

sulphuric-hydrofluoric method. The fusion process was, therefore, abandoned, partly on account of the difficulty of getting sodium and potassium carbonates free from silica. There is usually only a small amount of silica present in these rocks, often from 0.12 per cent. to 0.75 per cent. The paper referred to further shows that the evaporation to dryness and stirring to a fine powder is not necessary in these analyses, as the same result in silica can be obtained in two or three hours less time by simply dissolving the fine dolomite powder with hydrochloric acid, and considering the undissolved residue as silica, which it really is. This experiment, coupled with the work of the petrological microscope, showed that the silica present is not in the form of a silicate, but in the uncombined condition. The writer has worked with dolomites from various localities, but does not recall an instance where the silicate could not be decomposed by the digestion with hydrochloric acid. This, of course, would not be the case if the silicate consisted of particles of granite, syenite or similar rock.

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October 12, 1904.

REVIEW.

RECENT WORK IN INORGANIC CHEMISTRY.

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Received November 2, 1904.

THE past twelve months have been characterized by an unusually large number of papers in the various journals in the field of inorganic chemistry. These papers are increasingly concerned with the application of the methods and theories of modern physical chemistry to the solution of the problems of inorganic chemistry, or perhaps we should more correctly say that the so-called physical chemistry is being more and more incorporated as an integral part of general chemistry. The result is an almost new inorganic chemistry. Another division of the subject which is beginning to yield important results is that of mixed organic-inorganic compounds, such as "complex" salts with organic acids. The rapid breaking-down of the lines between the different divisions of chemistry progresses, a growing protest against the breaking-up of our chemical societies into those confined to special departments.

During the past year the subject of greatest interest has been.

radium and the various problems connected with it. The most important fact which has been presented to chemists for many years is that discovered by Sir William Ramsay (*Proc. Roy. Soc.*, 72, 204; 73, 346; *Compt. Rend.*, 138, 1388) that the emanation given off by radium contains helium. The emanation itself can be condensed by the use of liquid air and is luminous. It has an appreciable vapor pressure and obeys Boyle's law. Judging from its spectrum it appears to be a monatomic gas and for it Ramsay proposes the name of *Exradio*. From the emanation, which has an atomic weight of about 160, helium is given off, 1 gram of radium bromide furnishing in a year 0.0022 mg. of helium. Later, as yet unpublished experiments by Ramsay, indicate that there is also a substance given off from radium which possesses properties very similar to those of lead. If the average life of a radium atom is only 1,100 years, as estimated by Ramsay, a source of radium must be looked for in some atom of higher atomic weight such as uranium, as suggested by Thomson and Rutherford. Boltwood has examined a large number of uranium minerals (*Eng. Min. J.*, 77, 756; *Am. J. Sci.*, (4) 18, 97) and finds that the proportion of radium to the uranium present is quite constant. Barker (*Ibid.*, (4) 16, 161) had already examined a number of thorium minerals which were free from uranium, such as monazite sand from North Carolina, and found a complete absence of radio-activity, and Hofmann and Zerbau (*Ber. d. chem. Ges.*, 36, 3093) examining also thorium minerals, find that their radio-activity is proportional to the uranium they contain. The decay of the radium atom is considered at length from a theoretical standpoint by McCoy (*Ibid.*, 37, 2641). He finds it probable that the successive decomposition products are as follows: $Ur \rightarrow UrX \rightarrow Ra \rightarrow RaEm \rightarrow EmX \rightarrow He$. Since the decay of UrX , $RaEm$ and EmX is very rapid, their quantity in proportion to that of radium is very small. The amount of helium in uranium ores is not proportional to the amount of uranium on account of its diffusibility; the amount of radium is about $\frac{1}{300,000}$ part of the content of uranium. The experimental results of McCoy agree with those of Boltwood.

The spark spectrum of radium has been carefully studied by Runge and Precht (*Sitzungsber. Akad. Wiss.*, Berlin, 1904, p. 417; *Ann der Phys.* (4) 14, 418) and its character found to be that of an alkaline earth metal, while Crookes (*Proc. Roy. Soc.* 72, 295) has photographed the ultra-violet spectrum, and his photographs are reproduced in his paper. The electrical conductivity of radium bromide solutions has been found by Kohlrausch and Henning (*Verh. d. phys. Ges.*, 6, 144) to be very similar to that of barium, neither the high atomic weight nor the ionizing influence of radium having any especial effect upon its electrical conductivity. The calorific effect of radium has been further studied by Rutherford and Barnes (*Phil. Mag.* (6), 7, 202), and by

Precht (*Verh. d. phys. Ges.*, 6, 101). The former find the evolution of heat rather more than 100 cal. per hour per gram of radium. After expelling the emanation of radium by heat and condensing the emanation by liquid air they find that the radium and the emanation give complementary time curves. Seventy-five per cent. of the evolution of heat is to be attributed to the emanation and its decomposition products. The heat activity of radium, which has lost its emanation, gradually increases, while that of the emanation gradually decreases. The conclusion is drawn that the evolution of heat is a phenomenon which accompanies the successive transformations of radium. Precht, using three different methods and different radium preparations, obtains results which agree very closely (113.3 cal. per hour) and considers that the heat evolution of radium probably has the significance of a physical constant.

F. Rinne has examined (*Centrbl. f. Min. u. Geol.*, 1903, p. 134) radium bromide from a crystallographical standpoint and finds that it resembles in every respect the corresponding barium salt, so that he places the element chemically, spectroscopically, and crystallographically in the magnesium, calcium, strontium, barium group. Others also have confirmed this conclusion. The rapidity with which the stains caused by radium on glass disappear is found by Georgiewsky (*J. Russ. Phys. Chem. Soc.*, 36, 1) to increase with the temperature, but they also disappear very slowly at ordinary temperature. The same is true of the more slowly formed spots on quartz. Mica is superficially colored, while gypsum and Iceland spar are not colored at all. All these minerals are, however, affected in their optical properties, which Georgiewsky thinks is due to a dissociation. A thin sheet of aluminum was found by Orloff (*Ibid.*, 36, 41) after several months' exposure to radium bromide, to be covered with little drops which appeared to be melted metal. These drops were radio-active and retained this activity unchanged after washing, boiling with water, heating to 320°, and even after keeping for seven months. Crookes (*Proc. Roy. Soc.*, 74, 47) finds that diamonds are hardly affected by the β -rays of radium, but on embedding in radium bromide are colored dark on the surface. This layer of color was removed by the nitric acid-potassium chlorate mixture, but the whole mass of the diamond previously of yellowish tint, had become faintly bluish-green.

Regarding the other supposed radio-active elements, although much work has been put upon them the past year, notably by Marckwald, Debierne, Hofmann, Zerban, von Lerch and others, no definite results seem to have been obtained and much confusion still exists. Pellini (*Gazz. chim ital.*, 33, ii, 35) suggests that the anomalous high atomic weight of tel-

lurium is probably due to the presence of a small admixture of a radio-active element closely resembling tellurium, with an atomic weight of about 212, which it has been thus far impossible to isolate from tellurium.

Both Grüne (*Ber. d. chem. Ges.*, 37, 3076) and Hofmann (*Ibid.*, 37, 3407) have been able to prepare very strongly phosphorescing zinc blende by the addition of minute quantities of other elements to the zinc solution before precipitation with hydrogen sulphide. Grüne obtains the best results by using copper, while Hofmann uses magnesium in the presence of common salt. Both obtain striking results with manganese.

The electrical conductivity of non-aqueous solutions continues to attract some attention—not as much as it deserves—but no generalizations have as yet been reached, nor indeed any approach to them. Plotnikoff (*Ztschr. phys. Chem.*, 48, 220) has studied bromine as a solvent. Its solutions of the bromides of aluminum, arsenic, tin and sulphur are not conductors. Its solutions of the bromides of phosphorus and of antimony conduct, as well as those of the double compounds of aluminum bromide, with carbon bisulphide and ethyl bromide. In general the specific conductivity increases with concentration. In all these cases complex compounds seem to be formed and according to Plotnikoff the formation or presence of complex compounds appears to be the condition of conductivity. McIntosh, Walker and others (*Proc. Roy. Soc.*, 73, 450, 454; *J. Chem. Soc. (Lond.)*, 85, 1082, 1098, 1106) have worked with the liquid hydrogen compounds, HCl, HBr, HI, H₂S, and H₃P, and also with organic solvents. The hydrogen compounds dissolve mere traces of metallic salts, but many organic substances are readily dissolved, such as amines, amides, nitriles, alcohols, ketones, ethers, acids and esters. In every case where a conducting solution is formed, the solute contains an element which is capable of assuming a higher valence. Walker holds that so far from being a prerequisite of chemical action, ionization is to be looked upon as a generally necessary result of chemical action. Like Plotnikoff, he considers that the non-ionizing solvents become conductors only through reaction with the solute. The whole subject of the reactions of salts in non-aqueous solutions is being exhaustively studied by Naumann and his pupils (*Ber. d. chem. Ges.*, 37, 3605, 4328).

The question as to whether magnetism is capable of influencing chemical reactions has been taken up again, this time by Schweitzer (*Phys. Ztschr.*, 4, 852), and a series of experiments carried out on both silver and iron salts by the aid of a powerful electro-magnet. The silver halogen salts were used in the form of gelatine emulsion plates and of the iron salts the ferric oxalates and tartrate were studied in solution. In no case were any changes discoverable in

the magnetic field nor were the photochemical reactions accelerated or retarded.

A considerable amount of work has been done by Euler (*Ber. d. chem. Ges.*, **36**, 2878, 3400; **37**, 2391; *Arkiv. för Kemi, Min. och Geol.*, **1903**, i, 77) on the constitution of complex ions, particularly those containing silver, zinc and cadmium, and also on the change of trivalent nitrogen into quinquivalent. The latter he attempts to handle in a quantitative manner, based on the theory of electrolytic dissociation and the law of mass action. For the equilibrium of ammonia in aqueous solution he proposes the following equation,

$k = \frac{K_{H_2O}}{K_2 \cdot K'_2}$, where K_2 and K'_2 are the following constants,

$C_{NH_4^+} \cdot C_{OH^-} = K_2 \cdot C_{NH_3} \cdot C_H$ and $C_{NH_3} \cdot C_H = K'_2 \cdot C_{NH_4^+}$. Here the

assumption is made that the nitrogen atom can take up positive as well as negative charges, but this is only the expression of the fact that the nitrogen atom can unite with four positive and one negative atom to form a stable compound. Euler applies the same principle to other cases of variable valence. He also takes the position that the composition of all chemical compounds and molecular compounds is to be conceived of simply as a function of a valence force ("Valenzkraft") which is probably of an electrical nature, and also, according to van't Hoff, a function of the temperature, the pressure, and sometimes of the solvent. In his last paper, discussing certain platinum bases, he holds that as far as regards its basicity ammonia can play a passive rôle, just as water can at times be basic and not basic. A somewhat different mathematical treatment of complex compounds and ions is given by Bodländer (*Ber. d. chem. Ges.*, **36**, 3933), in which he makes use of what he calls ergochemical decomposition equations.

Cain (*Chem. News*, **90**, 39, 52) considers that in ammonium compounds the fourth hydrogen atom is not attached to the nitrogen and would express the hydroxide and chloride by the formulas $H_3N=OH_2$ and $H_3N=ClH$, the chlorine being trivalent and the oxygen quadrivalent. In ammonium sulphate the fourth hydrogen atoms are attached to the oxygen atoms which are here also quadrivalent. A similar reasoning is extended to the more complex ammonia compounds and used also as an explanation of the isomerism in one of these compounds. The subject is also treated by LeBel (*J. Chim. Phys.*, **2**, 340) from a stereomeric standpoint.

Some little work has been done upon other complex salts, but here again far less than the subject deserves. Smith has continued his researches (this Journal, **25**, 1223, 1227, 1229) upon the complex tungstic acids, preparing ammonium vanadico-phosphotungstates containing silicon, titanium, zirconium, thorium, and bivalent tin. He has also prepared ammonium vanadium tungstates in which the vanadium is in the V_2O_3 form and those in which the

vanadium is represented by V_2O_4 . Again he has prepared a series of complex tungstates with Al_2O_3 , Fe_2O_3 , Cr_2O_3 , Ni_2O_3 , Mn_2O_3 , and Bi_2O_3 . The aluminotungstates are very stable, and the bismuthotungstates separate as a yellow oil, which can be brought to crystallization. Kehrman (*Ztschr. anorg. Chem.*, **39**, 98) has investigated more fully the silicotungstates and finds that the composition of Marignac's potassium salt should be $7K_2O \cdot 2SiO_3 \cdot 20WO_3$. While Smith's manganese tungstates appear to contain Mn_2O_3 , Just (*Ber. d. chem. Ges.*, **36**, 3619), working in the presence of sodium persulphate, has obtained a manganese tungstate containing MnO_2 , to which he gives the formula $Mn(WO_4Na)_4 \cdot Na_2WO_4 \cdot 18H_2O$. He also has prepared complex salts in a similar way containing manganese and polytungstic acid, as well as metatungstic acid. Some attention has been paid to the complex salts with organic acids, Grossmann (*Ztschr. anorg. Chem.*, **41**, 43) having studied the molybdo-oxalates as well as tungsto-tartrates and citrates, especially with reference to their electrical conductivity. Mandel (*Ibid.*, **37**, 252) has examined quite a large series of complex salts of zirconium with organic acids. In the case of acids with hydroxyl groups attached to adjacent carbon atoms, as tartaric acid, he considers that the zirconium replaces the hydrogen of the hydroxyls.

Following out the work of Werner, Pfeiffer (*Ber. d. chem. Ges.*, **37**, 4255) has begun a series of researches upon the stereochemistry of chromium, basing his theories largely upon the study of the ethylene diamine bases. The work thus far prosecuted in every way substantiates the results which Werner has obtained with the platinum bases.

According to Werner, the compound $Pt(PCI_3)_2Cl_2$ is to be considered as analogous to $Pt(NH_3)_2Cl_2$, but the compound $Pt(PCI_3)Cl_2$ has no analogue in the ammonia series. Rosenheim (*Ibid.*, **37**, 394), from a study of the ethyl ester of phosphorous acid, concludes that the conjecture of Werner is correct. In the case of $Pt(PCI_3)Cl_2$ the platinum would seem to have a coördination number of four, but in the derivative ethyl ester compound molecular weight determinations, both by freezing and by boiling point in benzene, show that the formula must be doubled, so that it is probable that the formula of the chloride should be $PCI_3 \cdot Cl_2 \cdot Pt \cdot Pt \cdot Cl_2 \cdot PCI_3$. Oxidation with chlorine and bromine gave rise to platinum compounds of phosphoric ethers which form beautiful purple crystals. He also describes in the paper the preparation of pure $PtCl_4$ by heating dry chlorplatinic acid in chlorine at 275° in a diphenylamine bath, a method which gives excellent results.

Passing to a consideration of the elements and their simpler compounds, Tutton has continued his work on the relations that exist between the metals of the alkalis in their compounds and extended it to ammonium (*J. Chem. Soc. (Lond.)*, **83**, 1049).

Taking up ammonium sulphate and its constants he finds that in nine properties, which include solubility, molecular volume, and optical properties, ammonium lies between rubidium and cesium and nearer to the former. In some respects it stands slightly nearer cesium. He thinks it remarkable that the replacement of potassium by a group of five atoms should have less effect upon the molecule than its replacement by the single cesium atom. It is his view that either the atoms in the molecule have sufficient space at their disposal for the replacement of two atoms by ten without appreciably affecting the external dimensions of the molecule, or else the free space between the molecules must be sufficiently great for the addition of eight atoms to the molecule without increasing the distance between the centers of adjacent molecules. The possibility of atomic compression does not seem to be considered by him.

Two papers by Haber (*Ztschr. anorg. Chem.*, **38**, 377; **40**, 465), on glucinum, have appeared. In the first he gives the explanation of the discrepancies existing in the descriptions of glucinum hydroxide. He finds that it exists in two forms. When first precipitated by alkalis it is voluminous, absorbs carbon dioxide, and is easily soluble in potassium hydroxide and carbonate, in ammonium carbonate and acids. It gradually goes over into a more stable form in which it is granular, less affected by carbon dioxide and insoluble in potassium carbonate, dilute alkalis and dilute acids. In this condition it is rapidly dissolved by hot deka-normal potassium hydroxide. In the second paper he calls attention to the fact that if glucinum hydroxide is dissolved in glacial acetic acid, it can be, to a very large extent (about 90 per cent.), extracted by shaking with chloroform. This affords an easy separation from iron and aluminium. The solution of ferric hydroxide in acetic acid is also soluble in chloroform, but is not extracted by chloroform from the aqueous solution. Tanatar (*J. Russ. Phys.-Chem. Soc.*, **36**, 82) has repeated the work of Lacombe and Urbain (*Compt. Rend.*, **133**, 874; **134**, 772 (1902)) on the basic acetate of glucinum, and from this and his own investigations he comes to the conclusion that glucinum is probably a quadrivalent element with an atomic weight of 18.2. It will be recalled that Lacombe and Urbain drew the conclusion from their work that the ordinary view held of glucinum as a bivalent element is correct. Parsons (this Journal, **26**, 721) has made a study of this basic acetate and used it for the determination of the atomic weight of glucinum, and he has also used the glucinum acetylacetonate for the same purpose.

Baud has continued his researches on aluminium compounds (*Compt. Rend.*, **137**, 492; *Ann. chim. phys.* (8), **1**, 8), particularly on the double compounds of the chloride. He had already prepared compounds with NH_3 (four in number), H_2S , and C_2H_2 . He now finds two compounds with SO_2 ,— $\text{Al}_2\text{Cl}_6 \cdot 2\text{SO}_2$ and Al_2Cl_6 .

SO₂.—and also prepares calcium, strontium, barium and zinc salts of the type 2Al₂Cl₆.3MCl₂. A salt which separates from the hot, rather strongly acid solution of the sulphate, he finds to be Al₂O₃.4SO₃.4H₂O. This is soluble only with difficulty in water.

From determinations of the specific heat Sachs (*Ztschr. f. Krist.*, 38, 495) concludes that indium is trivalent and belongs to the aluminum group. The same is indicated by octahedra appearing in the metal as obtained electrolytically. Besides determining the atomic weight, Thiel (*Ber. d. chem. Ges.*, 37, 175; *Ztschr. anorg. Chem.*, 40, 280) has prepared several new salts, including the sulphides In₂S₃ and In₂S.

Many papers have appeared upon the subject of the rare earths and while some progress has been made, the solution of the problem of their nature seems as far as ever from attainment. Benedicks (*Ztschr. anorg. Chem.*, 39, 41), from a study of the atomic volumes of these elements, favors the suggestion of Brauner that these elements, as a group, take their place in the third and fourth groups between barium and tantalum, and that no maximum in the atomic volume curve occurs in this space. This would eliminate two of the horizontal rows of the Mendeléeff table of the periodic system. This is what has been called the asteroid theory of the rare earths, and it comes much nearer expressing the facts in the case than any other theory which has been proposed. One of the more important pieces of work which has been done upon the rare earths is the solution by Brauner (*Ibid.*, 38, 322; 39, 261) of the problem of the sulphates of cerium, and in particular the determination of the constitution of the puzzling cero-ceric sulphate. He finds that ceric sulphate, Ce(SO₄)₂, forms a complex acid with sulphuric acid (hypothetically H₄Ce(SO₄)₄) which forms, with certain trivalent elements, acid salts, the constitution of the cerium salt being Ce^{'''}HCe^{'''}(SO₄)₄.12H₂O. This is the cero-ceric sulphate. In addition to this Brauner prepared the lanthanum, praseodymium, and neodymium salts of this cerisulphuric acid. He has also prepared the acid sulphates of trivalent cerium, lanthanum, praseodymium, neodymium, samarium, and yttrium. The cerium salt has the formula H₃Ce(SO₄)₃ and should be considered as cero-sulphuric acid. The sulphates of the other metals are analogous. Šterba (*Ann. chim. phys.* (8), 2, 193) has continued his work on cerium, attempting to prepare pure cerous oxide, CeO, by heating the oxalate in a vacuum, or reducing ceric oxide with hydrogen or zinc. While some of the desired product is obtained, it is always contaminated with the higher oxide. Baskerville (this Journal, 26, 46, 54, 71, 67, 75) has examined the various methods of purifying praseodymium and neodymium. For the former he finds the best to be the heating of a saturated solution of citric acid in which impure praseodymium hydroxide is dissolved. Neodymium he precipitates fractionally

with hydrochloric acid gas. His attempts to prepare alums of these earths and of lanthanum were unsuccessful, but a number of new double sulphates were obtained. These contained in no case more than four molecules of water of crystallization. He has also obtained several lanthanates of the alkalis and of barium. Biltz (*Ann. Chem.* (Liebig), **331**, 334) has prepared and studied the acetylacetonates of the rare earths, which are well characterized compounds. He hoped to find the thorium compound well suited for atomic weight determination, but the difficulties were unsurmountable. By fractional crystallization of the magnesium double nitrates in the presence of bismuth Urbain and Lacombe (*Compt. Rend.*, **137**, 792; **138**, 84, 1166) resolved the gadolinium-samarium group and have prepared a considerable quantity of samarium for atomic weight determinations. Large quantities of the earths were fractioned by Muthmann (*Ann. Chem.* (Liebig), **331**, 1, 46, 58, 60) by the magnesium double nitrate method and by the electrolysis of the fused chlorides, the free metals obtained and their properties studied. Various alloys were made, as well as the hydride and nitrides of praseo- and neodymium. The best means of separation of the rare earths is found by R. J. Meyer (*Ztschr. anorg. Chem.*, **41**, 97) to be the potassium double carbonates, and he has studied several series of alkali double carbonates. Baskerville (this Journal, **26**, 922) has further investigated the products obtained by fractioning thoria with carbon in a current of chlorine, isolating a more volatile chloride, and a non-volatile unchanged oxide, while the greater portion distils at a high temperature as true thorium tetrachloride. The more volatile chloride is of a new element, berzelium, with an atomic weight of 212, while the element forming the non-volatile oxide is also new, and named carolinium. Its atomic weight is 255.6. The purified thorium shows an atomic weight of 220.6, or decidedly lower than that of the old thorium. Baskerville deems the elementary nature of berzelium and carolinium as probable, though not yet confirmed spectroscopically. While these are perhaps the more important researches upon the rare earths there have been many other papers on the subject, and it is evident that this difficult field is attracting more and more attention.

During the past year Moissan (*Compt. Rend.*, **137**, 292; **138**, 1558) has described two new carbides from his electric furnace. The first of these is a double carbide of chromium and tungsten. This may be prepared either from the elements or from the oxides. It is very resistant to reagents and scratches the ruby but not the diamond. The other of these products is a new carbide of molybdenum. It is prepared from the metal and carbon in the presence of aluminum. A lower current and shorter heating are used than in making the carbide Mo_2C . The new carbide has the formula

MoC, analogous to that of tungsten and is very resistant to reagents. Moissan thinks that this carbide in the form of a double carbide is present in molybdenum steel. Moissan (*Ibid.*, 138, 1299) has also determined the solubility of silicon in silver, which increases very rapidly with the temperature and is over 40 per cent. at 1470° . A portion of the silicon which crystallizes out is a new modification of the element, soluble in hydrofluoric acid. Dufour (*Ibid.*, 138, 1040, 1101, 1169) finds that at a temperature above the fusion point of silicon this element unites with hydrogen to form SiH_4 in very small quantities. SiO_2 is also reduced by hydrogen at a similar high temperature, as can be shown by passing hydrogen through a quartz tube heated in an oxygen blow-pipe. The apparent volatility of silicon in a Geissler tube in the presence of SiH_4 is really due to the successive decomposition and recombination of the SiH_4 and is not a true volatilization. Quite a number of interesting compounds of silicon have been prepared by Blix (*Ber. d. chem. Ges.*, 36, 4218, 4220), analogous to carbon compounds. Among these are silicon sulphobromide, SiSBr_2 , and silicon thiourea, $\text{SiS}(\text{NH}_2)_2$. The latter is a white amorphous powder which only slowly decomposes in the air. He has also prepared silicon imide, $\text{Si}(\text{NH})_2$; silicam, $\text{Si}_2\text{N}_3\text{H}$; and silicon nitride, Si_3N_4 . The silicam, which is an indifferent powder, unacted upon by water, is prepared by heating the imide in nitrogen to 900° , and by heating to 1200° it is itself converted into the nitride. The analogous titanium amide, $\text{Ti}(\text{NH}_2)_2$, was also obtained.

A boron imide, $\text{B}_2(\text{NH})_3$, is formed by Joannis (*Compt. Rend.*, 139, 364) by the action of ammonia on boron bromide at low temperature. Using phosphorus trichloride at -78° , a mixture of phosphorus amide and imide, or more probably a mixed amide-imide, NH.P.NH_2 , is observed, which above zero begins to decompose into phosphorus imide.

To the very small number of double nitrates known, Wallbridge (*Am. Chem. J.*, 30, 154) has added a double nitrate of potassium and barium which has the composition $\text{K}_2\text{Ba}(\text{NO}_3)_4$. Groschuff (*Ber. d. chem. Ges.*, 37, 1486; *Ztschr. anorg. Chem.*, 40, 1) finds that series of acid nitrates and the alkalis exist of definite composition, as $\text{KNO}_3.\text{HNO}_3$ and $\text{KNO}_3.2\text{HNO}_3$. He compares the latter to $\text{KOH}.2\text{HOH}$.

The effect of light upon the oxidation of metallic arsenic has been tested by Panzer (*Verh. Vers. d. Ntf. u. Aerzte*, 1902, ii, 79), who exposed arsenic mirrors obtained by Marsh's process, under different conditions. In the dark no change took place even in the presence of moisture, but in the sunlight the mirrors disappeared within a few days. The product formed was chiefly As_2O_3 . Cooke (*Proc. Chem. Soc.*, 19, 243) has tested the action of water and of

caustic soda upon metallic arsenic, both in the crystalline and amorphous forms. The action of water on the latter is very slight, but the alkali acts somewhat more strongly, especially when concentrated. The presence or absence of air seems to be without effect. Water and caustic soda are practically without action on crystalline arsenic in the absence of the air, but have some effect when air is present. Dilute alkali has no more effect than water alone. In all cases the arsenic goes into solution as As_2O_3 , and in no instance was arsine observed. Stock and Guttmann (*Ber. d. chem. Ges.*, **37**, 885, 901, 1957) have continued their work on stibine, and described in full its chemical and physical properties. Its decomposition, which may take place explosively, is studied from the standpoint of physical chemistry. Its physiological action was investigated and it was found to be even more poisonous than arsine. When decomposed by oxygen at -90° the yellow modification of antimony is formed very sparingly, and goes over into the black modification at -50° in a few seconds. The work of Koppel on quadrivalent vanadium, which was made note of last year, has been extended to the double oxalates and thiocyanates. The latter salts, of which $\text{K}_2\text{VO}(\text{CNS})_4$ may be taken as a type, are peculiar in that they crystallize with five molecules of water. The sulphates, double oxalates, and halides of trivalent vanadium are obtained by Bultenianu (*Ztschr. Elektrochem.*, **10**, 141) by the electrolytic reduction of vanadates. The alums, previously prepared by Piccini, are dimorphous, existing in a red and in a blue modification. They are convertible, one into the other, by recrystallization, and have the same composition.

Stähler (*Ber. d. chem. Ges.*, **37**, 4405, 4411) finds that in analogy with chromium the violet titanium trichloride is converted by boiling with hydrochloric acid and alcohol into a green modification. This could not be isolated, but the double rubidium and cesium salts were obtained, of the formula $\text{Rb}_2\text{TiCl}_5\cdot\text{H}_2\text{O}$. The corresponding vanadium salt, $\text{Rb}_2\text{VCl}_5\cdot\text{H}_2\text{O}$, was also prepared. The water appears to be an integral part of the molecule, replacing a chlorine atom. There is here an analogy with the violet-red chromium chloride series, $\text{M}_2\text{CrCl}_5\cdot\text{H}_2\text{O}$, of Neumann (*Ann. Chem. (Liebig)* **244**, 329) and the aquo chlorruthenate series, $\text{M}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$, of Howe. In the latter case also the conversion of the ordinary chloride into the aquo salt is by boiling with hydrochloric acid and alcohol.

Cryoscopic studies of the different modifications of sulphur in different solvents have been made by Popoff and by Timofejeff (*J. Russ. Phys.-Chem. Soc.*, **35**, 642, 644). In dimethylaniline and benzene the association of all three modifications is proportional to the concentration, being at a dilution of 0.5 per cent., equivalent to S_6 . By the boiling-point method the molecular

weight of rhombic sulphur corresponds to S_8 in chloroform, to S_8 in carbon bisulphide, while in benzene the value varies from S_8 to S_{10} . Gosio has continued his work on the reducing action of certain micro-organisms, and extended it to tellurium and selenium salts (*Atti. Accad. Lincei*, Rome, (5) 13 i, 422, 642). Tellurates are reduced within two or three minutes by *Hyphomycetes*, while fifteen to twenty minutes are required for arsenic compounds. Selenites are reduced more slowly. It is suggested that this bio-chemical reaction can be utilized to determine the viability of certain micro-organisms. Gutbier has suggested a new method for preparing telluric acid (*Ztschr. anorg. Chem.*, 40, 260), which is an improvement upon the chromic acid method in so far that it yields a purer product. It consists in dissolving the tellurium dioxide in warm caustic soda or potash, and then oxidizing with 15 per cent. hydrogen peroxide. The telluric acid can then be precipitated by nitric acid.

Double chromates with six molecules of water, corresponding to the double sulphates, have at last been prepared. Briggs (*J. Chem. Soc. (Lond.)*, 85, 677) has described several members of the nickel and the magnesium series. He has also prepared a number of the double chromates, as well as the double molybdates crystallizing with ammonia (two molecules). This work of Briggs affords some hope that chromate alums may yet be forthcoming. Working in the same direction as Briggs, Gröger (*Monatsh. Chem.*, 24, 483; 25, 520) obtains much more complex compounds, apparently due to his working at a higher temperature than Briggs. By the action of hydrogen peroxide on chromium hydroxide in the presence of ammonia, Hofmann (*Ber. d. chem. Ges.*, 37, 1663, 3405) obtains a salt of the composition $O_2Cr(OONH_4)_2$, to which he gives the name of "chromatodipersaures Ammonium." On treatment with dilute acetic acid the acid salt $O_2Cr(OONH_4)(OOH)$ is formed. The corresponding silver salt is relatively stable. These salts lose oxygen readily, going over into the chromates. With sulphuric acid in the presence of ether, the familiar blue solution of perchromic acid, $HCrO_5$, is obtained.

By electrolytic reduction Chilesotti (*Atti. Accad. Lincei*, Rome (5), 12 ii, 22) obtains from molybdic acid in hydrochloric acid solution, a solution of trivalent molybdenum, from which double salts can be prepared. The potassium salt has the formula K_3MoCl_6 , while the other alkali salts belong to the type $M_2MoCl_6 \cdot H_2O$, possibly of the same nature as the aquo salts. Engels (*Ztschr. anorg. Chem.*, 37, 125), continuing the work of V. Knorre on the tungsten bronzes of sodium and potassium, has prepared a series of these bronzes containing barium, strontium and calcium. The tungstates of the alkalies have also been further investigated by Schaefer (*Ibid.*, 38, 142).

Ruff and Plato (*Ber. d. chem. Ges.*, 37, 673) have overcome decided experimental difficulties in preparing the fluorides of titanium, tin, and antimony, by the reaction between the chlorides and hydrofluoric acid. The acid is obtained as a perfectly dry liquid by heating potassium hydrogen fluoride; the chloride of the reacting element is added directly to it and the mixture, after standing fractionally distilled. The physical constants of the fluorides were also obtained. For the preparation of anhydrous chlorides Matignon and Bourion (*Compt. Rend.*, 138, 631, 760) heat the oxide in a current of chlorine and sulphur chloride. If the chloride is difficultly volatile an excess of the chloride of sulphur is used; if volatile, an excess is avoided. In this way they have prepared SiCl_4 , 2AlCl_3 , SnCl_4 , ThCl_4 , VOCl_3 , VCl_4 , WO_2Cl_2 , WCl_4 , as well as chlorides of praseodymium, neodymium, samarium, chromium, nickel, iron, and cobalt. Oxides, as well sulphates, carbonates and other oxygen salts of most of the metals can be converted into chlorides. It is thus a method of general application. A paper which has filled out something of a gap in our chemical knowledge is by Hendrixson (this Journal, 26, 747) on the action of metals on chloric acid. In some cases hydrogen is evolved and in most cases at least a part of the chloric acid is reduced to hydrochloric acid. This acid shows no tendency to react with the chloric acid, as there is in no instance a production of chlorine nor were any of the lower oxides or acids of chlorine found. Defacqz (*Ann. chim. phys.* (8), 1, 337) has utilized the reaction between manganese fluoride and the halide salts of other metals to prepare fluorides and fluo-halides. Fluo-chlorides, fluo-bromides and fluo-iodides of the alkaline earth metals have been prepared as crystalline powders and the specific gravity of each has been determined. All have a formula analogous to CaF_2 , CaCl_2 .

From the fact that gold in nature is frequently accompanied by fluor spar, it would seem possible that a fluoride of gold might have played a part in the mineralization of veins. Leuher (this Journal, 25, 1136) has, therefore, tried many different methods to prepare a compound of fluorine and gold, but without success. He, however, calls attention to the fact that a number of years ago Moissan obtained, by the action of fluorine on gold at red heat, a yellow hygroscopic substance which decomposed easily into fluorine and gold. Some time ago Leuher showed that gold was soluble in selenic acid and in a solution of telluric acid in sulphuric or phosphoric acid. This solution might be caused by the splitting-off of oxygen in the nascent state, so Leuher (*Ibid.*, 26, 550) tried to effect the solution of gold by the use of sulphuric acid in presence of oxidizing agents such as MnO_2 , Pb_3O_4 , etc. Under these conditions gold was found soluble, easily when heated, but to some extent even at zero. In most cases phosphoric acid can be sub-

stituted for sulphuric. Berthelot (*Compt. Rend.*, **138**, 1297) finds that both platinum and gold are, to some extent, acted on by fuming hydrochloric acid in the light, especially where there is present a trace of some substance such as MnCl_2 , which can be further oxidized in the air. In complete darkness this action does not take place even when MnCl_2 is present. Quite an extensive study of the oxides of platinum has been made by Wöhler (*Ber. d. chem. Ges.*, **36**, 3475; *Ztschr. anorg. Chem.*, **40**, 423). Platinum has generally been classed as a metal which will not unite with oxygen directly at any temperature. Wöhler finds, however, that under circumstances it may be oxidized. The activity of platinum black seems to be in part due to the presence of an oxide and hydroxide of bivalent platinum. This oxide is very stable and begins to give up its oxygen only at 392° , being completely decomposed at 431° . Wöhler obtains the hexaoxyplatinic acid, $\text{Pt}(\text{OH})_6\text{H}_2$, by boiling chlorplatinic acid with excess of caustic soda and precipitating in the cold with acetic acid. Belluci (*Atti Accad. Lincei*, Rome, (5), **12** ii, 635) had already independently identified the hydrated oxide, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, of Topsoë as being the hexaoxyplatinic acid, and had prepared several of its salts. The only member of the chlorplatinic acid series remaining unknown is the trichlorplatinic acid, $\text{PtCl}_3(\text{OH})_3\text{H}_2$.

Moissan (*Compt. Rend.*, **137**, 229), by heating in the electric furnace a mixture of ruthenium and crystallized silicon, has prepared a ruthenium silicide, RuSi , which he describes as a very hard and exceedingly resistant body. It is peculiar in being the only known compound of ruthenium which is not attacked by potassium hypochlorite. Lind (this Journal, **25**, 928) has submitted potassium nitrosochlorruthenate to an examination from the standpoint of physical chemistry, and finds its behavior to be very much like that of the chlorplatinates. The nitrosochlorruthenates are the only class of halide compounds of ruthenium which form stable solutions. Howe (*Ibid.*, **26**, 543) has described the preparation of the chlorruthenates, M_2RuCl_6 , and the aquochlorruthenates $\text{M}_2\text{Ru}(\text{OH}_2)\text{Cl}_5$, and also of the bromruthenites, bromruthenates and aquobromruthenates. The chlorruthenates could be formed only by the action of chlorine upon the aquochlorruthenates, though Antony has prepared a potassium chlorruthenate by the action of HCl on K_2RuO_4 .

A large amount of interesting work has been done upon colloidal solutions, and this bids fair to attract more attention as time goes on. A rather new line of investigation has been opened up by Hausmann (*Ztschr. anorg. Chem.*, **40**, 110) on the formation of precipitates in jellies. It had been noticed by Liesegang in the case of silver nitrate and ammonium bichromate that the precipitate appeared in layers, and Hausmann finds that this is gen-

erally the case. A number of interesting problems are suggested by this line of work.

Finally mention may be made of the determination of the specific gravity of liquid and solid oxygen, nitrogen and hydrogen at very low temperatures by Dewar (*Proc. Roy. Soc.*, 73, 251), and of the determination of the compressibility of these same gases and of carbon monoxide, between one-half and one atmosphere pressure, by Lord Rayleigh (*Ibid.*, 73, 153). Calculated from these results the atomic weight of nitrogen becomes 14.003, which differs from the generally accepted atomic weight, 14.04, by an amount greater than can be accounted for by experimental errors. The cause of this discrepancy remains to be explained.

NEW BOOKS.

THE PURIN BODIES OF FOOD STUFFS. BY I. WALKER HALL, M.D., Owens College, England. Philadelphia: P. Blakiston's Son & Co. 1904. xiii + 201 pp. Price, \$1.50.

The book under consideration is a revision of the author's first edition of "Purine Bodies." It has been reissued, as the author states in his preface, to meet a popular demand. Several portions of the first edition have been rewritten, and the results of recent investigations included.

The greater part of the book is devoted to investigations undertaken by the author to obtain information as to the physiological action of purine bodies and their metabolism. The author has made estimations of the purine bodies present in the common food-stuffs, and studied their effects upon the metabolic processes in animals and man when introduced into the body subcutaneously or taken by the mouth.

A chapter on the action of drugs upon purine excretion is introduced, and an index and tables of analytical methods are appended.

A commendable feature of the work is the completeness of the literature references. The book is well written and remarkably free from typographical errors. The book should be of interest to all who are interested in physiological chemistry.

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