authors find that, when there is no sodium chlorate present, there is also no formation of lead chromate, lead peroxide being formed at the anode. It seems as though it were essentially a time phenomenon, the lead dissolving as chlorate and then precipitating as chromate. *W. D. B.*

Behavior of lead anodes in phosphoric acid. *F. Fischer. Zeit. Elektrochemie*, 8, *398* (*1902*). — When lead anodes are used in a dilute phosphoric acid solution having specific gravity 1.02, a gold yellow solution is obtained containing quadrivalent lead. This solution reacts with hydrogen peroxide evolving oxygen, precipitating white plumbous phosphate and becoming colorless. By adding to this yellow solution salts which do not decompose it, a yellow salt may be precipitated which is soluble in phosphoric acid. When this yellow salt is treated with water, lead peroxide is formed. *W. D. B.*

Electrolytic deposition of lead from phosphoric acid solutions. *A. F. Lynn. Jour. Am. Chem. Soc.* 24, *435* (*1902*). — The author finds that lead can be determined electrolytically from a solution prepared by precipitating lead phosphate with phosphoric acid and then dissolving this in an excess of the precipitating agent. *W. D. B.*

Contribution to the electrolytic analysis of mercury. *D. E. Bindschedler. Zeit. Elektrochemie*, 8, *329* (*1902*). — The author finds that one source of error in the electrolytic determination of mercury is the volatilization of the mercury. At 60° there may easily be a loss of 7 mgs. *W. D. B.*

On electrically prepared copper sulphide. *J. Rieder. Zeit. Elektrochemie*, 8, *370* (*1902*). — The author finds that when a copper wire imbedded in sulphur is made the cathode, an ever-increasing layer of blue-black copper sulphide is formed. *W. D. B.*

On the reactions during the formation of calcium carbide. *G. Gin. Zeit. Elektrochemie*, 8, *397* (*1902*). — At the highest temperatures, carbon monoxide cannot exist, and carbon reacts with lime forming carbide and oxygen. It is also known that calcium carbide reacts with lime, setting free calcium and carbon monoxide. In consequence of the first reaction, it is essential to take more lime than is called for by the equation as usually written. *W. D. B.*

The production of hitherto unknown metallic derivatives. *S. A. Tucker and H. R. Moody. Jour. Chem. Soc.* **81**, *14* (*1902*). — The authors have prepared the derivatives of zirconium, chromium, tungsten, and molybdenum by heating the metals with boron in an electric furnace. They did not succeed in preparing the boride of copper or of bismuth. *W. D. B.*

The fusion of carbon. *A. Ludwig. Zeit. Elektrochemie*, **8**, *273* (*1902*). — The author passed a current of 4 amp/mm^2 through carbon rods placed under a pressure of 1500 atmospheres. At the end of one and one-half hours each rod contained a core of dense graphite. The author has also tried heating a carbon rod electrically and plunging it suddenly into water under a pressure of 1400-1500 atmospheres. Under these circumstances there were found in the carbon rod colorless, transparent globules which may or may not have been diamonds. The author believes that the difficulty was due to too slow cooling, owing to the Leidenfrost phenomenon. *W. D. B.*

Investigations on the permanency of platinum and platinum iridium anodes in electrolysis of hydrochloric acid. *F. Bran. Zeit. Elektrochemie*, **8**, *197* (*1902*). — The author finds that the percentage decomposition of platinum anodes decreases the higher the current density. While the anode is more attacked the lower the current density, the cathode is converted into platinum black more rapidly the higher the current density. *W. D. B.*

Cathode disintegration in consequence of the formation of an alloy with a cathode material. *F. Haber and M. Sack. Zeit. Elektrochemie*, **8**, *245* (*1902*). — The authors believe that the decomposition of cathodes at high current densities is due largely to the formation of alloys with the alkali metals in solution. To prove this they show that lead, tin, thallium, and Rose's metal when alloyed with sodium and placed in water give the same general disintegration that is obtained by electrolysis of a caustic alkali solution with these metals as cathodes. Zinc and cadmium do not form alloys with sodium and they are not decomposed when used as cathodes. It is also shown that the formation of platinum black and of black mercury during the electrolysis is to be referred to the same cause, the formation of an alloy. *W. D. B.*

Electrically heated laboratory furnaces for high temperatures. *W. C. Heraeus. Zeit. Elektrochemie*, **8**, *201* (*1902*). — Electric furnaces which are heated above 200° by platinum wires do not last. The heating spiral being a round wire does not come in good contact with the tube to be heated and therefore has a much higher temperature than that. Owing to unequal contact, there is also unequal heating, and consequently a portion of the wire may easily be heated above the melting-point of platinum. All these differences are overcome by using platinum foil about 0.007 mm in thickness instead of platinum wire. Under these circumstances, it is possible to heat a tube 2-5 mm in diameter about 1400° in five minutes without damaging the tube. A temperature of 1700° can be reached without melting the foil, but as yet no tube can be found which will stand this without decomposition or without conducting. The use of platinum foil enables one to get along with about one-sixth the weight of platinum which will be necessary for wire heating. *W. D. B.*

An apparatus for electro-analytical purposes. *F. Hanaman. Zeit. Elektrochemie,* 8, *398* (*1902*). —The author describes a condensed form of apparatus for voltmeter, ammeter and variable resistances. *W. D. B.*

The electrical resistance of steel and of pure iron. *C. Benedicks. Zeit. phys. Chem.* 40, *545* (*1902*).—Equivalent quantities of different substances when dissolved in iron increase its resistance by the same amount. The iron carbide has no perceptible influence on the resistance of iron. Mild steel contains 0.27 percent of carbon in solution; but this is believed not to be stable unless there is a certain excess of iron carbide present. The author believes that the resistance of absolutely pure iron is about 7.6 micro ohms referred to a centimeter cube. *W. D. B.*

On the thermodynamics and dissociation theory of binary electrolytes. *M. Planck. Zeit. phys. Chem.* 41, *212* (*1902*).—The author first shows what relations between pressure, temperature, electromotive force and osmotic pressure hold for all concentrations and independently of any molecular theory. He then takes up the relations postulated by the electrolytic dissociation theory, the assumption of the gas law, and the mass law. In the third section he discusses the question of the calculation of the degree of dissociation from the electrical conductivity and takes the ground that no proof has ever been offered that the migration velocities of the ions are independent of the concentration. In consequence, we cannot calculate the percentage dissociation of any substances from the conductivity. He objects to the conductivity method still further on the ground that it is essentially a dynamic method and that a static method would be more satisfactory. *W. D. B.*

Liquid nitrogen peroxide as a solvent. *P. F. Frankland and R. C. Farmer. Jour. Chem. Soc.* 79, *1356* (*1901*). —

1. Nitrogen peroxide does not dissolve inorganic salts. On the other hand it is a good solvent for certain non-metallic elements and readily dissolves many organic compounds.
2. The perfectly anhydrous liquid is comparatively inert as a chemical reagent. Many organic compounds can be recovered unchanged from their solution in nitric peroxide.
3. Measurements of the electrical conductivity show that it is not "an ionizing solvent."
4. Molecular weight determinations show that many substances are associated to double molecules in this solvent. *W. D. B.*

The dissociating power of hydrogen sulphide. *W. T. Skilling. Am. Chem. Jour.* 26, *383* (*1901*). —The author finds that potassium chloride dissolves readily in liquefied hydrogen sulphide and that the solution does not conduct electricity. *W. D. B.*

The dissociation of certain acids, bases, and salts at different temperatures. *H. C. Jones and J. M. Douglas. Am. Chem. Jour.* 26, *428* (*1901*). — The authors have determined the conductivities of a number of salts over a wide range of temperature. From these conductivity measurements, they have calculated the percentage of electrolytic dissociation and find that this changes very slightly with the temperature. *W. D. B.*

On the conductivity of mixtures of electrolytes. *P. Sabat. Zeit. phys. Chem.* 41, *224* (*1902*). — The author has made a number of experiments to test Barmwater's formula for mixtures of electrolytes. The agreement between the facts and the theory is recognized by the author as not being very satisfactory. *W. D. B.*

On the antiseptic action of the hydrogen ion of dilute acids. *M. Bial. Zeit. phys. Chem.* 40, *513* (*1902*). — The author has studied the effect of dilute acids on the development of yeast. With each acid there is a concentration above which the yeast ferment does not develop, and this concentration appears to be a function of the concentration of hydrogen as ion. Addition of sodium chloride to a dilute hydrochloric acid solution first decreases the antiseptic power and then increases it. With a more concentrated acid, the first addition of sodium chloride increases the antiseptic action. As is well known, addition of sodium chloride to a hydrochloric acid solution increases the rate at which this acid inverts cane-sugar. From the author's experiments, he concludes that if these experiments were repeated with a sufficiently dilute acid, it would be found that addition of sodium chloride decreases the rate of inversion. The author finds, further, that while addition of sodium acetate to acetic acid solution decreases the antiseptic power, the addition of sodium acetate in sufficient excess causes it to decrease. *W. D. B.*

A new method for the determination of electrolytic dissociation. *R. C. Farmer. Jour. Chem. Soc.* 79, *863* (*1901*). — The author has determined the hydrolysis of hydroxyazobenzene by finding how much free hydroxyazobenzene is taken up by the benzene layer when an aqueous solution of a salt of hydroxyazobenzene is shaken with benzene. The results give a dissociation constant of 4.9×10^{-9}. *W. D. B.*

On the acid nature of acetylene. *J. Billitzer. Zeit. phys. Chem.* 40, *535* (*1902*). — The author hoped to determine the acidity of acetylene by observing the change of solubility when alkalies were added to the water. He finds, however, that barium hydroxide causes a slight increase in solubility, ammonia an almost imperceptible increase, and that sodium hydroxide and potassium hydroxide decrease the solubility. The assumption is made that this decrease of solubility in the case of sodium hydroxide and potassium hydroxide is the resultant of an increase of solubility due to the alkali nature and a decrease due to the specific precipitating power. He therefore measures the decrease of solubility of ethylene in solutions of caustic soda and potash, assumes that this specific action is the same for acetylene, and comes out triumphantly with a very slight increase of solubility for acetylene due to its acid nature. A conclusion of this sort is interesting but valueless. *W. D. B.*

The conditions determinative of chemical change, and of electrical conduction of gases, and on the phenomenon of luminosity. *H. E. Armstrong. Proc. Roy. Soc. 70, 99 (1902).* — The author believes that chemical action is reverse electrolysis or that chemical action can take place only when an electrolyte is present. The author points to the recent experiments with dried gases as confirming this view. Since water is not an electrolyte, he believes that the essential thing is not so much to remove the water vapor as to remove the conducting impurities which are present simultaneously. The author believes that luminosity and line spectra are the expression — visible signs — of the changes attending the formation of molecules from their atoms, or, speaking generally, that they are consequences of chemical changes. *W. D. B.*

Dielectricity and Optics

On the dielectric constant of dilute electrolytic solutions. *A. de F. Palmer. Phys. Rev. 14, 38 (1902).* — "It is highly probable that the dielectric constants of dilute electrolytic solutions of conductivity less than 2.5×10^{-4} are the same as that of pure water in electric fields varying at the rate of 10^6 oscillations per second." *W. D. B.*

Improvement of the apparatus for measuring dielectric constants by means of electrical waves. *P. Drude. Zeit. phys. Chem. 40, 635 (1902).* — The author's previous apparatus is improved by substituting a Tesla transformer for the induction coil and he gives directions for making the Tesla transformer. *W. D. B.*

On the relation between density and index of refraction of air. *H. G. Gale. Phys. Rev. 14, 1 (1902).* — The author finds that the equation of Gladstone and Dale holds in the case of air up to twenty atmospheres pressure with an error not exceeding 0.1 percent. *W. D. B.*

The rotation and dispersion of spontaneously active substances. *C. Winther. Zeit. phys. Chem. 41, 161 (1902).* — The three normal tartaric esters which were studied show abnormal dispersion. Formulas were obtained for the change of the specific rotations of these esters with the temperature and for the relation between specific rotation, wave-length and temperature. Tartaric acid and malic acid show normal dispersion at low temperatures, abnormal dispersion at a slightly higher temperature, and normal dispersion at yet higher temperature. The three tartaric esters, tartaric acid, and malic acid belong together in a group characterized by abnormal dispersion and by great variations of dispersion and rotation with temperature, concentration, and solvent. Potassium sodium tartrate is typical of another much larger group in which the dispersion is normal and varies but little with temperature, concentration, and solvent. *W. D. B.*

A comparative study of the spectra, densities, and melting-points of some groups of elements, and of the relation of properties to atomic mass. *H. Ramage. Proc. Roy. Soc. 70, 1 (1902).* — "The work and results now presented indicate that the properties of the elements are fundamentally due to the structure of the atoms as revealed by their spectra rather than the quantity of matter in them. It seems, for instance, inconceivable that the transition from calcium to strontium proceeds from the intermediate elements when we consider that the strontium molecules must have a similar structure to those of calcium. This structure is so simple that the fundamental Bunsen flame spectrum of each of these elements shows but a single line. The anomalies, according to Mendeléef's law in the atomic mass of tellurium and iodine, etc., are further evidence of this. The properties of tellurium and iodine may have nothing whatever to do with each other. They are, however, closely related but in an incorrect order with those of the elements and their respective groups as given above. The genesis was not in the direction of tellurium to iodine, but from, or perhaps through, oxygen and fluorine, respectively. So also with regard to the other groups.

"It is more probable that in the genesis of the elements, the properties of certain fundamental substances are modified by successive additions of matter to them, or by causes of which this is, to us, the apparent result. The regularity in the change in the properties of lithium, beryllium, boron, and carbon, as seen in the diagrams, is very remarkable. It, is, furthermore, very suggestive that the changes in properties are approximately proportional to the quantity of matter in the atom in excess of a constant (which is about 6), as if it were the same matter that is added in each case." *W. D. B.*

Optically active methoxy succinic acid and its derivatives. *T. Purdy and J. C. Irvine. Jour. Chem. Soc.* 79, *957* (*1901*). — The molecular rotation increases from the methyl form upward but tends toward a maximum. While the methoxy esters are less active than the ethoxy esters, the aqueous solutions of the two acids show nearly the same molecular rotation. "The molecular rotations of dilute aqueous solutions of the normal *d*-malates, *d*-lactates and *d*-tartrates are much higher in the dextro-sense than those of the corresponding free acids; in the case of alkylated derivatives, on the other hand, the rotations of the normal alkali salts are much lower, or, at most, only slightly higher than those of the free acids; that is to say, the rise of rotation produced by alkylation tells much more strongly on the hydroxy acids than on their salts." *W. D. B.*

Influence of the hetero-cyclic group on rotatory power. *P. F. Frankland and E. W. Aston. Jour. Chem. Soc.* 79, *911* (*1901*). — The authors have determined the rotatory power of di-ethyl and di-pyromucyltartrate and find that the rotatory effect of the heterocyclic furfuran ring is qualitatively similar to and quantitatively of the same order as that of the homocyclic benzene ring.

They have also devised a very pretty continuous automatic method for preparing esters of tartaric and other non-volatile acids, whereby the water formed in the reaction is taken up by dry potassium carbonate. *W. D. B.*

Ethyl *sec*-octyl tartrate and its dibenzoyl and di-acetyl derivatives. *J. McCrae. Jour. Chem. Soc.* 79, *1103* (*1901*). — The rotation of ethyl octyl tartrate increases with rise of temperature at about the same rate as that of di-ethyl tartrate. On comparing the rates of ethyl octyl tartrate and its derivatives with those of di-ethyl tartrate, it is seen that Guye's rule holds, namely, that substitution effected sufficiently far removed from the asymmetric carbon atom scarcely modifies the rotatory power. *W. D. B.*

The influence of solvents on the rotation of optically active compounds. *T. S. Patterson. Jour. Chem. Soc.* 79, *167*, *477* (*1901*). — In water, methyl alcohol, ethyl alcohol, and normal propyl alcohol, the rotation of dissolved ethyl tartrate alcohol diminishes as the molecular weight of the solvent increases. In very dilute glycerol solutions the rotation lies between the values found in methyl and ethyl alcohols. Molecular weight determinations showed that this variation of rotation in solution could not be referred to varying degrees of association of the dissolved substances. The author believes, however, that there is a connection between the internal pressure of the solvent and the specific rotation of the substances dissolved in it. When isobutyl alcohol and octyl alcohol are used as solvents, the same rule holds that the rotation of ethyl tartrate tends to diminish with increase of molecular weight of the solvent. *W. D. B.*

The magnetic rotation of some polyhydric alcohols, hexoses, and saccharobioses. *W. H. Perkin. Jour. Chem. Soc.* 81, *177* (*1902*). —

1. The influence of the magnetic rotation on successive hydroxyl groups in polyhydric alcohols diminishes as they increase in number, until about the seventh is reached when it becomes almost *nil*.

2. After the change has taken place, solutions of glucose and fructose give magnetic rotations which indicate that birotation is not due to hydration but that it is caused by a change in the constitution of these substances.

3. When in solution, galactose does not undergo isomeric change to so great an extent as glucose.

4. Sucrose is built up of the isomeric or β-forms of glucose and fructose by the elimination of the elements of a molecule of water.

5. Maltose is formed from one molecule of glucose in the aldehydic or α-condition, and one molecule in the isomeric or β-condition by the elimination of the elements of the molecule of water.

Lactose is similarly derived from one molecule of α-glucose and one of β-galactose. Both are constituted in a similar manner to that proposed by E. Fischer for lactose and these sugars undergo isomeric change when in solution, the α-portion becoming transformed, more or less, into the β-condition. This change accounts for the birotation and cupric reducing power of the two sugars. *W. D. B.*

The action of light on precious stones. *Chaumet. Comptes rendus*, 134, *1139* (*1902*). — The diamonds which give out the most light are those which show a distinct fluorescence when exposed to the violet light of the electric arc. It is found also that Burmah rubies show a marked fluorescence under these conditions while the Siamese rubies do not. It is possible in this way to distinguish sharply between the two grades. *W. D. B.*

Measuring higher temperatures by means of Stefan's law. *Féry. Comptes rendus*, 134, *977* (*1902*). — The author suggests that one might use for measuring very high temperatures the law of Stefan, $R = a(T^4 - t^4)$, where R represents the amount of heat emitted by a body radiating at an absolute temperature T, upon another at a temperature t, the emissive powers of the two substances being equal to unity, and a being the constant. For very high temperatures, this can be simplified to the relation $R = aT^4$. The author has checked this relation by comparison of the results thus obtained with the values obtained up to 1500° with a Le Chatelier pyrometer and finds that the error is less than one percent. Applying this to the temperature of the positive carbon in the electric arc he finds a temperature of 3490°. *W. D. B.*

On the induced radio-activity caused by the salts of radium. *P. Curie and A. Debierne. Comptes rendus*, 133, *931* (*1901*). — The activity of the walls of a closed vessel containing a solution of a radium salt depends upon the amount of salt present and on the air space inside the walls. *W. D. B.*

On the existence, in the radiation from a mixture of chlorides of radium and barium, of rays which can be reflected. *T. Tommasina. Comples rendus*, 133, *1299* (*1901*). — Experiments made with a mixture of chlorides of radium and barium seem to show that there are some rays which can be reflected by means of a mirror. *W. D. B.*

On radio-active substances. *P. Curie and S. Curie. Comples rendus*, 134, *85* (*1902*). — The general hypotheses which the authors have made in regard to the nature of radio-active phenomena are the following. They believe that radio-activity is an atomic property; that each atom acts as a constant source of energy; and that this activity does not vary with the time and is always the same when the radio-active substance is brought to the same chemical and physical state. They believe that it is inadvisable to form specific hypotheses in regard to the origin of the radio-active energy. *W. D. B.*

Conductivity of liquid dielectrics under the influence of radium rays and of Roentgen rays. *P. Curie. Comples rendus*, 134, *420* (*1902*). — The author finds that radium rays or Roentgen rays increase the conductivity of all liquid dielectrics, but that the amount of this increase varies very much with the nature of the liquid employed. *W. D. B.*

On the absorption of radium activity by liquids. *T. Tommasina. Comples rendus*, 134, *900* (*1902*). — Approximate experiments show the absorption of radium activity by different thicknesses of different liquids. *W. D. B.*

Crystallography, Capillarity and Viscosity

A method of measuring surface tension. *J. S. Stevens. Am. Jour. Sci.* (*4*) 10, *245* (*1900*). — "An iron wire is bent into the form of a T, and the cross allowed to float on the surface of water. The body of the T projects a little distance into the center of a coil of copper wire through which a current may pass. The part of the T forming the plunger is adjusted so that its weight is nearly sufficient to break through the liquid surface. A slight pull toward the center of the coil due to the passage of a current will then accomplish this. The system is raised and lowered by a rack and pinion so that it may be placed on the liquid surface as gently as possible. By means of a continuous resistance, the current may be applied in small increments and the amount required to break through read from a manometer." *W. D. B.*

ALLOYS OF LEAD, TIN AND BISMUTH

BY E. S. SHEPHERD

The first work done on these alloys consisted of some purely qualitative observations of their melting-points by d'Arcet, Rose, and others. Their observations were too crude, however, to possess other than purely historical interest, and the first really significant work is that of Rudberg[1] on the melting-points of binary alloys. He discovered that in binary alloys there were two pauses in the cooling curve, the upper break being variable and depending on the composition of the alloy, while the lower one was constant and independent of composition. He places this lower break as follows:

For lead-tin	187°	Composition	$PbSn_3$-$PbSn_4$
tin-bismuth	143°	"	"
lead-bismuth	129°	"	Pb_3Bi_4

For the ternary alloy he found the lowest fixed point at 98° and noticed that in this case there were two upper variable breaks in the curve.

The next property investigated was the variation of density with composition. Thompson,[2] Matthiessen,[3] Bolley-Pillichody[4], Kupferr,[5] Pohl,[6] and Riche[7] have studied the density of these and many other alloys. In every case the metals have been melted together in known proportions, cast into ingots, and the density determined. The results, except those of Thompson and Pillichody, agree surprisingly well, and I have thought it desirable to give the results of these determinations and plot the curves. Since several authors have sought to deduce the existence of compounds from the variations between the calculated and observed densities of these alloys, it is necessary to consider these determinations in some detail. By the theoretical density is meant the density which the alloys should have if, on mixing the two metals, neither expansion nor contraction occurs. And since density is not an additive property, while volume is, the theoretical density is to be calculated from the following formula:

$$D = \frac{A + B}{AV_1 + BV_2},$$

where A and B are the weights in grams or percentages of the metals A and B in the alloy, and V_1 and V_2 their specific volumes respectively. Ure gives the same formula in terms of densities, namely,

$$D = \frac{(A + B)d_1d_2}{d_1B + Ad_2},$$

where A and B are grams per hundred, and d_1 and d_2 the densities of A and B respectively.

For purposes of calculation and comparison we will assume the values given by Riche as densities of the pure metals:

	Density	Specific volume
Pb	11,364	0.08799
Bi	9,830	0.10173
Sn	7,300	0.13698

It is to be noticed that through a misprint the density of lead is quoted in his lead-antimony table as 12.364.

All who have determined densities give their results in terms of molecular proportions, and this accounts for the marked variations between the results of different workers. Since the atomic weights taken vary with the period at which such determinations were made, one may be misled in comparing different determinations.

I have recalculated these values into percentages and have tabulated the determinations made under the name of the observer. Kupferr used the atomic weights of Berzelius; Matthiessen, and apparently Riche, took Pb = 103.7, Sn = 58, and Bi = 208. Consequently the tin-lead alloys are nearly the same in percentage composition as would be calculated from our present atomic weights. Thompson's work shows the greatest variation from the mean value and must be due to using different atomic weights. Not having the original paper, I have omitted his figures.

TABLE I.

	Pct. Pb	Kupferr	Matthiessen	Riche	Pillichody	Calc.	Variation	
							M	K
Sn_4Pb	30.89	8.173	8.188	8.195	8.234	8.193	—0.01	—0.00
Sn_3Pb	37.34	8.391	——	8.414	8.408	8.407	——	0.00
Sn_2Pb	47.20	8.745	8.779	8.766	8.725	8.764	—0.00	0.00
Sn_3Pb_2	54.38	——	——	——	9.037	——	——	0.00
SnPb	62.73	9.425	9.460	9.451	9.433	9.454	—0.01	0.00
Sn_2Pb_3	72.84	——	——	——	9.797	——	——	——
$SnPb_2$	78.15	10.077	10.080	10.110	10.052	10.115	—0.03	0.00
$SnPb_3$	84.29	10.386	——	10.419	10.331	10.436	——	——
$SnPb_4$	87.73	10.555	10.590	——	10.595	10.626	0.03	——

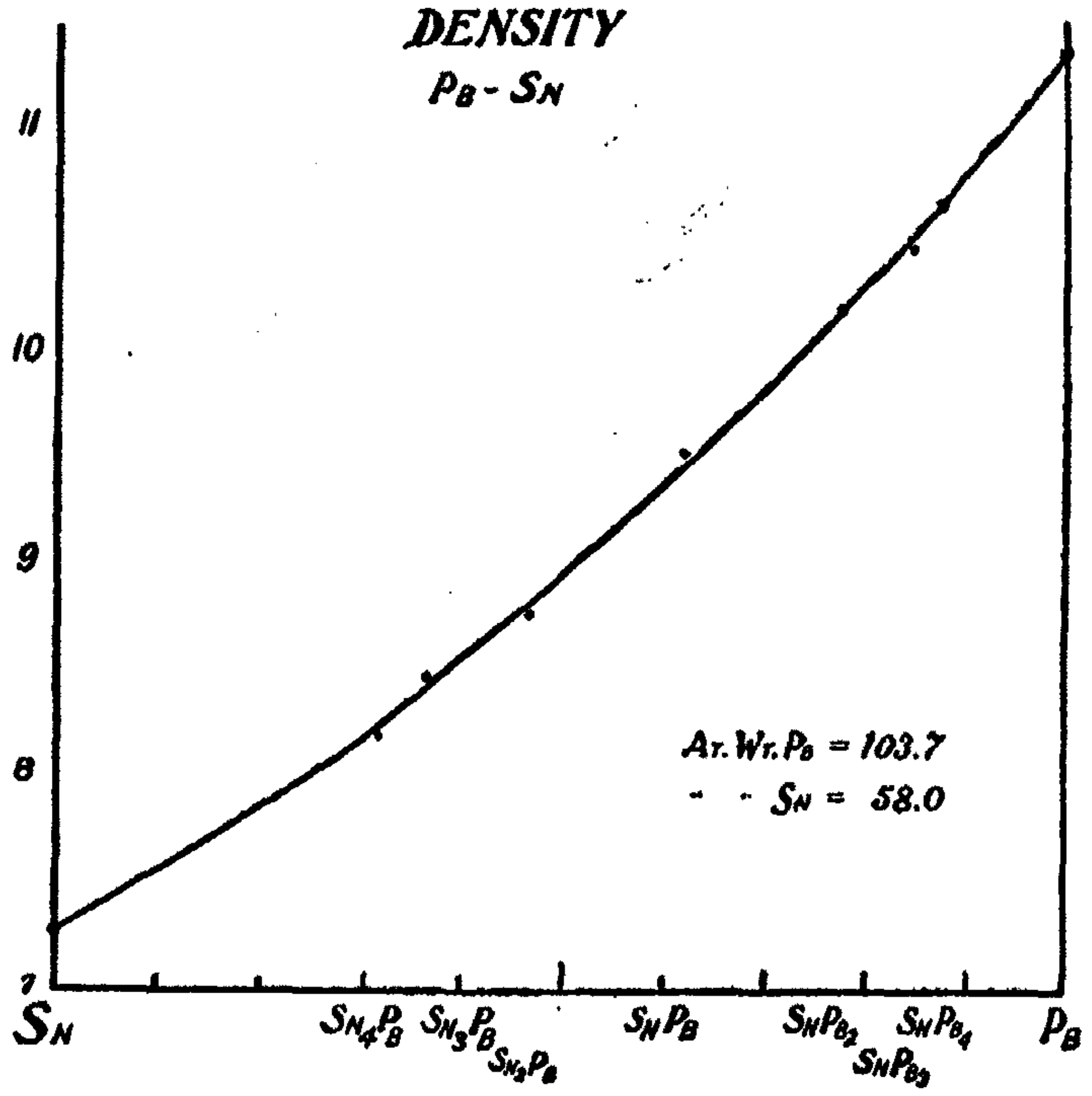

Fig. 1.

Since the theoretical densities are calculated on Matthiessen and Riche's alloys, the last column includes the variations from theory noted by them. As is seen, Riche got no variations in the second decimal place, while Matthiessen did. However, Matthiessen's variations are quite irregular and not greater than the possible errors in the composition of the alloy. Kupferr's figures do not vary more than can be accounted for from the different atomic weights used and consequent difference of composition. His data differ from the calculated by several hundreths of a unit, but he employed the picnometer method and apparently did not consider the purity of his metals. Everything considered, the densities agree very closely indeed. The percentages are calculated, using Matthiessen's atomic weights and the theory is calculated from the percents given.

The curve (Fig. 1) is that of the theoretical density and the observed data lie upon it.

In so far as densities are concerned, there is no evidence of a chemical compound between lead and tin. For bismuth and lead the densities are :

TABLE II.

	Pct. Pb	Density observed		Calc.	Diff.
		M	R		
Bi_6Pb	7.67	9.973	——	9.927	+0.046
Bi_4Pb	11.08	10.048	——	9.979	+0.069
Bi_2Pb	19.95	10.235	10.232	10.098	+0.137
BiPb	33.27	10.538	10.519	10.290	+0.248
$BiPb_2$	49.44	10.956	10.931	10.541	+0.415
$BiPb_3$	60.69	——	11.108	10.707	+0.401
$BiPb_4$	66.60	11.141	11.194	10.805	+0.336
$BiPb_6$	74.95	11.161	——	10.942	+0.219

The percentages here are based on the atomic weight ratios used by Matthiessen and the theoretical densities are his. It will be seen that there is a very marked difference between the observed and calculated densities, with a maximum value at $BiPb_2$. Riche got a maximum at $BiPb_3$, but this was through faulty calculation; his calculated value was 10.448 instead of 10.707 as it should be. His note that the alloy BiPb is more readily attacked by water is not significant. All are attacked readily.

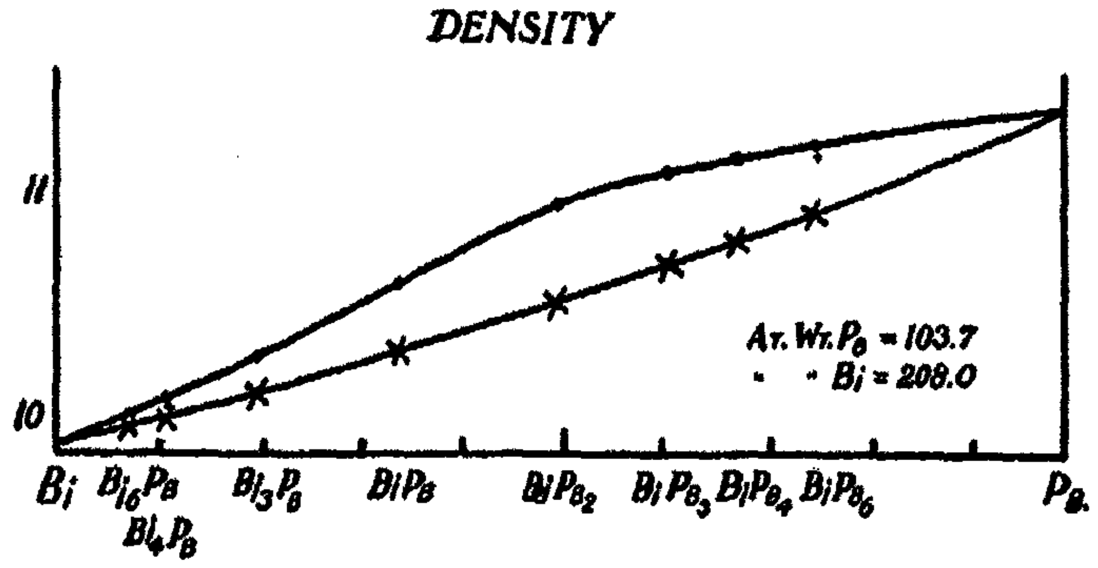

Fig. 2

For tin and bismuth the densities are:

TABLE III.

	Pct. Sn	Density observed		Mean	Theory	Diff.
		M	R			
Sn_6Bi	62.59	8.112	8.097	8.104	8.068	+0.036
Sn_4Bi	53.15	8.339	8.327	8.333	8.301	+0.032
Sn_3Bi	45.55	—	8.506	—	8.491	+0.015
Sn_2Bi	36.20	8.772	8.754	8.763	8.734	+0.029
SnBi	21.80	9.178	9.145	9.161	9.131	+0.030
$SnBi_2$	12.24	9.435	9.434	9.434	9.424	+0.010
$SnBi_4$	6.52	9.614	—	9.614	9.606	+0.008
$SnBi_6$	4.44	9.675	—	9.675	9.674	+0.001

Here again the percents are those used by Matthiessen and the theoretical values are based on them. As is seen, the variations are insignificant and irregular.

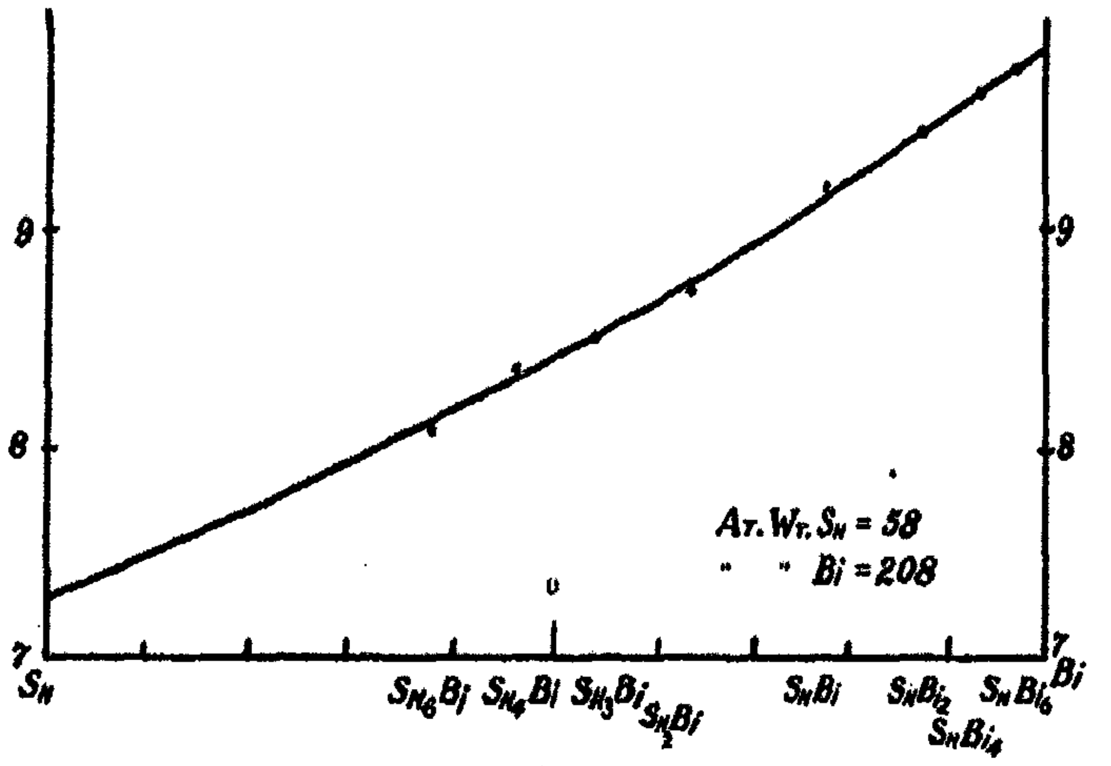

Fig. 3

I have redetermined the densities of these alloys up to 60 percent Sn and on plotting the specific volumes (Maey)[8] it is seen that the points lie almost exactly on the line connecting the specific volumes of the two metals.

TABLE IV.

Pct Sn	Density H_2O at 21.4° = 1	Specific volume
0.0	9.833	0.1017
11.67	9.461	0.1057
23.5	9.108	0.1098
34.2	8.814	0.1134
54.2	8.307	0.1204
59.9	8.170	0.1224
100.0	7.305	0.1369

These densities, of course, are not directly comparable with those of other workers, but since the specific volume is independent of temperature, so long as the density of the pure metals is taken at the temperature of the determination, the method allows us to dispense with much laborious calculation and correction, and has the further advantage that the variation from a straight line is more easily detected than the variation from a curve. It is open to objection that it is not very sensitive, a variation of one-tenth in the density of tin amounting to 0.002 in the specific volume, or a little over one percent. Since the density of a metal varies so much with its thermal and mechanical treatment, deductions as to the existence of compounds from variations in density of hundredths, or, as in some cases, even thousandths of units, are inexcusable. Thus one alloy which was examined had a density of 7.53 when cooled at a moderate rate; held at 100° for two days, its density changed to 7.51, although this alloy forms no compounds. A similar case of an alloy of tin and bismuth gave a density of:

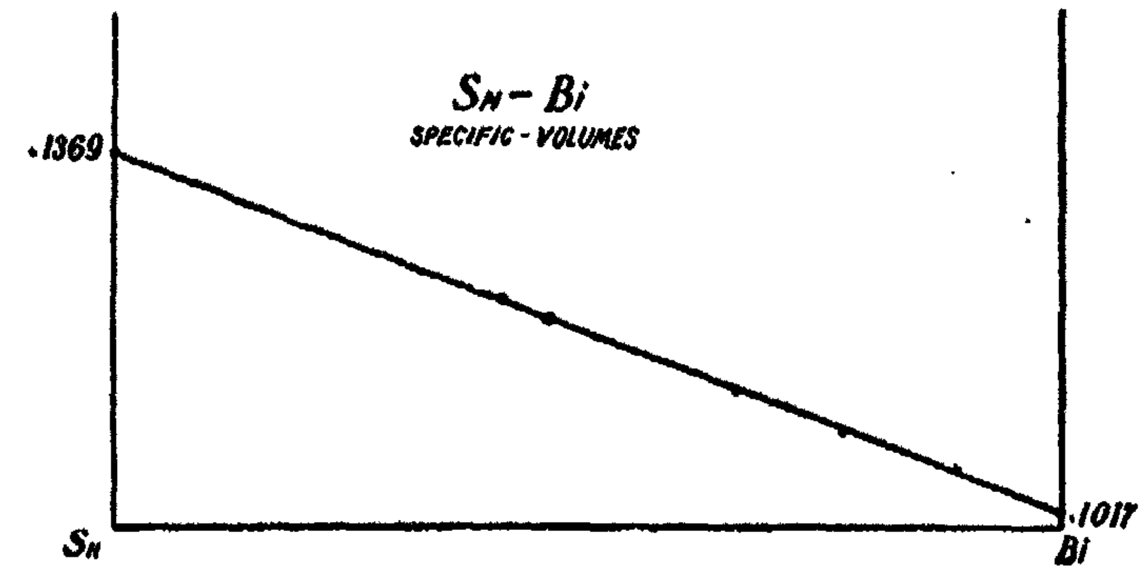

Fig. 4

1st day	8.176
2nd day	8.167
3rd day	8.159
4th day	8.157
5th day	8.154
Calculated	8.139

In this case the alloy when kept warm tended to crystallize and to assume its normal density. This crystallization would seem to account for the variation noted by Matthiessen and by Riche (see Table III). A better illustration are the densities of pure lead, tin and bismuth, as given by St. Claire-Deville.

	Cooled slowly	Cooled quickly	Difference
Pb	11.254	11.363	—0.109
Sn	7.373	7.234	+0.135
Bi	9.935	9.677	+0.258

Since the density of the pure metal may vary nearly three-tenths of a unit, depending on the rate of cooling, it becomes a question as to how far the divergence between the theoretical and observed density may be used as an indication of chemical combination; certainly not variations in the hundredths. Of course, if we work under about the same condition it is to be expected that the variations in density due to strains within the alloy in crystallizing and the subsequent growth of larger crystals, will introduce about the same error.

In a recent paper, E. Maey[9] has plotted the specific volumes of a number of alloys and has drawn conclusions as to the existence of definite compounds. Thus for Pb-Bi he finds by a peculiar extrapolation either BiPb or Bi_2Pb_3, while Riche found $BiPb_3$. The objection to Maey's work is that the specific volume, at the point where he predicts his compounds, has seldom been taken, and it is not clear why his iron-antimony curve is drawn to the particular point that it is. On the other hand, he must be given special credit for comparing his conclusions with those of others. In conclusion, the status of deductions from density would seem to be this.

1. If there is a distinct variation amounting to at least tenths of units, a compound, solid solution, or allotropic form of the metal must be present.

2. If there is no such variation, it proves nothing one way or the other, though taken in connection with the freezing-point curves and other properties, it is a useful guide; in any case, the final test will be analysis.

The freezing-point curves have been determined by several workers, those of Kapp[9] being probably the most accurate. They are perfectly smooth, and so far as they go might indicate that the metals crystallize pure from the freezing alloy. The eutectics as stated by Kapp are:

Bi-Pb at 57 pct Bi	136°
Sn-Bi at 56 pct Bi	124°
Sn-Pb at 66 pct Sn	186°

The freezing-points of the ternary alloy have been studied and the whole systematized by Charpy,[10] whose triangular diagram is here reproduced. His actually observed data are not given, but for all practical purposes the diagram is sufficiently accurate. As will be seen, the isotherms show no indications of compounds. Gautier[11] arrived at the same conclusion, as did also Le Chatelier[12].

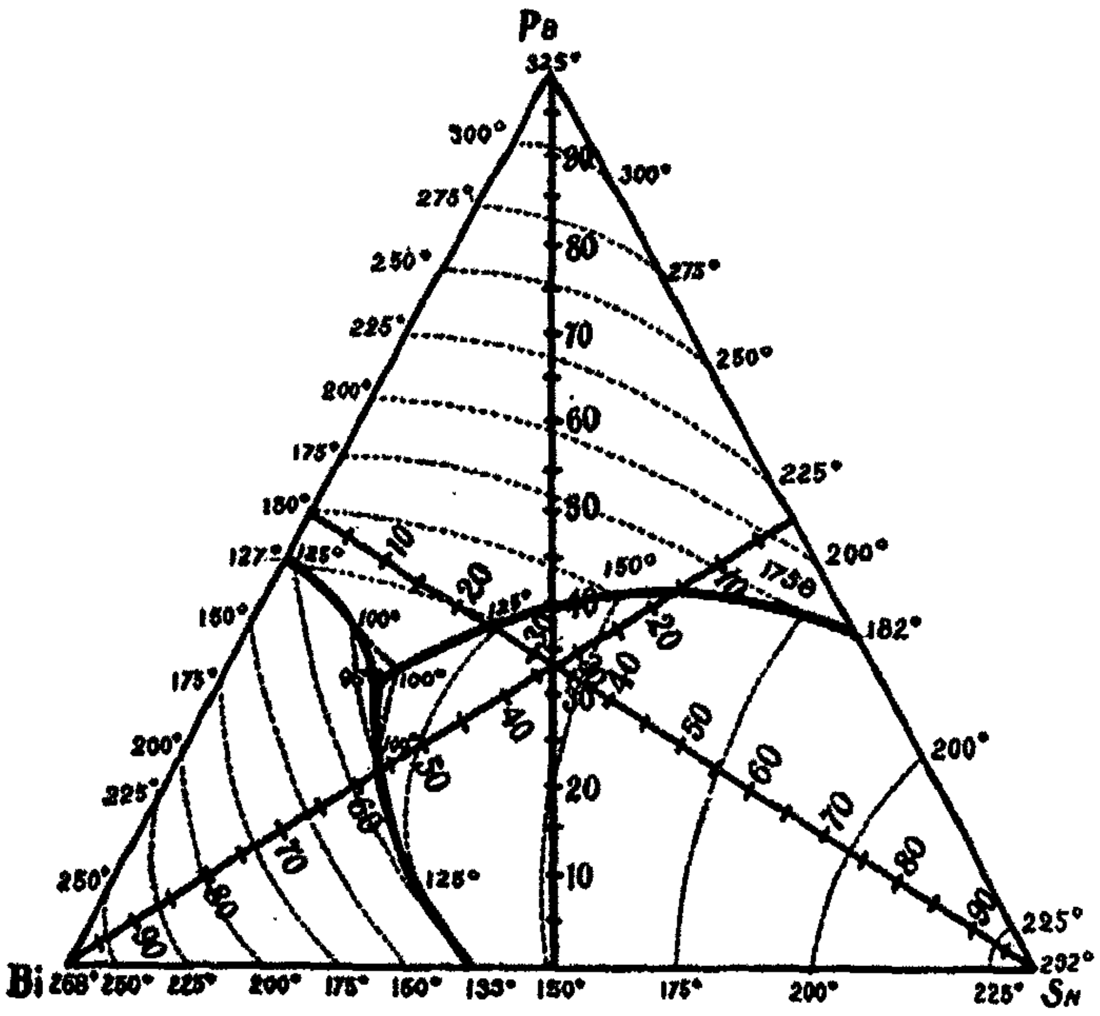

Fig. 5

Other methods of attack have been employed. Roberts[12] has studied alloys by means of the induction balance and gets a smooth curve for Pb-Sn, while alloys in which compounds are known to exist show very marked breaks. Laurie[13] has studied the electromotive force but gives no data.

Calvert and Johnson[14] have studied the hardness of alloys, using weights to force a fine point at given depth into the alloy in a given time, but from what we know of the tendency of alloys to liquate, it appears that this method can not lead to satisfactory results. Matthiessen[15] has studied the conductivity of a great many alloys and his plotted curves show, in some cases where compounds are indicated by other methods, distinct breaks and in other cases none. For Pb-Bi the curve is smooth, running to a minimum at 98 pct Bi; for Bi-Sn a small minimum at 99.4 pct. For Pb-Sn a smooth curve but with not nearly so many observations made. From what is known of the difficulty of getting a homogeneous sample, one can not but feel skeptical about his Pb-Sn alloy conductivities where the composition is varied by only tenths of a percent and where small variations in conductivity cannot be regarded as significant. In a later paper[16] he studies the effect of heat on the conducting power of alloys and finds that the conductivity of alloys rich in bismuth behave differently on different days. His measurements show, though he does not seem to have seen it, a steady increase of conductivity from day to day. The alloys were tested at different temperatures up to 100° and we are led to suspect a relation between crystallization in the wires and the increase of conductivity. He states that PbBi expands on cooling and that $PbBi_2$ does not; that $PbBi_3$ expands but little, while $PbBi_4$ and $PbBi_8$ contract. Heycock and Neville[17] in their study of the lowering of the freezing-point of metals by the addition of small quantities of other metals find that both tin and lead are normal in bismuth as solvent. Using lead as solvent, both tin and bismuth are abnormal, while lead and bismuth in tin as solvent give values that are only a little less than normal. These results are of the same order as those of Spring,[18] where he finds that molten alloys of lead and tin evolve more heat on cooling than calculated. Spring[19] has also studied the expansion of the alloys of Rose, d'Arcet, Lipowitz, and Wood with temperature. His paper is very interesting, though it would have been simpler had he studied the binary alloys also. However, on heating both the alloy $Bi_7Sn_6Pb_4$ and $Bi_{13}Sn_{10}Pb_8$ he finds the expansion rising rapidly to a maximum at 40° for the first of these alloys, then a decrease in volume until at 55° the volume is much less than at zero; then an expansion to the melting-point where the variations were too irregular to plot, and lastly a regular expansion. The second alloy expands up to 38° and the contraction is much less, the volume not falling below the volume at zero. Erman,[30] using the method of weighing in oil, finds the same contraction but at 69° C.

A similar peculiarity is noticed by Mazzotto,[20] who finds that the heats of fusion of $Bi_3Sn_2Pb_2$ and Bi_7Sn_2Pb do not agree with the values calculated for the mixtures. In a second paper[21] he finds that there is a heat change in the binary alloys *below* Rudberg's eutectic. It is notable, however, that this peculiarity occurred only in alloys containing *tin* and not in the bismuth-lead alloys. His table is as follows:

	F. P.	M. P.	T.
SnPb	180.0	182.0	150.0
SnZn	195.5	197.5	150.0
SnBi	137.0	140.0	95.0
BiPb	125.0	127.0	—

where F. P. signifies the lowest freezing-point, i. e., the eutectic, M. P. the melting-point, and T the temperature of the heat change.

Person[27] notes that Rose's alloy, cooled in water, will heat up spontaneously after being taken from the water and become hot enough to burn the fingers. This recalescence is accompanied by expansion.

Hiorns[28] notices this recalescence and says that it is destroyed by reheating *not* to the melting-point; that four tons pressure per square inch will prevent it, also that the fracture before the change is almost vitreous, afterwards crystalline.

Later Mazzotto[30] shows that the specific heat of Rose's alloy depends on whether it has been reheated to just below melting or not. If it has, its specific heat varies regularly over this range of temperature. See also van Aubel.[31]

Vicentini and Omondei[32] studied the expansion of the liquid alloy PbSn and found that it expanded regularly up to 252° where there was a sharp break in the curve, and they predict that the compound PbSn is in suspension in the alloy up to this point at which point it goes into solution. On cooling, the same break occurs at 245°. There is also a paper by Wiedemann[33] on the expansion of tin and lead-bismuth alloys, but his results are not of importance here, since he works only above 95°.

Foehr[34] gives a table of densities meant for determining quickly the approximate composition of tin-lead alloys.

Experimental

Following the method suggested by Professor Bancroft[24] and later applied to the case of salts in water by Mr. Browne,[25] I have undertaken to make similar measurements in the case of the alloy of lead, tin and bismuth in order to settle definitely whether or not there are compounds in the case of these metals.

I first tried a zero method. On taking the cooling curve of a ternary alloy, three breaks will be found, one where the first constituent separates, another where the first and second begin to separate together (the boundary curve), and a third at the ternary eutectic. If we let the metals be A, B, and C, and the breaks be respectively x, y, and z, and if A separate first, then the point x will be raised by remelting the alloy and adding more A, while the points y and z will remain unchanged. If we have not added the phase which is separating, both x and y will be displaced.

The alloy chosen had the initial composition

Sn	55.76 pct
Bi	14.80 pct
Pb	29.35 pct.

The cooling curve was determined twice, the upper break (x) came at 169° and the boundary curve was reached at (y) 157.1°, as a mean result of two determinations. Then tin was added and the upper break rose to 173.5° (x_1), but the boundary curve again appeared at 157°, showing that pure tin was separating. The alloy now had the composition II.

II.	III.
Sn 58.51 pct Bi 13.90 pct Pb 27.56 pct	Sn 57.83 pct Bi 13.84 pct Pb 28.43 pct

Enough lead was now added to bring the alloy to composition III. On redetermining the cooling curve, x changed slightly and y had changed to y'' at 159.2°. Between y'' and y there is a 19 percent change in the composition of the melt, corresponding in this case to about 77 grams of tin. Since the 3 grams of lead added caused a change of 2° in the location of B, then if one can locate the boundary curve to within one degree not more than 1.5 grams of lead can have separated with the tin, or the composition of the phase separating is known within 2 percent. In this particular case, one could pick up the boundary curve to within one-tenth of a degree, and therefore the tin separating could not have carried down with it more than two-tenths of a percent of lead. The accuracy of the method is limited by the accuracy with which one can pick up the boundary curve, and this varies greatly with alloys of different compositions. However, the method should prove serviceable in those cases where the analytical methods can not be applied.

I next applied the method of analyzing the mother-liquor at different points during the deposition of crystals. The metals used in making these alloys were carefully tested as to their purity. The alloy was brought to complete fusion and a sample sucked up into a narrow glass tube (previously heated) and this sample analyzed. The alloy cooled slowly with stirring, and when the greatest change of concentration consistent with pipetting off the mother-liquor had occurred, a sample was taken as before and analyzed.

Method of analysis

This method necessitates an accurate analysis of the alloy, since, as Mr. Browne has shown, a small error in the analysis will, depending on the change of concentration, extrapolate to large error in conclusions. And this is especially true when we plot our results on a triangular diagram, and the pure component is separating.

For the separation of any two of these metals very satisfactory methods have been devised; but such is not the case for the ternary alloy. The usual method of dissolving the alloy in nitric acid, weighing the stannic oxide, and subsequently separating the lead and bismuth by the basic nitrate process, gives incorrect results. The nature of the error thus introduced is very deceiving. The parallel analyses agree very well, and the summation is excellent. But if one starts with known quantities of the metals, the error becomes evident.

As is well known, the stannic oxide always contains lead and bismuth which can not be removed by prolonged boiling with nitric acid, while Hertzog[35] finds that the basic nitrate process may leave up to ten percent of lead in the bismuth and the sulphate method up to 2 percent bismuth in the lead. Since the atomic weights are so nearly the same, no error from this source appears in the calculations. Moreover, since the ratio of the stannic oxide to the lead and bismuth is always the same in any given alloy, the amount of these occluded is constant and the parallel analyses agree very well. But if to an alloy of known composition we add tin, analyze, and subtract the amount added from the amount found, the tin will always be found from 2 to 5 percent too high. Jannasch and others have separated lead and tin, and lead and bismuth, by distilling the chlorides in HCl, Cl_2, or bromine. I have extended the method to all three.

In passing it may be well to note that several methods have been proposed which call for the evaporation to dryness of solutions containing the chlorides of tin and bismuth. Fresenius notes that solutions can be completely freed from tin in this way though he gives a method elsewhere in which this is overlooked. I have been able to show that very appreciable quantities of bismuth can be lost in the same way.

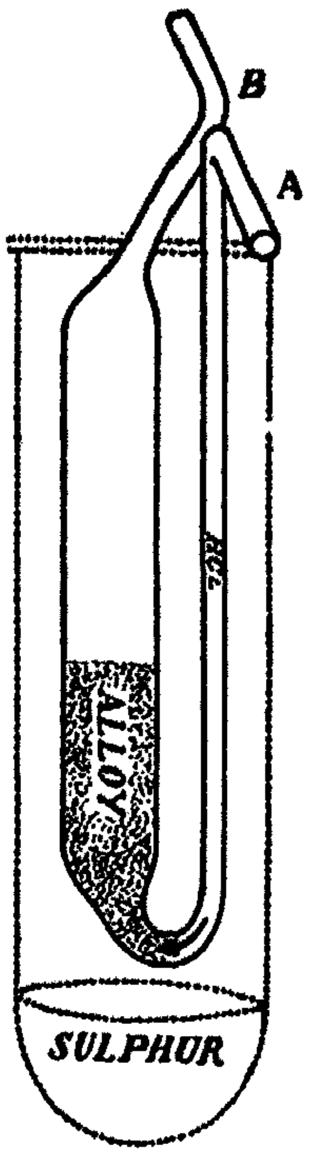

Fig. 6

Distillation in a combustion furnace is unsatisfactory, owing to the difficulty of regulating the temperature and I finally decided upon a bath of boiling sulphur as the most desirable and convenient temperature for the distillation. No temperature could be found at which tin and bismuth could be separated by distillation. The apparatus used consisted of a soft glass tube of about 15 mm internal diameter, and 15 cm long, drawn out at both ends to the shape of a solubility pig. To these ends were sealed narrower glass tubes and the joints well blown out. One of these tubes was bent back up over the pig forming a sort of U-tube which could easily be suspended in the 6 × 18 cm boiling tube used for the sulphur. This latter tube was jacketed with asbestos and provided with an asbestos lid.

About 0.7 g of alloy (cast in small sticks by sucking up in 3 mm glass tubes and let cool in a horizontal position) is placed in the pig and dissolved in aqua regia. Alloys rich in lead should be dissolved in HNO_3 and then HCl added. The end of the tube (*a*) connecting with the lower end of the pig is closed with a rubber tube and plug. When all the metal has disappeared, a thistle tube is connected to the other outlet, the pig placed in a small arsenic or combustion furnace, the thistle tube dipping under water, and the pig brought to dryness. A current of air is forced gently over the surface, and the heat applied *very* carefully. Alloys rich in tin or bismuth tend to 'bump'. When dry, the pig is transferred to the boiling tube. A slow current of HCl gas is passed in through (*A*), the current being more rapid after the bath has reached the boiling-point and bismuth begins to come over. The sulphur melts, thus warming the pig gradually, and the whole is finally brought to boiling. After the brown vapor of sulphur appears at the top of the boiling tube, the boiling is continued from an hour to two hours. The tin passes over quickly while the bismuth tends to collect in the exit tube (*B*) above the bath, and must be driven on over by the free flame. The process is finished when, after driving out all the bismuth from the exit tube, no more collects. On long runs, especially in alloys rich in lead, some lead chloride sublimes into (*B*), but it can be distinguished from the bismuth by its different appearance and the fact that the glass must be brought almost to melting in order to volatilize it. When the process is ended, the pig is lifted from the bath at once, letting the sulphur burn off, and allowed to cool with the HCl still passing. The tube is then disconnected and the thistle tube washed out with dilute HCl. The pig is inverted and acid run into the exit tube to wash out any bismuth left in that.

The lead chloride is dissolved out of the pig with hot concentrated HCl into a platinum dish, evaporated to dryness, dried at 110° and weighed.

The tin and bismuth chlorides are neutralized with NH_4OH, precipitated with an excess of $(NH_4)_2S$ (no free sulphur), digested several times with more sulphide, and the bismuth filtered off. The bismuth is dissolved in HNO_3, the excess of HNO_3 evaporated off, and then precipitated hot as carbonate. The precipitate should be granular, and in all cases the filtrate is to be warmed with $(NH_4)_2S$. If the amount of sulphide so obtained is small, it may be ashed with the paper, the carbon of which is sufficient to reduce it. Otherwise, it must be dissolved and re-precipitated. The carbonate is removed as completely as possible from the paper, the paper burned in strips over the crucible and the reduced bismuth dissolved in HNO_3 ignited slightly, the carbonate added, and the whole brought to constant weight.

The tin is precipitated by HCl, decanted several times on the filter (if in large quantity, on two or three papers), washed free of chlorides with water to which ammonium acetate has been added, and dried. The sulphide is separated as completely as possible from the papers, these ashed, and ignited. Then the remainder of the sulphide is added, and the ignition begun very gently. A two or three centimeter flame six centimeters from the crucible is best at starting.

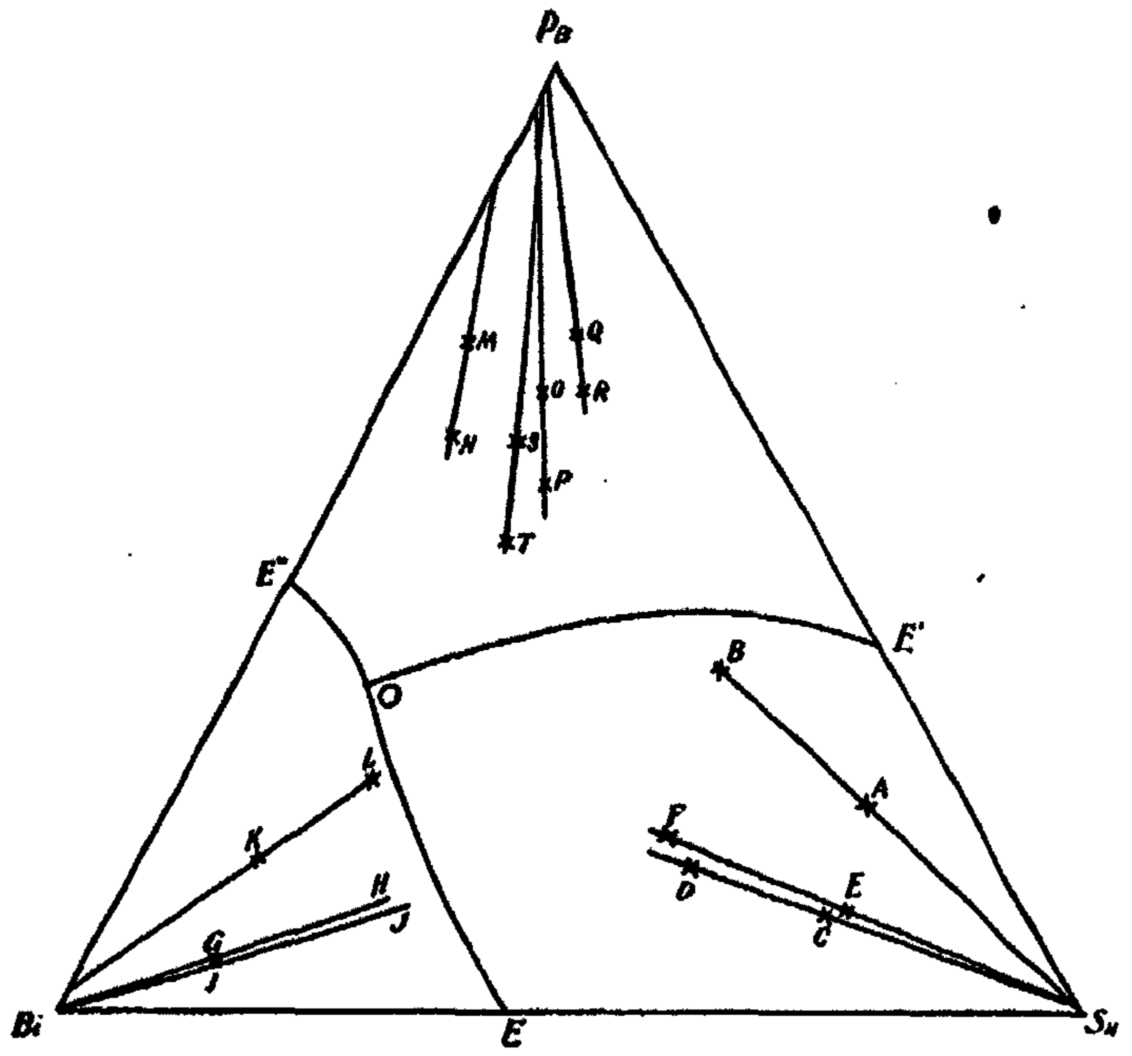

Fig. 7

This method is quite accurate, allowing a summation easily to 0.7 percent on the total analysis and from 0.2 to 0.5 percent on series. Thus we found the following:

	Sn	Pb	Bi	
Taken	18.00 pct	70.00 pct	12.00 pct	100.00 pct
Found	17.73 pct	70.00 pct	11.81 pct	99.61 pct

Out of twenty analyses by this method, the lowest was 99.24 percent and the highest 100.58 percent, with an average of 99.83 percent.

A satisfactory analysis being obtained, I then studied the solid phase crystallizing out on cooling different concentrations of the ternary alloys. The figures are given in the following tables.

TABLE V.

Point	Pb pct.	Sn pct	Bi pct	Total
A	21.67	67.16	10.50	99.33
B	36.21	46.97	16.81	99.99
C	10.00	70.00	20.00	Taken
D	15.22	54.23	—	—
E	10.16	71.88	17.64	99.68
F	18.51	50.05	—	—
G	5.11	12.84	82.55	100.50
H	11.24	25.90	62.55	99.69
I	5.14	13.32	80.78	99.24
J	—	28.74	60.21	—
K	16.90	11.27	71.89	100.06
L	24.75	18.74	56.17	99.66
M	70.61	5.55	23.49	99.65
N	60.41	—	30.85	—
O	65.23	15.76	19.58	100.58
P	55.42	20.85	23.52	99.79
Q	71.07	16.43	—	—
R	65.09	19.95	14.70	99.74
S	60.27	15.44	—	—
T	49.12	20.04	30.71	99.87

In Table 5 are the results of the analyses by which the points in the triangular diagram (Fig. 7) were determined. As will be seen, the solid phase in the lead and bismuth fields, PbE″OE′ and BiE″OE respectively, is not of constant composition, i. e., is a solid solution of about 5 percent content, while in the tin field the solid phase is pure tin. In several instances it has been necessary to determine the third component by difference, since the amount of mother-liquor which can be removed is usually too small to admit duplicate analyses. However, the possible error thus introduced is not thought to be serious. In pipetting off samples, unless the tube is well warmed and of narrow bore, liquation will occur and successive samples from the same rod will not agree in composition. The tubes were placed in a horizontal position during the solidifying of the sample.

Calculating these changes of concentration into the ratio of the changes of the two to the third as indicated by Mr. Browne.

	Bi/Pb	Sn/Pb	ΔBi	ΔSn	Bi in Sn
A	0.0484	3.099	0.002	1.802	0.063 pct
B	0.0464	1.297			
C	2.0	7.00	0.007	3.437	—0.118 pct
D	2.007	3.563			
E	1.736	7.075	0.038	4.493	0.845 pct
F	1.698	2.582			

ΔBi and ΔSn mean the change in concentration of the Bi or Sn; a negative value in the last column means that it was the lead which came out with the tin.

In the bismuth field we find

	Pb/Sn	Bi/Sn	ΔPb	ΔBi	Pb in Bi
G	0.3983	6.434	—0.0357	4.019	—0.89 pct
H	0.4340	2.415			
I	0.3859	0.3844	0.0015	3.969	0.058 pct
J	6.064	2.095			
K	1.499	6.379	0.178	4.11	4.35 pct
L	1.321	2.2693			

In the lead field, again referring concentrations to tin as unity:

	Bi/Sn	Pb/Sn	ΔBi	ΔPb	Bi in Pb
M	4.232	3.530	0.702	5.811	12.08 pct
N	12.723	6.912			
O	1.242	1.128	0.114	1.481	7.69 pct
P	4.139	2.658			
Q	0.7608	0.7368	0.024	1.063	2.26 pct
R	4.325	3.262			
S	1.572	1.532	0.040	1.541	2.59 pct
T	3.992	2.451			

In reviewing these results, the following points become evident:

1. That tin crystallizes pure from its alloy with lead or bismuth.

2. That bismuth crystallizes with up to four percent of lead as solid solution.

3. That lead crystallizes with about five percent of bismuth as solid solution. There are no compounds between Pb, Bi and Sn.

Having thus established the existence of the lead-bismuth solid solutions, it became desirable to demonstrate their existence in some other way. Accordingly, I undertook the microscopic examination. As it is extremely difficult to get polished preparations of alloys rich in lead, the observations were confined to the bismuth field. A binary alloy of lead and bismuth, containing four percent of lead was first examined. On freezing, these alloys expand and force out little buttons from the yet liquid center of the mass. If, therefore, the cooling be slow, giving the large bismuth crystals time to settle and the eutectic to collect in the center of the block, this eutectic will be forced out in the button and a microscopic examination of a section of the block and through this button should discover the eutectic, if this is present. There was, however, no trace of the eutectic. The specimen was both polished and etched, and since lead precipitates bismuth from its solutions, we should easily be able to find the dark eutectic between the crystals if it were present. The buttons consisted, apparently, of one large distorted bismuth crystal continuous with a similar one in the center of the block and the crystallization of the block was exactly like that of pure bismuth.

A ten percent alloy similarly treated gave a very marked eutectic, so that our microscopic evidence is in accord with that of our analyses. Matthiessen found a minimum in the conductivity of the lead bismuth alloy at 2 percent lead, which, making allowance for the possible irregular composition of his wires, coincides with the appearance of the eutectic. This fact may be only a coincidence, however. He found a similar minimum at 0.6 percent tin in the tin-bismuth combination. Since it is impossible to determine the existence of solid solutions of this magnitude by means of analysis, we examined a 0.4 percent alloy microscopically. Great care must be taken to get these alloys homogeneous on melting. On polishing the specimen and etching by electrolysis in ammonium sulphide solution, the blacked bismuth appeared surrounding the tin crystals, and *in greater amount* in the center of the block, thus showing that we do not have a solid solution in this case. An alloy of 2 percent tin in bismuth gave an easily seen eutectic. An alloy of 2 percent lead in tin gives a clearly defined segregation of the eutectic in the center of the block. M. Charpy in examining an alloy of about the composition Pb 20 percent, Sn 5 percent, Bi 70 percent, etched with hydrochloric acid, notes that we have the large plates of bismuth surrounded by a broken mass of lead and bismuth crystals side by side, and beyond these the gray eutectic of lead, tin, and bismuth. He notes that the lead crystals are dark, due to the deposit of lead chloride. M. Charpy may have overlooked the fact that both lead and tin precipitate bismuth from its solutions, even the chlorides, and during electrolysis with quite strong currents, so that it is quite possible that his gray masses are lead crystals, but concealed under a coating of bismuth.

In reviewing the work of others on these alloys we find the analytical data in agreement with the data obtained by other methods.

That tin crystallizes pure is shown by the density determinations, by the freezing-point curves, by the induction balance, by microscopic examination, and by analysis. That lead and bismuth form solid solutions is shown by the density determinations, and microscopic examination, as well as by analysis. Kurnakow[26] is of the opinion that tin and bismuth form solid solution because the lowering of the freezing-point for bismuth in tin is abnormal and because microscopic evidence shows "secondary crystals" of tin. As to the first, it is true that bismuth dissolved in tin gives a lowering of the freezing-point of 2.4 instead of 3 required by theory. But using bismuth as solvent, the lowering is 2.03 instead of 2.07 required by theory, this latter difference being quite within the limits of experimental error. Unfortunately, lead dissolved in bismuth gives 2.1, although it is known to form solid solutions with bismuth; and using lead as solvent, bismuth gives a lowering 3.02 instead of 6.4 theory, while tin in lead yields 1.6, though tin does not form a solid solution with lead and lead in tin is only 2.76 instead of 3.

Cady[30] has shown that the formula for the lowering of the freezing-point applies *only* when the heat of dilution is zero, and that the abnormal lowering of the vapor pressure of mercury when sodium, calcium, barium, etc., are dissolved in it, is due to this factor. While the lowering of the vapor pressure indicates an atomic weight of 15–21 for sodium, 19 for calcium and 75 for barium, the atomic weights become, if we will make the correction for the heat of dilution, normal. Further, if the dilution is accompanied by an absorption of heat, the atomic weight calculated from the fall of vapor pressure will be too high and vice-versa. The solution of molten tin in molten lead is accompanied by an absorption of heat (Mazzotto)[31] and tin dissolved in lead gives a value for the molecular lowering of one-fourth the normal, i. e., the molecular weight is Sn_4. Whatever the cause of this abnormal depression, be it polymerization or the heat of dilution, one is not justified in deducing the existence of solid solutions from the abnormal lowering of the freezing-point.

The irregular expansion of the alloy PbSn observed by Vicentini and Omondei is due to the fact that they were working with the partially molten alloy, since the melting-point of PbSn is at about 245°, the point where the break in the rate of expansion occurred being therefore the point where the last of the lead melted.

From the preceding, the advantages of the analytical method of attack becomes evident. Some care, must, of course, be exercised in applying it. It is absolutely necessary to prevent any alteration in the composition of the melt by oxidation or volatilization. This is especially true in the case of high melting alloys. For example, in the case of the bronzes, work on which is now under way, if one uses lead as the third component, the results may be completely reversed unless great care be taken to prevent oxidation. This source of error can be diminished by pipetting off the samples at short intervals, although this necessitates very great accuracy in the analysis. But applied with care, the method gives us our absolute proof of the existence of compounds or solid solutions crystallizing from the molten alloy, and, as in the case studied, it demonstrates the existence of such phases where the microscopic and other methods give only indications, or fail completely. The method does not apply to the case of compounds or solid solutions instable in the presence of the melt.

PART II.

Molecular rearrangements below the eutectic temperature

It is interesting to notice for how many years promising observations may be overlooked. As early as 1827 Erman[30] observed both the abnormal expansion of the ternary alloy and its recalescence. This peculiar property was recorded and let lie. In 1876 Spring[19] repeated Erman's work in detail, confirmed his results, and still no one seems to have taken up the problem.

At first sight the case is very simple. On cooling down from the melt, we have an expansion with an evolution of heat and on reheating a contraction occurs,—apparently a simple reversible phenomenon. However, a study of the published data shows that the recalescence occurs at different temperatures, depending on the composition of the alloy. Thus for Rose's alloy, Bi 48.9, Sn 23.5, Pb 27.5, the recalescence is at 57° (Person); Spring places it at 54°; and with carefully corrected thermometer and under the same conditions I have had it rise as high as 59° and fall as low as 52°. Spring finds 54° for d'Arcet's alloy Bi 49.27, Sn 21.2, Pb 27.5 percent, but while the Rose alloy held his calorimeter at 54°–54.75° for five minutes, d'Arcet's alloy held it at 54° only two minutes, while Lipowitz's alloy recalesced at 31° and Wood's gave but a slight effect at about 29°. The contraction of the alloy on reheating takes place at 48°–53° for the Rose alloy and a much smaller contraction at 38°–43° for d'Arcet's alloy, while Lipowitz's alloy begins to contract at 25°, and Wood's at 5°.

Erman found the contraction to begin at 43° and reach the maximum at 68°, while he places the recalescence at 57°. There is, therefore, no definite transition point either for the contraction or expansion. Apparently, it depends on the composition of the alloy. Hiorns[28] (he misquotes Erman's temperatures which were on the Reaumur scale, giving the temperatures in Fahrenheit degrees and marking them Centigrade) states that the recalescence is destroyed by three or four reheatings, but is reproduced by remelting the alloy. He says that the fracture of the alloy before recalescence is almost vitreous but crystalline afterwards. This I can confirm only in part. Its fracture is finely crystalline before recalescence and coarsely so afterwards. He notes that the tensile strength is one ton per square inch before and that the recalescence can be prevented by a pressure of four tons per square inch.

There remains the work on the specific heat of this alloy. (The alloys of Lipowitz and Wood are introduced only for comparison and will not be further treated here.)

Spring[18] has determined these as follows:

	Temperature	Specific heat
Rose alloy	29.0°	0.0474
	38.5°	0.0562
	68.2°	0.0545
	100.0°	0.0881
d'Arcet's	29.0°	0.0621
	41.5°	0.0528
	56.5°	0.0650
	101.3°	0.0901

In both cases we observe a minimum value. Van Aubel[30] remarks on the difference between Spring's values for Lipowitz's alloy and those of Mazzotto.[33] Mazzotto replies[32] that the value depends on whether or not the alloy has been reheated. The following tables show the effect of reheating:

Lipowitz's alloy

Spring		Mazzotto			
Cooled from melt	Specific heat	From melt	Specific heat	Reheated	Specific heat
28.0°	0.0634	60°-45°	0.0446	——	——
50 0°	0.0554	45°-35°	0.0504	50°-30°	0.0359
90.5°	0.0625	35°-30°	0.0697		
		30°-25°	0.2408	30°-20°	0.0352
		25°-20°	0.0869		
		20°-15°	0.0476	20°-15°	0.357
		15°-10°	0.0384	15°-10°	0.351
		10°- 5°	0.0374	10°- 5°	0.0353

It will be seen that the alloy which has been heated to melting possesses a very marked difference in specific heat, also that the alloy heated to just below melting has *lost* this peculiar nature, even though held just below the melting-point for fourteen hours (Mazzotto).

The first step in the solution of this problem raises the question, "Are we dealing with a reversible phenomenon?" Is there any relation between the expansion, with recalescence, and the contraction on reheating? If this is a true inversion point, the temperature must be fixed. Take the case of the Rose and d'Arcet alloys which have nearly the same composition. Let us assume that a compound or stable allotropic form changes over at the point of recalescence. This being a three-component system, we know, from the phase rule that when five phases are present we have an invariant system. Supposing there is present a compound BiPb, then we have present four solid phases, Bi, Pb, Sn, BiPb, and vapor; the system is invariant and the recalescence point must be the same for both alloys, since the percentages of the phases present make no difference. But the recalescence point varies anywhere between 80° and 20° for the same alloy, as observed above. Moreover, the alloy when melted, and, without being allowed to cool down, held at 80° over night, will cool down *without* recalescence. That is, the change took place at 80° instead of 57°. In trying to obtain the density of the alloy before recalescence, the alloy was melted, cooled to 70° and the weight determined by the hydrostatic method. The density first obtained was 9.538 and soon dropped to 9.416, where the observations ceased. Another alloy gave 9.532 at 70, falling to 9.366, and finally to 9.267 in about an hour. That is, the recalescence occurred as easily at 70° as at 57°. The density of the recalesced and reheated alloy used as a check was 9.243 for nearly the same composition. These densities are referred to H_2O at 4° = 1. In other words, the recalescence is not a stable inversion point, and it is not reversible since reheating does not *restore* the recalescence nor the contraction. We are dealing, therefore, with a distinct, non-reversible phenomenon.

The source of the contraction is easily determined. As we have seen from our analytical data, lead and bismuth form solid solutions, and this solid solution shows a tendency to crystallize on standing. In nearly all cases, the alloys have been cast, giving no time for equilibrium to be reached. We know, further, that the solid solution is formed with contraction. If, therefore, we heat an alloy containing lead and bismuth, crystallization and contraction will occur and the temperature at which this takes place will vary with the conditions. This offers an explanation for the fact that with Rose's alloy Spring gets the maximum density at 55°, that Erman finds it at 68°, and that d'Arcet's alloy should show it at 43°. But does this contraction actually occur with a lead-bismuth alloy? It does. The following table gives the volume and temperature of a lead-bismuth alloy containing 33 percent Bi (Rose's alloy 64 percent):

I. 30 percent Bi	II. 33 percent Bi	III. 33 percent Bi
32° = 1.00000	35° = 1.00000	75° = 1.00617
45° = 1.00152	40° = 1.00025	80° = 1.00659
53° = 1.00754	45° = 1.00070	85° = 1.00420
56° = 1.00578	50° = 1.00135	85° = 1.00403
60° = 1.00303	55° = 1.00180	87° = 1.00275
70° = 1.00547	60° = 1.00250	
75° = 1.00648	64° = 1.00286	
80° = 1.00661	71° = 1.00360	
	75° = 1.00437	
	80° = 1.00335	

The volumes were determined by Erman's method. As is seen from the tables, the lead-bismuth solid solution undergoes readjustment at different temperatures depending somewhat on its composition. We are justified therefore in attributing the contraction of these alloys to the bismuth-lead solid solution and can see why it is not a reversible phenomenon. Both Erman and Spring worked with rising temperature and Spring carried the temperature past the melting-point of the alloy. Consequently they always obtained this readjustment on reheating. To see if this adjustment was permanent, a specimen of the Rose alloy was examined. If we take the volume of the freshly cast alloy as unity, after heating at 70° for twelve hours, the volume became 0.99808 and did not show any reverse change on standing for a week at room temperature. The change was, apparently, permanent.

E. Wiedemann[37] studied this alloy by means of a large dilatometer and arrived at results quite different from others. He finds a contraction on freezing, requiring three or four hours for completion, then on further cooling, an expansion began at 50° and in some cases at 70°. This expansion was complete only after 24–36 hours. On reheating he obtained a contraction beginning at 70° which lasted for days (compare with Matthiessen's conductivity of lead-bismuth alloys.) He obtained the expansion and presumably the recalescence whether heating to fusion or to 85°. Rapid heating to 88° caused the oil to rise higher in the dilatometer tube than when slowly heated, and on holding the temperature constant at 88° a contraction quickly took place until the oil column indicated the same position that it attained by slow heating. Sudden cooling to 20° produced the inverse phenomenon.

From these data Wiedemann concludes that the 'Rose' alloy exists in two modifications, α and β, of which α is the one stable at lower temperatures, and β at higher (above 88°). These two modifications change slowly, the one into the other, and that is why we get the recalescence at temperatures between 80° and 20°. On reheating, the reverse change (the contraction) begins at about 70° (Ermann found it to begin at 43°, Spring at 48°) and before the alloy melts, the change of α into β takes place. Regardless of observed data, his conclusions must be wrong. One will admit that, if β ought to change into α at 88° on cooling down, the change might easily occur below that point as at 57°. But one can not admit that β, which is instable below 88°, will begin to be formed below that temperature on reheating. Of course, α might continue to exist above 88° just as β does below it. This would be quite in keeping with the transformation of gray tin into the crystalline form, Cohen[41] having shown that the two will exist together even at 100°, the change being very slow. But one would hesitate before saying that the gray tin began to form from the crystalline *above* 20°. There are a few criticisms of Wiedemann's method which may account for the disagreement between his results and others. In the first place, he gives none of his data. It is easily possible that the readjustments of the apparatus were not as rapid as he thought. The metal was enclosed (melted) in a glass tube and this placed in the dilatometer, the whole then sealed. My own observations have shown, as was expected, that the glass of a large dilatometer (50 cc) continues to change for a long time. When he heated the alloy rapidly, the metal and oil may well have reached equilibrium before the glass did and the quite rapid contraction back to the normal value when the temperature was held at 88° would then be accounted for by the gradual expansion of the glass and the cooling of the oil column forced suddenly into the capillary tube. Thermometers often act in this way. On cooling, the metal contracted more rapidly than the glass envelope and the volume registered too low. Such an explanation will account for his unique results. Then, too, the capillary tube was 1.5 meters long and not calibrated. Its bore is not given and this leaves us in the dark as to just what his figures mean. The thermometer with which he did the succeeding piece of research on melting-points of a tin-lead alloy registered 5° too low. (Thus it read the freezing-point of tin at 227°.) The effect of the tightly fitting glass envelope on the expansion of the metal is another evident source of error and, as he said at the start, the readings were qualitative.

Kopp[39] has examined the Rose alloy but admits that the alloy contained air cavities and evolved bubbles. He gives its density as 8.9. It is nearer 9.3, and consequently his work is not satisfactory. Weber[38] examined the conductivity of these alloys at different temperatures. The liquid alloy has a very slight temperature coefficient, that of Rose = 0.0007 and Lipowitz = 0.005. But on freezing, the resistance drops rapidly and then decreases regularly to the recalescence point where it drops again. It then becomes regular. On reheating, the resistance increases *regularly* up to the melting-point. In accordance with the observation that the freezing-point is three degrees lower than the melting-point, the resistance curve shows the break at 96° on melting and 93° on freezing.

As further evidence that the lead-bismuth alloy changes on being heated and that the change is irreversible, we have Matthiessen's temperature conductivity data which show a steady increase in conductivity when the alloys are held at about 90° for several days, and they do not regain their original conductivity on cooling down.

Lead-tin alloys also show a similar increase of conductivity and in this case it approaches rapidly the theoretical conductivity of the alloys. This seems to be good evidence of crystallization.

Calvert and Johnson[40] find a similar effect of crystallization on the conducting power of lead-tin alloys for heat and the variation between the theoretical conducting power for heat and the found value is less than the difference between a cast and crystallized metal. Their data again confirm our conclusions, that lead and tin form no compounds.

Since the contraction is due to the lead and bismuth, and since tin crystallizes pure from both, recalescence must be due to the tin. It has been shown above that this change is irreversible and takes place with a decrease of density.

That this is not due to the crystallization of liquid tin which had hardened as an amorphous solid, is shown by the facts that:

1. The alloy is crystalline before recalescence.
2. Crystals of Pb, Bi and Sn added at freezing do not destroy the recalescence.
3. Recalescence occurs whether cooled slowly or rapidly.
4. The alloy has a definite melting-point.

However, there are many other properties which lead one to suspect that we are here dealing with an allotropic form of tin, instable at any temperature, the case being analogous to that of $Na_2SO.7H_2O$, which has no inversion temperature, but changes over at any time, depending on the conditions. Nor need it be necessary that one obtain this form of tin from the pure metal, any more than that one obtain the red selenium from the melt.

Such an hypothesis will account for the variable transition point and the crystalline structure of the alloy before recalescence. It will also explain the heat change *below* the eutectic observed by Mazzotto for alloys of tin with either bismuth, lead, or zinc, while he got no such change with bismuth lead alloys. We know also that the heat of fusion of lead-tin alloys is not that calculated from the heat of fusion of lead and tin. Spring and Mazzotto find the heat of fusion to be abnormal in the case of the alloys of tin with Zn and Bi. We have also another peculiarity which need not be due to an allotropic form of tin, but which falls promptly in line if we assume its existence, namely, the difference between the freezing-point and melting-point of the ternary eutectic, the freezing-point of which is 93.7° and the melting-point 96°. A possible analogy between tin and carbon and silicon will help us, since we know that both carbon and silicon, which stand above tin in the periodic table, crystallize from metals in different allotropic forms. Since bismuth expands on freezing, the tin is under enormous pressure while crystallizing, and this favors the formation of the denser form and this is in accord with Hiorns's observation that pressure prevents the recalescence. It further accounts for the "secondary crystals" of tin observed by Kurnakow, in tin-bismuth alloys, since, if as Hiorns states, the recalescence is not completed at the first cooling down of the alloy, the denser crystals might still be present on microscopic examination.

Spring[18] has studied the heat content of the lead-tin alloys between 100° and 260° and finds in every case that it is greater than the calculated value. The value he obtains consists of the heat contained in the alloy because of its temperature plus the heat of fusion. Person[42] states that the heat of fusion is not constant for different temperatures so that the source of the "extra" heat may be this. On the other hand, if tin crystallizes as an allotropic form from lead alloys, it is then quite probable that the heat content would not be the same as the value calculated from the ordinary form of tin. That his variations which amount to as much as five hundred calories (though irregular as compared to percentage composition) are not due to experimental error is shown by his determinations for the fluid alloys where the values differ by not over one percent. In two cases the variation is greater, but neither of these alloys was above its melting-point, hence the disagreement. Spring calculates the heat content on the assumption that instead of pure tin he has the compound $PbSn_3$ or Pb_4Sn present, and finds that neither of these will account for the facts. He then concludes that we must have polymerization in the case of pure tin or pure lead, and that on mixing them the larger molecule is broken up. On the other hand, if the abnormal lowering of the freezing-point is not due to the heat of dilution, then tin dissolved in lead may be polymerized to the molecule Sn_4. Such an hypothesis does not in any way conflict with that of tin crystallizing from its solutions in lead in an allotropic form. As a result of these data we are forced to conclude that tin crystallizes from these alloys in a denser, allotropic form, and have thought it desirable to calculate the possible density of this form of tin.

An alloy of the following composition was prepared:

Sn 27.72 pct
Pb 23.06 pct
Bi 49.22 pct.

and its density was found to be 9.36 at 21.46°. The density of the lead-bismuth solid solution should be 10.51, the percent of lead in the bismuth being 31.9 percent. If one considers the lead bismuth as one component and the tin as the other, the specific volume of the tin will be given by the expression

$$V_2 = \frac{A + B - DAV_1}{DB},$$

where A and V are the percent and specific volume of the lead-bismuth portion, D the density of the ternary alloy, A = 72.28, B = 27.72. The calculated density for the tin in this alloy is D = 7.28. That is, tin has its normal density and the denser allotropic form has by similar calculation a density of 7.98. This is assuming that the ternary alloy has a density about three-tenths higher before recalescing. We have also assumed that the lead-bismuth alloy in the presence of tin has the same density that it has alone, and this is perhaps untrue, since it is quite probable that it would be more nearly the theoretical value for a mixture of pure lead and bismuth. That is, the density would be less than 10.5. If it were 10.4 the density of tin after recalescence would be 7.4. But it would not affect the relative densities of the two forms of tin. A similar calculation for the density of tin, based upon Spring's figures, gives a density of tin in the Rose alloy to be 7.15, so that the form of tin in the recalesced alloy seems to be of the ordinary form, and the instable allotropic form must have a density of about 8.

It was thought that the addition of tin to the alloy just as it froze would destroy the recalescence. It did not do so, though the rate of cooling from the freezing-point was slower, indicating slow transformation and also the recalescence was less marked. Neither lead nor bismuth affected the recalescence. That the tin does not instantly destroy the instable form does not conflict with the fact that such a form exists, since, as is well known, gray tin will exist in contact with the crystalline, for a long time, even at 100°.

The practical importance of this allotropic form of tin is at once apparent since the tin crystallizes from the melt in a denser form, and this form tends to change over, on cooling down. The strain which will be produced on a casting by this expansion *after* freezing must materially alter its strength. The unexplained weakness of certain brass castings may find an explanation in this behavior of tin, and it is of great importance that the exact conditions for the formation and transformation of the allotropic forms of tin be thoroughly investigated.

The case just studied is a striking example of the importance of the phase rule as a guide in the study of alloys.

As a final summing up: —

1. From alloys containing lead, bismuth and tin, the tin crystallizes pure, but often in an instable denser form.

2. Lead and bismuth form two series of solid solutions, in each case with contraction. When the fused alloys are cooled fairly rapidly, the saturation concentrations are not reached.

In conclusion, I desire to thank Professor Bancroft, under

whose direction this work has been carried out, for his very patient criticism and encouragement. I wish also to thank Dr. Carveth for much kindly assistance, Dr. Chamot for similar aid in the microscopic investigations, and Mr. A. R. Middleton for valuable suggestions on the analytical problems involved.

Cornell University,
June 15, 1902.

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INFLUENCE OF THE SOLVENT IN ELECTROLYTIC CONDUCTION

BY HARRISON EASTMAN PATTEN

INTRODUCTION

The theory of electrolytic dissociation of Arrhenius[1] has suggested and guided much of the research in chemistry since 1887; but it has also diverted attention from the study of the electrical conductivity of non-aqueous solutions and of concentrated aqueous solutions. On the basis of this theory Nernst and Thomson have attempted to show that the dielectric constant of the solvent determines its so-called electrolytic dissociating power. Brühl attributes "dissociating power" to spare valences of the solvent. Dutoit and Aston claim that electrolytic conduction takes place in solutions whose solvents are associated. Beyond this no part in the process of electrolytic conduction has been assigned to the solvent by the supporters of the theory of Arrhenius and by writers of current text-books holding this hypothesis. Nevertheless a mass of experimental data exists in the literature indicating that chemical action between solvent and solute undoubtedly takes place in the production of solutions.

In 1893 D. Konowalow[2] published a research in which he maintained that chemical union of solvent and solute was the determining factor in electrolytic conduction. Since that time, Dutoit and Friderich,[3] Kahlenberg and Lincoln,[4], Euler,[5] Walden,[6]

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[1] Zeit. phys. Chem. 1, 481 (1887).

[2] Wied. Ann. 49, 733 (1893).

[3] Bull. Soc. Chim. (3) 19, 321 (1898).

[4] Jour. Phys. Chem. 3, 12 (1899); also Trans. Wis. Acad. Sciences, Arts a. Letters, 12, 395; and Jour. Phys. Chem. 3, 457 (1899).

[5] Zeit. phys. Chem. 28, 619 (1899).

[6] Zeit. anorg. Chem. 25, 213 1900.

Werner,[1] Franklin and Kraus,[2] Kahlenberg,[3] Walden,[4] and Smits,[5] working upon various solutions by the electrical conductivity method, and in some cases using cryoscopic and ebullioscopic methods as a check, have established facts which render the theory of electrolytic dissociation untenable. More recently L. Kahlenberg[6] has shown that instantaneous precipitation takes place as well in solutions which are non-conductors of electricity as in the best electrolytes. In another paper Professor Kahlenberg[7] takes the position that mutual attraction between the solvent and solute is the essence of the so-called osmotic pressure and is the cause of the process of solution. The influence of the solvent on the change in concentration at the electrodes in an electrolytic cell is clearly shown in the work of H. Schlundt.[8] Moreover, A. Ponsot[9] has proved that van 't Hoff's relation $PV = iRT$ is on a weak basis, theoretically as well as experimentally, and G. Quincke[10] has called into question the efficiency of the semipermeable membranes used by Pfeffer[11] and others in determining the osmotic pressure of solutions. Nernst, Garrard and Oppermann[12] find that diffusion is a complex process in which the solvent takes a part; and J. W. Brühl[13] has shown that the solvent influences the change of isomers in solution. Lastly Hans Wolf[14] has studied the influence of several neutral solvents upon the conductivity of a few aqueous electrolytes, but without accomplishing any marked advance.

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[1] Zeit. anorg. Chem. 15, 1 (1897).

[2] Bull. Soc. Chim. (3) 19, 334 (1898).

[3] Bull. Univ. Wis. No. 47 (Science Series), Vol. 2, No, 5, 297 (1901).

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[7] Ibid.

[8] Jour. Phys. Chem. March (1902).

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[10] Wied. Ann. 3, 631 (1902).

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

[14] Zeit. Elektrochemie, 8, 117 (1902); Zeit. phys. Chem. 40, 2, 222 (1902).

The main purpose of this investigation is to establish further facts concerning the influence of the solvent upon the process of conduction in electrolytes, which may be of use in framing a more adequate theory of solution and of electrolytic conduction.

Method and apparatus

The problem was attacked experimentally in two ways: (1) It was determined what relation exists between the amounts of various solvents required to alter the specific electrical conductivity of a given solution—liquid in liquid or solid in liquid—to a stated degree. (2) It was determined how the specific electrical conductivity of solutions of two homogeneous liquids, which are miscible in all proportions and are known to form compounds according to the law of definite proportions, varies with their percentage composition.

The Kohlrausch method was used for measuring the electrical conductivity,[1] an Arrhenius cell with a tightly fitting cover being employed. The temperature of the cell was kept at 25° C to within one-tenth of a degree by an Ostwald thermostat.

In preparing the solutions the cell was weighed, approximately to the fourth place, absolutely to the third place, a quantity of liquid sufficient to cover the electrodes was then introduced and the cell again weighed. After making the conductivity measurements, a small portion of the second liquid was run in from a burette and a third weighing of the cell made. The liquids were well mixed by moving the electrodes up and down, and after the temperature had been adjusted the conductivity was measured. By repeating this process the specific conductivity of solutions varying from rather dilute to exceedingly concentrated was determined.

In general, molecular conductivities were not determined: (1) because the concept of molecular conductivity is based on the assumption that the solute alone—or its parts, the "ions" of

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[1] See Ostwald's Hand u. Hilfsbuch f. physico-chemische Messungen.

Arrhenius — conduct the electric current through a solution; and as stated in the introduction, this assumption is not warranted by the experimental facts; and (2) because in the one case calculated (Fig. 10, curve 1, pyridine and acetic acid) the molecular conductivity does not approach a maximum at infinite dilution. Similar exceptions to the theory of electrolytic dissociation are abundant in the literature, so it is deemed more profitable to work along the lines that will be presented.[1]

Sources of error

In order to ascertain the extent to which the conductivity of an electrolyte in an Arrhenius cell is changed by varying the depth of the liquid above the upper electrode, the following measurements were made in both the cells employed in this investigation, using an aqueous *n*/50 potassium chloride solution, the conductivity of which was 0.00277 reciprocal ohms.

Cell No. 1			Cell No. 2		
H	R	A	H	R	A
0.2	60	49.71	0.3	60	47.20
0.9	60	49.70	3.0	60	47.25
4.5	60	49.75	6.0	60	47.20
6.0	60	49.65			

In the above table H is the height of the surface of the liquid above the upper electrode in centimeters; R the resistance of the rheostat; and A the bridge reading corresponding to the A used in Ostwald's tables for Wheatstone's bridge.

The variations of the bridge readings (columns A) clearly fall within the limits of experimental error. From the above results the "capacity factor," K, for cell No. 1 is 0.1693 and for cell No. 2, 0.1863.

As far as possible the settings were made near the middle of the bridge so as to reduce the errors in the bridge readings to a minimum.

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[1] The specific gravities of the liquids worked with are all known, so any one wishing to do so can easily calculate the approximate molecular conductivity.

The error due to variation in temperature is great. A 13.07 percent[1] solution of aniline in acetic acid showed a specific conductivity of 3.107×10^{-3} at 24.9°, and of 3.121×10^{-3} at 25.1° — a change of 0.22 percent per 0.1 degree. A 23.5 percent solution of acetic acid in pyridine gave a specific conductivity of 7.250×10^{-5} at 25.1°, and of 7.300×10^{-5} at 25.2° — a variation of 0.69 percent for 0.1 degree. To control this error the thermostat was delicately adjusted; the thermometer, which was near the cell, was closely watched, and check readings on the conductivity were made.

The error due to bubbles of gas collecting on the electrodes was avoided by moving the electrodes about till the bubbles were dislodged. In the solvents studied, bubbles are not so prone to form as in aqueous solutions. In the most viscous solutions there is undoubtedly a small error of this sort, since it is well nigh impossible to get the last bubbles off the electrodes without allowing the solution to stand for a considerable time — too long, in fact, to be permissible. From the slight differences in the readings when the electrodes were still visibly coated with bubbles, when only a few bubbles remained, and finally when, after long standing, all the bubbles had cleared away, I consider the neglect of this error perfectly justified.

The pyridine used probably contained a trace of picolene. With this exception the solvents employed were in a high state of purity.

The solutions studied could be left ten hours over a water-bath in the cells used without a readable change in the conductivity, showing that the covers of the cells fitted securely. But the curves with a great number of points nevertheless show a slight influence of the presence of moisture, since it was necessary to continue the readings through several days in order to have the curve continuous. The necessary addition and abstraction of material to get the different percentages renders some exposure to the air unavoidable. I have assured myself

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[1] In this research the percentage strength of solution always means the number of grams of solute contained in 100 grams of the solution.

that the error thus incurred was not sufficient, however, to necessitate greater refinement of method for the present purpose.

In a few cases the conductivity did not at once become constant on mixing the liquids because of a measurable speed of chemical reaction between the substances. This will be discussed further below.

Consideration of the foregoing sources of error shows that it is unnecessary to compute the specific conductivity to more than three digits. Accordingly the calculations were made with a slide-rule, using Ostwald's tables for Wheatstone's bridge.

Materials

Two liters of Kahlbaum's C. P. acetic acid containing 99.41 percent acid (by a potassium hydrate test) was cooled till about one-half had crystallized. The liquid was poured off, the crystals melted and again frozen and the remaining liquid poured off. These last crystals were melted and dehydrated with a little phosphorus pentoxide. The acid was poured off from the phosphorus pentoxide and distilled. The fraction amounting to some 700 cc, which came over at 116°-117° under a pressure of 738.7 mm, was used. Its melting-point was 16.59°; its specific conductivity was less than 2×10^{-8}; and its specific gravity was 1.0463 at 25° as compared with water at the same temperature.

The pyridine, quinoline, amylamine, isobutylamine, aniline, dimethylaniline, and xylidine used were dried in each case over fused potassium hydrate for at least a week, and then allowed to stand over freshly broken potassium hydrate. If the sharp corners of the caustic showed signs of rounding off, the drying of the liquid was continued until no such action was observed on freshly broken pieces of the caustic. The pyridine boiled between 114° and 117° at 738.5 mm pressure; the quinoline (synthetic according to Skraup) at 232° under 746 mm; the amylamine at 96° under 738 mm; the isobutylamine at 67° to 69° under 745 mm; the aniline at 117° under 88 mm; the dimethylaniline at 123° under 87 mm; and the xylidine at 214° under 744.5 mm. The latter substance had a specific gravity of 0.9747 at 25° as compared with water of the same temperature.

The following preparations used were of the best C. P. varieties of standard manufacturers — Kahlbaum, Schuchardt, or Merck. A few of the compounds were prepared in this laboratory. All the substances were thoroughly dried with dehydrating agents, phosphorus pentoxide being used in case of benzene, toluene and xylene, and fused calcium chloride in all the other cases except the alcohols, which were dried with lime, distilled, and finally redistilled after adding some metallic sodium. The acetone was dried for months over anhydrous copper sulphate. The boiling-points of these liquids were as follows: benzene 79.4° to 79.5° at 746.9 mm; toluene 108° to 110° at 744.5 mm; xylene 134.4° to 135.5° at 743 mm; cymene 167° to 169° at 740.2 mm; amylene 40° at 724 mm; methyl alcohol 65° to 66° at 749 mm; ethyl alcohol 77.6° to 77.8° at 738.2 mm; acetone 55.5° to 56° at 738.2 mm; methyl acetate 54° at 742.3 mm; methyl nitrate 64.4° at 730 mm; isobutyl nitrate 120° to 124° at 728 mm; chloroform 60° at 747.9 mm; carbon tetrachloride 75.2° to 75.7° at 740.4 mm; bromoform 144° to 146.2° at 740.6 mm; ethyl bromide 37.4° to 41° at 732.4 mm; propyl bromide 69° to 71° at 740.1 mm; amyl bromide 118.5° to 119° at 742 mm; ethylene bromide 128.5° to 128.7° at 741.2 mm; butylene bromide 150° to 152° at 741.2 mm; methyl iodide 41° to 43° at 742.7 mm; ethyl iodide 71° to 71.1° at 747 mm; amyl iodide 127° to 128° at 740.3 mm; benzonitrile 187° to 188° at 737.9 mm; nitrobenzene 205° to 205.5° at 743.8 mm; benzaldehyde 173.4° to 173.7° at 729.9 mm; amylsulphydrate 115° at 742.8 mm; ethyl xanthogenate 194° to 196° at 742.8 mm. The naphthalene used was resublimed; and the distilled water employed was carefully prepared in this laboratory.

Results

The first series presents the experimental results showing how the specific electrical conductivity of a solution consisting of 17 percent pyridine and 83 percent acetic acid is changed by diluting the solution with various solvents. A mixture of pyridine in acetic acid was chosen because such a solution was found to be miscible with a relatively large number of solvents. The solution was made to contain 17 percent pyridine and 83 percent acetic acid because this particular strength was found to have the highest specific conductivity of any mixture of these two liquids.

A solution containing 19.303 g pyridine to 93.654 g acetic acid was made up, corresponding to 17.07 percent pyridine to 82.93 percent acetic acid. The specific conductivity of this solution was 8.70 × 10^{-3} at 25°.

A second solution containing 18.412 g pyridine to 89.892 g acetic acid was made up, corresponding to 17 percent pyridine to 83 percent acetic acid. The specific conductivity of this solution at 25° was 8.70 × 10^{-3}. The bridge reading was exactly the same as for the first solution.

A third solution containing 17.425 g pyridine to 85.083 g acetic acid was prepared corresponding to 16.998 percent pyridine to 83.002 percent acetic acid. The pyridine used was not the same sample as in the first two solutions; neither was the acetic acid. The pyridine distilled at 115° to 117° under 745.3 mm. The acetic acid came over at 117° under 739 mm. The specific conductivity of this solution was 8.66 × 10^{-3} at 25° C.

The solution containing 17 percent pyridine to 83 percent acetic acid was diluted with different amounts of various solvents and the specific electrical conductivity of each resulting solution was measured at 25°. The results thus obtained are given in Table I. which follows. The headings of the table are self-explanatory. Each of the pure solvents used had a specific conductivity of less than 2 × 10^{-8}, except water (4 × 10^{-6}); methyl alcohol (5.2 × 10^{-5}); acetone (8.22 × 10^{-6}); methyl nitrate (4.52 × 10^{-6}); benzonitrile (9.40 × 10^{-6}); and benzaldehyde (1.00 × 10^{-6}).

To facilitate a comparison of the numerous results given in Table I., these are presented in graphic form in Figs. 1 to 5 following the table.

TABLE I.

Specific conductivity of solution containing 17 percent pyridine and 83 percent acetic acid on dilution with various solvents.

(Percents indicate number of grams of dilutant in 100 grams of resulting solution. Specific conductivities are multiplied by 10^6.)

1. Benzene		2. Toluene		3. Xylene	
Percent	Sp. cond.	Percent	Sp. cond.	Percent	Sp. cond.
0.00	866.0	0.00	866.0	0.00	866.0
5.92	697.0	3.42	769.0	5.79	685.0
17.60	368.0	13.06	479.0	11.51	495.0
32.06	100.0	27.80	140.0	22.12	297.0
37.02	44.6	39.42	26.7	35.5	52.3
45.75	9.02	46.75	6.75	38.8	28.4
				41.4	18.4

4. Cymene		5. Naphthalene		6. Amylene	
0.0	870.0	0.0	870.0	0.0	870.0
16.0	410.0	5.94	719.0	22.2	204.0
29.0	93.5	11.60	581.0	38.0	121.0
37.6	29.2	—	—	—	—
43.0	12.2	—	—	—	—

7. Water		8. Methyl alcohol		9. Ethyl alcohol	
0.0	870.0	0.0	870.0	0.0	871.0
0.42	898.0	7.2	901.0	23.8	871.0
0.84	923.0	24.7	768.0	34.8	246.0
1.25	955.0	52.0	392.0	46.1	92.8
1.74	994.0	68.6	224.0	70.8	36.0
2.15	1020.0	—	—	—	—
4.07	1150.0	—	—	—	—
5.99	1260.0	—	—	—	—

10. Acetone		11. Methyl acetate		12. Methyl nitrate	
0.0	870.0	0.0	866.0	0.0	872.0
18.0	555.0	28.5	340.0	27.0	521.0
30.5	338.0	46.1	73.6	50.9	216.0
48.6	136.0	62.7	15.6	62.3	138.0

TABLE I.—(*Continued*)

13. Isobutyl nitrate		14. Chloroform		15. Carbon tetrachloride	
Percent	Sp. cond.	Percent	Sp. cond.	Percent	Sp. cond.
0.0	872.0	0.0	870.0	0.0	870.0
21.6	347.0	17.65	541.0	29.7	251.0
34.6	149.0	28.60	337.0	49.4	31.0
51.6	34.8	36.9	205.0	52.7	18.4
—	—	43.6	123.0	55.8	9.75
—	—	49.00	72.0	—	—
—	—	53.60	43.2	—	—
—	—	57.20	26.0	—	—
—	—	60.30	16.0	—	—
16. Bromoform		17. Ethyl bromide		18. Propyl bromide	
0.0	870.0	0.0	870.0	0.0	871.0
38.5	386.0	48.8	80.3	18.1	578.0
56.8	144.0	53.0	54.3	39.6	172.0
68.0	45.4	61.5	19.7	52.0	56.9
73.4	18.6	—	—	60.5	19.8
—	—	—	—	65.6	9.65
19. Amyl bromide		20. Ethylene bromide		21. Butylene bromide	
0.0	871.0	0.0	872.0	0.0	870.0
14.37	489.0	24.3	477.0	32.8	272.0
25.05	266.0	41.6	230.0	47.9	90.0
36.60	143.0	56.8	73.4	52.0	60.6
45.60	44.1	66.9	20.2	57.8	31.2
50.10	25.6	—	—	61.3	18.3
53.95	15.2	—	—	—	—
22. Methyl iodide		23. Ethyl iodide		24. Amyl iodide	
0.0	870.0	0.0	870.0	0.0	870.0
40.6	299.0	40.0	157.0	23.6	308.0
54.6	141.0	63.0	28.9	41.2	86.0
65.6	62.9	72.0	13.6	50.8	35.3
72.8	31.5	—	—	58.3	20.0
80.4	14.2	—	—	—	—

TABLE I.—(*Continued*)

25. Benzonitrile		26. Nitrobenzene		27. Benzaldehyde	
0.0	870.0	0.0	866.0	0.0	867.0
20.7	515.0	27.4	408.0	6.7	661.0
34.8	285.0	43.4	227.0	24.2	426.0
39.9	216.0	55.8	128.0	37.2	245.0
61.3	113.0	—	—	49.4	129.0
72.0	64.3	—	—	—	—
78.3	42.2	—	—	—	—

28. Amyl sulphydrate		29. Ethyl xanthogenate	
0.0	866.0	0.0	870.0
9.57	543.0	29.5	170.0
20.00	253.0	43.8	47.0
43.3	20.2	49.9	26.0
—	—	53.3	14.7

Naphthalene dissolves with some difficulty in the solution of pyridine in acetic acid. To façilitate solution: The cell containing the pyridine-acetic acid solution and the naphthalene was set in a dish of hot water until solution was complete, then cooled to 25° and the conductivity determination made. That this solution was not supersaturated within the limits investigated was shown by the fact that no naphthalene crystallized out when crystals of naphthalene were added. Addition of more than 11.6 percent of naphthalene causes a mass of crystals to separate out on cooling this solution to 25°.

There is without question a pronounced reaction between the methyl iodide and the pyridine-acetic acid solution. The conductivity is at first lowered to the figure given in Table I., and then on allowing the solution to stand the conductivity rises rapidly. After each successive addition of methyl iodide the conductivity sinks again to the figure given in the table. When these figures are plotted a smooth curve is obtained. On allowing the solution to stand, a crystalline substance separates out. It is readily soluble in water and gives a precipitate of silver iodide with silver nitrate. Doubtless it is an addition product of methyl iodide and pyridine. The conductivity of this solution affords good opportunity to study the speed of this reaction.

In the case of ethyl iodide a crystalline substance separated out from the 72 percent solution (Table I.). This body is analogous to that obtained with the methyl iodide, and is probably pyridine ethyl iodide. The reaction proceeds much slower than in the case of methyl iodide.

No solid separates out from the solution containing 58.3 percent of amyl iodide. On standing for two hours, the conductivity had increased, showing that a slow reaction was in progress.

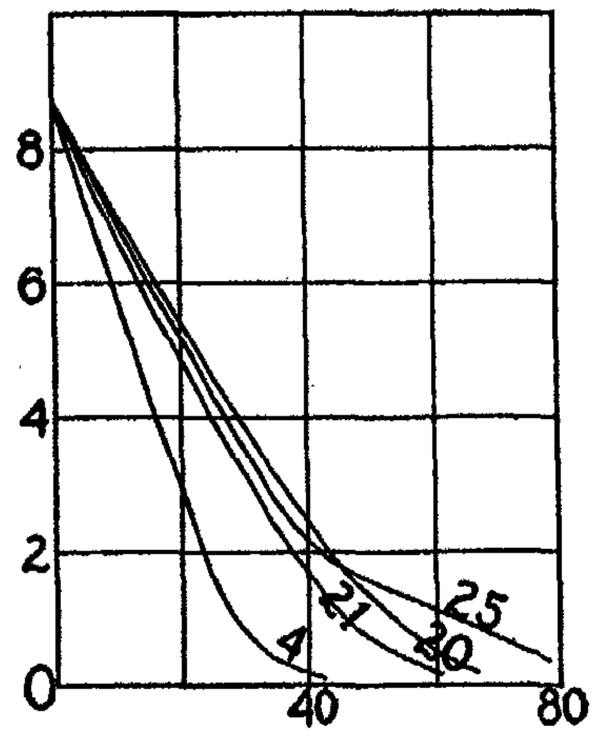

Fig. 1

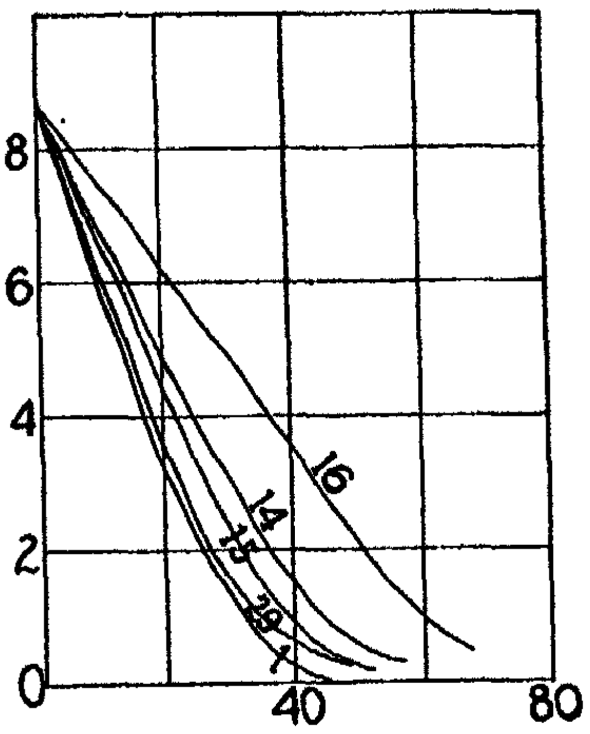

Fig. 2

In Figs. 1 to 5, which present graphically the results in the foregoing table, the ordinates represent specific conductivity multiplied by 10^3, and the abscissas, the percent of dilutant (see heading of Table I.). The curves are numbered to correspond with the numbers of the solvents listed in Table I. Curve 1 is that of benzene, toluene and xylene; their points are not exactly coincident, but nearly so, hence but one curve was plotted. Similarly 20 is the curve of ethylene bromide and of ethyl bromide.

The general trend of the results can readily be seen by inspection of Figs. 1 to 5. In order to present more clearly the relations existing between the results in this series and the physical and chemical properties of the dilutants, Table II. was prepared. In this table under the heading "Dilutant" are given the various solvents employed, — the order is the same as in Table I. The next column contains the molecular weights usually attributed to these solvents, and the third column their

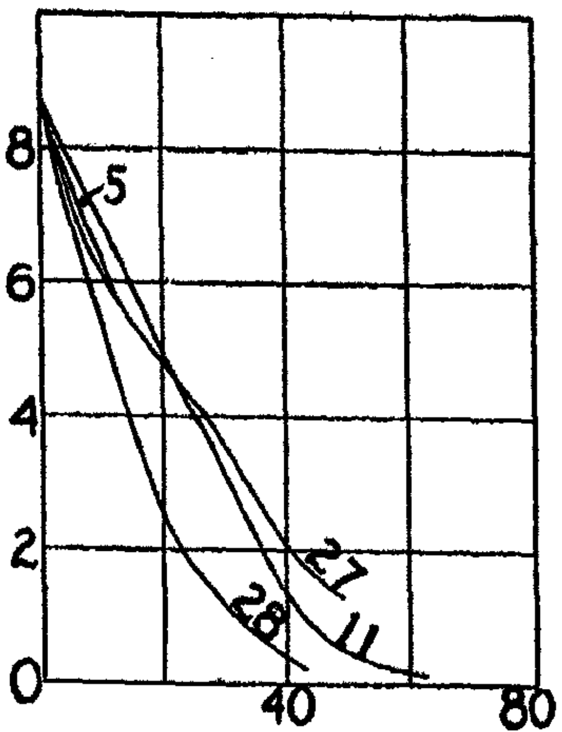

Fig. 3

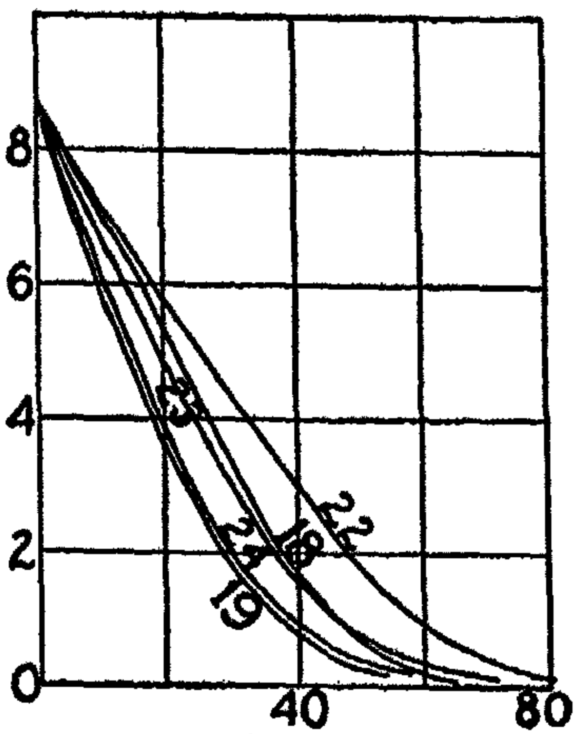

Fig. 4

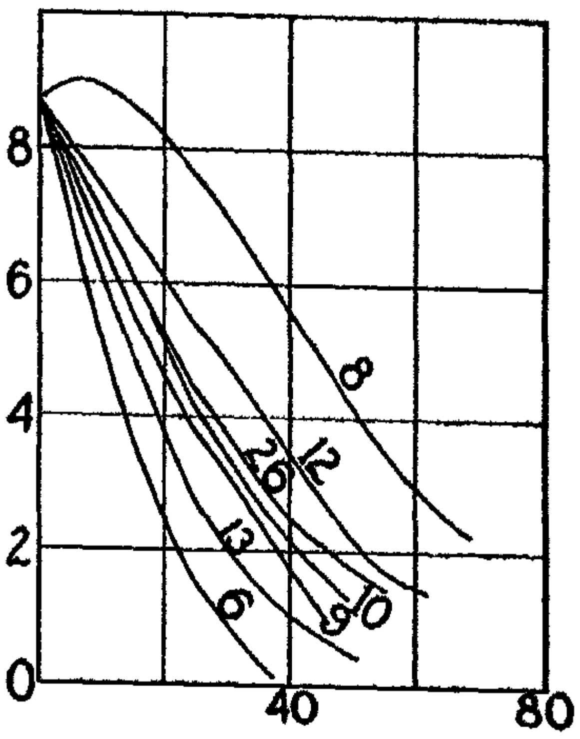

Fig. 5

formulas. Their specific gravities, dielectric constants, specific conductivities and coefficients of association follow in the next four columns. Under G_{200}, G_{400}, G_{600} are given the weights in grams of each solvent which added to 100 grams of the solution (of pyridine 17 percent — acetic acid 83 percent) will produce a lowering of the specific conductivity to 200×10^{-5}, 400×10^{-5} and 600×10^{-5}, respectively. The values given for G are taken from the curves in Figs. 1 to 5. Under M_{200}, M_{400}, M_{600} are given the fractions of a gram-molecule of a solvent required to effect a lowering of the specific conductivity to 200×10^{-5}, 400×10^{-5}, 600×10^{-5}, respectively. The M's were obtained by dividing the G's by the formula weight of the solvent in each case. Under V_{200}, V_{400}, V_{600} are given the volumes in cubic centimeters of solvent required to lower the specific conductivity to 200×10^{-5}, 400×10^{-5}, 600×10^{-5}, respectively; they were obtained by dividing the G's by the specific gravity in each case. The abbreviations used are P, for Palaz; N, Negreano; D, Drude; L & J, Landolt & Jahn; T, Tereschin; Ro, Rosa; Tw, Thwing; Sh, Schlundt; R & S, Ramsay and Shields.

Table II, shows that no simple relation exists between the dielectric constant of a solvent and its power to lower the conductivity. The coefficient of associations of the solvent, also gives no indication of its effect on the conductivity. That the alteration of the conductivity is not due merely to dilution — i. e., to a thinning out of the conducting particles — is shown by the different volumes of dilutants required to produce the same effect. (Columns V_{200}, V_{400}, V_{600}, Table II.). Substances like methyl alcohol, ethyl alcohol, methyl nitrate, acetone, etc., require a large number of gram-molecules to effect the same lowering as one gram-molecule of cymene, for instance. In general, such solvents are capable of yielding conducting solutions.[1] Their behavior will be considered in the general discussion.

Columns M_{200}, M_{400}, M_{600}, show that for *chemically analogous* compounds the lowering of the specific conductivity is roughly

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[1] A. T. Lincoln (Dissertation). Trans. Wis. Acad. Sciences, Arts, and Letters, Vol. XII., pp. 395-453.

TABLE II.

Dilutant	Mol. wt.	Formula	Sp. gr. 25°	D. C.	Sp. cond. $\times 10^{-8}$	Coeffi. Ass'n.	G_{200}	G_{400}	G_{600}	V_{200}	V_{400}	V_{600}	M_{200}	M_{400}	M_{600}
Benzene	78	C_6H_6	0.8869	2.34 P	< 2	1.01 R&S	35.9	19.9	10.4	40.5	22.4	11.7	0.46	0.26	0.13
Toluene	92	C_7H_8	0.8615	2.36 P	< 2	—	35.9	19.9	10.4	41.7	23.1	12.0	0.39	0.22	0.11
Xylene	106	C_6H_{10}	0.8600	2.28 N	< 2	—	35.9	19.9	10.4	41.8	23.2	12.1	0.34	0.19	0.10
Cymene	134	$C_{10}H_{14}$	0.8817	2.47 N	< 2	—	31.1	19.5	10.3	35.2	22.1	11.6	0.23	0.15	0.08
Naphthalene	128	$C_{10}H_8$	—	—	—	—	—	—	12.9	—	—	—	—	—	0.10
Amylene	70	C_5H_{10}	0.6645	2.30 L&J	< 2	0.96 R&S	28.7	16.3	7.9	43.2	24.5	11.9	0.41	0.28	0.13
Water	18	H_2O	1.0000	81.0	400.0	2.53 R&S	—	—	—	—	—	—	—	—	—
Methyl alcohol	32	CH_3OH	0.7931	32.65 T	1070.0	3.43 R&S	280.0	106.8	58.0	35.3	134.7	73.2	8.75	3.34	1.81
Ethyl alcohol	46	C_2H_5OH	0.7906	25.7 Ro	520.0	2.74 R&S	61.3	32.6	15.1	79.9	41.2	19.1	1.33	0.71	0.30
Acetone	58	C_2H_6CO	0.7890	20.7 D	822.0	1.26 R&S	70.5	35.2	18.9	89.4	44.5	24.0	1.21	0 61	0.33
Methyl acetate	74	$C_3H_6O_2$	0.9200	7.75 T	337.0	—	56.3	33.7	17.1	61.1	36.7	18.6	0.76	0.46	0.23
Methyl nitrate	77	CH_3NO_3	1.2003	23.5 Sh	452.0	—	108.3	55.5	26.6	90.0	46.3	22.2	1.41	0.72	0.35
Isobutyl nitrate	119	$C_4H_9NO_3$	1.0072	11.7 Sh	< 2	—	50.0	23.9	11.9	49.6	23.8	11.8	0.42	0.20	0.10
Chloroform	119.5	$CHCl_3$	1.4805	3.95 Tw	< 2	0.94 R&S	58.5	33.3	16.6	39.5	22.5	11.2	0.49	0 28	0.14
Carbon tetrachloride	154	CCl_4	1.5867	2.2 T	< 2	1.01 R&S	47.9	30.0	16.0	33.1	18.9	10.1	0.31	0.20	0.10
Bromoform	253	$CHBr_3$	2.8220	4.43 D	< 2	—	104.5	59.2	27.5	37.0	21.0	9.8	0 41	0.23	0.11
Ethyl bromide	99	C_2H_5Br	1.4450	8.74 D	< 2	—	79.9	41.2	19.9	55.3	28.5	13.8	0.81	0.42	0.20
Propyl bromide	123	C_3H_7Br	1.3389	—	< 2	—	61.0	36.2	19.8	45.5	27.1	14.8	0.49	0.29	0.16
Amyl bromide	150.7	$C_5H_{11}Br$	1.1790	—	< 2	—	40.1	21.8	10.6	34.0	18.5	9.0	0.27	0.15	0.07
Ethylene bromide	188	$C_2H_4Br_2$	2.1735	—	< 2	0.95 R&S	79.9	41.2	19.9	36.7	19.0	9.2	0.42	0.22	0.11
Butylene bromide	216	$C_4H_8Br_2$	1.7670	—	< 2	—	61.3	33.3	15.7	34.7	18.9	8.9	0.28	0.15	0.07
Methyl iodide	142	CH_3I	2.2661	—	< 2	—	93.5	48.1	22.4	41.1	21.2	9.9	0.66	0.34	0.16
Ethyl iodide	156	C_2H_5I	1.9293	7.42 D	< 2	—	57.8	32.5	16.0	30.0	16.8	8.3	0 37	0.21	0.10
Amyl iodide	198	$C_5H_{11}I$	1.1189	—	350.0	—	50.0	23.8	12.4	44.7	21.2	11.0	0.25	0.12	0.16
Benzonitrile	103	C_6H_5CN	1.0068	26.0 D	940.0	—	73.0	31.2	18.1	72.6	31.0	17.9	0.71	0.30	0.17
Nitrobenzene	123	$C_6H_5NO_2$	1.1967	32.19 Tw	< 2	1.13 R&S	70.5	35.2	18.9	59.0	29.4	15.8	0.57	0.29	0.15
Benzaldehyde	106	C_6H_5COH	1.0456	14.48 Tw	100.0	0.97 R&S	69.5	36.1	11.6	66 5	34.5	11.1	0.66	0.34	0.11
Amyl sulphydrate	104	$C_5H_{11}SH$	0.8336	4.355 Sh	< 2	—	29.5	16.7	8.3	35.4	20.0	10.0	0.28	0.16	0.08
Ethyl xanthogenate	118	$C_5H_{10}S_2O$	1.0812	—	< 2	—	36.2	22.4	11.2	33.5	20.7	10.4	0.31	0.19	0.10

proportional to the number of gram-molecules dissolved. The individuality of the curves in Figs. 1 to 5 shows that the chemical constitution of the substance is a very important factor in determining the trend of the curve. At the same time the different specific gravities of the solvents cause great variation of the volume added to get the same effect on the conductivity. As dilution is undoubtedly one factor in the alteration of the conductivity, too much reliance is not to be placed on a casual inspection of curves charted on the basis of percentage by weight. But the regularities which appear in Table II. are only the more remarkable because of this fact.

The foregoing solvents and others were next added to a 0.1 normal solution of silver nitrate in pyridine in order to ascertain how such additions affect the electrical conductivity. The solution of silver nitrate in pyridine was chosen because it can readily be prepared; it conducts fairly well; it mixes with a goodly number of solvents; and it represents a solution of an inorganic salt in a solvent other than water. Silver nitrate dissolves in pyridine with liberation of much heat, and on evaporation, addition products of silver nitrate with pyridine crystallize out, so that no doubt can be entertained that chemical combination between silver nitrate and pyridine occurs.

One hundred cc of 0.1 normal solution of silver nitrate in pyridine was carefully prepared at 25°. The pyridine used boiled at 114.7° to 117° under a pressure of 746.3 mm, and the silver nitrate had been dried by carefully fusing it. Expressed in percent by weight this solution is made up of 1.74 percent $AgNO_3$ to 98.26 percent C_5H_5N. The specific conductivity of this solution was 2.75×10^{-3} at 25° C. A second solution, prepared in the same flask when the first was exhausted, had a specific conductivity of 2.76×10^{-3}.

Preliminary qualitative tests were made to ascertain which solvents are miscible with the solution just described. It was found that ethyl iodide first gives a yellow precipitate, and on standing a mass of crystals forms throughout the solution. Ethylethyl xanthogenate is immediately decomposed, free sulphur and a black precipitate forming. Carbon disulphide gives a black precipitate. Normal pentane and normal hexane do not mix with the pyridine-silver nitrate solution. Ethyl bromide causes the silver nitrate to separate out from the solution; the same is true of turpentine. Careful addition of bromoform to silver nitrate solution in pyridine causes a white precipitate to form, which redissolves immediately to a brown liquid on stirring. Addition of propyl bromide beyond 53 percent of the total weight of the resulting solution causes a solid to separate out. In the case of amyl bromide 41 percent causes a solid to deposit; and in the case of butylene bromide, addition of 36 percent results in the deposition of a solid. It is of course very likely that the solutions were supersaturated before these solids actually separated out.

Table III. shows how the conductivity of 0.1 *n* silver nitrate solution in pyridine is altered by adding various solvents. The results are also presented graphically in Figs. 6, 7, and 8 immediately following the table. In the figures ordinates represent specific conductivity multiplied by 10^3, and abscissas the percent of dilutant added as indicated in Table 3. The curves are numbered to correspond with the numbers attached to the solvent in Table III.

The curves of destruction of conductivity as plotted in Figs. 6, 7 and 8 are smooth. Their individuality gives evidence of the chemical nature of the process of solution. The fact that the curve of methyl alcohol, Fig. 8, curve 7, lies higher than that of water, Fig. 7, curve 6, is of considerable interest. The fact that amylene, an unsaturated hydrocarbon, will mingle with these solutions (silver nitrate pyridine solution, and pyridine acetic acid solution) while the saturated hydrocarbons of the fatty series refuse to dissolve, would further indicate that solution is a union of solvent and solute.

Table IV. has been compiled from the curves in Figs. 6, 7 and 8 in the same manner as Table II. was formed from Figs. 1 to 5, except that in the case of Table IV. the specific conductivity was lowered to a different degree, i. e., to 120×10^{-5}, 160×10^{-5},

TABLE III.

Specific conductivity of 0.1 *n* silver nitrate in pyridine on dilution with various solvents.

(Percents indicate number of grams of dilutant in 100 grams of resulting solution. Specific conductivities are multiplied by 10^5.)

1. Benzene		2. Toluene		3. Xylene	
Percent	Sp. cond.	Percent	Sp. cond.	Percent	Sp. cond.
0.0	275.0	0.0	275.0	0.0	275.0
21.3	102.0	14.3	147.0	10.4	177.0
31.6	48.9	28.9	58.0	17.5	124.0
37.8	28.1	34.0	38.2	24.6	76.2
41.6	19.2	38.0	23.8	30.9	47.0
—	—	—	—	39.5	20.8

4. Cymene		5. Amylene		6. Water	
0.0	276.0	0.0	276.0	0.0	275.0
7.3	187.0	8.53	141.0	35.0	206.0
17.2	108.0	27.9	55.0	47.0	192.0
25.9	59.5	34.7	30.8	54.0	186.0
32.0	37.6	—	—	70.8	154.0
35.7	22.9	—	—	—	—

7. Methyl alcohol	
0.0	276.0
14.5	312.0
28.0	287.0
41.3	252.0
55.8	207.0
72.9	143.0

11. Isobutyl nitrate	
0.0	276.0
6.35	242.0
25.45	151.0
41.60	92.5

8. Ethyl alcohol	
0.0	276.0
11.0	256.0
14.8	246.0
16.0	241.0
18.0	236.0
20.8	227.0
23.0	219.0
28.2	201.0
33.6	183.0
36.0	176.0
39.3	165.0
43.9	150.0
57.5	110.0
65.6	89.0

9. Acetone	
0.0	276.0
16.2	273.0
30.8	254.0
40.9	222.0

10. Methyl acetate	
0.0	276.0
12.0	237.0
20.2	206.0
34.6	156.0
52.4	101.0

TABLE III.—*Continued.*

12. Chloroform		13. Carbon tetrachloride		14. Bromoform	
Percent	Sp. cond.	Percent	Sp. cond.	Percent	Sp. cond.
0.0	275.0	0.0	275.0	0.0	275.0
8.2	246.0	17.2	169.0	46.0	98.0
29.8	173.0	33.1	85.5	64.1	42.9
36.2	150.0	42.5	48.2	70.1	28.6
48.3	108.0	53.2	20.2	73.6	21.4
62.4	64.9	—	—	—	—
77.0	25.6	—	—	—	—
15. Propyl bromide		16. Amyl bromide		17. Ethylene bromide	
0.0	275.0	0.0	275.0	0.0	275.0
29.3	142.0	11.6	193.0	52.5	81.2
45.5	75.3	20.7	140.0	59.5	56.6
53.0	48.5	27.0	93.2	65.1	40.8
—	—	35.0	62.8	71.8	24.5
—	—	41.0	36.4	—	—
18. Butylene bromide		19. Nitrobenzene		20. Benzaldehyde	
0.0	275.0	0.0	276.0	0.0	276.0
36.6	116.0	20.4	237.0	12.7	237.0
—	—	43.6	175.0	30.1	173.0
—	—	54.1	142.0	49.3	115.0
—	—	62.3	115.0	—	—

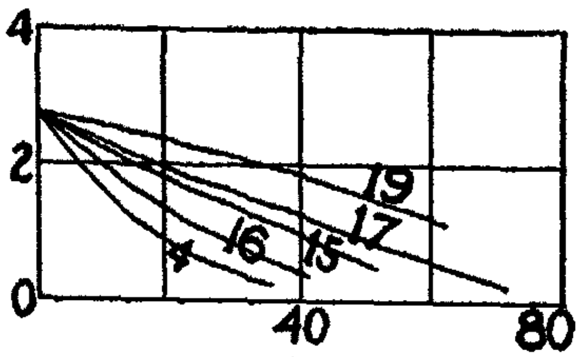

Fig. 6

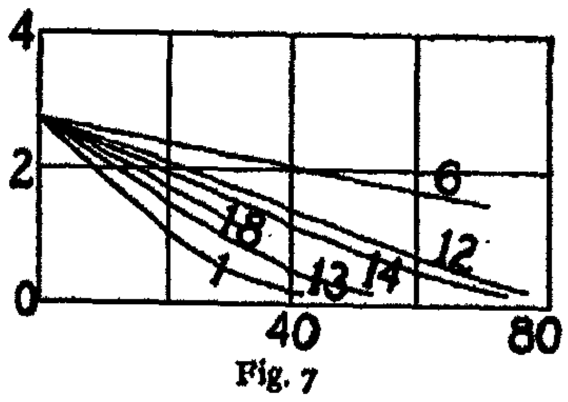

Fig. 7

and 200 × 10^{-5}, respectively, as indicated by the subscripts to the letters G, V, and M, which head the columns. The explanations given in connection with Table II. will make the headings of

Table IV. perfectly intelligible. The molecular weights, formulas, specific gravities, dielectric constants and coefficients of association of the dilutants in Table IV. have already been given in Table II., so that repetition would be superfluous.

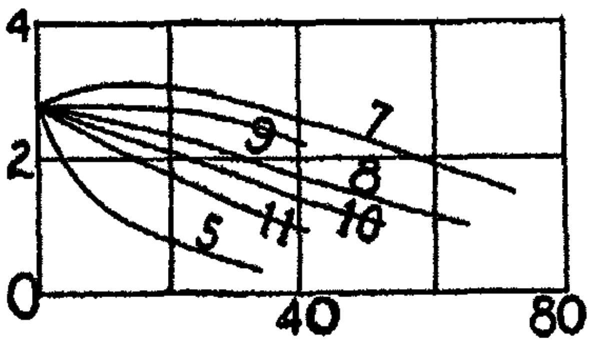

Fig. 8

TABLE IV.

Dilutant	G_{120}	G_{160}	G_{200}	V_{120}	V_{160}	V_{200}	M_{120}	M_{160}	M_{200}
Benzene	22.1	15.6	9.4	25.0	17.6	10.6	0.28	0.20	0.12
Toluene	22.1	15.6	9 4	25.6	18.1	10.9	0.24	0.17	0.10
Xylene	22 1	15.6	9.4	25.7	18.2	11.0	0.20	0.15	0.09
Cymene	18.5	12.0	7.1	21.0	13 6	8.0	0.14	0.09	0.05
Amylene	13.1	7.1	3.8	19.8	10.6	5.8	0.19	0.10	0.06
Water	—	207.3	71.0	—	207.3	71.0	—	11.50	3.94
Methyl alcohol	—	219.5	135.3	—	277.0	174.0	—	6.85	4.23
Ethyl alcohol	134.2	78.6	46.0	170.0	99.5	58.2	2.92	1.70	1.00
Acetone	—	—	81.8	—	—	103.2	—	—	1.41
Methyl acetate	85.2	52.2	29.2	92.6	56.8	31.7	1.15	0.75	0.39
Isobutyl nitrate	48.4	30.4	17.5	48.0	30.1	17.4	0.41	0.25	0.15
Chloroform	84.5	52.1	28.2	52.1	35.2	19 0	0.71	0.44	0.24
Carbon tetrachloride	34.8	23.5	14.0	21.9	14.8	8.9	0.23	0.15	0.09
Bromoform	62.1	39.9	22.1	21.5	13.9	7.7	0.25	0.16	0.09
Propyl bromide	53.4	33.9	19.2	39.9	25.3	14.3	0.43	0.28	0.16
Amyl bromide	29.9	19.5	11.6	25.4	16.5	9.9	0.20	0.13	0.08
Ethylene bromide	73.1	43.3	22.2	33.6	19.9	10.2	0.12	0.23	0.39
Butylene bromide	46.1	29.9	17.5	26.1	16.9	9.9	0.21	0.14	0.08
Nitrobenzene	151.3	93.1	52.7	126.5	78.5	44.0	1.23	0.76	0.43
Benzaldehyde	85.2	52.2	29.2	81.5	50.0	26.9	0.81	0.49	0.28

Table IV. shows that the lowering of the specific conductivity is not proportional to the dielectric constant of the dilutant or to its coefficient of association. Nor does the specific conductivity stand in any simple relation to these properties, even as to general trend. The gradual decrease of the number of gram-molecules required to produce the same lowering of conductivity, with increase of the number of CH_3 side-chain groups in benzene, toluene, xylene and cymene shows the constitutive character of this lowering phenomenon.

In a third series the specific electrical conductivity of solutions consisting of various organic bases dissolved in acetic acid in all proportions was determined. In the case of pyridine and acetic acid solutions, specific gravity determinations were also made and the molecular conductivity calculated on the basis that pyridine is doing the conducting — an assumption which is, however, not warranted by the results obtained. The molecular weight of pyridine in acetic acid was further determined by the freezing-point method for several concentrations; and a curve was plotted to facilitate comparison with the molecular conductivity curve.

Table V. gives the specific conductivity of solutions of pyridine and acetic acid. The first column indicates the percent acid by weight calculated on the total weight of solution. The specific conductivity multiplied by 10^5 is given in the second column. The sp. cond. of the pure acid was less than 2×10^{-8}; the same is true of the pure pyridine employed.

Curve 1 in Fig. 9 shows the general trend of the results in Table V. In Fig. 9 ordinates represent specific conductivity in reciprocal ohms multiplied by 10^3; and abscissas, the percent of organic base by weight, calculated on the total weight of the solution.

In Fig. 9, curves 2 to 6 were similarly obtained, using organic bases other than pyridine. So curve 2 is that of dimethylaniline; 3, that of isobutylamine; 4, that of amylamine; 5, that of quinoline; and 6, that of aniline.[1] These curves will be considered in their turn below.

In order to calculate the molecular conductivity of pyridine

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[1] Isopropylamine, dipropyl amine and piperidine were tried with acetic acid, but their acetates do not redissolve in excess of the base, so nothing further was done with them.

in acetic acid, specific gravity determinations were made which are contained in Table VI. and from them a specific volume curve[1] was charted.

TABLE V.

Specific conductivity of pyridine dissolved in acetic acid

Percent acid	Sp. cond. $\times 10^6$	Percent acid	Sp. cond. $\times 10^6$	Percent acid	Sp. cond. $\times 10^6$
99.70	0.9567	92.92	494.6	47.47	87.08
99.43	2.508	92.68	516.4	45.17	68.56
99.18	5.303	92.42	532.0	42.98	52.06
98.86	9.614	92.19	566.4	40.51	37.29
98.55	16.68	92.02	580.1	38.28	29.19
98.27	25.13	91.68	586.1	36.15	21.36
97.98	36.64	91.43	602.2	33.52	15.24
97.74	50.71	91.18	621.2	31.17	11.28
97.47	65.39	90.99	638.3	28.73	8.680
97.20	83.16	90.74	688.6	25.77	6.083
97.04	83.51	89.98	708.3	23.43	4.617
96.76	102.3	89.78	719 5	19.73	2.981
96.49	122.1	88.15	780.3	16.56	2.060
96.23	142.7	86.76	828.1	13.13	1.80
95.95	165.5	85.56	834.8	11.16	1.45
95.69	188.8	83.04	877.8	9.48	1.02
95.54	198.4	80.55	868.5	7.51	0.613
95.28	240.9	76.02	843.1	5.50	0.414
95.03	268.7	74.03	786.2	3.36	0.253
94.78	309.2	70.39	684.5	1.14	0.1326
94.56	324.1	67.01	581.5		
94.27	344.2	63.66	481.8		
94.19	383.2	61.37	387.2		
93.89	403.1	58.36	260.6		
93.64	425.8	56.03	248.5		
93.36	450.1	54.35	171.1		
93.14	469.5	50.00	122.8		

TABLE VI.

Specific gravity and specific volume of pyridine dissolved in acetic acid, at 25° C, as compared with water at 25° C.

(The percent given is that of pyridine calculated on the total weight of solution.)

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[1] This curve is not reproduced in this paper.

Percent	Specific gravity	Specific volume
0.0	1.0463	0.9558
4.82	1.0494	0.9529
16.82	1.0566	0.9464
30.31	1.0629	0.9409
37.43	1.0575	0.9457
50.01	1.0372	0.9641
63.67	1.0180	0.9830
78.06	0.9995	1.0005
100.00	0.9768	1.0235

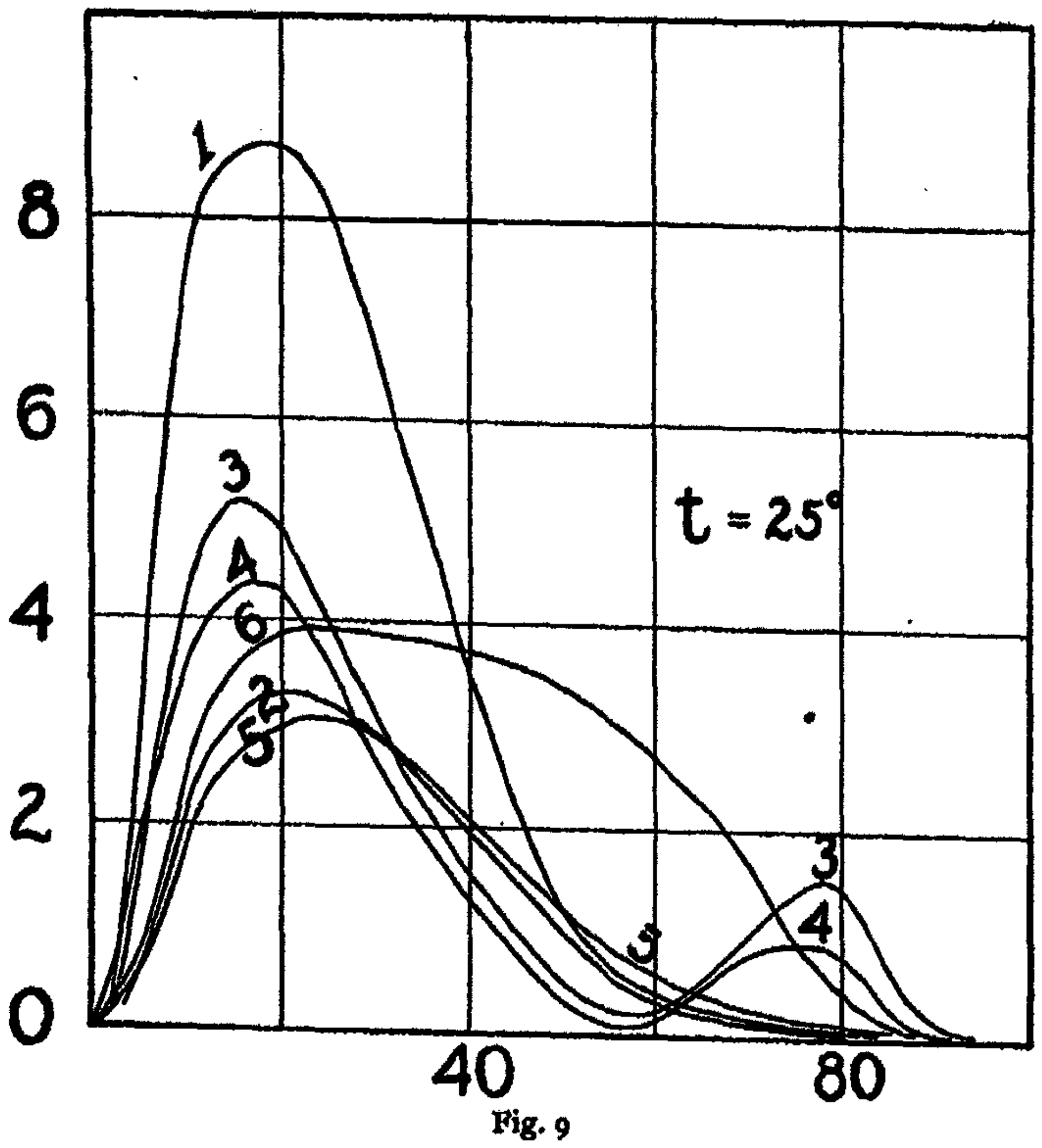

Fig. 9

With values taken from this curve and from curve 1, Fig. 9, the molecular conductivities were calculated as set forth in Table VII.

TABLE VII.

Molecular conductivity of pyridine dissolved in acetic acid

$\mu \times 10^3$	V_c	Sp. cond. $\times 10^6$	Percent
4200.0	1.502	280.0	5
5490.0	0.752	730.0	10
3240.0	0.372	870.0	20
1660.0	0.248	670.0	30
673.0	0.187	360.0	40
182.0	0.152	120.0	50
51.2	0.128	14.0	60
15.6	0.112	4.0	70
2.97	0.099	3.0	80
0.890	0.089	1.0	90
0.340	0.085	0.4	95

In Table VII., μ is the molecular conductivity and V_c, as usual, is the volume in liters in which one gram-molecule of pyridine is dissolved. These results are charted in curve 1, Fig. 10. The ordinates are given to the right in terms of μ; the abscissas below in terms of $V_c \times 10$. Curve 2 is the trend of the molecular weights of pyridine dissolved in acetic acid determined by the freezing-point method, which results will be given in Table VIII. following Fig. 10; ordinates are in terms of molecular weight, M; abscissas, in V_f, the volume in liters containing one gram-molecule of pyridine.

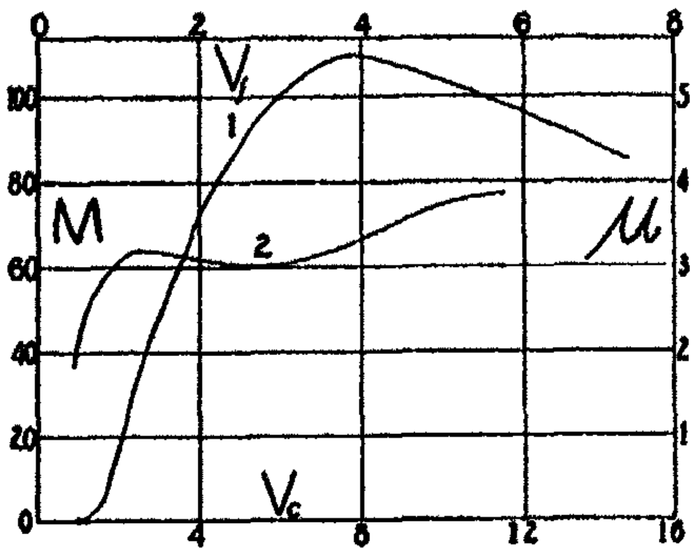

Fig. 10

The depression of the freezing-point was determined according to Raoult's method, using a Beckmann thermometer graduated to 0.01° and enabling estimation to 0.001°. The formula $M = \frac{SK}{L\Delta}$ was used, where M is the molecular weight; S, the weight of the solute; L, the weight of the solvent; Δ, the observed depression; and K, the molecular depression of the solvent 33.80.[1] The pyridine and acetic acid used were from the stock supply described under "Materials."

TABLE VIII.

Molecular weight of pyridine in acetic acid by the freezing-point method.

S	L	P_c	Δ	M	V_f
0.2030	15.504	1.29	0.663	77.0	5.840
0.7736	28.840	2.60	1.784	60.0	2.895
1.1639	16.214	6.69	4.366	63.8	1.123
3.0095	23.927	11.10	9 002	54.0	0.675
2.9620	19 337	13.20	12.399	48.2	0.567
18.412	89.892	17.00	19.1	36.0	0.438

In Table VIII., S is the weight in grams of pyridine dissolved in the weight of acetic acid given in column L; P_c is the percent of pyridine in the resulting solution; Δ, the observed lowering of the freezing-point; M, the molecular weight calculated from Δ, S, and L; and V_f the volume (of solution) in liters containing one gram-molecule of pyridine.

Comparison of curves 1 and 2, Fig. 10, shows that the agreement between freezing-point and conductivity determinations on which much of the confidence in the theory of electrolytic dissociation is based, is in this instance lacking to a marked degree.

The smoothness of my pyridine-acetic acid curve (1, Fig. 9) casts doubt upon the breaks which Konowalow[2] claims in the curves of specific conductivity reproduced from his plate in Fig. 11.

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[1] Calculated from the latent heat of fusion, $K = \frac{0.02T^2}{W}$.

[2] Wied. Ann. 49, 733 (1893).

In Fig. 11 the ordinates are in specific conductivities expressed in reciprocal Siemens units multiplied by 10^8; the abscissas in percent of base in 100 grams of solution. Curve 1 is that of methylaniline in acetic acid; curve 2 that of aniline in acetic acid; curve 3 that of dimethylaniline in acetic acid; curve 4 that of toluidine in acetic acid; curve 5 that of aniline in propionic acid; curve 6 that of aniline in butyric acid.

To set at rest this doubt, Konowalow's aniline-acetic acid curve was experimentally reproduced. The results found are contained in Table IX. The specific conductivities are multiplied by 10^5. Where two values of the conductivity are given for one concentration, the conductivity changed from the upper figure to the lower. The figures 5′, 15′, etc., give the time in minutes which elapsed between these two readings for the conductivity. The percents given in the columns headed "Aniline + acetic acid" are for *acetic acid* calculated on the total weight of solution; the percents in the column headed "Acetic acid + aniline" are for *aniline*, based on the total weight of solution. In the first case, acetic acid was gradually added to aniline; in the second case, aniline was added to the acetic acid.

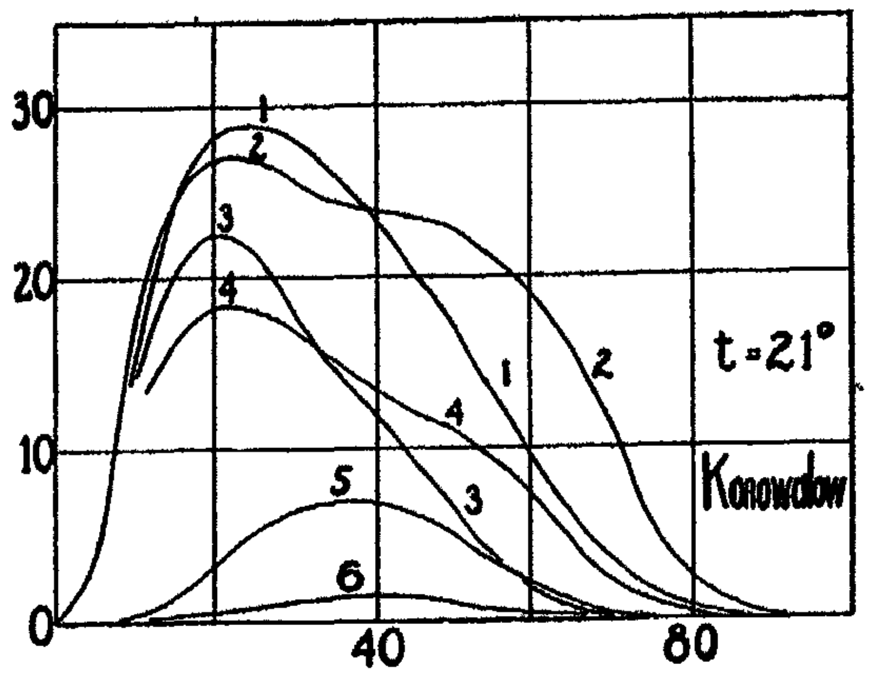

Fig. 11

The results in Table IX. are charted in curve 6, Fig. 9, using in every case the specific conductivity after it had become constant. Comparison of Konowalow's acetic acid-aniline curve (Reproduced in curve 2, Fig. 11) with curve 6, Fig. 9 shows that one of the curves must be incorrect. Table IX. shows that at several points on the curve a reaction whose speed can be followed by the change in the electrical conductivity of the solution is in progress.

TABLE IX.

Specific conductivity of aniline dissolved in acetic acid

Aniline + acetic acid				Acetic acid + aniline	
Percent	Sp. cond.	Percent	Sp. cond.	Percent	Sp. cond.
2.29	0.00809	37.7	256	0.8	1.30
4.74	0.272	38.8	267	2.5	5′ { 9.97 10.30 ↓
7.06	0.707	39.6	273	5.6	5′ { 77.3 7.60 ↓
7.20	1.64	40.6	280	7.1	5′ { 125.0 124.0 ↓
11.35	2.92	41.4	284	8.4	172.0
13.32	6.50	42.2	295	9.8	216.0
15.2	12.2	43.0	295	11.1	255.0
17.0	20.3	43.9	297	12.4	296.0
18.7	30.5	44.7	306	13.3	338.0
20.3	43.0	45.4	315	16.1	355.0
21.9	58.6	46.9	318	17.2	370.0
23.4	73.7	47.6	320	18.4	378.0
24.8	91.9	48.3	322	19.5	382.0
26.3	110.0	49.0	322	20.5	387.0
27.5	130.0	49.6	319	22.6	396.0
28.9	148.0	50.3	326	24.6	387.0
30.2	168.0	51.6	343	26.4	385.0
31.4	180.0	53.0	10′ { 307 342 ↓	36.1	381.0
32.5	195.0	60.7	365	43.6	365.0
33.7	209.0	64.7	9′ { 372 342 ↓	52.7	330.0
34.7	222.0	75.5	11′ { 414 380 ↓	59.6	278.0
36.8	249.0	83.3	10′ { 358 348 ↓	73.0	108.0

If the curve be determined by adding aniline to acetic acid the conductivity given is in general too high; if the acid be added to the aniline, the conductivity is low and on standing rises to its constant value; as, for instance, at 53 percent of aniline in Table IX., the specific conductivity rose in ten minutes from 307 to 342 ($\times 10^{-5}$), a variation of 10.2 percent, and more than sufficient to account for all the sag in Konowalow's acetic acid-aniline curve (2, Fig. 11). It is worthy of note that at 60.78 percent of aniline, the concentration corresponding to one molecule of aniline to one of acetic acid, where the solution is in fact a fused salt comparable with molten KNO_3, NaCl, or $SnCl_2$, there is no sudden break in the specific conductivity curve. The final conductivities obtained after equilibrium is established lie on the same curve whether the solution be prepared by adding acid to base or base to acid, and this curve is smooth. This of course is what one would expect. At first it was thought that this readily measurable speed of reaction might be due to the formation of some acetanilide; but on standing over night the solution containing 83.3 percent of acetic acid to 16.7 percent aniline had a specific conductivity of 355×10^{-5}, showing that the rate of formation of acetanilide is so slow that its influence on the trend of the acetic acid-aniline curve may be neglected; and that in accounting for the presence of a measurable speed of reaction upon mixing aniline and acetic acid the formation of acetanilide cannot be advanced as an explanation.[1] To investigate further this measurable change in the conductivity, the determinations given below in Table X. were made.

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[1] The most natural explanation of this changing conductivity is that the process of neutralization of acetic acid by aniline requires an appreciable time for its completion. On page 751, Wied. Ann. 49 (1893), Konowalow says with reference to the heat of neutralization, "Um den Wärmeaustausch zu beschleunigen, war im Gefässe ein Rührer aus Platin angebracht, mit dessen Hülfe die Lösung in rasche Bewegung versetzt wurde. Letzterer Umstand war im gegebenen Falle von grosser Bedeutung, denn ich hatte *mit sehr zähen Lösungen zu thun, welche ihre Wärme nur langsam abgaben.*" The slow evolution of heat, together with the measurable change in the electrical conductivity in these acid-aniline solutions, would indicate that the neutralization takes place slowly. On the other hand, in the region of large excess of acid there are cases where the conductivity rises (53 percent acid, Table IX.) on allowing the solution to stand. In this region of the curve formation of more salt molecules lowers the conductivity, so this rise in the conductivity is incompatible with the assumption that a slow neutralization is taking place. This subject will be taken up further on after more data have been presented.

The percents of acid are based on the total weight of solution; the specific conductivities are multiplied by 10^5.

TABLE X.

Rate of variation of the specific conductivity of aniline dissolved in acetic acid. (The percents are of acetic acid.)

Percent	Sp. cond.	Min.	Percent	Sp. cond.	Min.	Sec.
50.14	360	0	62.00	395	0	0
	364	5		376	2	0
	339	10		372	3	30
	337	17		368	4	45
	337	38		364	9	20
				365	235	—
57.55	407	0				
	384	2	73.10	424	0	0
	365	4		402	1	30
	361	7		394	5	0
	358	8		391	6	30
	352	18.5		386	12	0
	355	120.0		383	31	30

During the intervals between the conductivity determinations the cell containing the solution was maintained at 25° in the thermostat. These results are charted in Fig. 12. The ordinates are specific conductivities in reciprocal ohms multiplied by 10^3, the abscissas are in minutes. Curve 1 is that of 50.14 percent of acid; curve 2 of 57.55 percent of acid; 5 is a similar curve for 38.80 percent of amyl amine in acetic acid; 6 is another curve for amyl amine, 46.4 percent in acetic acid; 7 is the curve for 52.62 percent of isobutyl amine in acetic acid. The results from which curves 5, 6 and 7 were plotted will be given following Fig. 12.

Table XI. contains the specific conductivities of solutions of amyl amine dissolved in acetic acid. The percents of amyl amine are calculated on the total weight of solution; the specific conductivities are multiplied by 10^5. In every case the conductivity was allowed to come to a constant value. These results are charted in curve 4, Fig. 9, which is seen to be smooth, having two crests similar to those of the sulphuric acid-water curves of F. Kohlrausch[1] and of E. Bouty.[1]

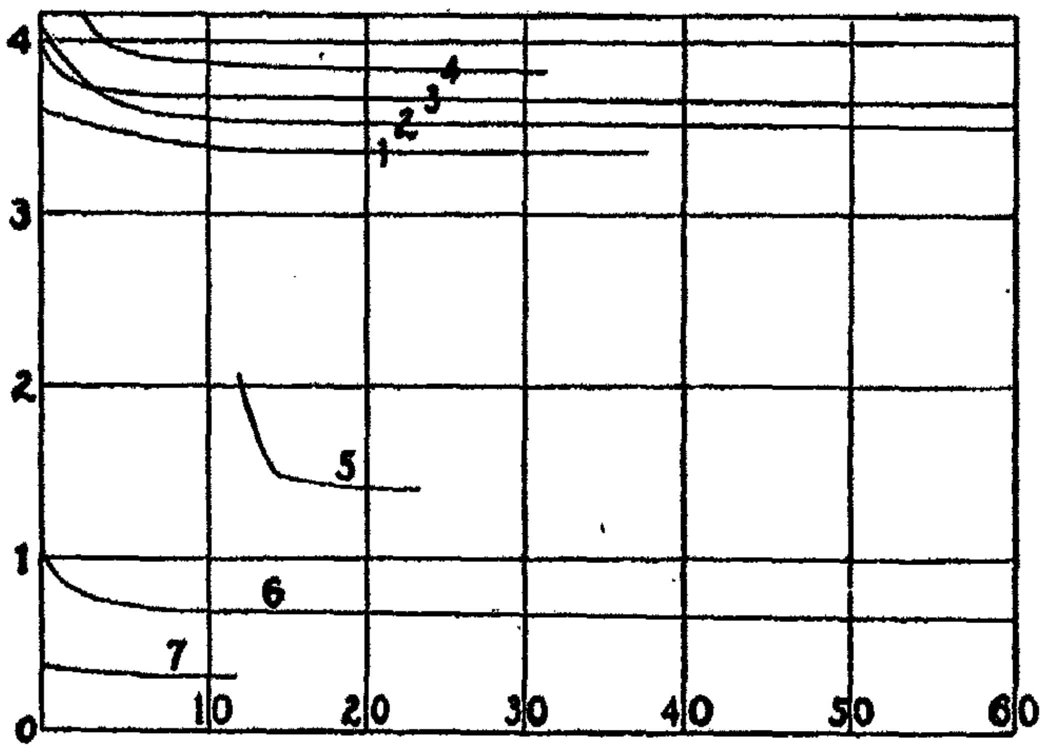

Fig. 12

TABLE XI.

Specific conductivity of amyl amine dissolved in acetic acid.

Percent amine	Sp. cond. $\times 10^6$	Percent amine	Sp. cond. $\times 10^6$
00.0	$<2 \times 10^{-8}$	20.75	410.0
00.87	2.23	24.60	372.0
01.40	6.07	30.90	247.0
01.97	12.8	38.80	140.0
03.15	41.0	46.40	65.2
04.23	81.6	62.30	21.8
05.82	154.0	67.20	56.2
06.93	202.0	76.70	92.0
07.86	252.0	83.02	60.3
09.25	282.0	88.70	1.17
09.99	329.0	94.60	0.315
11.53	378.0	100.0	$<2 \times 10^{-8}$
12.90	409.0		
14.70	434.0		
15.50	435.0		
18.60	438.0		

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[1] See Landolt u. Börnstein, tables.

While waiting for the solutions of amyl amine in acetic acid to give a constant conductivity, measurement of the rate of change of conductivity was made in two instances, as follows in Table XII. The specific conductivity is multiplied by 10^5; the percent given is that of amyl amine.

TABLE XII.

Rate of change of conductivity of amyl amine dissolved in acetic acid.

Percent amine	Sp. cond.	Minutes	Seconds
46.4	104.0	0	
	88.4	1	
	81.9	2	
	78.0	3	
	74.3	5	
	68.0	8	
	68.0	18	30
	68.7	22	
	65.2	60	
38.8	(?)	0	
	206	12	
	146	14	15
	143	17	30
	140	23	30

These results are plotted in Fig. 12, as stated above in connection with Table X.; 5 is the curve for 38.8 percent amyl amine; and 6 that of 46.4 percent amyl amine. Before discussing the results in Tables XI. and XII., I wish to present some data of a similar character obtained with solutions of isobutyl amine and acetic acid.

Table XIII. contains the specific conductivities (multiplied by 10^5) of isobutyl amine dissolved in acetic acid. In every case the solution was allowed to stand until the conductivity became constant. From 81.22 percent of acid to 97.34 percent of acid no measurable change in the conductivity was observed on allowing the solutions to remain for a considerable time in the thermostat. Throughout the rest of the curve a decrease in the conductivity after mixing the liquids and allowing the solution

TABLE XIII.

Specific conductivity of isobutyl amine dissolved in acetic acid

Percent acid	Sp. cond.	Percent acid	Sp. cond.
2.95	0.1316	68.56	282.0
5.82	1.337	72.09	353.0
11.45	27.2	74.09	391 0
13.77	54.8	77.11	438.0
15.88	93.2	79.00	476.0
17.92	122.6	80.18	492.0
20.00	145.1	81.22	501.0
22.95	154.2	82.09	510.0
27.87	121.9	83.19	516.0
30.92	79.5	84.57	517.0
34.43	54.6	84.79	522.0
38.33	24.1	85.02	510.0
41.42	14.74	88.32	458.0
47.38	32.7	91.41	343.0
51.96	64.5	94.18	196.0
56.49	105.0	95.69	108.2
63.03	192.0	97.34	19.4
65.87	232.0		

TABLE XIV.

Speed of reaction. Isobutyl amine dissolved in acetic acid

Percent acid	Sp. cond.	Minutes	Seconds
11.45	27.9	0	
	27.4	2	0
	27.2	9	0
13.77	56.2	0	
	54.9	2	30
	54.8	7	30
47.38 See Fig. 12, curve 7	37.9	0	
	34.7	4	0
	32.6	8	30
	32.6	12	0
51.96	68.2	0	
	65.8	2	30
	64.9	6	45
	64.9	10	0

to come to 25° was noted, the greater the excess of base, the greater the decrease. The specific conductivity of the pure isobutyl amine was less than 2×10^{-8}; the percents are by weight as in the foregoing tables.

This isobutyl amine acetic acid curve is smooth. It has two crests, similar to those of the amyl amine acetic acid curve.

TABLE XV.

Specific conductivity of dimethyl aniline dissolved in acetic acid

Percent	Sp. cond.	Percent	Sp. cond.
13.4	0.0851	50.7	104.0
14.7	0.115	51.3	110.0
16.0	0.163	51.9	116.0
17.2	0.220	52.5	126.0
19.0	0.259	53.1	128.0
20.9	0.670	53.8	132.0
22.5	1.03	54.2	139.0
24.1	1.67	54.7	146.0
25.7	2.70	55.3	152.0
27.1	3.80	55.9	156.0
28.6	5.15	56.4	161.0
30.0	6.55	57.6	171.0
31.8	8.80	58.3	181.0
32.6	11.0	59.2	188.0
33.5	13.6	60.7	198.0
35.2	16.6	62.5	217.0
36.3	19.8	64.0	232.0
37.4	23.2	66.0	250.0
38.5	27.0	68.6	276.0
39.1	31.6	71.1	295.0
40.2	36.3	73.1	302.0
41.1	43.4	75.2	315.0
42.2	45.7	76.6	321.0
43.1	50.0	77.8	327.0
43.9	58.1	80.1	327.0
44.7	62.6	85.8	311.0
45.5	68.0	88.2	229.0
46.2	73.0	90.5	168.0
47.1	78.0	92.3	138.0
47.9	83.2	93.1	107.0
48.5	89.9	94.0	75.4
49.0	94.1	95.7	41.7
49.8	99.8	97.0	18.2

For several concentrations readings were made to ascertain the rate at which the conductivity varied while the cell was maintained at 25° C. These results are given in Table XIV. below. The percents of acid are calculated on the total weight of solution and the specific conductivities are multiplied by 10^5.

TABLE XVI.

Specific conductivity of quinoline dissolved in acetic acid

Percent acid	Sp. cond.	Percent acid	Sp. cond.	Percent acid	Sp. cond.
0.00	0.512	27.6	13.2	55.2	162.0
0.16	0.512	28.1	14.9	55.9	168.0
0.33	0.522	28.9	16.9	56.3	175.0
0.49	0.531	29.8	18.6	58.2	188.0
0.65	0.538	30.5	20.2	58.7	197.0
0.81	0.541	31.3	21.9	59.8	207.0
1.45	0.552	31.9	24.0	60.8	215.0
2.26	0.630	32.7	26.1	62.0	229.0
3.03	0.675	33.3	28.0	63.7	240.0
3.82	0.740	34.0	30.4	64.3	250.0
4.75	0.815	34.6	32.8	66.2	259.0
5.32	0.910	35.2	34.9	67.3	268.0
6.30	0.991	36.0	37.0	68.2	272.0
6.77	1.13	36.5	39.6	69.2	280.0
7.46	1.23	37.3	42.2	70.4	286.0
8.17	1.32	37.8	45.2	71.2	292.0
8.80	1.44	38.4	48.6	72.0	295.0
9.50	1.56	39.5	53.8	72.8	297.0
10.18	1.73	40.8	60.8	73.8	299.0
10.81	1.83	41.7	67.0	75.0	300.0
12.13	2.16	43.0	73.4	76.1	304.0
13.22	2.47	44.1	80.4	78.0	299.0
14.31	2.88	45.0	87.0	78.7	296.0
15.67	3.25	46.0	93.3	80.5	295.0
16.95	3.76	47.1	101.0	82.5	278.0
18.0	3.85	48.1	106 0	84.7	253.0
19.2	3.92	48.9	113.0	86.2	228.0
20.4	4.41	50.0	116.0	87.4	205.0
21.3	4.95	50.6	123.0	88.7	184.0
22.2	6.91	51.2	128.0	89.5	164.0
23.2	7.76	52.0	132.0	90.1	145.0
24.2	8.60	52.8	139.0	91.1	132.0
24.9	9.60	53.6	145.0	92.1	106.0
25.7	10.8	54.0	153.0	94.3	64.5
26.7	12.5	54.6	157.0	97.4	12.8

Thus it is seen that a measurable speed of reaction on mixing is not peculiar to aniline and acetic acid, but that a similar retardation of reaction occurs in the case of amyl amine and acetic acid, and of isobutyl amine and acetic acid. As these amines are not known to form compounds analogous to the anilides, it seems hardly probable that the formation of acetanilide causes this continued diminution of the speed of reaction. Tables IX. to XIV. show the possibility of finding such breaks as Konowalow indicates in his curves (Fig. 11), but it does not follow that these peaks necessarily lie on the true conductivity curve. As a further test Konowalow's dimethyl aniline acetic acid curve was experimentally reproduced, as given in Table XV. and charted in curve 2, Fig. 9. The conductivities are multiplied by 10^5; the percentage of acid is calculated on the total weight of solution.

The above results as charted in curve 2, Fig. 9, show no such breaks as Konowalow claims. To secure more data, the specific conductivity of quinoline dissolved in acetic acid was determined. These results are given in Table XVI., which follows, and charted in curve 5, Fig. 9. Specific conductivities are multiplied by 10^5; percents, as usual, are calculated on the total weight of solution.

This quinoline acetic acid curve, too, is smooth. The retardation of reaction on mixing the quinoline and acetic acid was less marked than in the other cases mentioned; the values given are for conductivities after they had become constant. Thus it appears that the discontinuity of curve upon which Konowalow bases his theory of chemical combination between solvent and solute according to the law of definite proportions has no foundation in fact — at least as far as indicated by the electrical conductivity. The time required for the completion of the reaction explains his error. The lack of this discontinuity does not, however, shut out the argument for a chemical union of solute with solvent. *In fact, a smooth curve is what we should expect to find in case such union takes place.*

In summing up the results of his work, Konowalow[1] says

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[1] Wied. Ann. 49, 733 (1893).

(1) "The curves which express the electrical conductivity of these solutions (amines in acids) as a function of the percentage composition are not symmetrical. They are displaced toward the side of the liquid which has the less molecular weight and (molecular) volume; and the more (displaced) the greater the difference in the molecular weight and volume is." (2) "The peculiar properties of aqueous solutions appear to be due to the low molecular weight and volume of water."

In Table XVII., given below, I have compared the molecular volumes of the solute (column V_m) with the percent of solute which with acetic acid gives the maximum conductivity (column M_{ax}), for the solutions studied by Konowalow and by myself. Column D contains the difference between the molecular volume of the solute and that of acetic acid. Where the molecular volume of the solute is greater than that of acetic acid a plus sign is prefixed to the difference given in column D; where less, a minus sign. Columns "Fig." and "Curve" will assist the reader in locating the curves of the substances.

TABLE XVII.

	V_m	D	M_{ax}	Fig.	Curve
Pyridine	81.0	+23.6	17.0	9	1
Quinoline	117.7	+60.3	23.9	9	5
Aniline	90.0	+32.6	23.0	9	6
Methyl aniline	109.4	+52.0	25.0	11	1
Dimethyl aniline	126.5	+69.1	20.0	9	2
Amyl amine	116.0	+58.6	18.6	9	4
Isobutyl amine	100.0	+42.6	25.2	9	3
Acetic acid	57.4	—	—	—	—
Water[1]	18.0	−39.4	84 0	—	—

The conclusion of Konowalow[2] that the greater the difference between the molecular volume of the base and that of the acid, the greater the displacement of the crest toward the side

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[1] The percent of water in acetic acid which gives the maximum conductivity was taken from the curve determined by F. Kohlrausch and given in Landolt and Börnstein's tables.

[2] Wied. Ann. 49, 733 (1893).

of the acid, is not borne out by my experiments. For instance, pyridine with a molecular volume of 81 has its maximum at 17 percent; methyl aniline, molecular volume 109.4, has its crest at 25 percent; and quinoline, molecular volume 117, has its maximum at 23.9 percent. It is true that the curve of acetic acid and water is far displaced toward the water, but since Konowalow's rule holds in no case save that of water, it is, to say the least, premature to attribute the singular behavior of aqueous solutions to the low molecular weight and volume of water.

In the paper referred to above Konowalow says, "The conductivity of liquids at ordinary temperature is brought about by the chemical affinity between the dissolved electrolyte (solute) and the excess of the solvent. The peculiar condition of the unstable combinations (in these electrolytes) favors the chemical exchange, without which electrolytic conduction is impossible."

Concerning the curves of heat of neutralization he says, "In no case does the maximum correspond to a relation of one molecule of acid to one molecule of amine and is always displaced toward the side of the solution with the greater acid content."

My experiments show that there is no direct proportionality between the electrical conductivity of solutions and the degree of intensity with which the solute combines with the solvent as measured by the thermal change. For example, the heat of solution of pyridine in acetic acid is much less than the heat of solution of amyl amine,[1] and yet pyridine shows nearly twice the conductivity of amyl amine at its maximum (compare the pyri-

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[1] I determined the heat of neutralization of amyl amine, 19 percent, in acetic acid, 81 percent, the composition corresponding to the crest of the specific conductivity curve. 4.3785 g amyl amine boiling at 96° under a pressure of 738 mm added to 19.127 g acetic acid which boiled at 117° under a pressure of 739.9 mm evolved 713.8 small calories at the mean temperature of 20.6° C. Further, 3.913 g pyridine boiling at 115°-117° under a pressure of 745.3 mm, added to 19.105 g of the same sample of acetic acid — a composition corresponding to the crest of the specific conductivity curve — gave out 244.5 small calories as a mean temperature of 20.5° C. In each case the heat was evolved slowly, indicating that the neutralization is *not* instantaneous.

dine, curve 1, Fig. 9, with that of amyl amine, curve 4, Fig. 9).

I find, as Konowalow did, that the composition of these solutions at the crest of each curve does not follow the law of definite proportions.

That the electrical conductivity comes into existence suddenly, at a point corresponding to molecular proportions of solute to solvent, I do not find to be true, going from base to acid or from acid to base. The electrical conductivity increases with perfect regularity as more and more of the solute is added.

In explanation of the crests observed in Fig. 9, I conceive that as more and more of the base is added to the acetic acid, more and more molecules of a complex body are formed. These molecules will require a definite amount of the acid and base for their formation, and upon them will depend the conductivity of the solution. The excess of acid is not to be thought of as playing no part here, that is, as serving merely as so much space for these molecules to exist in. The intensity of combination between the solvent and solute shades off from (1) the strong union of solvent molecules, in close proximity to the solute molecule, with that molecule; to (2) the weaker union between this same solute molecule and the more remote solvent molecules. After the crest of the conductivity curve is reached, a rapid decrease in the conductivity occurs as more and more base is added. It seems likely that here we have different orders of compounds formed between the acid and the base. The molecules of one compound favor the transfer of electricity through the solution; the molecules of another compound, and of the original solvent (there may be more than two compounds formed) tend to retard the passage of electricity through the solution.

The fact that the crests of the conductivity curves given in Fig. 9 are all in the region of excess of acetic acid raises the question whether the addition of a second base would increase the conductivity by forming more salt molecules. To answer this question a solution of 2.396 g aniline to 8.165 g acetic acid corresponding to 22.7 percent aniline to 77.3 percent acetic acid — the concentration giving the maximum specific conductivity

— was prepared. Its conductivity was determined, and weighed amounts of pyridine added and the conductivity again determined. The results are given below in Table XVIII.; the percents are for total base calculated on the total weight of solution; the specific conductivities are multiplied by 10^5.

TABLE XVIII.

Specific conductivity of aniline and pyridine dissolved in acetic acid.

Base	Percent	Sp. cond.
Aniline	22.7	394.0
Aniline and pyridine	24.7	440.0
	34.1	601.0
	43.2	485.0
	60.4	57.4

Clearly, then, the power of the acetic acid to yield solutions of higher conductivity is not exhausted at the crest of the aniline acetic acid curve (6, Fig. 9). To ascertain whether this is true of the other curves in Fig. 9, the following experiment was performed. 2.102 g quinoline was added to 6.256 g acetic acid, corresponding to 25.2 percent quinoline.[1] The sp. cond. of this solution was 3.05×10^{-3}. Now aniline was run in until it ceased to cause an increase in the conductivity; then amyl amine, and finally pyridine. Each base in turn is seen to unite with the acid and raise the conductivity; and each base, too, ceases after a certain quantity of it is added, to raise the conductivity, although a large excess of acetic acid is present and consequently it must continue to unite chemically with the base as more and more of the latter is added. These results are given in Table XIX. which follows. Percents are for total base calculated on the total weight of resulting solution; specific conductivities are multiplied by 10^5.

In each case tried so far the base added raised the conductivity. When, however, xylidene is added to the pyridine acetic

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[1] The quinoline used distilled at 230° to 233° under a pressure of 745.3 mm. The pyridine came over at 115° to 117° under a pressure of 746.3 mm. The other bases were from the stock supply. All were thoroughly dry.

acid solution at its concentration of maximum conductivity, a sharp diminution in the conductivity is produced, as shown in Table XX. below. The percents are for total base calculated on the total weight of solution; the specific conductivities are multiplied by 10^5.

TABLE XIX.

Base	Percent	Sp. cond.
Quinoline.	25.2	305.0
Quinoline and aniline	27.7	360.0
	30.1	362.0
	32.3	364.0
	36.3	343.0
Quinoline, aniline and amyl amine	37.1	362.0
	38.0	332.0
Quinoline, aniline amyl amine and pyridine	42.1	359.0
	47.5	319.0
	52.9	222.0
	57.5	139.0
	69.3	39.7
	80.1	18.6

TABLE XX.

Base	Percent	Sp. cond.
Pyridine	17.0	873.0
Pyridine and xylidene	20.3	785.0
	40.2	346.0
	53.2	192.0

On standing eleven minutes and thirty seconds the conductivity of the solution containing 53.2 percent total base had diminished to 168×10^{-5}, although no crystals were visible. Finally after an hour and a half a mass of crystals separated from the solution. This change in the conductivity, followed by the separation of crystals, indicates that possibly there is an arrangement of the constituents in solution into crystalline groups before such groups appear as solid crystals.[1] On the

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[1] In this connection see G. Wyrouboff. Bull. Soc. Chim. (Paris), (3) 25-26, 2, 105 (1901). O. Lehmann on liquid crystals. Wied. Ann. 2, 6,6 (1900). Ibid. 5, 236 (1901). G. Tammann. Ibid. 4, 524 (1901). Ibid. 5, 103 (1902).

other hand, the decrease in conductivity observed in the case of amyl amine and isobutyl amine, together with the slow evolution of heat on mixing pyridine, amyl amine or aniline with acetic acid, points strongly to slow neutralization of base by acid as the cause of this measurable change in conductivity in these solutions.

The results in Tables XVIII., XIX., and XX. are plotted in Fig. 13. The ordinates are in specific conductivity multiplied by 10^3; the abscissas in percent of total base in solution in acetic acid.

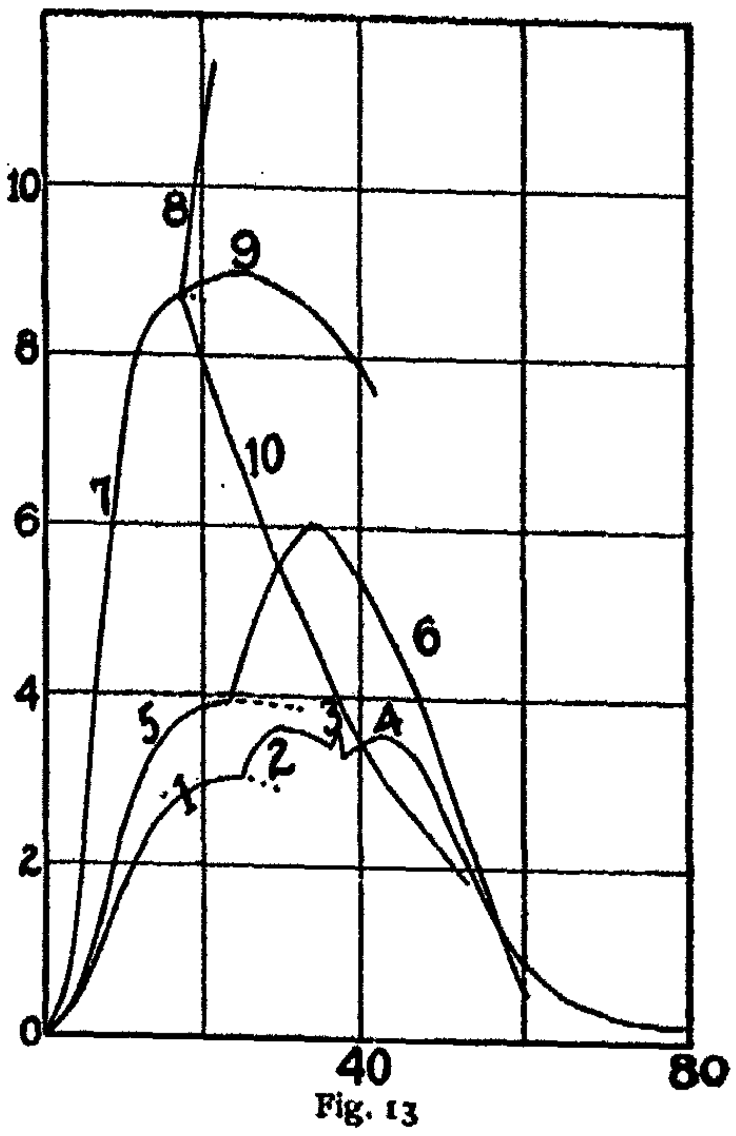

Fig. 13

The curve 1-2-3-4 is produced by successive addition of quinoline, aniline, amyl amine and pyridine to acetic acid. Curve 5-6 is produced by successive addition of aniline and pyridine to acetic acid. Curve 8 is that of water added to the pyridine acetic acid solution at its composition of greatest conductivity, shown by curve 7,—see also Table I., solvent 7; 9 is a similar curve for methyl alcohol; and 10 is a like curve for xylidene.

The results given in Tables XVIII., XIX., and XX. and charted in Fig. 13 show that by adding another base we can form new molecules which aid in electrical conduction sufficiently to materially raise the conductivity curve. On the other hand, the xylidene curve (Fig. 13, curve 10) shows that new molecules formed in precisely the same way may lower the conductivity of the solution. The effect produced depends upon the kind of molecules which the new base added forms; and possibly upon the arrangement of the atoms in these molecules.

Returning to Fig. 9, it appears that as the 60 percent point of base is passed in curves 3 and 4, the electrical conductivity again increases. The fact that the crest of the curve does not correspond to a definite molecular ratio between the acid and base clearly does not preclude the formation of a chemical combination between the substances. The observed conductivity is the resultant of the power of some of the molecules to transfer electricity and of some others to oppose this transfer. The assumption that the excess of the solvent is loosely combined with the salt molecules which are formed by the close combination of acid and base, does not necessitate that the power of these molecules of solvent to oppose the transfer of electricity is completely lacking. The conductivity of a solution also depends upon the *kind* of solvent molecules and upon the *number* of solvent molecules which are in combination with a solute molecule. The crests in Fig. 9 show that a definite excess of solvent united with a salt molecule gives a maximum conductivity. The number of solvent molecules united with a salt molecule will be greater the greater the amount of solvent present, according to the law of mass action. Therefore in solutions containing a great excess of acetic acid, and exhibiting a lower conductivity than that given at the crest of the curve, we have very complex molecules which conduct electricity less well than the simpler molecules which exist at the crest of the conductivity curve.

Further, in the region of excess of acid, in Fig. 9, beyond the crest of any curve and toward the base side of the figure, a smaller excess of solvent with the salt molecule is seen to give a lower conductivity than that at the crest of the curve. This means that there exists a perfectly definite ratio of solvent to salt molecule for which the conductivity is a maximum. Excess of solvent above this ratio or below this ratio gives a lower conduction. The continued change in the conductivity observed and noted in Tables IX., X., XI., XII., and XIV. and charted in Fig. 12 may be simply explained on this basis: When excess of either solvent is added to an acid amine solution, the conductivity may not immediately attain its full value although the liquids be thoroughly mixed mechanically — as happened in certain regions of the aniline acetic acid curve; or a high temporary value may be obtained — as in the case of the isobutyl amine and amyl amine curves (5, 6, and 7, Fig. 12). In the first case the salt molecules have not combined with the full amount of solvent with which they are capable of uniting. As more and more solvent is added to these salt molecules their tendency to transfer the electric current is changed in consequence of their different chemical constitution. Hence the rise in the electrical conductivity with lapse of time. In the second case, where the conductivity decreases, the same chemical action is in progress, i. e., more of the solvent is adding itself to the salt molecule, and the complex molecule of salt and solvent grows until, when equilibrium is reached, the amount of solvent in this complex molecule is greater than the amount required for maximum conductivity. Therefore the conductivity of the solution is less than at first.

The best conception we have of conduction in metallic conductors is that the particles of metal transfer electrical charges from one to the other. The ether hypothesis furnishes us with a picture of the mechanism of this charge transference. This ether hypothesis has not been applied to conduction in electrolytes because of the appearance of products of decomposition on passing a current. But now that electric currents may be induced in electrolytes with no accompanying decomposition of the electrolyte, we are not justified in saying that the current is carried through the electrolyte by convection in the form of "electrical charges on the backs of the ions."

The character of the curves of alteration of specific conductivity, Figs. 1 to 8, is explained by this same assumption, that the observed conduction of electricity is a resultant of the insulating power of one set of molecules and the conducting power of other molecules.

In the case of the water curve in Fig. 13, curve 8, the high insulating power of water itself gets no chance to lower the conductivity. The water combines to form molecules with power of conduction, and the curve of conductivity rises rapidly. Water is known to form a compound with pyridine, $C_5H_5N - 3H_2O$,[1] and the difficulty in keeping acetic acid anhydrous shows how strong is the tendency of water to unite with it; pyridine acetate also dissolves very readily in water.

In the curve for water, Fig. 7, curve 6, in the silver nitrate pyridine solution the conductivity is seen to be very gradually lowered. Here it seems that the power of water to form new conducting molecules is exhausted sooner than in the pyridine acetic acid solution, and little by little the insulating power of the non-conducting molecules of water prevails.

Throughout all the curves of destruction of conductivity the influence of chemical constitution is clear. Each substance has its own individual curve. A dilutant which is known to yield solutions which conduct electricity lowers the conductivity less than a dilutant whose solutions will not conduct.

The principle that the properties of a compound are resultants of the properties of its constituents has been used hitherto with some success. It would seem that we must work along this line if we are to formulate general principles by which to predict whether a given system will conduct electricity, and to what extent.

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[1] Calm-Buchka, "Chemie des Pyridins," p. 50. Also G. M. Wilcox. Jour. Phys. Chem. 5, 8, 593 (1901).

General observations

The results collected in Tables I. to IV. may be expressed in the following law: *For chemically analogous substances the lowering of the specific electrical conductivity in solutions is roughly proportional to the number of gram-molecules of dilutant added.* This law holds in a number of cases even in solutions up to 40 percent of dilutant by weight. A new method of molecular weight determination is thus at hand. Like all other methods extant, it has limitations. The choice of the solution whose conductivity is to be lowered is important: first, the dilutant must mingle with it; second, no sharp chemical reaction should take place between the dilutant and the constituents of the solution. While in the rough this property of altering the conductivity of solutions is colligative for analogous compounds, the influence of constitution is also clearly in evidence.

The curves charted in Fig. 13 are of interest in that they show that the power of solutions to conduct electricity does not depend upon the intensity with which the various constituents unite to form the solution, but rather upon the property of the compound formed.

So many exceptions to the theory of Arrhenius, which need not be detailed here, have appeared in the literature that I have not discussed my results in the light of that theory; especially as the results as charted in Fig. 10 also show a lack of agreement between the cryoscopic and conductivity methods in the determination of the degree of "electrolytic dissociation."

Summary

The results of this investigation may be summed up briefly as follows:

(1) The lowering of the specific electrical conductivity of non-aqueous solutions by addition of a pure solvent has been found to be approximately proportional to the number of gram-molecules of solvent added. Application of this principle offers a new method of molecular weight determination.

(2) The curves of alteration of the specific electrical conductivity are peculiar to each solvent used. The alteration depends upon the chemical character of the solvent employed, all degrees of this chemical influence of solvent on the original solution being observed, from water to benzene.

(3) Four new conductivity curves of bases in acetic acid have been determined.

(4) The idea has been advanced that electrical conductivity is the resultant of (1) the tendency of some molecules to transfer the charge produced by an impressed electromotive force, and (2) the resistance offered to this transfer of charge by other molecules.

(5) Konowalow's conclusion that the small molecular volume of water stands in a definite relation to the power of aqueous solutions to conduct electricity is shown to be unwarranted.

(6) The discontinuity of curve found by Konowalow in acid-base solutions for the electrical conductivity is shown to be due to a measurable speed of reaction overlooked by him.

(7) Konowalow's conclusion that the magnitude of the electrical conductivity of solutions is proportional to the intensity of the chemical combination between solvent and solute as measured by the heat effect, is found to be untenable.

(8) It is shown that the conduction of electricity by solutions depends upon the fact that a compound is formed by the solvent and solute when solution takes place; and that the degree of electrical conductivity depends upon the constituents in this compound, and possibly upon their arrangement.

I wish to take this opportunity of expressing my hearty thanks to Prof. Kahlenberg for the many courtesies he has conferred upon me during this research. The work was undertaken at his suggestion and has been carried out under his direction. Also he has greatly facilitated my work by putting at my disposal the extensive collection of solvents in his laboratory. His presence has been a constant source of inspiration. I further thank Dr. Schlundt for the use of some solutions prepared by him, and for many other kindnesses done me; also Prof. Hillyer and Prof. Kremers for similar favors; and Mr. Walter D. Patton for his careful assistance in making the freezing-point determinations.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
May, 1902.

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.

Crystallography, Capillarity and Viscosity

The surface tension of water above 100°. *C. T. Knipp. Phys. Rev.* 11, *129* (*1900*). — The water was placed inside a platinum-lined steel tube and the principle employed was that of lifting a platinum vane partly submerged in the water. The critical temperature was found to be 359° and the critical pressure 205 atmospheres. There is a gradual decrease in surface tension until near the critical temperature when it drops suddenly to zero. *W. D. B.*

Surface tension at the interface of two liquids determined experimentally by the method of ripple waves. *F. R. Watson. Phys. Rev.* 12, *257* (*1901*). — The author made determinations of the surface tension at the surface between mercury and water, mercury and alcohol, water and petroleum, and water and benzene. It was found impossible to measure mercury and benzene, and mercury and petroleum. *W. D. B.*

The variation with temperature of the surface energies and densities of liquid oxygen, nitrogen, argon, and carbon monoxide. *E. C. C. Baly and F. G. Donnan. Jour. Chem. Soc.* 81, *907* (*1902*). — The authors have determined the change with the temperature of the surface energy of liquefied oxygen, nitrogen, argon and monoxide. The resulting relation is linear, the constants for *k* being 1.917, 2.002, 2.020 and 1.996 respectively. These liquids are therefore practically normal. The lines cut the temperature axis at 153.77°, 124.99°, 145.44°, and 132.47° abs, while the critical temperatures are oxygen 154.2, nitrogen 124°, argon 155.6° and carbon monoxide 137.4°. *W. D. B.*

On the cohesion of liquids. *A Leduc and P. Sacerdote. Comptes rendus*, 134, *589* (*1902*). — From experiments in a capillary tube the authors find the cohesion of water to be greater than 24 cm of water. In a mercury barometer the break took place between the glass and the mercury and the mercury itself was not torn apart. A column of 30 centimeters of mercury was held up as it was and there is reason to suppose that the actual limit is much higher. *W. D. B.*

On the laws of viscosity. *L. Natanson. Phil. Mag.* [6] 2, *342; Zeit. phys. Chem.* 38, *690* (*1901*). — The present mathematical theory of viscosity has as its fundamental concept the ideas of Poisson regarding the nature of the fluid state, and a development of the purely descriptive method of Maxwell. It is shown that the present work leads to a generalized theory of viscosity of which the generally accepted theory is a particular case. The author hopes to give ultimately some applications. *H. T. B.*

Studies on the relation between the viscosity of liquids and the absolute temperature. *A. Batschinski. Reprint, 1901.* — Out of one hundred and forty-four substances, most are found to follow fairly closely the formula $\eta T^3 = constant$. The anhydrides, acids, alcohols, and water are exceptions.

W. D. B.

On the viscosity of helium and the variation with temperature. *H. Schultze. Drude's Ann.* **6**, *302* (*1901*). — Experiments are carried out in a similar way to the author's experiments on the viscosity of argon. The results agree well with those of Lord Rayleigh, and show that Sutherland's formula for the effect of temperature is correct. *H. T. B.*

A determination of the viscosity of water. *E. R. Drew. Phys. Rev.* **12**, *114* (*1901*). — The author rotated co-axial cylinders at a constant rate, the water being placed in the space between the two cylinders. In this way a value of 0.01022 was obtained for the coefficient of viscosity of water at 20°.

W. D. B.

On the influence of pressure on the viscosity of water. *L. Hauser. Drude's Ann.* **5**, *597* (*1901*). — The method of study was that of the discharge from capillary tubes as in the classical experiments of Poiseuille. The pressure was supplied by a Cailletet pump from Ducretet, reading to 1000 atmospheres, and the compression cylinder was enclosed in a constant temperature device. Some interesting points in regard to the effect of pressure on the viscosity of water are brought out, the experiments ranging up to 400 and 500 atmospheres. It appears that the effect of pressure is to increase the viscosity for temperatures above 32° C, becoming more pronounced as the temperature rises. The total amount is 4 percent at 100° C for 400 atmospheres. As has been well known, the effect of pressure is to diminish the viscosity for temperatures below 32° C, but at this point it is shown that pressure has no effect at all. This minimum point, as the author points out, is near the point of minimum specific heat and otherwise indicates a change in the physical state of the water. *H. T. B.*

The elasticity and viscosity of ice. *Hans Hess. Drude's Ann.* **8**, *405* (*1902*). — Small slabs of ice are cut and the bending moment obtained by loading in the middle and observing the deflection produced, the movement being magnified by mirror and telescope. It is found that a permanent bend occurs in addition to the elastic movement. Experiments are also tried on the metal tin with very similar results. Experiments on the rate of flow of ice were tried with interesting results. Under steady pressure the velocity of flow increases with the time, so that after a large initial pressure to start the flow a small pressure suffices to continue it. Various conclusions are drawn with regard to the movement of glacial ice. *H. T. B.*

ON THE PASSAGE OF A DIRECT CURRENT THROUGH AN ELECTROLYTIC CELL

BY S. L. BIGELOW

The occurrences within an electrolytic cell, including as they do all changes in the electrolyte and on the electrode, in other words, the mechanism of current transference, electrolysis, and polarization have been the subject of many investigations. We have most plausible and useful theories bearing upon these subjects, the fundamental idea concisely stated being that when a current passes it is carried by the ions, which, in the neighborhood of the electrodes, unite to form neutral molecules giving up their charges. Certain facts to be described below do not appear to be readily explainable on this simple hypothesis, but require some modification or extension of it. The present condition of our knowledge is admirably summed up by Nernst,[1] who also points out wherein our hypotheses are lacking. For instance he says:[2] "We state that the ions separate at the electrodes, but how do they give up their charges?" * * * "are we not forced to the conclusion that the electric charges are capable of independent existence for an instant at least, or cannot the electrical elementary atoms exist by themselves without being attached to matter?" In the third edition of his text-book[3] he offers an hypothesis, which gives greater definiteness to the dissociation theory, ascribing an atomistic structure to electricity, and assuming the existence of two new univalent elements without weight conveniently called positive and negative electrons. According to this theory the free ions in a solution are to be considered as chemical compounds of these elements with the dissociated parts of the electrolyte and electrolysis becomes a breaking up of these compounds at the electrodes, the

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[1] Ber. chem. Ges. Berlin, 30, 2, 1547 (1897).

[2] loc. cit. 1562.

[3] Nernst. Theoretische chemie, Dritte Auflage, 1900, p. 346.

massless electrons passing through the metallic conductor and giving rise to the usual phenomena of electrical currents.

Thomson's corpuscular theory[1] is another plausible hypothesis which may lead to a more complete understanding of occurrences within an electrolyte. Certain attempts have been made to apply it to solutions and Thomson[2] concluded that the charge on the gaseous hydrogen ion was the same, "or at any rate of the same order as the charge carried by the hydrogen ion in electrolysis." Lengfeld[3] has offered suggestions as to how the corpuscular theory might be applied to "the ionic theory, the solution tension theory, and the periodic law," but his article is speculative and no experiments are made nor cited. A number of experimental facts are known however pointing to the advantage, if not the necessity, of applying this theory to solutions, and it is hoped that this article, with another to succeed it shortly, may make this clear as well as contribute some new experimental evidence.

It was thought that it might lead toward the end in view to study particularly the current which passed through an electrolyte when the electromotive force at the electrodes was relatively small, say one volt. Le Blanc[4] made it appear probable that there was a fixed and definite minimum electromotive force required for the electrolytic decomposition of each electrolyte and the determination of these decomposition points or intensities of fixation was continued notably by Glaser[5] and Bose[6] under Nernst's direction. On the other hand Wiedeburg[7] and others deny the existence of such a point on theoretical grounds. In any solution there is a variety of ions and the theory demands that when a gradually ascending electromotive force is applied

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[1] For an excellent summary of Thomson's work see Crew, Astrophysical Journal, 11, 170 (1900).

[2] Phil. Mag. 46, 544 (1898).

[3] Jour. Phys. Chem. 5, 639 (1901).

[4] Zeit. phys. Chem. 8, 299 (1891); 12, 333 (1893).

[5] Zeit. Elektrochemie, 4, 355, 373, 397, 424 (1898).

[6] Ibid. 5, 153 (1898).

[7] Wied. Ann. 51, 302 (1894); Zeit. phys. Chem. 14, 174 (1894).

to electrodes immersed in the solution, that anion and that cation the sum of whose intensities of fixation is the least must separate out first, and until this minimum electromotive force is reached that nothing can separate out, i. e., no current can pass, assuming Faraday's law to hold. This is contrary to universal experience, for it is found that with no matter what electrolyte and no matter how low an applied electromotive force a current does pass; it may be small, but is measurable.[1] Any of the published data plotted on a coordinate system with volts on one axis and current quantity on the other show this, but also show a more or less rapid increase in current quantity at or about the decomposition point noted by Le Blanc. That this rapid increase in current occurs in every instance at the same electromotive force which the electrodes and the electrolytes will give as a source of electrical energy is strong evidence that the point is characteristic and that some new process begins there.

This objection, that small currents do pass below the decomposition point, has been met in several ways. It has been suggested by a number of investigators, for example Salomon[2] that solutions act to a slight extent as conductors of the first class, i. e., as metals, and Faraday himself was of this opinion, but the best authorities are opposed to this view and Ostwald[3] says: "Insbesondere ist für die von verschiedenen Forschern als möglich angesehene 'metallische,' d. h. von der Ionenbewegung unabhängige Elektrizitätsleitung nicht das kleinste Anzeichen gefunden worden." This hypothesis may be rejected as highly improbable and there remain two alternatives, either electrolysis does occur at voltages below the decomposition point or the currents in question are merely piling up ions in the immediate neighborhood of the electrode, forming a sort of a condenser or "electrical double layer" while no ions actually discharge. The formation of these double layers must be accompanied by a detectable transference of elec-

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[1] See for instance Sokolow. Wied. Ann. 58, 209 (1896).

[2] Zeit. phys. Chem. 24, 55 (1897).

[3] Grundriss, Dritte Auflage, 1899, p. 380.

trical energy and such transference is indubitably an exception to Faraday's law as stated by Wiedeburg, who says:[1] "Es müsste ja zu dem eben ausgesprochenen Satz noch der fernere, dass stets die gesamte herangeführte Ionenmenge an den elektroden zersetzt werde, hinzutreten, um das Faraday'sche Gesetz in seiner gewöhnlich angeführten, für die Praxis berechneten Form zu Stande zu bringen, und dem wiederspricht im Grunde schon die Annahme, dass sich an den Elektroden elektrische Doppelschichten bilden." But such double layers cannot account for all the current observed below the decomposition point of water because, no matter how large the capacity of such a condenser may be assumed to be owing to the closeness of the layers, it must be finite and so the current would have to cease eventually. This however does not happen and no matter how long the circuit is left closed a residual current, or 'Reststrom' still passes. The conclusion appears inevitable that electrolysis of some sort occurs even with the smallest electromotive forces.

The other alternative, that electrolysis occurs at any electromotive force, is in accord with our osmotic theory of galvanic cells for we have only to assume the solution pressure from electrode into the solution sufficiently small to be exceeded by the reverse pressure from within the solution outward. When the products of electrolysis are gases such a current must continually increase the concentration within the electrode until an equilibrium is reached and then it should cease. This condition of equilibrium would correspond to a maximum of polarization, a thing often sought for but never yet found. Since a residual current passes for an indefinite time, we must assume that the electrolysis which occurs is of a nature not taken into account by our present osmotic theory. Again, this theory does not satisfactorily account for the suddenness with which the current increases at the decomposition point.

The argument has been advanced that as much energy must be required to decompose water as is evolved upon the formation of water, and the quantity of electrical energy being

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[1] Zeit. phys. Chem. 14, 179 (1894).

determined by Faraday's law the intensity factor or electromotive force must be determined also; otherwise we could electrolyze with a low voltage and then, allowing the cell to deliver a current while water was formed, regain the same quantity at a higher voltage, thus gaining energy, an obvious impossibility. These considerations led Tommasi[1] to express the opinion that water is in some measure dissociated into hydrogen atoms and oxygen atoms, in a manner resembling that in which gases dissociate, and that it is the separation of these atoms at the electrode which supports the current below the point calculated from the heat of formation of water. He considers electrolysis occurring below this point in a sense parallel with the evaporation of a liquid below its boiling-point. It is generally conceded that the fallacy in the above reasoning lies in its application to a reaction which is not reversible, while it would hold only for a reversible reaction. But the statement that it is not reversible leaves open the question as to what the exact nature of the reaction is, and it would be a more definite and satisfactory explanation of many rather troublesome points if it could be proven that electrolysis below the decomposition point of water differed in kind from that above it.

The residual current.

The residual current has received by no means the attention it deserves and but few investigations have been reported. The most important is that of Helmholtz[2] who found that one Daniell cell (electromotive force about 1.1 volts) could send a measurable current through an electrolytic cell with platinum electrodes in distilled water or in dilute sulphuric acid for weeks at a time. He furthermore found that sealing up the cell completely made little difference, but that when he removed practically all the dissolved gases from the electrolyte with a mercury pump the current was much smaller. He fails to give the details as to the strength of the current after definite

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[1] Electrical Review, 44, 293 (1899).

[2] Pogg. Ann. 150, 483 (1873); Wiss. Abhandl. 1, 823.

times. Danneel[1] worked on the same problem and gives the current he observes and the corresponding volts but does not state the time elapsed between the closing of the circuit and the observation, though it is to be assumed from the context that he waited until the current became practically constant. Salomon[2] worked with silver electrodes in silver nitrate solution and his results bearing upon the movement of a metal ion between electrodes of the same metal cannot be of much assistance in discussing the problem of the residual current in solutions between electrodes such as platinum which are not supposed to go into solution.

Helmholtz's explanation of the residual current is as follows. Assume that the solution contains dissolved hydrogen, or that the electrodes contain occluded hydrogen, then at the electrode to which oxygen is driven by the current it combines with the hydrogen present to form water. At the same time an equivalent amount of hydrogen is liberated at the other electrode and will either dissolve in the electrolyte or be occluded. Although electrolysis thus takes place neither of its products appear and the electromotive force does not have to do the work implied by the decomposition of water into its components, in other words, a current may pass although the electromotive force is less than that required for the latter purpose. The hydrogen freed may diffuse through the liquid until it reaches the other electrode and so by a constant circulation support the current. If, at the start, the solution or electrodes contain oxygen instead of hydrogen, the reasoning will be the same. To this process he gives the name of electrolytic convection. This explanation has been accepted as fundamentally correct by both Salomon and Danneel who made it the basis of calculations as to what the strength of the residual current should be. But neither one found any satisfactory agreement between calculated and observed values, and Danneel working with dissolved gases found currents uniformly two to three times as large as those calculated.

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[1] Zeit. Elektrochemie, 4, 211, 227 (1897).

[2] loc. cit. and Zeit. Elektrochemie, 3, 264 (1896).

Assuming some oxygen present at the outset, either occluded in the electrode or dissolved in the electrolyte, or both, we may readily see how it could facilitate the discharge of hydrogen ions and the formation of water at the cathode, but the law of mass action would lead us to expect that it would hinder the formation of more oxygen at the anode. According to our present theories the discharge of each cation must be accompanied by the simultaneous discharge of an equivalent anion, so it would seem that the passage of the current should be determined largely by the concentration of the ion present in least amount. Therefore dissolved oxygen, or dissolved hydrogen, might be expected to diminish rather than increase quantity of current transmitted. But this is contrary to the actual facts. Again, assuming oxygen present and that it assists in the transference of the current by facilitating the discharge of hydrogen ions, it is obvious that a great increase in the concentration of these ions should be accompanied by a corresponding increase in the current quantity. Experiments to be described below demonstrate that increasing the concentration of the sulphuric acid used as electrolyte a hundredfold makes practically no difference in the residual current. The conclusion appears to be justified that the convection current theory is not a fully satisfactory explanation of the phenomena. In the opinion of the writer it is at least probable that either dissolved oxygen or dissolved hydrogen as such is able to transfer electrical energy, and further, that either one in solution furnishes *both anions and cations*, or charged particles analogous to these.

It seemed desirable to increase the amount of experimental data in the hope of nearing an answer to the questions, is there or is there not a true decomposition point, and if there is, what supports the current at lower voltages?

Apparatus.

Two storage cells of eighty ampere hours capacity each were connected in parallel and the circuit was closed through a nickelin wire wound on a drum as in the Kohlrausch bridge. The resistance of this wire was about 30 ohms and consequently the current taken from the cells was small (1/15 ampere) and their electromotive force proved to be practically constant for three months and more. By means of a wheel contact any electromotive force less than two volts could be taken off for the experiments.[1]

In order to be sure that the electromotive force was constant, a Weston standard laboratory voltmeter was kept connected at the electrodes of the experimental cell all the time. This voltmeter, having a large scale and a total range of three volts, was easily readable to within two millivolts. It was calibrated several times against a Clark and against a Weston cell with certificates from the Reichsanstalt and finally, when the work was broken off, it was compared with a new Weston voltmeter. During the work it did not vary more than two millivolts. A key, such as is commonly used with the capillary electrometer, threw a galvanometer into the circuit with the experimental cell whenever an observation was to be taken. The mirror galvanometer, read with a telescope, was of the d'Arsonval type made by R. W. Paul, and an exceptionally dead beat and serviceable instrument. Its internal resistance was 500 ohms and, as set up, it showed a deflection of one scale division for 0.022 micro ampere. As current strengths extending over a wide range had to be measured, a resistance box was inserted as a shunt with the galvanometer and different resistances were taken out such that at no time did the galvanometer deflections much exceed 100 scale divisions, within which range experiment showed the deflections to be directly proportional to the currents. For the sake of clearness and ready comparison the shunts used and the actual galvanometer deflections will be omitted, and the results will be given in micro am-

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[1] The more common form of a wire stretched on a meter stick with a sliding knife contact was used at first, but with nickelin wire the contact proved to be unreliable, and platinum wire had to be so fine as to be inconveniently breakable in order to give a moderately high resistance. In the final arrangement both the nickelin wire and the wheel were gold-plated and the contact left little to be desired. The plating reduced the resistance of the wire from about 36 to about 30 ohms.

peres as calculated from the galvanometer calibrations. The probable error in the galvanometer readings may be taken as amounting to two to five units in the last significant figure. Cells of different forms were used and they will be described with the individual experiments. Figure 1 is a diagram of the connections and shows how several experiments were controlled and read with the one galvanometer and voltmeter. One volt was used in each experiment unless otherwise mentioned, this value being chosen for two reasons, first, because it is below the electromotive force of the hydrogen oxy-

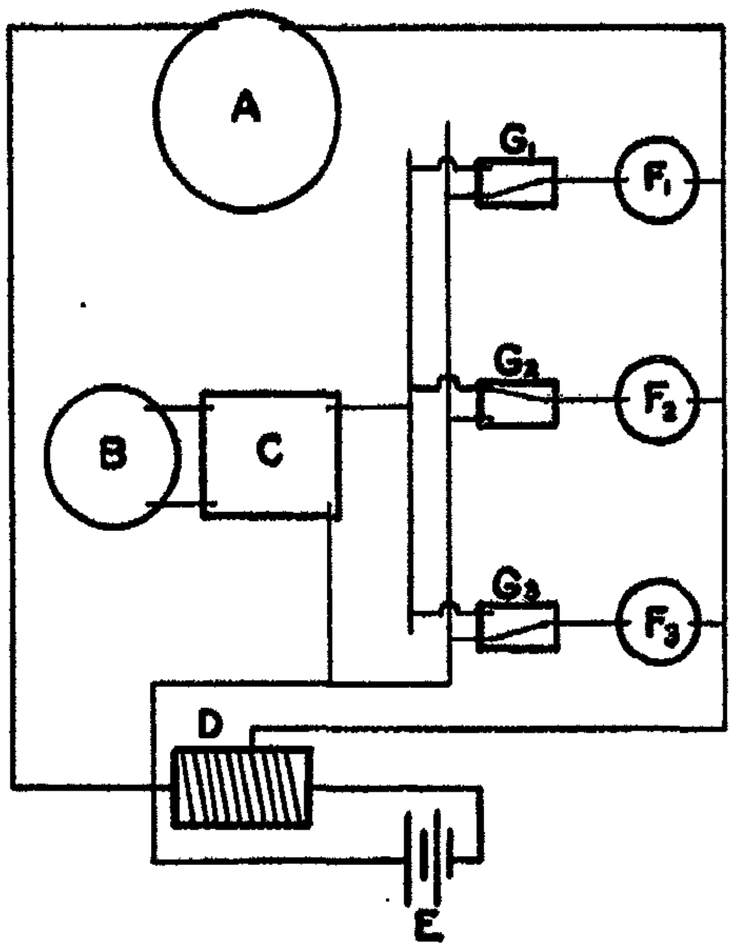

Fig. 1

A, voltmeter.
B, galvanometer.
C, resistance box as shunt.
D, drum wound with nickelin wire.
E, storage battery.
F_1, F_2, F_3, experimental cells.
G_1, G_2, G_3, switches or keys to throw galvanometer into circuit with cells (G_2 in position to determine circuit passing through F_2).

gen cell (1.08 volts),[1] and second because a fairly high voltage was desired in order that the currents should be as large as compatible with the other conditions and so more readily and more accurately measurable.

Experiment No. 1

Electrodes of platinum, each 17 mm square, 11 mm apart. Platinum wires welded on them were fastened with sealing wax through a hard rubber cover, copper wires were soldered on outside the cover. The electrodes were heated to redness just before immersing in the electrolyte, which was *n*/200 (molecular) H_2SO_4 contained in a small jar, the diameter of which was just large enough to admit them. Both voltmeter readings and temperature are given, as the former varied somewhat and the latter has a marked effect on the residual current, as will be shown later.

Time	Temp.	Volts	Micro amperes	Expt. No. 5	
				Micro'p'rs.	Time
24 min	17.5	0.980	64.5	56.4	10 min
17 hours	16.0	1.000	20.3	6.69	19 hours
43 "	14.5	0.998	14.3	4.01	66 "
91 "	13.5	1.010	7.39	4.08	90 "
95 "	15.0	1.000	6.96	4.34	
114 "	16.0	1.006	6.62	3.42	
119 "	17.0	1.008	7.08	—	
6 days	16.0	1.004	4.72	2.75	
7 "	15.0	1.000	3.67	2.63	
8 "	17.0	1.002	3.41	2.06	
9 "	14.0	1.000	2.63	1.77	10 days
11 "	14.0	1.000	1.85	1.72	
12 "	16.0	1.000	1.53	(4.23)	
15 "	17.0	1.000	1.33	1.91	
16 "	20.5	1.000	1.24	1.56	17 days
18 "	20.5	1.000	1.64	1.00	19 "
20 "	18.0	1.000	0.77	1.02	
21 "	17.0	1.000	1.28	0.84	
22 "	17.0	1.000	0.79	—	
25 "	15.0	1.000	0.45	0.66	24 days
27 "	17.5	1.000	0.418	0.66	26 "
29 "	17.0	1.000	0.242	0.550	28 "
32 "	16.0	1.000	0.218	0.453	31 "

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[1] Smale. Zeit. phys. Chem. 14, 577 (1894).

At this point unfortunately an imperfection developed in the contacts which must have allowed the cell to become partly depolarized as the current ran up to 7.18 micro amperes. The trouble was quickly remedied and the experiment was continued, but the times are now from the date of this interruption.

Time	Temp.	Volts	Micro amperes	
				Expt. No. 5
5 days	19.0	1.004	2.27	0.427
12 "	18.5	1.000	0.968	0.297
19 "	19.0	1.002	0.414	0.238
20 "	19.0	1.002	0.403	0.255
21 "	20.0	1.000	0.277	0.229
22 "	20.0	1.000	0.253	0.293
23 "	19.0	1.000	0.249	0.275
59 "	21.0	1.000	0.196	0.178
63 "	23.0	0.998	0.242	0.264
68 "	21.6	0.998	0.185	0.163
70 "	22.5	0.998	0.185	0.180
71 "	23.0	0.998	0.189	0.136
72 "	22.5	1.000	0.169	0.088
76 "	23.0	1.000	0.262	0.257
82 "	19.0	1.000	0.218	0.134

This experiment shows that there is a residual current, small but measurable, and that this current does not grow indefinitely smaller. Rather, it tends to a minimum which here appears to have been reached in the second part of the experiment after 72 days and amounts to 0.169 micro ampere.

The difficulty of holding all conditions so constant as not to affect the residual current is apparent from the fact that there is not a regular falling off to a constant minimum value, but a fluctuation hard to control though not hard to account for. The most evident source of variations is from mechanical disturbance. It has been observed repeatedly that shaking the electrodes causes an increase in the residual current. The following experiment is a further demonstration of this and shows also what the amount of the effect may be.

Experiment No. 2

Electrodes, platinum wire 1 mm in diameter immersed in *n*/200 (molecular) H_2SO_4, a length of about 4 cm. Cell, a U-tube of inner diameter 1 cm.

Time	Temp.	Volts	Micro ampere
18 hours	15.5	1.008	0.794

The cathode was shaken vigorously, at the same time the greatest deflection of the galvanometer was observed. This corresponded to a current of 1.252 micro amperes. The anode was shaken just as vigorously and the greatest deflection obtained corresponded to a current of 1.054 micro amperes. In 20 minutes the current had fallen practically to what it was before shaking and measured 0.856 micro ampere. The cell was then left for three days with the circuit closed, after which the following measurements were made, showing the limits within which the cell was constant when left alone.

Time	Temp.	Volts	Micro ampere
91 hours	15.0	0.998	0.238
95 "	16.5	1.004	0.242
96 "	16.0	1.000	0.220

The cathode was shaken as before and the maximum current was 0.704 micro ampere and fell to 0.231 micro ampere in two minutes after the shaking was stopped. The anode was then shaken and the maximum current obtained was 0.594 micro ampere. In the attempt to increase this current the anode was shaken more violently than the cathode and the failure of the attempt indicates that it is harder to increase the current by shaking the anode than by shaking the cathode. In two minutes the current had fallen again to 0.286 micro ampere, showing further that the recovery of polarization is somewhat slower on the anode than on the cathode. This shaking must owe its effect to a partial destruction of the layer of ions held near the electrode by the condenser action and could hardly have any effect on the alteration which had occurred in the electrode.

The anode was lifted out until only about 0.4 cm remained in the electrolyte and the current fell from 0.242 to 0.088 micro ampere, or a reduction of the electrode surface to one-tenth the original was accompanied by a reduction of the current to one-third. Probably if more time had been given for the current to reach a constant value it would have fallen in direct proportion, agreeing with Danneel's[1] observation that the residual current is proportional to the electrode surface. Lifting out the cathode in the same manner gave similar results.

When the current measured 0.242 micro ampere again the cathode was entirely removed from the solution, wiped off with filter paper, and then replaced. The maximum current observed while the cathode was being immersed was 1.365 micro amperes and the recovery was much more rapid than had been anticipated, the current falling to 0.290 micro ampere in three minutes. Removal of the anode and wiping it off with filter paper was more effective, as a maximum current of 3.566 micro amperes was observed while the anode was being immersed and a yet greater current might have obtained, but it was replaced more gradually than the cathode for fear of damaging the galvanometer. Recovery in this case was less rapid than in the former.

These observations are in accord with the well known fact that the polarization of platinum electrodes under such circumstances is largely a matter of occlusion of hydrogen by the cathode and of oxygen by the anode. The occluded gases of course could not be wiped off, and as much of the polarization as was due to them remained, while all of that due to banking up of ions opposite the electrodes as a "double layer" must have been removed. It is evident that the formation of a condenser by the accumulation of ions near the surface of the electrodes is capable of supporting but a small residual current and for but a short time. It appears to be in fact negligible as compared to the long-continued residual currents observed.

The cell was then left with the circuit closed for 78 days

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[1] loc. cit.

more. It would be tedious to give the almost daily measurements and it will be sufficient to state that the results were perfectly analogous to those given in full under Experiment 1, and that the smallest current was 0.066 micro ampere observed at the end of the 26th, 60th, and 78th days.

Other experiments were tried, shaking the electrodes of cells of different forms, but as the results merely confirm those just stated the details may be omitted.

Helmholtz[1] showed that upon completely exhausting the air from the electrolyte the residual current was greatly diminished; in fact he says that it practically vanished after a time. But his galvanometer was by no means sensitive; that used in these experiments had at least 100 times the sensibility of his and he did not give the dimensions of his cell. The following experiment was performed to verify his results and obtain some numerical data.

Experiment No. 3

The cell consisted of wide bore combustion tubing rather more than 30 cm long and drawn out at both ends. A capillary stopcock with mercury seal was sealed on to the top and a small bore tube sealed to the bottom connected with a rubber tube and leveling bulb filled with mercury. The platinum wires leading to and welded on the electrodes were sealed through the sides of the combustion tubing. The electrodes, of platinum, were 101 mm long and 15.5 mm wide. Owing to their length and the difficulties of sealing them in, they were not parallel but bulged toward each other near the middle. The shortest distance between them was about 2 mm and the longest about 8 mm. By raising and sinking the leveling bulb the electrolyte (*n*/200 H_2SO_4) was introduced from the top. When enough had been drawn in to completely submerge the electrodes to above the point where the platinum wires were sealed through the glass, the stopcock was closed, the leveling bulb was lowered and the dissolved gases came off copiously under the diminished pressure. The bulb was then raised, the stopcock opened, and

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[1] loc. cit.

the gases driven out by the rising liquid. This process was repeated a number of times for two days, the cell being left under diminished pressure over two nights. Upon raising the leveling bulb the last time no trace of a bubble of gas appeared in the capillary beneath the stopcock and though the exhaustion probably was not so complete as that obtained by Helmholtz the amount of gas left was small. An electromotive force of 1 volt (± 0.004) was applied as in the other experiments, and observations were made for 97 days. The current fell off rapidly, amounting to but 6.471 micro amperes after 6 hours, a value not far removed from the smallest, which was 3.235 micro amperes noted at the end of the 29th day. The current varied between these limits, several times rising to the larger value but not again falling quite to the minimum, thus failing to show any indication of vanishing in any finite time.

To compare the results of this experiment with those of Experiment No. 1 in spite of the marked difference in the size of the electrodes in the two cells the expedient was adopted of determining the conductivity of samples of the same electrolyte, *n*/200 H_2SO_4, in each by the usual Kohlrausch conductivity method. The cell of Experiment No. 1 showed a resistance of 54.5 ohms and the cell of this experiment 10.4 ohms. Thus the latter cell has a conductivity about five times that of the former and for comparison the results with cell of No. 1 must be multiplied by five or the results with cell of No. 3 must be divided by five. In this manner it is seen that a fall in current strength occurred in No. 3 in six hours which required 15 to 16 days in No. 1. But another fact appears, namely, that the minimum of No. 3 equaling 3.245 micro amperes even when divided by five is nearly four times the minimum of 0.169 obtained in No. 1.[1]

Experiment No. 4

Two platinum electrodes not carefully measured but of

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[1] No particular stress can be laid upon this observation, for raising the bulb at the end of the experiment, it was found that some air had leaked in through the stopcock, rather invalidating the results and making a repetition desirable. The next experiment, however, bears out the main conclusions.

somewhat smaller surface area than those used in No. 1 were sealed through the sides of a large test-tube so as to be approximately 1 cm apart. The tube was nearly filled with *n*/200 molecular H_2SO_4, drawn out at the upper end, connected with the water pump and gently warmed. When about one-half of the electrolyte had boiled away and it was thought that almost all the dissolved gases had been removed the tube was sealed off, and after it had cooled to the temperature of the room the experiment was begun as usual. The following figures again show how much the initial current is diminished by the removal of dissolved gases and how much more rapidly the current falls off in their absence.

Time	Temp.	Volts	Micro amperes
1½ min	19.0	1.004	3.57
2 "	—	1.002	2.762
3 "	—	—	2.256
4 "	—	—	1.992
5 "	—	—	1.782
6 "	—	—	1.648
7 "	—	—	1.545
8 "	—	—	1.463
9 "	—	—	1.397
11 "	—	—	1.309
41 "	—	—	0.942
1 day	—	—	0.231
5 "	—	—	0.143

The experiment was run for 81 days with almost daily measurements, showing after the fifth day sometimes larger, sometimes smaller currents without any discoverable regularity, but of the later values none exceeded 0.143 micro ampere, though this value was reached twice again. The minimum value was 0.075 micro ampere observed on the 56th day.

A measurement of the conductivity with *n*/200 H_2SO_4 showed the cell to have a resistance of 72.4 ohms, therefore the factor by which the readings should be multiplied to make them comparable with those of Experiment No. 1 is 724/545 or roughly 4/3. After 41 minutes we find here 0.942 micro ampere, which multiplied by 4/3 gives 1.256 micro amperes, reached in Experiment No. 1 only after 15 to 16 days. The minimum of 0.075 multiplied by the same factor gives 0.100, a value less than the minimum of 0.169 obtained in No. 1.

The experiments so far described suffice to prove the overwhelming importance of the dissolved gases in supporting a current below the usually accepted decomposition point of water, a fact recognized by Helmholtz.[1] Kohlrausch and Heydweiller,[2] working of course with electromotive forces much above one volt, noted the marked increase in the specific conductivity of their best waters when in contact with air and measured the difference due to the air as about 0.5 to 0.6 × 10^{-6}. They say (p. 215) "Nach * * * würde man nicht für unmöglich halten, dass schon die Sauerstoffabsorption das Leitvermögen beeinflusst." But it does not seem to have been realized that this necessitates a modification or expansion of our dissociation theory which states that the current is transported through an electrolyte solely by the ions due to dissociation. Before entering further into this discussion an experiment will be described intended to determine the influence on the residual current of greatly increasing the concentration of the ions present in the electrolyte.

Experiment No. 5

A cell was constructed as nearly identical with that used in Experiment No. 1 as possible; all four electrodes were cut out at the same time and were necessarily of the same size and the difference in distance apart was less than half a millimeter. Care was taken to have all the conditions the same except that the electrolyte in this new cell was *n*/2 molecular H_2SO_4. The results are given by the side of those of No. 1, but the experiment was started one day later and, as the times were not always the same, they also are given when they differed.

The current is distinctly less with the stronger electrolyte in the earlier stages, but becomes about the same after 11 days. The rise and fall in current from day to day without apparent

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[1] loc. cit.

[2] Wied. Ann. 53, 209 (1894).

cause is more marked in No. 5 than in No. 1 and makes it hard to decide whether or not, if all conditions could be held constant, the current would become the same. It appears probable from the figures that they would, and this idea is further supported by the fact that after the 59th day the rise and fall is practically parallel in the two cells.[1]

The results of Experiment No. 5 appear to show that the current which passes through an electrolyte below the decomposition point of water is not carried by the ions resulting from the dissociation of the electrolyte, but *by a form of ions due to the dissolved gases hitherto unrecognized.*

Some experiments were made in connection with the troublesome irregularities in the currents to determine the effect of temperature on the residual current.

Experiment No. 6

The cell was a small wide-mouth Jena flask almost globular in form but with a flat bottom and containing 125 cc when filled to the neck as it was in all experiments. The electrodes were of platinum, 20 × 25 mm, 15 mm apart at the top and varying between 17 and 19 mm apart at the bottom. Stout platinum wires led from the electrodes to heavy copper rods which passed through a cork holding them rigidly in place. The electrolyte was *n*/200 H_2SO_4. A short thermometer graduated in fifths of a degree was inserted through the cork so that its bulb was in the electrolyte between the electrodes. The whole cell was supported by a clamp in the center of a battery jar which served as a bath. An electromotive force of one volt was applied and at the end of eight days, the change in quantity of the residual current during three or four hours was but slight. The bath was stirred with a feather and care was taken not to shake the cell. The measurements were not made until the thermometer in the

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[1] These irregularities caused much annoyance throughout the work and many unavailing attempts were made to eliminate them. Whenever possible connections were made by soldering or by mercury cups and all other contacts were repeatedly cleaned with emery paper and chamois, but even with these precautions it cannot be stated with certainty that some of the variations did not arise from faulty contacts.

cell had remained constant to within two-tenths of one degree for 10 minutes and then successive readings were taken sometimes extending over an hour. These readings agreed with each other in all instances to within five units of the last significant figure given and the average for each temperature is given below.

Temperature	0.0°	4.6°	8.0°	10.4°	16.4°	17.4°
Micro amperes	1.08	1.31	1.70	2.08	3.59	4.08

The cell was then allowed to polarize for 35 days more when a residual current of 2.77 micro amperes was found to be passing through it at a temperature of 20.2°. It was immersed in a freezing mixture of salt and ice and five measurements were made between – 4.2° and – 4.4° extending over 45 minutes, the largest current observed was 0.78, the smallest 0.76, or say 0.77 micro ampere for – 4.3°. The ice was then taken out and the temperature allowed to rise slowly while the galvanometer and the thermometer were read as nearly simultaneously as possible. A few of the results are tabulated below:

Temperature	–4.3°	0.4°	2.4°	3.0°	5.5°	7.0°	8.0°	9.0°	10.4°	12.0°	14.5°	16.0°	18.2°	—
Micro amperes	0.77	0.88	0.95	1.02	1.13	1.26	1.32	1.46	1.58	1.77	2.08	2.16	2.59	—

The cell was left for a day with one volt as usual, and at the end of this time the current passing was 2.42 micro amperes, while the temperature was 20.4°. It was then immersed in ice water and a number of measurements were made to determine the current near 0°, after which the ice was removed and observations were made as before at different temperatures.

Temperature	0.2°	8.0°	12.2°	16.4°	25.5°
Micro amperes	0.85	1.03	1.44	1.93	3.80

The original object of these experiments was to find a mathematical expression for the connection between current strength and temperature, and while any one of the above series plotted on a coordinate system gives a fairly regular curve, it was not considered that they checked well enough together to make the attempt at a formulation promising. Furthermore, the current quantity being so dependent upon the amount of dissolved air two sets of values could be obtained, one with a solution saturated with air at a definite temperature, and another with a solution saturated at each temperature. The results given approximate to the first case because much air could neither have been dissolved nor given off during the observations. Some estimate may be formed as to the rate at which the conductivity increases with the temperature. It about doubles for an increase of ten to fifteen degrees. This is greatly in excess of the average rate of increase in conductivity for acids which has been determined as between 0.9 and 1.6 pct per degree by Kohlrausch's method,[1] they presumably owing their increased conductivity to an increased dissociation and increased velocity of the ions. A much higher temperature coefficient for purest water, distilled in vacuo, was found by Kohlrausch and Heydweiller[2] amounting at 18° to 5.8 pct. The above figures show a temperature coefficient between 7 and 10 pct, that is, much larger than either, and this again indicates that the ions due to ordinary dissociation are not what supports the residual current. This temperature coefficient is more comparable with that of the velocity of many chemical reactions which is known to double and treble for an increase of about ten degrees.[3]

The following experiments were carried out to determine the effect upon the residual current at one volt of temporarily altering the electromotive force.

Experiments No. 7, *a*, *b*, *c*, *d*.

The cell was the same one used in Experiment No. 6 and the temperature was held constant within 2/10 of a degree during each experiment. The method of procedure when not otherwise stated was to alter the voltage by means of the rolling contact, make a reading after five minutes, then immediately return to one volt, wait five minutes, read, then apply a new voltage, read, and so on. A stop watch was used to measure the

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[1] Kohlrausch und Holborn. Leitvermögen der Elektrolyte, p. 118.

[2] loc. cit.

[3] van 't Hoff. Vorlesungen, Erstes Heft, p. 223.

time. The cell was sufficiently polarized at the beginning to allow of the assumption that if left to itself the residual current would not alter perceptibly in the time required for the experiment. The observations are given in the order in which they were made.

Experiment No. 7, *a* (Temp. 21.3°)

Volts	1.000	1.020	1.000	1.040	1.000
Micro amperes	4.520	5.690	4.620	7.076	4.512
Volts	1.060	1.000	1.080	1.000	1.100
Micro amperes	8.884	4.435	11.114	4.458	13.91
Volts	1.000	1.120	1.000	1.140	1.000
Micro amperes	4.474	17.08	4.489	22.55	4.428

Experiment No. 7, *b* (Temp. 19.8°)

Volts	1.000	0.980	1.000	0.960	1.000
Micro amperes	4.358	3.681	4.451	3.142	4.335
Volts	0.940	1.000	0.920	1.000	0.900
Micro amperes	2.934	4.481	2.703	4.528	2.626
Volts	1.000	0.800	1.000	0.700	1.000
Micro amperes	4.605	2.195	5.305	1.502	6.006
Volts	0.600	1.000	0.500	1.000	—
Micro amperes	1.232	7.384	0.554	8.609	—

Experiment No. 7, *c* (Temp. 21.8°)

Volts	1.000	1.200	1.000	1.300	1.000
Micro amperes	4.682	46.7	5.182	86.3	5.529
Volts	1.400	1.000	1.500	1.000	—
Micro amperes	106.1	6.591	133.1	7.300	—

Experiment No. 7, *d*

To eliminate the possibility of errors due to the rolling contact, the storage battery was short-circuited through a resistance box and the wires leading to the cell were attached at one end and the middle. By removing or inserting plugs the electromotive force on the cell could be altered at will. The results given are those taken just two minutes after the voltage was altered. As the electromotive force was not changed at regular intervals the times that the individual voltages were maintained are given in the third line. The initial residual current is less than in the preceding experiments owing to the fact that the cell had been polarizing several days longer.

Temperature 22.5°

Volts	1.001	1.097	1.001	1.118	1.001
Micro amperes	3.596	10.595	3.457	12.921	3.334
Min. maintained	——	47.0	6.0	10.0	4.0
Volts	1.152	1.001	1.176	1.001	1.238
Micro amperes	18.441	3.442	26.06	3.402	30.82
Min. maintained	5.0	5.0	6.0	4.0	5.0
Volts	1.001	1.308	1.001	1.386	1.001
Micro amperes	3.665	88.86	3.966	112.31	4.197
Min. maintained	5.0	3.0	6.0	2.0	5.0
Volts	1.476	1.001	1.576	1.001	1.696
Micro amperes	120.17	4.882	137.6	5.914	172.8
Min. maintained	2.0	3.0	2.0	3.0	2.0
Volts	1.001	——	——	——	——
Micro amperes	7.161	——	——	——	——
Min. maintained	——	——	——	——	——

It may be seen that temporary and not too great variations in the electromotive force, either up or down, do not produce any lasting effects on the residual current at one volt. For instance in No. 7, *b*, after the electromotive force had been lowered to 0.920 and returned to 1,000, five minutes sufficed for the residual current to come within 4 pct of its initial value; in No. 7, *a*, where the electromotive force was raised to 1.140, five minutes back at 1.000 brought the current to within 2.3 pct of the initial. This last result is rather remarkable and some more definite change might have been expected as 1.08 volts, the electromotive force of the hydrogen oxygen cell, was passed. When the electromotive force was altered through wider limits more permanent changes in the current at one volt were noted. No. 7, *b* shows that a decided lowering of the electromotive force considerably increases the residual current, this increase amounting to about 100 pct after the electromotive force had been at 0.500, undoubtedly because the lower electromotive force allowed a partial loss of polarization. But the same train of reasoning would lead us to expect that after high electromotive forces had been applied polarization would be greater and hence cause smaller residual currents at one volt. This is not the case and the application of higher voltage is followed by a marked increase in the residual current. In No. 7, *c*, after the application of 1.500 volts, the residual current at one volt shows an increase of 56 pct of the initial, and in No. 7, *d*, after the application of 1.696 volts, an increase of nearly 100 pct of the initial.

The interpretation given to these results is that at some point considerably below 1.67 volts (the minimum value generally accepted for the visible electrolysis of water) hydrogen and oxygen are freed and remain in solution supporting the one volt current. This point appears to lie above 1.140 volts (see Expt. No. 7, *a*) which indicates that the gases are not freed and left in solution at 1.08 volts. Recent work shows that the value 1.08 volts is too low for the reversible decomposition and formation of water and Bose[1] suggests 1.1392 ± 0.0150 volt as a better approximation.

Kohlrausch and Heydweiller[2] noticed that when they passed direct currents of 40 to 200 volts through conductivity water or through solutions the resistance diminished to a minimum and then rose again. They accounted for this in the case of salt solutions on the basis that an acid was formed at the anode, a base at the cathode, and these immediately dissociated, increasing the conductivity; but the hydrogen ions and the hydroxyl ions, owing to their great velocities of migration, met somewhere in the middle forming an almost insulating layer of purest water. But this explanation would not apply for their conductivity water, and after rejecting the theory that the phenomenon was due to impurities, and finding by experiment that the formation of hydrogen peroxide was not the cause, they concluded that complex hydrogen and hydroxyl compounds must be formed.

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[1] Zeit. Elektrochemie, 7, 673 (1901).

[2] loc. cit. Also Wied. Ann. 54, 385 (1895).

If we assume that these "compounds" are simply hydrogen and oxygen and grant that these elementary gases as such will conduct, their difficulty vanishes. Sufficiently high electromotive forces produce the gases in the solution and the conductivity increases, but as the current passes, polarization also increases until a point must be reached where the conductivity will diminish.

There is another phenomenon in connection with these experiments not shown by the above figures. After the electromotive force had been held for five minutes at a high voltage and then returned to one volt, a number of readings were taken, at one minute, two minutes, and so on. Without exception, when the electromotive force had been 1.2 or higher, the first readings at one volt showed a smaller current than the later, the current increasing for a short time to a maximum and then falling off again. The following figures will suffice to illustrate this behavior.

Electromotive force had been held at 1.2 for five minutes and then returned to one volt.

Minutes	1.0	3.0	5.0	7.0	10.0	12.0	15.0	17.0	20.0	——
Micro amperes	4.967	5.128	5.205	5.282	5.313	5.328	5.244	5.167	5.09	——

Electromotive force had been held at 1.3 for five minutes and then returned to one volt.

Minutes	1.0	2.0	3.0	5.0	7.0	10.0	12.0	15.0	20.0	25.0
Micro amperes	5.144	5.352	5.429	5.529	5.613	5.752	5.760	5.752	5.690	5.613

Electromotive force had been held at 1.5 for five minutes and then returned to one volt.

Minutes	1.0	3.0	5.0	7.0	10.0	12.0	15.0	20.0	25.0	——
Micro amperes	6.491	7.030	7.292	7.646	7.954	7.946	7.877	7.739	7.700	——

When the preceding voltage had been less than one nothing of the sort appeared, the current sinking gradually from the beginning. A possible explanation is that at the higher voltages the concentration of neutral hydrogen in solution about the cathode was increased and hindered the formation of more neutral hydrogen, while the neutral oxygen formed about the anode acted similarly. But diffusion setting in then gradually diminished this effect. Perhaps this phenomenon might be utilized in a new method for determining the lowest electromotive force necessary to form the neutral gases in solution.

Conclusion

The following theory is suggested as furnishing a satisfactory explanation of the facts and harmonizing some apparent contradictions and therefore serviceable until the advent of a better. A dissolved gas is in a condition analogous to a rarefied gas, some of whose molecules Thomson has shown are capable of carrying plus electric charges, others minus. Using the phraseology of the corpuscular theory, we may have a hydrogen molecule plus a corpuscle of electrical energy which is then negatively charged, and a hydrogen molecule minus a corpuscle which is then positively charged. The process of solution is sufficient to occasion this differentiation into molecules plus corpuscles and molecules minus corpuscles with undoubtedly a large residue of neutral molecules. Why this should occur is a question which may be answered simultaneously with that as to why electrolytes are dissociated upon solution.

When a charged molecule comes in contact with the metal of the electrode its corpuscle passes to the metal, or a corpuscle passes from the metal to the positively charged molecule as the case may be. The molecule which has lost its charge may be occluded or remain in solution; in the latter case it increases the concentration of the neutral molecules and thus induces a further differentiation into molecules plus corpuscles and molecules minus corpuscles according to the law of mass action. If no external electromotive force be present, as many corpuscles are given up as are acquired by each electrode in unit time and no currentis observed. If the smallest external electromotive force be present there will be a tendency for one electrode to attract plus charged molecules and for the other to attract minus charged molecules, more corpuscles will then be given up to one electrode than are given out by it and a current will be observed. Though the charge on the individual molecule is probably the same as that on the ion as indicated by Thomson's work already quoted, the former are present in such small numbers that the total current carried by them is much less than that carried by the ions when the decomposition point is once passed, in fact negligible in all ordinary work.

This theory is thought to offer a more plausible explanation of the facts described in this article than any other we have. If it be accepted, it enables us to say that there is a real and definite decomposition point for each pair of ions, of course somewhat variable according to the osmotic theory of galvanic cells, but a fixed and constant value for any given conditions; any current observed before this value is reached being due to the charged molecules present.

Furthermore this conception is not necessarily limited to hydrogen and oxygen nor to gases. Any substance in dilute solution in any solvent is analogous to a rarefied gas and so may be susceptible to a differentiation into molecules plus corpuscles and molecules minus corpuscles, thereby becoming able to conduct electricity without dissociation as usually understood. This would account for Kahlenberg's[1] interesting discoveries of solutions conducting while the boiling- or freezing-point methods failed to indicate any corresponding dissociation. Other instances of such, at present anomalous behavior are multiplying rapidly.

It is far from the writer's intention to invalidate or supplant in any manner our dissociation theory, but rather to support it by offering a small addition explaining some apparent exceptions.

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Sept., 1902.

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[1] Jour. Phys. Chem. 3, 379 (1899).

ON THE CRITICAL STATES OF A BINARY SYSTEM

BY PAUL SAUREL

The conditions which are satisfied when a system of two phases formed from two independent components reaches a critical state were given by Gibbs in his memoir "On the Equilibrium of Heterogeneous Substances." Of the two conditions given by Gibbs only the first has been used by subsequent writers, and yet some of the most interesting of the theorems relating to the critical state are consequences of the second condition. These theorems, however, are well known, but heretofore they have been obtained as consequences of hypotheses which are less simple than those of Gibbs. In the present note we shall give a simple demonstration of Gibbs' conditions and we shall then show their importance in the theory of the critical state.

In what follows we shall suppose that the systems considered have been formed from two independent components. Moreover, by the term concentration of a phase we shall understand the mass of the first component which is present in the unit of mass of the phase.

The fundamental assumption of Gibbs may be stated as follows: For any given pair of components there exists an analytical function ζ of the variables T, Π and x, such that if T, Π and x denote the temperature, the pressure and the concentration of a homogeneous phase in equilibrium, ζ is equal to the thermodynamic potential of the unit of mass of that phase. This function is, in general, many-valued. Thus, for any given values of T and Π, we may represent the relation between ζ and x by a number of continuous curves in the $\zeta\, x$ plane. To each branch of the ζ function there corresponds a ζ curve.[1]

It can be shown that, when a homogeneous phase is in

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[1] On the Equilibrium of Heterogeneous Substances, p. 178.

equilibrium, its specific entropy η, its specific volume v and what for convenience we shall call its chemical potential μ, are given by the equations

$$-\eta = \frac{\partial\zeta}{\partial T}, \quad v = \frac{\partial\zeta}{\partial\Pi}, \quad \mu = \frac{\partial\zeta}{\partial x}. \tag{1}$$

Moreover, when the homogeneous phase is in stable equilibrium, we must have, for any virtual change which leaves the temperature and the pressure unchanged,

$$\delta\zeta > \mu\delta x, \tag{2}$$

in which the variations are to be construed strictly.[1] But, on the other hand, it follows, from the definition of ζ, that in passing from one state of equilibrium to an adjacent state of equilibrium at the same temperature and under the same pressure, we must have

$$\delta\zeta = \frac{\partial\zeta}{\partial x}\delta x + \frac{1}{2}\frac{\partial^2\zeta}{\partial x^2}\delta x^2 + \cdots, \tag{3}$$

in which the omitted terms are of the third and higher degrees in δx. From 1, 2 and 3 it follows at once that when a homogeneous phase is in stable equilibrium at a given temperature and under a given pressure,

$$\frac{\partial^2\zeta}{\partial x^2} > 0. \tag{4}$$

Thus at every point which corresponds to a phase in stable equilibrium the ζ curve is convex toward the x axis.

If the system consists of two phases in equilibrium it can be shown that

$$\left(\frac{\partial\zeta}{\partial x}\right)_1 = \left(\frac{\partial\zeta}{\partial x}\right)_2, \tag{5}$$

$$\zeta_1 - x_1\left(\frac{\partial\zeta}{\partial x}\right)_1 = \zeta_2 - x_2\left(\frac{\partial\zeta}{\partial x}\right)_2, \tag{6}$$

in which the subscripts 1 and 2 refer to the two phases. The geometrical interpretation of these conditions is that the tangents at the points 1 and 2 coincide. Moreover, it can be shown

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[1] On the Equilibrium of Heterogeneous Substances, p. 166.

that if the system is in stable equilibrium, condition 4 is satisfied at each of the points 1 and 2.

The points 1 and 2 may belong to the same or to different ζ curves. By varying the temperature and the pressure it may be possible to change the relative position and the shape of the ζ curves so that finally the points 1 and 2 are brought into coincidence. If the points which are thus made to coincide belong to different ζ curves we reach an indifferent state of the system;[1] if, on the other hand, the two points which are brought into coincidence belong to the same ζ curve we reach a critical state of the system.[2] In the first case, it is easy to see that, although x_1 and x_2 become equal, η_1 and η_2, v_1 and v_2 do not. For $-\eta_1$ and v_1 are equal to the derivatives with respect to T and Π of that branch of the ζ function which corresponds to the first ζ curve, while $-\eta_2$ and v_2 are equal to the derivatives with respect to T and Π of that branch of the ζ function which corresponds to the second ζ curve. In the second case, however, not only x_1 and x_2 become equal, but also η_1 and η_2, v_1 and v_2.

Let us consider the second case. If we remember that at each of the points of contact of the double tangent the curve is convex toward the x axis, it follows that a line parallel to the double tangent and slightly above it cuts the curve in four points. Accordingly, if the points 1 and 2 be made to coincide, the tangent to the curve at the limiting point will have with the curve a contact of the third order. The conditions for this are well known; they are

$$\frac{\partial^2\zeta}{\partial x^2} = 0, \quad \frac{\partial^3\zeta}{\partial x^3} = 0. \qquad (7)$$

These are Gibbs' conditions.[3]

Before discussing these conditions let us return to the consideration of equations 5 and 6. As these equations give two conditions between the four quantities T, Π, x_1 and x_2, it follows that two of these quantities, T and Π, for example, can be chosen

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[1] On the Equilibrium of Heterogeneous Substances, p. 183.

[2] van Rijn van Alkemade. Zeit. phys. Chem. 11, 298 (1893).

[3] On the Equilibrium of Heterogeneous Substances, p. 191.

arbitrarily. Accordingly, if we take three rectangular axes in space along which we shall measure T, Π and x, the values of x_1 and x_2 which correspond to different pairs of values of T and Π will determine two surfaces which we shall call the concentration surfaces.

Equations 7 give us two relations between the three quantities T, Π and x. Accordingly, the points in the T Π x space which correspond to critical states of the system, all lie on a curve. This curve may, with propriety, be called the critical line. Moreover, from the manner in which the critical states have been defined, it follows that the critical line is common to both of the concentration surfaces.

The equations which connect the simultaneous changes in T, Π and x as we pass from point to point on the concentration surfaces are due to van der Waals.[1] He has shown that they can be written in the following simple form:

$$v_{21}d\Pi = \eta_{21}dT + (x_2 - x_1)\left(\frac{\partial^2\zeta}{\partial x^2}\right)_1 dx_1, \tag{8}$$

$$v_{12}d\Pi = \eta_{12}dT + (x_1 - x_2)\left(\frac{\partial^2\zeta}{\partial x^2}\right)_2 dx_2, \tag{9}$$

in which

$$v_{21} = v_2 - v_1 - (x_2 - x_1)\left(\frac{\partial v}{\partial x}\right)_1, \tag{10}$$

$$v_{12} = v_1 - v_2 - (x_1 - x_2)\left(\frac{\partial v}{\partial x}\right)_2, \tag{11}$$

$$\eta_{21} = \eta_2 - \eta_1 - (x_2 - x_1)\left(\frac{\partial \eta}{\partial x}\right)_1, \tag{12}$$

$$\eta_{12} = \eta_1 - \eta_2 - (x_1 - x_2)\left(\frac{\partial \eta}{\partial x}\right)_2. \tag{13}$$

If we suppose that the system has reached an indifferent state we have

$$x_1 = x_2, \qquad \eta_1 \neq \eta_2, \qquad v_1 \neq v_2. \tag{14}$$

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[1] Archives néerlandaises, 24, 15 (1890). Zeit. phys. Chem. 5, 143 (1890). Archives néerlandaises, 30, 267 (1896). Die Continuität des gasförmigen und flüssigen Zustandes, 2, 108, 112, 179 (1900).

Equations 8 and 9 both reduce to the form

$$(v_2 - v_1)d\Pi = (\eta_2 - \eta_1)dT. \tag{15}$$

Thus the points in the $T\Pi x$ space which correspond to the indifferent states of the system lie on a line which is common to the two concentration surfaces. This line may be called the indifferent line of the system. From equation 15 it follows that along the indifferent line the two concentration surfaces have a common tangent plane and that this plane is constantly perpendicular to the $T\Pi$ plane. Further, the slope of the projection upon the $T\Pi$ plane of the indifferent line is given by equation 15 or, in more familiar form, by the equation

$$\frac{d\Pi}{dT} = \frac{\eta_2 - \eta_1}{v_2 - v_1}. \tag{16}$$

This extension of Clapeyron's equation to the indifferent states of a bivariant binary system is due to Gibbs.[1]

Let us consider next the manner in which the two concentration surfaces meet along the critical line. At every point of the critical line we have

$$x_1 = x_2, \qquad \eta_1 = \eta_2, \qquad v_1 = v_2, \tag{17}$$

$$\frac{\partial^2 \zeta}{\partial x^2} = 0, \quad \frac{\partial^3 \zeta}{\partial x^3} = 0. \tag{18}$$

The coefficient of every term in equations 8 and 9 is thus equal to zero. However, if we refer to equations 10, 11, 12 and 13 and if we expand v_2, v_1, η_2 and η_1 by Taylor's theorem, we find that the following approximate relations hold:

$$v_{21} = \tfrac{1}{2}(x_2 - x_1)^2\left(\frac{\partial^2 v}{\partial x^2}\right)_1, \tag{19}$$

$$v_{12} = \tfrac{1}{2}(x_1 - x_2)^2\left(\frac{\partial^2 v}{\partial x^2}\right)_2, \tag{20}$$

$$\eta_{21} = \tfrac{1}{2}(x_2 - x_1)^2\left(\frac{\partial^2 \eta}{\partial x^2}\right)_1, \tag{21}$$

$$\eta_{12} = \tfrac{1}{2}(x_1 - x_2)^2\left(\frac{\partial^2 \eta}{\partial x^2}\right)_2. \tag{22}$$

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[1] On the Equilibrium of Heterogeneous Substances, p. 155.

Equations 8 and 9 then take the form

$$\left(\frac{\partial^2 v}{\partial x^2}\right)_1 d\Pi = \left(\frac{\partial^2 \eta}{\partial x^2}\right)_1 dT + \frac{2}{x_2 - x_1}\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_1 dx_1, \qquad (23)$$

$$\left(\frac{\partial^2 v}{\partial x^2}\right)_2 d\Pi = \left(\frac{\partial^2 \eta}{\partial x^2}\right)_2 dT + \frac{2}{x_1 - x_2}\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_2 dx_2. \qquad (24)$$

To find the limiting value of the least term in equation 23 we observe that we have approximately

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_1 = \frac{\partial^2 \zeta}{\partial x^2} + (x_1 - x)\,\frac{\partial^3 \zeta}{\partial x^3}\,, \qquad (25)$$

in which the point to which x refers is any point on the ζ curve in the immediate neighborhood of the point 1. If we suppose that the point to which x refers is one of the two points on the ζ curve between 1 and 2 for which

$$\frac{\partial^2 \zeta}{\partial x^2} = 0,$$

the first term on the right-hand side of equation 25 disappears and the coefficient of dx_1 in equation 23 becomes

$$2\,\frac{x_1 - x}{x_2 - x_1}\;\frac{\partial^3 \zeta}{\partial x^3}. \qquad (26)$$

Since $x - x_1$ is not larger than $x_2 - x_1$ it follows that the limit of their ratio cannot be infinite. It follows then from the second of equations 18 that the limit of expression 26 is zero. Accordingly, at the limit, equations 23 and 24 reduce to the same form, viz:

$$\frac{\partial^2 v}{\partial x^2}\, d\Pi = \frac{\partial^2 \eta}{\partial x^2}\, dT. \qquad (27)$$

Accordingly, along the critical line the two concentration surfaces have a common tangent plane, and this plane is constantly perpendicular to the T Π plane.

From the fact that along the indifferent and the critical lines the tangent plane to the two concentration surfaces is perpendicular to the T Π plane, we can derive at once several interesting theorems. In the first place, if the indifferent and the critical lines intersect, their projections upon the T Π plane will be tangent to each other. In the second place, if the section of the concentration surfaces made by a plane parallel to the $T\Pi$ plane cut either the indifferent or the critical line, the projection of this curve upon the $T\Pi$ plane will be tangent to the projection of the indifferent or of the critical line. Finally, a section of the concentration surfaces by a plane parallel to the Tx plane or parallel to the Πx plane has at the points in which it cuts the indifferent and the critical lines tangents which are parallel to the x axis.

The theorems which we have deduced as consequences of Gibbs' conditions are well known. Demonstrations of them have been given by van der Waals[1] and by Duhem.[2]

New York, July 9, 1902.

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[1] Archives néerlandaises, 30, 266 (1896). Die Continuität des gasförmigen und flüssigen Zustandes, 2, 131-146 (1900).

[2] Traité élémentaire de Mécanique chimique, 4, 109–121 (1899).

DEDUCTION OF THE MAGNITUDE OF THE OSMOTIC PRESSURE IN DILUTE SOLUTIONS ACCORDING TO THE KINETIC THEORY

BY PETER FIREMAN

If the kinetic energy of the moving molecules of the dissolved substance is practically the only factor which determines the magnitude of the osmotic pressure in dilute solutions, and if besides it is known from experience that this pressure is equal to the gas pressure of a number of molecules equal to that of the dissolved substance and occupying at the same temperature a volume equal to that of the solution, it would appear that the theoretical deduction of the magnitude of the osmotic pressure should be a rather simple problem. I mean a deduction which is not based on thermodynamical reasoning,[1] but on the consideration of, to use the words of Nernst, the molecular forces and the molecular motion[2] involved. And yet the attempts made in this direction do not appear to have been successful. Nernst[3] discusses those of Boltzmann,[4] Riecke,[5] and Lorentz,[6] and considers them as rather provisional (vorläufig). Any way they seem to lack simplicity and persuasiveness.

In the following the present writer attempts a very simple theoretical deduction of the magnitude of the osmotic pressure in dilute solutions by a consideration of the individual factors and particular conditions concerned.

The magnitude of the osmotic pressure in dilute solutions being determined by the kinetic energy of the solute, our problem

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[1] van 't Hoff gave us a thermodynamical deduction (Zeit. phys. Chem. 1, 488) which, after the manner of such demonstrations, does not enter upon the nature of the osmotic pressure.

[2] Theoretische Chemie, Second Edition, 1898, p. 240.

[3] loc. cit.

[4] Zeit. phys. Chem. 6, 474 (1890); 7, 88 (1891).

[5] Ibid. 6, 564.

[6] Ibid. 7, 36.

would be solved if we were able to ascertain the mean kinetic energy of the molecules of the solute and the number of impacts which they produce in unit of time on unit of area of the semipermeable wall.

The first question then is: How great is the molecular kinetic energy of the solute at a given temperature? Obviously it will depend on three things: 1st, on the molecular kinetic energy of the solvent; 2d, on the mutual attraction between the molecules of the solvent and the solute; and 3d, on the temperature. As to the first, after equilibrium is established between the solvent and solute, the molecules of either will give as much as take and, therefore, have the same kinetic energy. But how great will this common kinetic energy be? Let us consider what the molecular kinetic energy of the solvent would be if it were alone. In that case it would, we may safely assume, depend on the temperature and the mutual attractions of its molecules. It is easy to see that these mutual attractions cannot influence the velocity of the molecules. For each molecule of a liquid, except in the surface, while constantly tossed about, is in all its positions equally attracted in all directions by the surrounding molecules; and, therefore, the total effect of these attractions on its motion is the same as if there were none. Hence the molecular kinetic energy of a liquid will depend only on its temperature, just as in the case of gases, and be, we must conclude, equal to that of gases at the same temperature.[1]

Thus the molecular kinetic energy of the solvent, before the addition of the solute, will have been equal to that of a gas at the same temperature.

As to the dissolved substance we cannot but assume that it will tend to develop a molecular kinetic energy also equal to that of a gas at the same temperature.

It follows that the solvent and the solute have to be considered as contributing to the solution equal molecular kinetic

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[1] This conclusion is in entire harmony with the interpretation of the liquid state as deduced, on the hand of van der Waals's equation, from the fact of the mutual interconvertibility of the gaseous and liquid states.

energy. Moreover, this kinetic energy cannot be affected, for reasons similar to those given above, by the mutual attractions of the solvent and solute. Consequently the molecular kinetic energy of the dissolved substance is equal to that of a gas at the same temperature.[1]

The second question is: How great is the number of impacts produced by the molecules of the solute in unit of time per unit of area of the semipermeable wall? At the first thought one is inclined to conclude that the number of impacts, owing to the presence of the solvent which retards the forward progress of the molecules of the solute, causing them to less frequently traverse the volume of the solution, will be less than that produced by an equal number of molecules moving with the same velocity in the absence of the solvent. But on reflection it is easy to see that this conclusion is erroneous. For if a given number of molecules are uniformly distributed in a given space — which in cases under consideration they always must be — and if they move with a given velocity, then the number of molecules passing a unit of time through unit of area of a mathematical plane within that space, will be the same regardless of the circumstance whether a liquid is present which retards their forward progress or not. The consequence of the presence of the liquid can merely be this that the molecules of the solvent will linger and be tossed about for a longer time in one and the same region.

Thus liquid or no liquid, the number of molecules passing through unit of area in unit of time and hence the number of impacts on unit of area of a wall within the containing vessel depends only on the number of molecules present and their velocity.

Having proved thus that the kinetic energy of the molecules of a solute in dilute solution is equal to that of a gas at the same temperature and that the number of impacts with the same kinetic energy depends only on concentration, regardless of the presence of the solvent, we have also proved that the os-

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[1] A conclusion shared by a number of authors.

motic pressure of a substance in dilute solution is equal to the corresponding gas pressure of that substance.[1]

Appendix

Molecular kinetic energy of a liquid

By reversing the order of reasoning given above and starting with the magnitude of the osmotic pressure, as found by experiment, a new and perhaps more rigorous proof than those hitherto advanced, can be obtained that the kinetic energy of the molecules of a liquid is equal to that of a gas at the same temperature.

The osmotic pressure in dilute solution is, as the experiment shows, equal to the corresponding gas pressure. The osmotic pressure, like the gas pressure, is a product of the mean molecular kinetic energy and the number of molecular impacts in unit of time per unit of area. Since one of the factors — the number of impacts produced by a given number of molecules of the solute —is, as shown in the foregoing, independent of the presence of the solvent and is the same for the solute in solution as it would be for it in the gaseous state, then the other factor — the kinetic energy of the molecules of the solute in solution must also be equal to that of a gas at the same temperature.

Now the molecular kinetic energy of the solute is bound to be the same as that of the solvent. Hence the molecular kinetic energy of the solvent must also have been equal to that of a gas at the same temperature. This means that, in general, the kinetic energy of the molecules of a liquid is equal to that of gas molecules at the same temperature.[2]

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[1] In the above deduction we had in mind only substances which do not dissociate in solution.

[2] Of the two factors of the known osmotic pressure one — the number of impacts — is known, whence the other factor — the molecular kinetic energy — becomes known. This deduction of the molecular kinetic energy of the solute is more than merely speculative. This feature renders my reasoning in this appendix essentially different from a speculation of Ostwald (Allgem. Chemie, 2d Edition, Vol. I., 699) to which it is similar in form and conclusion.

NAME INDEX

To Papers and Reviews

NAME INDEX

to New Books

SUBJECT INDEX

Exclusive of New Books