## REVIEWS

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

#### General

The atomic weight of radio-active barium. S. Curie. Comptes rendus, 131, 382 (1900).—The atomic weight of barium from barium chloride came out 138, while a specimen of the same salt containing a large amount of radium gave 174 as against 146 previously obtained (4, 400).

W. D. B.

The true atomic weights of ten elements deduced from recent publications. G. Hinrichs. Comptes rendus, 131, 34 (1900). — The following atomic weights are adopted: H I. C I2, O I6, Cl 35.5, Br 80, S 32, Na 23, Ag 108, Ba 137, Bo II. The author maintains that the difference between the 'atomic ratio' and the 'analytical ratio' falls within the limit of experimental error in the recent determinations of the atomic weight of boron, and that, therefore, the value of II.00 is the correct one.

W. D. B.

Thermochemistry of the ethylene diamines. M. Berthelot. Ann. Chim. Phys. (7) 20, 163 (1900). — Reviewed (4, 415) from Comptes rendus, 129, 687, 694, 743 (1899).

On the mercury alkyls. M. Berthelot. Ann. Chim. Phys. (7) 20, 158 (1900). — Reviewed (4, 401) from Comptes rendus, 129, 918 (1900).

Investigations in the uric series. M. Berthelot. Ann. Chim. Phys. (7) 20, 189 (1900). — Reviewed (4, 401) from Comptes rendus, 130, 360 (1900).

Studies on the isomerism of the sulphocyanates. M. Berthelot. Ann. Chim. Phys. (7) 20, 197 (1900). — Reviewed (4, 401) from Comptes rendus, 130, 441 (1900).

Investigations on the metallic derivatives of acetylene. M. Berthelot and M. Delépine. Ann. Chim. Phys. (7) 19, 5 (1900). — Reviewed (4, 401) from Comptes rendus, 129, 361 (1899).

Thermochemistry of lactic acid. M. Berthelot and M. Delépine. Ann. Chim. Phys. (7) 20, 149 (1900). — Reviewed (4, 401) from Comptes rendus, 129, 920 (1899).

Thermochemical studies on the chief alkaloids of opium. E. Leroy. Ann. Chim. Phys. (7) 21, 87 (1900). — Reviewed (4, 219, 401) from Comptes rendus, 128, 1107; 129, 220 (1899).

Heat of neutralization of hydrocarbonyl ferrocyanic acid compared with that of hydroferrocyanic acid. J. A. Müller. Ann. Chim. Phys. (7) 20, 377 (1900).

— Reviewed (4, 416) from Comptes rendus, 129, 962 (1899), but ascribed by a misprint to J. A. Miller.

Model to illustrate the movement of ions. F. Kohlrausch. Zeit. phys. Chem. 34, 559 (1900).—A mechanical model for lecture demonstration. The relative movements of the ions are illustrated by means of small metal cylinders hung on strings which pass over concentric pulleys at different diameters.

A . P . S .

Model to illustrate the movement of ions. W. L. Miller and F. B. Kenrick. Zeit. phys. Chem. 35, 440 (1900). — The mechanical principle on which this model is constructed is the same as that employed by Kohlrausch (see preceding review), but this appears to be, on the whole, a more serviceable piece of apparatus for lecture demonstration than the other.

A. P. S.

### One-Component Systems

Note on the melting-point of lithium. G. W. A. Kahlbaum. Zeit. anorg. Chem. 23, 220 (1900).—A sample prepared by A. Guntz of Nancy, melted at 186°. The value given by Bunsen and Mathiessen was 180°. W. D. B.

The boiling-points of zinc and cadmium. D. Berthelot. Comptes rendus, 131, 380 (1900). — By means of electric heating, the error due to radiation is reduced to a minimum. The mean of five measurements gives 920° as the boiling-point of zinc. The corresponding value for cadmium is 778°. W. D. B.

Studies on the vapors given off by the two forms of mercuric iodide. D. Gernez. Ann. Chim. Phys. (7) 20, 384 (1900).—Reviewed (4, 220) from Comptes rendus, 128, 1516 (1899).

Note on the article of B. Woringer entitled: On the vapor-pressure of a series of benzene compounds. A. Winkelmann. Zeit. phys. Chem. 35, 480 (1900).—Contains a correction of certain statements in the article (3, 73) regarding previous work by Winkelmann.

A. P. S.

On two loci relative to the densities of liquid carbonic acid and its saturated vapor. E. H. Amagat. Comptes rendus, 131, 91 (1900).—It is pointed out that what M. Mathias has proved is that the diameter of the curve for the densities of liquid and vapor, and the diameter for points at which liquid and vapor have the same volume, cannot both be straight lines. It is possible, however, that either may be curved and the other straight, or that both may be slightly curved.

W. D. B

The law of corresponding states. D. Berthelot. Comptes rendus, 131, 175 (1900).—A statement of the belief that the law of corresponding states is absolutely accurate if we displace the zeros of volume and temperature by amounts varying with each substance [See 4, 546].

W. D. B.

Some points on isomerism in the aromatic series. Oechsner de Coninck. Ann. Phys. Chim. (7) 20, 136 (1900).— "Aromatic isomers fall into pairs

whether one studies the qualitative reactions, solubilities, melting- and boiling-points, densities, heats of solution, heats of formation, or whether one considers their tendency to react or not to react."

W. D. B.

## Two-Component Systems

On the alloys of antimony and tin. W. Reinders. Zeit. anorg. Chem. 25, 113 (1900). — The freezing-point curve rises steadily from the melting-point of pure tin, 232°, to that of pure antimony, 622°. There are three quadruple points, at about 243°, 310°, and 430°. The first and last solid phases are mixcrystals of antimony in tin and of tin in antimony respectively. The two intermediate phases are not known definitely, but the author inclines to SbSn and Sb<sub>1</sub>Sn<sub>3</sub> or Sb<sub>5</sub>Sn<sub>4</sub>. To the reviewer SbSn<sub>2</sub> seems quite as probable from the evidence as SbSn. From 10-40 percent Sb we have cubical crystals which by forty percent are beginning to change. At fifty percent there are no cubes left, the mass being chiefly flat plates, the edges not forming right angles. This seems inconsistent with the views of the cubes being SbSn. The author is non-committal as to the cubes and plates being identical or not. If they are not identical, the cubes cannot have the formula SbSn. If they are identical, then there is nothing in the paper to show the crystalline form of the second set of compounds.

W. D. B.

Contributions to our knowledge of amalgams, II. W. Kerp and W. Böttger. Zeit. anorg. Chem. 25, I (1900). — The authors have determined the freezing-point curves from o° to 100° for a number of amalgams and have analyzed the coexistent solid and liquid phases. With sodium amalgam, NaHg<sub>6</sub> is apparently solid phase up to about 40.5°; from there to about 150° we have NaHg<sub>5</sub>. LiHg<sub>5</sub> is solid phase over the whole range, o° to 100°. Below o' KHg<sub>14</sub> is stable; from about oo to 71°, we have KHg12; from 71° to 75°, KHg10; and above 75° a solid solution. Below o° RbHg<sub>12</sub> separates; but it is not certain whether the solid phase above this temperature is a solid solution or not. Below 30° we have SrHg<sub>12</sub>; above 30° a solid solution. Below 30° the solid phase is BaHg<sub>13</sub>; from 30° to 100° it is BaHg<sub>12</sub>. Cadmium amalgam crystallizes as Cd2Hg; from oo to about 44°; at higher temperatures, a solid solution is formed. No definite results could be obtained for zinc amalgam because the composition of the solid phase appeared to vary with the time. This would seem to indicate the formation of an instable precipitate which reached equilibrium very slowly.

In the case of the solid sodium amalgams, a little less sodium is found than is called for by the formulas. This is very probably due to the presence of mother-liquid. On the other hand, pressing the crystals changes the composition. The authors attribute this to a lowering of the inversion point. While this is possible, a change of 40° under moderate pressure is surprising and seems less probable than a change of composition of a solid solution. The matter could easily be settled definitely by holding the amalgam at 0° under constant pressure until equilibrium is reached and seeing whether the final composition was or was not NaHg<sub>5</sub> [Cf. following review].

W. D. B.

The amalgams of sodium and potassium. A. Guntz and Ferée. Comptes

rendus, 131, 182 (1900). — The authors deny the statement of Kerp, that different crystals of sodium amalgam are obtained under moderate pressure. They believe in the existence of NaHg<sub>8</sub> at temperatures below zero, of NaHg<sub>8</sub> at ordinary temperatures; of NaHg<sub>5</sub> at temperatures above 100°. Under pressures of 200–1200 kg cm², both NaHg<sub>6</sub> and NaHg<sub>5</sub> pass into NaHg<sub>4</sub>. At 19° a potassium amalgam KHg<sub>18</sub> is obtained. At ordinary pressures, KHg<sub>12</sub> is the stable form passing under pressure into what is thought to be KHg<sub>10</sub>. The authors are distinctly handicapped in their work by their ignorance of the phase rule.

W, D, B.

Cryoscopic and ebullioscopic studies. A. Battelli and A. Stefanini. Nuovo Cimento, (4) 9, 5 (1899); Ann. Chim. Phys. (7) 20, 64 (1900). — After a long discussion of the sources of error in freezing-point determinations, the authors describe their own experiments with dilute sugar solutions. Their apparatus was protected on all sides, including the top; they used boiled-out water; the stirring was mechanical; corrections were applied for convergence temperature, etc. At different times they used a Beckmann thermometer, a resistance thermometer, and a thermopile. For solutions containing from 0.7 to 14 g of sugar per liter they find a molecular depression rising from 1.84 to 1.88. As a more dilute solution (0.34 g) gave 2.02, they conclude that the value is constant at 1.87. Boiling-point measurements with potassium antimony tartrate were made at dilutions of eight, sixteen, and thirty-two liters. The molecular weights were 287, 304, 329, which they call practically constant at 322, though one does not quite see why there should not be electrolytic dissociation. The accuracy of the results seems to stand in no obvious relation to the precautions which they took.

Note on the solubility of mercury halides and especially mercuric iodide in organic solvents. O. Sulc. Zeit. anorg. Chem. 25, 399 (1900). — A few experiments were made to determine the solubility of the chloride, bromide, iodide, and cyanide of mercury in chloroform, carbon tetrachloride, bromoform, ethyl bromide, ethyl iodide, and ethylene dibromide. Mercuric iodide was then determined in nineteen solvents. The author states that these last measurements were made at the boiling-points of the solvents; but this could only be strictly true in case mercuric iodide were absolutely insoluble, because the solutions were heated on a water-bath. Since the solid phase was sometimes yellow crystals and sometimes yellow and red crystals mixed, it seems fair to assume that these so-called solubility determinations are fortuitous data referred to fictitious temperatures.

W. D. B.

Solubility of cupric chloride in organic solvents. Oechsner de Coninck. Comptes rendus, 131, 58 (1900). — Qualitative experiments. W. D. B.

Liquefaction of methyl chloride and sulphur dioxide. F. Caubet. Comptes rendus, 131, 108 (1900).—A diagram showing the boiling curves and dew curves for seven mixtures of methyl chloride and sulphur dioxide. Two of the curves show loops, there being a temperature and pressure at which liquid and vapor of the same composition are in equilibrium. Others of the curves show transitions from this type to the normal. Owing to the very slight

difference between the boiling pressures and the dew pressures, the phenomena of retrograde condensation could not be observed experimentally. W. D. B.

The extraction of oxygen by solution at low temperature. G. Claude. Comptes rendus, 131, 447 (1900).— Attempts have been made to find a solvent which should dissolve oxygen much more readily than nitrogen at low temperatures; but all efforts have proved fruitless.

W. D. B.

Preparation and properties of two borides of silicon:  $SiB_3$  and  $SiB_6$ . H. Moissan and A. Stock. Comptes rendus, 131, 139 (1900). — The authors have prepared the borides  $SiB_3$  and  $SiB_6$  by heating boron in electrically fused silicon. These compounds scratch the ruby, but do not scratch the polished face of a diamond. The density of  $SiB_3$  is 2.52 and that of  $SiB_6$  is 2.47. Both substances conduct electricity. W. D. B.

On the composition by volume of hydrofluoric acid. H. Moissan. Ann. Chim. Phys. (7) 19,531 (1900). — Reviewed (4,409) from Comptes rendus, 130,544 (1900).

## Poly-Component Systems

Action of hydrogen on the sulphide of arsenic. H. Pélehon. Comptes rendus, 131, 416 (1900).— Above 300°, hydrogen and the sulphide of arsenic reacts, and the reaction is reversible. At 610° the percentage of hydrogen in the gas is about 93 percent of the total, provided hydrogen is in excess and there is still liquid sulphide of arsenic in the tube. If arsenic in excess be added, the ratio falls to 78.7. With an excess of arsenic and no liquid sulphide, the ratio is 64.9.

W. D. B.

The equilibrium between lead, zinc, and their fused chlorides. W. Reinders. Zeit. anorg. Chem. 25, 126 (1900). — On electrolyzing fused mixtures of zinc and lead chlorides, the resulting alloy does not have the equilibrium concentration. The actual concentrations at equilibrium were therefore determined by direct experiment. When the fused mixture contains over 0.1 percent lead chloride, the metal in equilibrium is practically pure lead. The author has also measured the electromotive force of cells of the type  $Zn + Pb \mid ZnCl_2 + PbCl_2 \mid PbCl_2 \mid Pb$ . W. D. B.

Solubility of a mixture of salts having a common ion. C. Touren. Comptes rendus, 131, 259 (1900).—Assuming complete dissociation for potassium carbonate, the curve for the solubility of potassium nitrate in potassium nitrate in solutions coincides for part of its course with those for potassium nitrate in solutions of potassium chloride and potassium bromide. The solubility of potassium nitrate is increased by carbonic acid, so the solubility isotherm for the salt in presence of potassium bicarbonate is not comparable with the others.

W. D. B.

On the solubility of the carbonates of the alkaline earths in water containing carbon dioxide. G. Bodländer. Zeit. phys. Chem. 35, 23 (1900).—A discussion of the experimental results of Schloesing [Comptes rendus, 74, 1552 (1872); 75, 70 (1872)] on the solubility of carbonates of calcium and barium, and of

Engel [Comptes rendus, 100, 144 (1885)] on magnesium carbonate. Van't Hoff's formula (Vorlesungen, 1, 149) applied only for infinite dilution; the author deduces a formula which applies for finite dilutions. In the case of calcium carbonate it takes the form:

$$HCO_3' = 12.69 \, 1^{3} \, K_1 CO_2$$
.

The first dissociation of the bicarbonate into  $Ca^{\cdot\cdot}$  and  $2HCO_3'$  is found to be about 20,000 times greater than the second into  $H^{\cdot}$  and  $CO_3''$ , so that the concentration  $HCO_3'$  is practically a measure of the total concentration.  $CO_2$  in the formula represents the pressure of carbon dioxide in atmospheres. The formula holds for all those carbonates of the group which are very sparingly soluble; only the value  $K_1$  is different for different individuals. A. P. S.

Absorption, V. J. M. van Bemmelen. Zeit. anorg. Chem. 23, 111 (1900). — Colloidal metastannic acid absorbs hydrochloric acid in a marked fashion. The distribution ratio is not constant. At 15° and in presence of saturated water vapor, the colloid contains 2.2 reacting weights of H<sub>2</sub>O to one of SnO<sub>2</sub>. If we consider the whole of this water as solvent, the concentration of potassium chloride in the colloid is less than in the solution. It is not certain, however, that the colloid contains so much water in concentrated solutions, or that the whole of it should be considered as water. If half of it is part of the stannic acid, the concentration of potassium chloride in the colloid is greater than in the solution. However one calculates it, the distribution ratio for potassium chloride is approximately constant and thus differs markedly from the corresponding ratio for hydrochloric acid.

W. D. B.

Absorption, VI. J. M. van Bemmelen. Zeit. anorg. Chem. 23, 321 (1900). — A general discussion of the phenomena attending the absorption of solutes by colloids. This includes a study of the qualitative distribution of a solute between an absorbing substance and a solution. The case of colloids in colloids is treated first; then the absorption of crystalline substances. In the latter case, it is shown that the absorption depends on the nature and state of the colloid, on the nature of the liquid solvent, on the nature and concentration of the solute, and on the temperature. A special section is devoted to the absorption of two substances with resulting chemical reactions, and yet another to the case of absorption with hydrolysis. The last three pages treat of the change in absorption when the gel changes, either by passing into another modification or into the crystalline state.

W. D. B.

The effect of neutral salts on the partial pressure of ammonia in aqueous solutions. W. Gaus. Zeit. anorg. Chem. 25, 236 (1900).— The author has determined the change in the partial pressure of ammonia when neutral salts are added to aqueous ammonia. The change was measured by passing electrolytic gas through the solution into hydrochloric acid and determining the conductivity of the acid. With the salts of the alkalies, an increase of pressure is observed; with other salts a decrease, the decrease being largest with the silver and copper salts.

W. D. B.

Equilibrium phenomena in the distribution of an acid between ammonia and sparingly soluble metal hydroxides. W. Herz. Zeit. anorg. Chem. 23, 222;

24, 123 (1900). — When zinc sulphate, nitrate or chloride reacts with ammonia, the resulting equilibria cannot be represented by the theoretical formula  $\text{Zn 1.5.NH}_4 = const$ . On the other hand, the empirical formula  $\text{Zn NH}_4 = const$  represents the facts very well so long as ammonia is not present in excess.

Beryllium hydroxide is so insoluble that ammonia precipitates it quantitatively from solutions of beryllium salts. Cadmium salts behave like the corresponding zinc salts.

W. D. B.

Aqueous tin chloride solutions. W. von Kowalewsky. Zeit. anorg. Chem.

23, 1 (1900). — The reaction between tin tetrachloride and water is a reversible one, less acid being formed the higher the temperature. The author concludes that the colloidal stannic hydroxide reduces the conductivity of hydrochloric acid about twenty-five percent.

W. D. B.

On the behavior of some halide compounds of the carbon group analogous to stanuic chloride. W. von Kowalewsky. Zeit. anorg. Chem. 25, 189 (1900).

— The reaction between titanium tetrachloride and water is a reversible one; but if the solution be heated, titanic acid precipitates and does not react on cooling. With silicon tetrachloride and water, the reaction runs practically to an end.

W. D. B.

On the determination of sulphuric acid in presence of iron; a note on solid solutions and on the hydrolysis of chromium and iron. T.W.Richards.Zeit. anorg. Chem. 23, 383 (1900). — Attention is called to the fact that Küster and Thiel in their papers (3, 251; 4, 150, 411) have overlooked important papers by Richards, by Schneider, and by Gladding. It is further pointed out that the distribution ratio, if any, must refer to the undissociated salt, a view which is confirmed by the influence of hydrochloric acid on the occlusion of barium chloride by barium sulphate. While Küster and Thiel assume that  $Ba[Fe(SO_4)_2]_2$  is occluded, the author inclines to the view that it is really a basic salt because acidifying the solution decreases the occlusion, while increased hydrolysis due to dilution increases the occlusion.

The determination of sulphuric acid in presence of iron, IV. F. W. Küster and A. Thiel. Zeit. anorg. Chem. 25, 319 (1900). — The authors state that they did not overlook the paper by Jannasch and Richards, and that they do not accept the hypothesis of Richards (preceding review). W. D. B.

Some complex silver salts. K. Hellwig. Zeit. anorg. Chem. 25, 157 (1900). — Silver iodide, cyanide, chloride, sulphocyanate, and bromide are soluble in silver nitrate solutions in the order named, the iodide being the most soluble. Silver cyanide, sulphocyanate, iodide, and bromide are soluble, in the order named, in solutions of the potassium salts of the corresponding acids, the cyanide being the most soluble. In all these cases, complex salts exist to a greater or lesser extent in solution, as shown by boiling-point determinations. The following double salts were prepared:  $Ag_3I(NO_3)_2$ ,  $Ag_2I(NO_3)$ ,  $Ag_2Br(NO_3)$ ,  $Ag_3CN(NO_3)_2$ ,  $Ag_3CN($ 

The oxidation of cobalt and cerium salts in alkaline solution. A. Job. Ann. Chim. Phys. (7) 20, 205 (1900). — Ferric salts dissolve in sodium pyrophosphate solution and are then colorless. In such a solution, it is easy to titrate ferrous iron with permanganate. Cobalt salts dissolve in concentrated solution of potassium bicarbonate with a pink color. On adding chlorine or hydrogen peroxide, the color changes to a green, very like that of concentrated solutions of nickel salts. This is due to the formation of a cobaltic salt. In acid solutions, the cobaltic salt is reduced by hydrogen peroxide.

Cerous salts, dissolved in aqueous potassium carbonate, oxidize in the presence of air to perceric salts, which latter react with the former, making ceric salts. In acid solutions, hydrogen peroxide changes ceric salts into stable perceric salts. From potassium carbonate solutions of perceric salts, a stable perceric double carbonate crystallizes, which decomposes only at 200°. We thus have salts corresponding to cerous oxide, Ce<sub>2</sub>O<sub>3</sub>, ceric oxide, CeO<sub>2</sub>, perceric oxide CeO<sub>3</sub>. In addition, the behavior of perceric solutions in the presence of hydrogen peroxide indicates the existence of a salt corresponding to the oxide CeO<sub>4</sub>, This is a most interesting and valuable paper, and the work has been done in a very creditable manner.

W. D. B.

Hydrogenization of acetylene and ethylene by finely divided platinum. P. Sabatier and J. B. Senderens. Comptes rendus, 131, 40 (1900). — Cold platinum black acts on a current of mixed acetylene and hydrogen, forming chiefly ethane when hydrogen is in excess, and chiefly ethylene when acetylene is in excess. At higher temperatures, the reaction takes place more readily and condensation products are also formed. Platinum black reduces hydrogen and ethylene at first to ethylene, but owing to slight carburation, soon ceases to be active unless heated.

W. D. B.

The action of reduced nickel on acetylene. P. Sabatier and J. B. Senderens. Comptes rendus, 131, 187 (1900). — When no hydrogen is present, nickel only reacts to any extent with acetylene when the temperature is raised above 180°. A number of substances are formed, including liquids as well as gases. When hydrogen is present, its reaction with acetylene makes the nickel incandescent and a series of complex reactions takes place.

W. D. B.

Action of finely divided platinum, cobalt, and iron on acetylene and ethylene. P. Sabatier and J. B. Senderens. Comptes rendus, 131, 267 (1900).— The action of finely divided platinum, cobalt, and iron on acetylene and on ethylene is very similar to that of nickel except that the nickel puffs up much more than the other metals.

W. D. B.

Correction to the systematic detection of anions. R. Abegg and W. Herz. Zeit. anorg. Chem. 25, 405 (1900). — A few modifications of the original scheme (4, 636) have been introduced in order to obviate some difficulties brought up by Fresenius.

W. D. B.

Action of hydrofluoric acid and of fluorine on glass. H. Moissan. Ann. Chim. Phys. (7) 19, 516 (1900).—Reviewed (4, 412) from Comptes rendus, 129, 799 (1900).

On the simultaneous phenomena of oxidation and hydration in organic compounds under the influence of oxygen and light. M. Berthelot. Ann. Chim. Phys. (7) 20, 42 (1900). — Reviewed (4, 412) from Comptes rendus, 129, 627 (1899).

#### Velocities

Periodic phenomena in the solution of chromium in acids, I. W. Ostwald. Zeit. phys. Chem. 35, 33 (1900). — Hittorf has shown that chromium exists in three different modifications; in one of them the metal appears as a readily oxidizable substance standing between zinc and cadmium in the electrochemical series and dissolving readily in acids with formation of chromous compounds and hydrogen; in the second it is about like mercury in its position in the electro-chemical series, is not attacked by acids, but when made the anode in a current of sufficient pressure, it dissolves forming chromic acid; while in the third form it yields chromic compounds.

Ostwald, in repeating some of Hittorf's experiments with the first of these varieties, noticed that the velocity of reaction with acids varied periodically. In the ordinary case of the solution of a metal in an acid, if the velocity of reaction be measured by the rate of evolution of hydrogen, it will be found that this is at first slow, then more or less rapidly increases to a maximum, after which it gradually falls, reaching in the end zero, where either the acid or the metal is all used up. In the case of chromium the reaction begins in the usual way, the maximum is reached, and the velocity of evolution then diminishes; but instead of dropping continuously to zero, it turns at a certain point and begins to rise again, and this process, repeating itself an indefinite number of times, gives rise to a series of maxima and minima.

The acids used by Ostwald were mainly hydrochloric and sulphuric. The ingenious arrangement made use of by him to render the reaction self-registering cannot be described here.

The results lead to the conclusion that the seat of the phenomenon is in the metal and not in the acid used. Two pieces of metal in the same solution give a curve representing the sum of their velocities of reaction; and since the periods at which the maxima recur are not the same for the two pieces, the curve resulting evidently has the form of two curves superposed on one another. If the two pieces of metal be brought into contact, the curve at once becomes simple and takes on the period which is the smaller of the two. A piece of "active" chromium brought into contact with a piece which is "inactive," transforms it into the active variety. The length of period characteristic of a given piece of the metal depends partly on the treatment to which it has previously been subjected; but it does not follow that pieces which have received the same treatment will show the same behavior. On the contrary, when three pieces were treated as nearly as possible alike and then put into acid, they gave curves showing the widest differences. Since previous treatment has no constant effect, the peculiarity must lie in the substance of the metal and not on its surface.

At this stage of the investigation, some new and purer material was taken up, and the whole phenomenon at once ceased to make its appearance; the metal dissolved like any other, and all attempts to cause it to take on the pecu-

liarities previously observed were in vain. It was therefore necessary to return to the older material in order to continue the work. The method by which this peculiar form of chromium may be produced will be made the subject of a special article by Ostwald and Goldschmidt later on.

Some pieces gradually lose the property of "vibrating" in the process of solution, and, while they may be made active again by being taken out of the liquid and brought into contact with an active piece, the property is gradually lost when they are further dissolved. The influence of the concentration of the acid is in the direction that the periods are longer the more dilute the acid employed. A rise in temperature shortens the length of the period, and this change is, in some cases, in quantitative agreement with the general rule that a rise of 10 degrees causes approximately a doubling of any reaction velocity; this rule, however, is not invariable here.

The chapter on the influence of added substances is a complex and surprising one. Even the mixing of the two acids, sulphuric and hydrochloric, gives rise to a considerable increase in complexity of the curves, and in every case to a dying out of the vibration after the lapse of a certain time. Addition of potassium chromate, colloidal platinum, or copper chloride had little effect. On the other hand, the addition of potassium iodide caused a marked retardation of the periods and beyond a certain concentration causes the disappearance of the vibrations altogether. Potassium sulphocyanate and cyanides show much the same effect; but formaldehyde is the most powerful of all these "retarders," and its effects are noticeable even at very great dilution. Other substances on the contrary cause a decrease in the length of the periods, i. e., they hasten the recurrence of the maxima. Such are nitric acid and the nitrates, chlorates, bromates, etc. These are all oxidizing agents, while the retarders are all reducing agents; it is of interest to note that hydrogen peroxide falls into the latter class according to its action here.

The vibrations may also be observed when a galvanometer is put in circuit with the dissolving chromium and a platinum electrode placed in the vessel. The maxima and minima correspond to a potential difference in the metal of about 0.1 V.

A. P. S.

Periodic phenomena in the solution of chromium in acids, II. W. Ostwald. Zcit. phys. Chem. 35, 204 (1900). — Pursuing the investigation, the author finds that a piece of chromium in the first stage of solution apparently gives up to the acid its power of calling forth the phenomenon of vibration; for if the same piece of metal be washed and transferred to fresh acid, it vibrates for a time and then becomes dormant, but if it be allowed to carry with it a small quantity of the original acid, the vibrations continue for a considerably longer period. If after it has become dormant it is again transferred to the original acid, the vibrations begin anew; and the acid which has already been in contact with a vibrating piece, acts the same as the original acid. This "active" acid retains its property for weeks, but can be weakened by dilution with fresh acid. The property is shown not to be due to chromium or hydrogen in solution. It is not regained by a dormant piece when allowed to remain in the air. These results which seemed to involve the whole problem in a further degree of com-

plexity, were at last found to be due to the influence of the little bags in which the pieces of chromium were hung, for when these were suspended in glass they were no longer active; this refers however only to one preparation of the metal, made by fusion with gypsum, for the original stock showed the phenomenon of vibration, no matter how suspended. It was found then that the material of the bags contained starch, and this as well as dextrine was shown to have a very marked influence in bringing about the phenomenon of vibration. The influence of dextrine is noticeable even at a dilution of 0.00001 per cent. Inorganic colloids have no effect, but analogous organic substances, such as gum arabic, gum tragacanth, etc., show a marked action; the experiments on these substances lead in the end to the conclusion that the "dextrine" action is a property of all carbohydrates, and is the more developed the higher the molecular weight. The action of these bodies was not the same on the original first sample of chromium, with which their action brought forth great irregularities.

The rest of the article is given up to a more exact study of the described curves, and the conditions favorable or unfavorable to their uniformity.

A. P. S.

Action of bromine on phenyl-sulphon-acetic acid in phenyl-sulphon-propionic acid in aqueous solution; a contribution to chemical kinetics. L. Ramberg. Zeit. phys. Chem. 34, 561 (1900). — The reaction, which results in the formation of dibrom-methyl-phenyl-sulphone, carbon dioxide, and hydrobromic acid, probably occurs in one of two ways:

(a) 
$$C_6H_5SO_2CH_2COOH + 2Br_2 = C_6H_5SO_2CHBr_2 - CO_2 + 2HBr$$
.

In this case it is truly a trimolecular reaction, and should give a constant when the ordinary formula is applied.

- (b) It may go on in stages, as:
  - (1)  $C_6H_5SO_2CH_2COOH + Br_2 = C_6H_5SO_2CHBrCOOH + HBr.$
  - (2)  $C_6H_5SO_2CHBrCOOH + Br_2 = C_6H_5SO_2CBr_2COOH + HBr$ .
  - (3)  $C_6H_5SO_2CBr_2COOH = C_6H_5SO_2CHBr_2 + CO_2$ .

In this case, if (1) goes on with measurable velocity and (2) instantaneously, the reaction will be purely bimolecular; if the velocities of (1) and (2) are alike, the reaction velocity follows a more complex formula which contains two constants. Since the concentration of unchanged bromine is the value used to determine the course of the change, reaction (3) does not come into consideration at all. The reaction of bromine on  $\alpha$ -phenyl-sulphon-propionic acid, which results in the formation of the substance  $CH_3(C_6H_5SO_2)CBrCO_2H$  is also studied, and the author is led to the following conclusions: The first of the two reactions goes on in several stages, while the second is a case of simple substitution. For very dilute solutions the reaction velocity is in both cases approximately proportional to the product of the concentration of the substances; but in concentrated solution to the product of the concentration of the acid and the square root of the concentration of the bromine. The relative velocity of the reaction increases with increasing dilution.

A. P. S.

On the velocity of solution of solid bodies. L. Bruner and S. Tolloczko.

Zeit. phys. Chem. 35, 283 (1900). — The authors have determined the rate of solution of a number of substances and are led to give their support to the theory of Noyes and Whitney, that the whole question is one of diffusion; that the dissolving substance is always surrounded by a thin layer of saturated solution, and hence that the problem of a direct action between solid and unsaturated solution is beyond our reach. The formula employed contains a factor representing the area exposed at the beginning, and gives a very satisfactory constant; yet the surfaces show erosion at the end, hence the actual area suffers considerable change during the process; this lends support to the assumption that the action is really between a film of saturated solution and the surrounding medium, and not between this and the surface of the solid itself.

A. P. S.

The effect of hydrobromic acid on the rate of reaction of bromine on trimethylene. G. Gustavson. Comptes rendus, 131, 273 (1900). — The addition of traces of HBr5H<sub>2</sub>O causes bromine at first to react very readily with trimethylene. The author attributes the final decrease in the reaction velocity to the breaking up of the combinations of bromine with hydrobromic acid, an explanation which is so vague as not to deserve the name of an explanation at all.

W. D. B.

The combustion of gases. S. Tanatar. Zeit. phys. Chem. 35, 340 (1900). — It is well known that a mixture of gases which explode — say hydrogen and oxygen — in combining proportions will do so in the presence of a foreign gas, or of an excess of one of these gases themselves, only when the quantity of the inactive gas is below a certain percentage, generally a moderately high one. The author finds that as little as 11-12 percent of propylene prevents the explosion of hydrogen and oxygen, and gives as an explanation that the oxygen goes to the combustion of the propylene and not of the free hydrogen, the products being carbon monoxide and water.

A. P. S.

On the velocity of the explosion wave in acetylene. M. Berthelot and H. Le Chatelier. Ann. Chim. Phys. (7) 20, 15 (1900). — Reviewed (4, 413) from Comptes rendus, 129, 427 (1899).

On the explosion of potassium chlorate. M. Berthelot. Ann. Chim. Phys. (7) 20, 11 (1900). — Reviewed (4, 413) from Comptes rendus, 129, 926 (1899).

## Electromotive Forces

On the electrocapillary functions of aqueous solutions. Gony. Comptes rendus, 131, 255 (1900). — The author has studied the form of the pressure-potential curve for different electrolytes in capillary tubes. The variation in the height of the column from the value for sulphuric acid is as much as ten percent in some cases. The curves are not symmetrical, the positive side and the maximum varying with the nature of the anion, while the nature of the cathode determines the form of the negative side.

W. D. B.

The potential of silver in solutions of its mixed salts. F. W. Küster and A. Thiel. Zeit. anorg. Chem 23, 25 (1900).—The potential of difference between silver and a solution obtained by precipitating silver nitrate with varying

relative amounts of potassium chloride and bromide varies continuously with the amount of bromide. [Cf. 4, 635].

W. D. B.

On the potential of the iodine electrode. F. W. Küster and F. Crotogino. Zeit. anorg. Chem. 23, 87 (1900). — A preliminary notice. The complete paper was reviewed (4, 697) from Zeit. anorg. Chem. 24, 225 (1900).

The decomposition voltage of fused and solid electrolytes. C. C. Garrard. Zeit. Elektrochemie, 6, 214 (1899); Zeit. anorg. Chem. 25, 273 (1900).— The author has determined the decomposition points for fused lead chloride, lead bromide, lead iodide, cadmium chloride, cadmium bromide, cadmium iodide, silver chloride, silver bromide, silver iodide, sodium iodide, potassium iodide, zinc chloride, zinc bromide, cuprous chloride; for solid lead bromide and silver iodide; for saturated solutions of lead chloride, cadmium chloride, and oxalic acid

Some of the salts showed two decomposition points. With lead bromide and with oxalic acid a marked increase of internal resistance was obtained as soon as the decomposition point was passed.

W. D. B.

The thermo-electricity of steels. G. Belloc. Comples rendus, 131, 336 (1900). — The change of the electromotive force with the temperature shows two minima and one maximum for soft iron containing only a trace of carbon, soft steel containing three-tenths percent carbon, and hard steel containing 1.25 percent carbon.

W. D. B.

## Electrolysis and Electrolytic Dissociation

Study of the electrolysis of alkali chloride solutions, with a diaphragm. F. Foerster and F. Jorre. Zeit. anorg. Chem. 23, 158 (1900). — An exhaustive discussion of the losses due to the evolution of oxygen, formation of hypochlorites, and diffusion of caustic potash into the anode chamber. This last is the most serious difficulty and one that seems unavoidable unless one invents a diaphragm impermeable to hydroxyl as ion, discovers a non-aqueous solution corresponding to pyridine for lithium chloride, or uses a mercury cathode. Experiments are also given illustrating the theoretical views. With platinum iridium anodes, the yield in alkali drops rapidly from about ninety to about fifty-five percent, while the yield of chlorine is somewhat lower. Carbon anodes, if of good quality, do not alter the conditions appreciably, though there is of course some evolution of carbon dioxide, also some disintegration. The diaphragm used was Pukall's material and probably gave better results than would any of the substances used in technical work.

W. D. B.

The electrolysis of fused salts. R. Lorenz. Zeit. anorg. Chem. 23, 97 (1900). — Attention is called to the sources of error in the electrolysis of fused salts. Owing to diffusion and distillation the yield may drop to zero and the determinations of decomposition values may be worthless. For more extensive experimental data, see the paper by Helfenstein (4, 636).

W. D. B.

Electrolysis of concentrated hypochlorite solutions. A. Brochet. Comptes rendus, 131, 340 (1900). — When a concentrated sodium hypochlorite solution

is electrolyzed, the reduction is at first greater than the oxidation. This ceased to be the case as soon as the hypochlorite concentration fell below seven percent.

W. D. B.

Electrolytic precipitation of bismuth. D. Balachewsky. Comptes rendus, 131, 179 (1900). — The important points in getting a good adherent deposit of bismuth are: slightly acid solution; absence of large amounts of Cl, Br, and I; maximum current density 0.00060 amp/cm<sup>2</sup>; matt electrodes. W. D. B.

Electrolytic determination of cadmium. D. Balachewsky. Comptes rendus, 131, 384 (1900). — Cadmium can be precipitated quantitatively on a copper cathode from a cadmium sulphate solution acidified with nitric acid, the current density changing from 0.004 amp/cm² at the beginning to 0.006 amp/cm² at the end of the operation. A method similar to that for bismuth (preceding review) can also be used.

W. D. B.

On the dissociating powers of some inorganic solvents. P. Walden. Zeit. anorg. Chem. 25, 209 (1900). — The author has investigated the solvents BCl<sub>3</sub>, PCl<sub>3</sub>, PBr<sub>3</sub>, SbCl<sub>5</sub>, SiCl<sub>4</sub>, SnCl<sub>4</sub>, SO<sub>3</sub>, Br<sub>2</sub>, POCl<sub>3</sub>, AsCl<sub>3</sub>, SbCl<sub>3</sub>, S<sub>2</sub>Cl<sub>2</sub>, SOCl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>, the first eight of which show no dissociating tendency, while the remaining six dissociate binary salts to a greater or lesser extent.

The following empirical conclusions are formulated:

Binary salts are the most easily dissociated electrolytically.

Acids, ternary salts, and quarternary salts are often practically undissociated in solvents in which binary salts conduct well.

The dissociating power of a solvent is a function of its nature, and of the type and nature of the solute.

If we arrange the inorganic solvents according to the periodic system, we find that the elements N, P, As, and Sb of the fifth group, and O and S of the sixth group, in combination with one another, with hydrogen, or with the halides, are the ones which furnish the dissociating solvents.

W. D. B.

The effect of non-electrolytes on the conductivity of electrolytes. A. Hantzsch. Zeit. anorg. Chem. 25, 332 (1900).—Addition of small amounts of urea, alcohol, acetone, ether, urethane or pyridine to solutions of sodium chloride, potassium chloride, sodium hydroxide or hydrochloric acid causes changes of conductivity of less than ten percent. Pyridine and thiourea decrease the conductivity of silver nitrate thirty percent or more, while ammonia has a very slight effect. From this, the author concludes that all three substances form compounds in solution with silver nitrate. Something more than "logic's priceless gift" is to be discerned here.

W. D. B.

Salt formation in alcoholic solution. S. Tanatar and B. Klimenko. Zeit. phys. Chem. 35, 94 (1900). — The authors bring forward some further material in support of certain observations recorded in an earlier paper (3, 431). The data here recorded are the heats of neutralization of potash and ammonia with five organic acids.

A. P. S.

#### Dielectricity and Optics

On uranium radiation. H. Becquerel. Complex rendus, 131, 137 (1900). —

The author mixes uranium chloride with barium chloride and then precipitates the barium as sulphate (method of Debierne). The barium sulphate carries down with it a radio-active substance. After eighteen such operations, the uranium salt in solution is found to be only one-sixth as active as at first. It is therefore uncertain whether the activity of uranium salts is or is not due to uranium.

W. D. B.

An artificial radio-active barium. A. Debierne. Comptes rendus, 131, 333 (1900).—If barium chloride be allowed to stand in a solution containing a very active salt of actinium, it becomes itself active and this activity may be intensified by recrystallization. The spectrum of this barium chloride does not show the lines of radium and the salt loses its activity in time.

II. D. E.

The spectrum of radium. E. Demarçay. Comples rendus, 131, 258 (1900).

— A sample of fairly pure chloride of radium showed a weak barium spectrum while the radium lines, especially 3814.7, 4340.8 and 4683.2, were very distinct. No new radium lines were detected.

W. D. B.

Gadolinium. E. Demarçay. Comptes rendus, 131, 341 (1900).—The author has prepared a considerable quantity of the double nitrate of magnesium and gadolinium, and gives in tabular form the spectral lines of gadolinium and their relative intensities. The most persistent are 3549.3 and 3545.7.

W, D, B,

On some new spectra of the rare earths. E. Demarçay. Comptes rendus, 131, 386 (1900). — The wave-lengths are given for eight lines belonging presumably to turbium. There is also a discussion of several groups of rays which cannot be assigned definitely to any element. W. D. B.

On organic solutions of ferric chloride. Oechsner de Coninck. Comptes rendus, 131, 275 (1900).—In solutions containing no water and no methyl alcohol, dissolved ferric chloride gives off chlorine only after long exposure to sunlight.

##. D. B.

New investigations on argon and its compounds. M. Berthetot. Ann. Chim. Phys. (7) 19, 66 (1900). — Reviewed (4, 419) from Comptes rendus. 129, 71 (1899).

On the combination of carbon bisulphide with hydrogen and with nitrogen. II. Berthelot. Ann. Chim. Phys. (7) 19, 145 (1900).—Reviewed (4, 419) from Comptes rendus, 129, 133 (1899).

Note on the combination of nitrogen with oxygen. *M. Berthelot. Ann. Chim. Phys.* (7) 19, 154 (1900).—Reviewed (4, 419) from Comptes rendusing, 137 (1899).

Action of argon and of nitrogen on mercury alkyls. M. Berthelot. Ann. Chim. Phys. (7) 19. Sg (1900). — Reviewed (4, 419) from Comptes rendus, 129, 378 (1899).

# Crystallography, Capillarity and Viscosity

On the composition of the surface layers of aqueous solutions. J. v. Zawidski. Zeit. phys. Chem. 35, 77 (1900). — Saponine was added to solutions of hydrochloric and acetic acids in water, and air bubbles were then blown through. The foam was collected and analyzed. It was found to be more concentrated than the original solutions, though the difference is small.

A. P. S.