

Inorganic Chemistry.

Oxyhalogen Compounds. IV. Reaction between Chlorine Peroxide and Iodides. WILLIAM BRAY (*Zeit. physikal. Chem.*, 1906, 54, 731—749. Compare this vol., ii, 221—222).—The nature of the reaction between chlorine peroxide and iodide depends on the nature of the medium in which it takes place. In an alkali hydrogen carbonate solution saturated with carbon dioxide, the reaction is represented by the following equation: $\text{ClO}_2 + \text{I}' = \text{ClO}_2' + \text{I}$ (*a*). When the reaction takes place in a so-called "neutral" solution of chlorine peroxide, which, however, contains traces of acid, the action is represented by $3\text{ClO}_2 + 5\text{I}' = 2\text{IO}_3' + 3\text{I} + 3\text{Cl}'$. When, finally, the reaction takes place in an ordinary acid solution, it is represented by $\text{ClO}_2 + 5\text{I}' + 4\text{H}' = 5\text{I} + \text{Cl}' + 2\text{H}_2\text{O}$. The first stage in all cases is probably $2\text{ClO}_2 + \text{I}' + \text{H}_2\text{O} = 2\text{HClO}_2 + \text{IO}'$, which in a hydrogen carbonate solution saturated with carbon dioxide is immediately followed up by $\text{IO}' + \text{I}' + 2\text{H}' = \text{I}_2 + \text{H}_2\text{O}$, giving (*a*). When a slightly larger trace of acid is present, (*a*) is followed by $3\text{HClO}_2 + 2\text{I}' = 2\text{IO}_3' + 3\text{HCl}$, the only reaction in which a rapid oxidation of iodide to iodate in an acidified potassium iodide solution takes place.

It has been found that iodine is oxidised to iodate in the following reactions: $\text{ClO}_2 + \text{I} + \text{H}_2\text{O} = \text{HIO}_3 + \text{HCl}$ and $5\text{HClO}_2 + 4\text{I} + 2\text{H}_2\text{O} = 4\text{HIO}_3 + 5\text{HCl}$. It is probable that in these cases it is hypiodous acid and not iodine that is the really active substance.

For the detailed evidence in support of the foregoing equations the original must be consulted. There, too, are described methods for the determination of chlorite in the presence of iodate.

It is noteworthy that the reaction between chlorous acid and an iodide is retarded by increasing the concentration of the iodide and is accelerated by the presence of free iodine. It is probable that chlorous acid does not react primarily with hydriodic acid, or does so very slowly, and that an oxidation of the iodide is induced by a primary reaction between chlorous acid and iodine (or hypiodous acid).

J. C. P.

Electrochemical Equivalent of Iodine. GINO GALLO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 24—35).—The author has determined the electrochemical equivalent of iodine by electrolysing a solution of potassium iodide in a specially designed apparatus, the voltage being chosen so that no oxygen was evolved at the anode. The iodine

separating was estimated volumetrically by means of sodium thiosulphate solution, and the silver deposited in a silver voltameter run in series with the potassium iodide cell was also measured. The values obtained in this way for the atomic weight of iodine, compared with $O=16$, vary from 126.82 to 126.98, the mean of the 24 numbers obtained being 126.89. One equivalent of iodine corresponds to 96537 coulombs.

T. H. P.

Change of State of Liquid Sulphur. FRIEDRICH HOFFMANN and R. ROTHE (*Zeit. physikal. Chem.*, 1906, 55, 113—124).—The authors have observed that liquid sulphur about 160° exhibits a behaviour which is probably to be attributed to the transformation of one modification into another (compare Smith and his pupils, *Abstr.*, 1905, ii, 382, 580). When fused sulphur is heated above 160° and is then allowed to cool, not too slowly, it is observed that at about 160° the liquid divides into two layers separated by a meniscus, and thermometric investigation reveals a discontinuity in the cooling curve at this point. If, however, the rate of cooling is diminished, the separation into two phases becomes less distinct and the discontinuity in the cooling curve is less marked. If the rate of cooling is sufficiently slow, neither phenomenon can be observed. Hence, the two modifications must, under ordinary conditions, be completely miscible with each other, and the temperature of 160° cannot be a transition point in the ordinary sense.

J. C. P.

The System Sulphur—Sulphates. KAMILLO BRÜCKNER (*Monatsh.*, 1906, 27, 49—58).—The author has examined the products obtained on heating the anhydrous sulphates of various metals with excess of sulphur. The mixtures were heated in a porcelain crucible, or, when higher temperatures were required, in a hard glass tube through which a current of sulphur vapour was passed.

The sulphates of lithium, sodium, and potassium react at a red heat; sulphur dioxide is evolved and the alkaline residue contains sulphide, thiosulphate, and polysulphide. The sulphates of the alkaline earth metals yield similar products, but react less readily. Magnesium, glucinum, and aluminium do not react at a red heat. Chromic sulphate gives a black sulphide insoluble in hot concentrated hydrochloric acid, cerium sulphate a reddish-brown sulphide decomposed by hydrochloric acid, and uranyl sulphate a mixture of uranous oxide and uranoso-uranic oxide. The sulphates of manganese, zinc, cadmium, iron (ferrous and ferric), nickel, copper, lead, mercury, thallium, silver, and cobalt are converted into sulphides with evolution of sulphur dioxide. Bismuth and antimony sulphates yield bluish-grey sulphides of metallic appearance, but in the case of bismuth, the metal is obtained when a smaller proportion of sulphur is employed.

The mode of formation of the various products is discussed.

H. M. D.

Selenium obtained with Organic Reducing Agents. WILLIAM OECHSNER DE CONINCK and CHAUVENET (*Bull. Acad. Roy. Belg.*, 1906, 601—603).—When selenic acid is heated with formic,

oxalic, malonic, or pyruvic acid, paraldehyde, formaldehyde, trioxymethylene, ænanthaldehyde, benzaldehyde [dissolved in alcohol], or with an aqueous solution of dextrose or lævulose, it is reduced to selenium. Neither succinic nor acetic acid reduces selenic acid.

T. A. H.

Behaviour of Selenium towards Light and Temperature.

II. ROBERT MARC (*Zeit. anorg. Chem.*, 1906, 48, 393—426).—A more detailed account of work already published (this vol., ii, 226).

G. S.

Selenium Dioxide. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1906, 142, 571—573).—One part of selenium dioxide dissolves in 2·67, 2·6, and 2·54 parts of water at 11·3°, 14°, and 15·6° respectively; in 9·84 parts of alcohol (93°) at 14°, in 15 parts of methyl alcohol at 11·8°, in 23 parts of crude acetone at 15·3°, and in 90 parts of acetic acid at 12·9°. The specific gravities of 1—10 per cent. solutions of selenium dioxide in water are tabulated in the original. Reddish-brown amorphous selenium, insoluble in carbon disulphide, separates slowly when aqueous solutions of the dioxide are exposed to light.

Selenium dioxide is converted by nitric acid into selenic acid, by hot sulphuric acid into selenium sulphoxide, SeSO_3 , hydrogen selenide, and some amorphous, reddish-brown selenium; by phosphorus pentachloride into selenium tetrachloride, and by phosphorus trichloride into brown, amorphous selenium. Phosphorus oxychloride is formed in the last two reactions. With hydrazine, the dioxide yields nitrogen and black, amorphous selenium, and when warmed with hydroxylamine hydrochloride, nitrogen is evolved and reddish-brown, amorphous selenium separates.

T. A. H.

Action of Nitrogen Peroxide on Ammonia and on Some Ammonium Salts. ADOLPHE BESSON and GEORGES ROSSET (*Compt. rend.*, 1906, 142, 633—634).—Liquid ammonia reacts explosively with solid nitrogen peroxide at -80° , but if a current of gaseous ammonia at -20° is passed over the peroxide, the reaction is moderated and the products are nitrogen, nitric oxide, water, ammonium nitrate, and a trace of ammonium nitrite. Nitrogen peroxide reacts slowly with ammonium chloride in the cold; the reaction is, however, complete in sealed tubes at 100° with the formation of chlorine, nitrogen, nitrous oxide, nitrogen trioxide, nitrosyl chloride, water, and nitric acid. When ammonium nitrate or sulphate replace the chloride in the above reaction, the products are nitrogen and nitric acid or nitrogen, and a mixture of nitric and sulphuric acids respectively.

M. A. W.

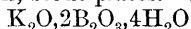
An Instance of Choke Damp free from Carbon Dioxide. BERTRAM BLOUNT (*J. Hygiene*, 1906, 6, 175—178).—"Choke damp" or "black damp" in mines and wells is air deficient in oxygen and rich in carbon dioxide. Very few cases of deficiency in the latter gas have been described. In the present instance it was noticed that

candles would not burn in a room used for cold storage. On analysis, the air was found to contain 17.6 per cent. of oxygen, and the remainder inert gas (nitrogen, argon, &c.). This would account for the extinction of a light, but the amount of oxygen was sufficient not to endanger the lives of workers there, who apparently suffered no inconvenience. The amount of carbon dioxide was negligible and can be accounted for by the presence of workmen. The gas came from a disused well shaft in communication with the room. The clay through which the shaft passed contained iron pyrites, which accounted for the loss of oxygen. Either no carbon dioxide was formed from the carbonates of the clay, or, if any was formed, it must have been subsequently absorbed by the mud and water.

W. D. H.

Borates of the Alkali Metals and of Ammonium. ALBERT ATTERBERG (*Zeit. anorg. Chem.*, 1906, **48**, 367—373).—The work described in this communication was carried out more than thirty years ago, and the author has been induced to publish it in accessible form by the appearance of Auerbach's recent paper (*Abstr.*, 1904, ii, 118) on the same subject. Only mono-, di-, and penta-borates of the metals above mentioned could be obtained; they all melt to clear glasses at a high temperature.

Potassium monoborate, $K_2O, B_2O_3, 3H_2O$, separates from a strongly alkaline solution in small, stout plates. *Potassium diborates*:



occurs in lustrous, six-sided prisms; $K_2O, 2B_2O_3, 5\frac{1}{2}H_2O$ forms short, hexagonal prisms; $K_2O, 2B_2O_3, 6H_2O$ occurs in short, monoclinic prisms. *Potassium pentaborate*, $K_2O, 5B_2O_3, 8H_2O$, crystallises in rhombic octahedra.

Sodium monoborates: $Na_2O, B_2O_3, 4\frac{1}{2}H_2O$ forms four-sided prisms; $Na_2O, B_2O_3, 5\frac{1}{2}H_2O$, long prisms; $Na_2O, B_2O_3, 8H_2O$ forms small, six-sided crystals. *Sodium diborates*: $Na_2O, 2B_2O_3, 5H_2O$, octahedral borax; $Na_2O, 2B_2O_3, 10H_2O$, ordinary prismatic borax. *Sodium pentaborate*, $Na_2O, 5B_2O_3, 10H_2O$, obtained in the form of prismatic crystals, is partially hydrolysed in aqueous solution.

Ammonium diborate, $(NH_4)_2O, 2B_2O_3, 5H_2O$, occurs in tetragonal pyramids; *ammonium pentaborate*, $(NH_4)_2O, 5B_2O_3, 8H_2O$, in rhombic double pyramids.

Barium monoborates: $BaO, B_2O_3, 2H_2O$, a crystalline powder; $BaO, B_2O_3, 4H_2O$, short, four-sided prisms. *Barium sesquiborate*, $2BaO, 3B_2O_3, 7H_2O$, was obtained by interaction of boric acid and excess of barium hydroxide as a voluminous, amorphous precipitate.

G. S.

Hydrates of Sodium Thiosulphate. STEWART W. YOUNG and W. E. BURKE (*J. Amer. Chem. Soc.*, 1906, **28**, 315—347. Compare *Abstr.*, 1905, ii, 32, and Young and Mitchell, *Abstr.*, 1905, ii, 31).—An account is given of twelve crystalline hydrates of sodium thiosulphate and the anhydrous salt. The methods of preparing the various hydrates are described, and the solubility of each has been determined at intervals of 5°, from 0° upwards. Transition points have been determined from the intersections of the solubility curves and in many

cases have also been measured directly. A number of observations has been made with reference to super-cooling and super-heating of the different forms, and it is shown that super-heating is as common in this system as super-cooling and that both probably occur in the neighbourhood of every transition point; both phenomena are probably transitory.

The hydrates are classified in groups on the basis of their behaviour in undergoing transition with rising temperature, and are accordingly termed primary, secondary, tertiary, &c. The following is a list of the hydrates with their transition and melting points. Primary pentahydrate (formerly called α -pentahydrate), m. p. $48\cdot45^\circ$, transition point into the primary dihydrate, $48\cdot17^\circ$. Primary dihydrate (α -dihydrate), transition point into the anhydride, $66\cdot5^\circ$. Secondary pentahydrate (β -pentahydrate), transition point into the secondary tetrahydrate, $30\cdot22^\circ$. Secondary tetrahydrate (originally known as the *d*-form), m. p. $41\cdot65^\circ$, transition point into the secondary monohydrate, $40\cdot65^\circ$. Secondary monohydrate (α -monohydrate), transition point into the anhydride, $56\cdot5^\circ$. Tertiary hexahydrate, which also acts as a quaternary form and was formerly regarded as γ -pentahydrate, m. p. $14\cdot35^\circ$, transition point into the quaternary $4/3$ -hydrate, $14\cdot3^\circ$, and into the tertiary sesquihydrate, $14\cdot25^\circ$. Tertiary sesquihydrate, transition point into the tertiary monohydrate, $48\cdot5^\circ$. Tertiary monohydrate (β -monohydrate), transition point into the anhydride, 61° . Quaternary $4/3$ -hydrate, $3\text{Na}_2\text{S}_2\text{O}_3\cdot 4\text{H}_2\text{O}$, originally called the *c*-form, transition point into the anhydride, 58° . Quintary dihydrate (β -dihydrate), transition point into the quintary monohydrate, $27\cdot5^\circ$. Quintary monohydrate (γ -monohydrate), transition point into the quintary hemihydrate, 43° . Quintary hemihydrate, transition point into the anhydride, 70° .

The paper is illustrated with curves and diagrams.

E. G.

Presence of Chlorate in Sodium Nitrate. LÉON GRIMBERT (*J. Pharm. Chim.*, 1906, [vi], 23, 98—100).—Small quantities of chlorate were found in three samples of commercial sodium nitrate. It is pointed out that this impurity should be guarded against when sodium nitrate is employed in destroying organic matter as a preliminary to the estimation of chlorine in organic products.

T. A. H.

Density of Solutions of Sodium Carbonate and Sodium Hydroxide. II. RUDOLF WEGSCHEIDER (*Monatsh.*, 1906, 27, 13—30. Compare Abstr., 1905, ii, 521).—The interpolation formulæ previously given for the densities of solutions of sodium carbonate and sodium hydroxide were deduced on the false assumption that Lunge's data represent density values referred to water at 4° . The formulæ are now corrected.

H. M. D.

Preparation of Metallic Lithium. OTTO RUFF and OTTO JOHANNSEN (*Zeit. Elektrochem.*, 1906, 12, 186—188).—The electrolysis of mixtures of lithium salts with salts of the other alkali metals always yields impure lithium; the electrolysis of pure lithium chloride is inconvenient on account of the volatility and high resistance of this salt;

the addition of lithium fluoride increases the resistance. The best electrolyte is a mixture of lithium bromide with 13 per cent. of lithium chloride; this is the mixture of lowest melting point (520°), pure lithium chloride and bromide melting at 606° and 546° respectively. With this mixture and using a carbon anode and iron cathode a current of 100 amperes can be maintained with an *E.M.F.* of 10 volts. The current efficiency is about 80 per cent. The metal contained 0.17 per cent. of sodium, but was otherwise pure; its melting point was 180° (corr.). T. E.

Sulphides of Rubidium and Cæsium. WILHELM BILTZ and ERNST WILKE-DÖRFURT (*Zeit. anorg. Chem.*, 1906, 48, 297—318).—In a former paper (Abstr., 1905, ii, 162), the preparation of the pentasulphides of these two metals has been described; in the present communication, an account of the other sulphides is given.

Rubidium monosulphide, $\text{Rb}_2\text{S}\cdot 4\text{H}_2\text{O}$, and the corresponding *cæsium* salt, $\text{Cs}_2\text{S}\cdot 4\text{H}_2\text{O}$, are obtained in colourless, deliquescent crystals on allowing the concentrated aqueous solutions to remain for some time in a desiccator over calcium chloride. The *hydrosulphides*, RbSH and CsSH , obtained in a similar manner from the aqueous solutions, also occur in colourless, deliquescent crystals. Anhydrous monosulphides could not be obtained.

Rubidium tetrasulphide, $\text{Rb}_2\text{S}_4\cdot 2\text{H}_2\text{O}$, was obtained from an aqueous solution containing calculated amounts of the monosulphide and sulphur; it forms small, prismatic, yellow crystals which dissolve unchanged in water, but undergo decomposition on dehydration. *Cæsium tetrasulphide*, Cs_2S_4 , prepared in an analogous manner, forms reddish-yellow prisms, soluble in water without decomposition. No other sulphides of uniform composition could be isolated from monosulphide solutions containing varying proportions of dissolved sulphur, but *disulphides* are apparently obtainable on heating the pentasulphides for some time in a current of hydrogen at $700\text{--}800^{\circ}$.

With the object of determining in a more definite way what sulphides of these metals exist, freezing-point curves of the systems were constructed. In the case of rubidium, the curve starting from the disulphide shows one distinct maximum at a point corresponding with the composition of the pentasulphide, as well as four eutectic points; from the shape of the curve, the conclusion is drawn that tri-, tetra-, and hexa-sulphides also exist; unlike the pentasulphide, they dissociate into their components at temperatures below their melting points. The curve of the system cæsium—sulphur indicates the existence of the same sulphides as in the case of rubidium, but both the penta- and hexa-sulphides give distinct maxima. No indication of the existence of other sulphides than those referred to has been obtained. G. S.

Silver and Arsenic. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1906, 3, 192—195).—The freezing-point curve for alloys containing from 0 to 19 per cent. of arsenic has been determined, and shows only a descending branch, corresponding with the separation of silver crystals. The eutectic horizontal is at 527° , and is unbroken. Within the limits examined, there is no evidence of the existence of a compound of silver

and arsenic, and the existence of a compound Ag_3As (Descamps, Abstr., 1878, 705) is disproved. Microscopic sections show only silver and the eutectic.

Alloys of the same character, containing 87.2—89.5 per cent. of arsenic, are obtained on reducing silver arsenate with potassium cyanide at a low temperature. C. H. D.

Silver-zinc Alloys. G. I. PETRENKO (*Zeit. unorg. Chem.*, 1906, 48, 347—363. Compare Heycock and Neville, *Trans.*, 1897, 71, 417; Herschkowitsch, *Abstr.*, 1898, ii, 582).—The investigation was carried out by Tammann's method of thermal analysis, and the results were controlled by microscopic observations. The observed temperatures of initial crystallisation agree very closely with those obtained by Heycock and Neville.

There are five breaks in the freezing-point curve, at 28.1, 37.7, 47.6, 60, and 95 per cent. by weight of zinc, the first four of which correspond with the compounds Ag_3Zn_2 , AgZn , Ag_2Zn_3 , and Ag_2Zn_5 respectively. The compound AgZn forms complete series of mixed crystals with the compounds Ag_2Zn_3 and Ag_3Zn_2 ; on the other hand, the compounds Ag_2Zn_3 and Ag_2Zn_5 have only a limited mutual solubility, which is also true of the latter compound and zinc, so that there are breaks in the series of mixed crystals. Within certain limits, the structure of the alloys depends on the velocity of cooling, thus, when the compound Ag_3Zn_2 is allowed to cool slowly below 640° , it decomposes into AgZn and a saturated mixed crystal. The compound AgZn exists in two forms which have a transition point at 260° .

The hardness of these alloys reaches its maximum between 47.6 and 60 per cent. by weight of zinc, and the brittleness is also greatest between these limits; the degree of hardness does not depend on the rate of cooling.

Photo-micrographs of several of the alloys are given in the paper.

G. S.

Silver Oxide and Silver Suboxide. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1906, 28, 139—158. Compare *Abstr.*, 1905, ii, 578).—Guntz (*Abstr.*, 1899, ii, 418) has described experiments from which he concluded that when silver oxide is heated in a closed tube at 358° , it decomposes into the suboxide and oxygen, and that the suboxide then suffers partial decomposition until equilibrium is attained. It is now shown that silver suboxide is not produced under these conditions, and that Guntz's results are capable of a different interpretation.

The decomposition pressure of silver oxide has been determined at 302° , 325° , and 445° , and the results show that the equilibrium pressures in the system, silver oxide, silver, oxygen, are approximately 20.5, 32, and 207 atmospheres respectively at these temperatures. Silver suboxide was not produced in any of the experiments, and is probably incapable of existence at these temperatures. From the change of equilibrium pressure with the temperature, the heat of formation of silver oxide has been calculated and found to be 6.4 Cal. It is shown that the average of five determinations of this quantity based on the available calorimetric data is 6.34 Cal., and it is therefore

concluded that the silver oxide which exists between 302° and 445° is, from a thermodynamical point of view, identical with that existing at the ordinary temperature. The decomposition pressure of silver oxide at 25° has been calculated and found to be 5×10^{-4} atmospheres.

E. G

Alloys of Calcium. L. STOCKEM (*Metallurgie*, 1906, 3, 147—149. Compare Quasebart, this vol., ii, 229).—Calcium dissolves in molten cast iron with great development of heat, but when large quantities are used the metal is rapidly coated with a crust of calcium carbide which prevents further action. Some calcium carbide always remains mechanically entangled in the iron. Ferric oxide reacts vigorously with an excess of metallic calcium; the iron formed is pure and ductile, and does not contain a trace of calcium.

Calcium alloys with copper in all proportions. The products are brittle, an alloy containing 20 per cent. of calcium being pure white and crumbling on exposure to air. Copper-calcium may be advantageously employed in place of phosphor-copper for deoxidising copper.

Aluminium and magnesium also alloy with calcium in all proportions. When 10 per cent. of calcium is present, the alloys are so brittle as to be easily powdered in a mortar.

C. H. D.

Hydration of Portland Cement. PAUL ROHLAND (*Zeit. angew. Chem.*, 1906, 19, 327—331. Compare Abstr., 1905, ii, 319).—A study of the influence of a number of different salts on the rate of hydration of Portland cement has shown that sodium carbonate and aluminium salts increase the rate of hydration; moreover, the increase produced by pairs of salts such as sodium carbonate and aluminium chloride or aluminium sulphate and chloride acting together is considerably greater than would be expected from a summation of their individual effects. On the other hand, when two salts such as potassium dichromate and borax, each of which taken alone produces a retarding influence, are allowed to act together, the retardation is less than can be accounted for by adding together the effects due to each one separately. The paper is brought to a close with a theoretical discussion regarding the mechanism of the influence of these various salts, for details of which the original should be consulted.

P. H.

Combustion of Cadmium. WILHELM MANCHOT (*Ber.*, 1906, 39, 1170—1171).—When cadmium is burnt at as low a temperature as possible, the smoke, which consists mainly of cadmium oxide, contains also some cadmium peroxide.

W. A. D.

Oxides of Thallium. I. OTTO RABE (*Zeit. anorg. Chem.*, 1906, 48, 427—440).—When an alkaline solution of a thallos salt is treated with a 3—5 per cent. solution of hydrogen peroxide, anhydrous thallic oxide, Tl_2O_3 , separates as a dark brown, flocculent precipitate which slowly changes to small, lustrous crystals of chocolate-brown colour. If precautions are taken to keep the temperature low and the peroxide is used in excess, the yield is almost quantitative; the excess of hydrogen peroxide undergoes decomposition in a catalytic manner

without affecting the thallic oxide. When, on the other hand, the experiment is carried out at 80—100° in strongly alkaline solution (10—35 per cent. of potassium hydroxide), a black modification of the same oxide is obtained as a heavy, sandy, practically anhydrous powder.

The brown oxide is easily, the black much less readily, soluble in dilute mineral acids; in both cases the process is accompanied by slight reduction to thallos salt. The brown oxide also undergoes partial reduction on boiling with water, whilst the black oxide is scarcely affected. The specific gravities were determined with the pycnometer by displacement of xylene, and are, for the brown modification 9·65 at 21°, for the black 10·19 at 22°. G. S.

Decomposition of an Aqueous Solution of Copper Sulphate by Aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1906, 142, 575—577. Compare *Abstr.*, 1905, ii, 526).—Quantitative investigation of the reactions resulting in the evolution of hydrogen and precipitation of copper, which take place when a bismuth-aluminium alloy containing 94 per cent. of the latter metal is placed in an aqueous solution of copper sulphate, showed that these may be represented by the equations $\text{Al}_2 + 6\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{H}_2$; $\text{H}_2 + \text{CuSO}_4 = \text{H}_2\text{SO}_4 + \text{Cu}$, and $3\text{CuSO}_4 + \text{Bi}_2 = \text{Bi}_2(\text{SO}_4)_3 + 3\text{Cu}$. With a magnesium-aluminium alloy, on the contrary, the whole of the hydrogen produced by the action of the magnesium on the water is evolved, and the copper precipitated is solely the result of the action of the aluminium on the copper sulphate, thus: $3\text{Mg} + 6\text{H}_2\text{O} = 3\text{Mg}(\text{HO})_2 + 3\text{H}_2$ and $3\text{CuSO}_4 + \text{Al}_2 = \text{Al}_2(\text{SO}_4)_3 + 3\text{Cu}$. With a tin-aluminium alloy, hydrogen is evolved and metallic copper is precipitated, but the reaction soon stops owing to the formation on the surface of the alloy of an insoluble layer of alumina. In all three cases, the alloys used were previously filed to produce roughened surfaces. A polished and re-heated fragment of the magnesium-aluminium alloy, when immersed in the copper sulphate solution, acquired after ten hours a hard coat of copper which could readily be separated as a coherent film (0·09 mm. thick) with a knife blade. T. A. H.

Calcium and Strontium Mercuric Iodides. ANDRÉ DUBOIN (*Compt. rend.*, 1906, 142, 573—574).—*Calcium mercuric iodide*, $\text{CaI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$, obtained by slow evaporation at atmospheric temperature of a solution containing calcium 3·97, mercury 21·84, iodine 52·8, and water 21·39 per cent., crystallises in transparent needles 5 cm. long and has a sp. gr. 3·25 at 0°.

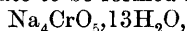
Strontium mercuric iodide, $\text{SrI}_2 \cdot 5\text{HgI}_2 \cdot 8\text{H}_2\text{O}$, was obtained in small crystals, together with mercuric iodide, by slightly cooling a solution (sp. gr. 2·5 at 16·5°) containing strontium 7·12, mercury 20·4, iodine 45·63, and water 26·85 per cent. When strongly cooled, the solution deposits the same salt in iridescent lamellæ, having a sp. gr. 4·66. This strontium salt may also be obtained in larger quantity by saturating the solution with mercuric iodide at 70° and allowing the liquid to cool.

A second *strontium mercuric iodide* [$\text{SrI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$] was obtained in long prisms, having a sp. gr. 3·22 to 3·36, by slowly evaporating a

liquid having the composition strontium 7·85, mercury 21·22, iodine 50·44, and water 20·49 per cent. T. A. H.

Action of Silicon Tetrachloride on Cobalt. ÉMILE VIGOUROUX (*Compt. rend.*, 1906, 142, 635—637. Compare this vol., ii, 32).—Silicon tetrachloride is reduced by cobalt at the temperature of the electric furnace with the formation of cobalt chloride, which is volatile, and a residue of a cobalt silicide. At 1200° to 1300°, the reaction is complete, and ceases when the cobalt is converted into the silicide, Co_2Si (compare Abstr., 1896, ii, 176; Lebeau, Abstr., 1903, ii, 80), which has a sp. gr. 7·28 at 0° and differs from the corresponding iron silicide in that it is not attracted by a magnet (compare Moissan, Abstr., 1896, ii, 173). M. A. W.

Alkali Chromates. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1906, 55, 71—98).—The bulk of this work has been already reported (Abstr., 1905, ii, 818, 820; this vol., ii, 24). The various equilibria at 30° in the system $\text{Na}_2\text{O} + \text{CrO}_3 + \text{H}_2\text{O}$ have also been studied, and the results are now communicated. The solid phases which at one concentration or another are in equilibrium with the solution are: $\text{NaOH}, \text{H}_2\text{O}$; Na_2CrO_4 ; $\text{Na}_4\text{CrO}_5, 13\text{H}_2\text{O}$; $\text{Na}_2\text{CrO}_4, 4\text{H}_2\text{O}$; $\text{Na}_2\text{Cr}_2\text{O}_7, 2\text{H}_2\text{O}$; $\text{Na}_2\text{Cr}_3\text{O}_{10}, \text{H}_2\text{O}$; $\text{Na}_2\text{Cr}_4\text{O}_{13}, 4\text{H}_2\text{O}$, and CrO_3 . All these sodium chromates are soluble in water without decomposition. An interesting point brought out by the author's work, and made evident in the triangular diagram usually employed, is the following. When chromium trioxide is added to a saturated solution of sodium hydroxide, the first chromate to be formed is Na_2CrO_4 , not



as might be expected. Further addition of chromium trioxide is necessary to convert Na_2CrO_4 into $\text{Na}_4\text{CrO}_5, 13\text{H}_2\text{O}$. That is to say, one chromate is converted by addition of chromium trioxide into another chromate which contains less chromium than the first. This is possible only because of the high percentage of water contained in the second chromate. J. C. P.

Gold-zinc Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1906, 48, 319—332. Compare Heycock and Neville, Trans., 1897, 71, 419).—The complete freezing-point curve of the system has been constructed and the conclusions arrived at by Tammann's method of thermal analysis have been confirmed by microscopic observations and by chemical analysis.

The freezing-point curve shows a eutectic point at 14 per cent. by weight of zinc, a distinct maximum at 25 per cent., and three breaks at 33, 77, and 88·5 per cent. of zinc respectively. The maximum corresponds with a compound of the formula AuZn , and besides this two other compounds exist, the respective formulæ and composition of which are: Au_3Zn_5 , 35·6 per cent. of zinc, and AuZn_8 , 72·6 per cent. of zinc. It is remarkable that the composition of none of the compounds corresponds with the ordinary valencies of the component elements.

From 0—12·5 per cent. by weight of zinc, mixed crystals separate

out; from 12.5—16 per cent., the primary separation of the saturated crystals is followed by the appearance of a eutectic, the second component of which is a new series of mixed crystals containing the compound AuZn ; from 16—25 per cent. of zinc, the new series separates alone. From 25—31 per cent., a third series of mixed crystals separates; from 31—35.6 per cent., the primary separation of the latter is followed by the appearance of the compound Au_3Zn_5 . The latter compound enters into a fourth series of mixed crystals from 35.6—61 per cent. of zinc; from the latter point to 72.6 per cent., the primary separation of these crystals is followed by the appearance of the compound AuZn_8 , beyond which point no mixed crystals are formed.

The alloys rich in gold have about the same hardness as the latter, but are not quite so tenacious. Between 31 and 61 per cent. of zinc, they are extremely hard and brittle, due to the compound Au_3Zn_5 ; above the latter point, the hardness and brittleness gradually diminish.

G. S.

Gold-cadmium Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1906, **48**, 333—346. Compare Heycock and Neville, *Trans.*, 1892, **61**, 883, and preceding abstract).—The freezing-point curve of the system shows two breaks at 623° and 30 per cent. and 493° and 63 per cent. by weight of cadmium respectively, and a eutectic point at 303° and 87 per cent. of the same metal. The first break corresponds with a compound of the formula Au_4Cd_3 , the second with a compound AuCd_3 .

From 0—18 per cent. by weight of cadmium, mixed crystals separate; at the latter point they are saturated, and from 18—30 per cent. the primary separation of the saturated mixed crystals is followed by the separation of the compound Au_4Cd_3 ; from 30—51 per cent., a second series of mixed crystals appears, and from 51—63 per cent. the separation of these crystals is followed by the appearance of the compound AuCd_3 ; beyond this point no mixed crystals form, the components of the eutectic mixture at 87 per cent. being the compound AuCd_3 and cadmium.

Heycock and Neville (*loc. cit.*), by distilling off the excess of cadmium from an alloy of the two metals, obtained a residue which corresponded approximately with the composition CdAu , and considered the existence of a compound of this formula as proved, but the author points out that this method of procedure is only applicable when the vapour pressure of the volatile metal alters in a discontinuous way at a point corresponding with the composition of the compound, a condition which is not fulfilled when, as in this case, mixed crystals with the volatile component are formed.

The hardness reaches its maximum in the alloys containing 18—30 per cent. and 51—63 per cent. of cadmium respectively; the remaining alloys have about the same degree of hardness as the metals themselves. Some of the alloys are extremely brittle; this property attains its maximum at 51—63 per cent. of cadmium.

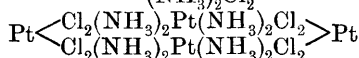
Photo-micrographs of several of the alloys are given in the paper.

G. S.

Action of Hot Sulphuric Acid on Platinum and Iridium Salts in the Presence of Ammonium Sulphate. MARCEL DELÉPINE (*Compt. rend.*, 1906, 142, 631—633. Compare this vol., ii, 24, 93).—A platinum-iridium alloy containing 10 per cent. of the latter metal is dissolved to the extent of 0.10 gram per hour per square decimetre by sulphuric acid at 365°. On boiling the solution with ammonium sulphate, the platinum is deposited in the spongy form, and the residual solution exhibits the beautiful green colour changing to a deep violet on the addition of nitric acid which is a characteristic reaction of iridium salts. From the green solution, the author has isolated three ammonium iridosulphates: a greenish-blue salt which gives a blue precipitate with barium or strontium salts and is slowly decomposed by ammonia; a green salt which gives no precipitate with neutral barium chloride, but a greenish-brown precipitate with the reagent in the presence of alkalis; and an olive-brown salt which gives no precipitate with neutral barium chloride, and a brown precipitate in the presence of ammonia. M. A. W.

A New Red Compound Isomeric with Magnus' Green Salt. SOFUS M. JÖRGENSEN and SÖREN P. L. SÖRENSEN (*Zeit. anorg. Chem.*, 1906, 48, 441—445).—Magnus' green salt is usually obtained by the action of potassium platinous chloride on platodiammine chloride, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, in aqueous solution, but the authors have observed that in certain circumstances the same substances interact with formation of an isomeric red salt. The conditions favourable for the production of the latter are absence of potassium platinichloride (traces of which are often present in the platinous salt) and very dilute neutral or slightly ammoniacal solution. The precipitate is washed with aqueous and finally with absolute alcohol, and forms small, ill-defined needles, rose-red in colour. The same salt is obtained in well-defined, small, tetragonal prisms by interaction of the yellow plato-dimethylamine-ammine platinous chloride (compare this vol., i, 338) with platodiammine chloride in the presence of a large excess of water.

The red salt is anhydrous, and in the dry condition is very stable, but on boiling with water it is changed quantitatively into the green salt; the converse change has not been observed. Both salts contain the residues $\text{Pt}''(\text{NH}_3)_4$ and $\text{Pt}'\text{Cl}_4$, and the authors consider it probable that the formulæ $\text{Pt} \left\langle \begin{array}{c} (\text{NH}_3)_2\text{Cl}_2 \\ (\text{NH}_3)_2\text{Cl}_2 \end{array} \right\rangle \text{Pt}$ and



are to be ascribed to the red and green salts respectively. G. S.

Colloidal Nature of the Black Palladium Solution obtained by means of Carbon Monoxide. JULIUS DONAU (*Monatsh.*, 1906, 27, 71—74. Compare Abstr., 1905, ii, 462).—The blackish-brown solution obtained by passing carbon monoxide into an aqueous solution of palladous chloride containing 0.005—0.05 per cent. of palladium has the same colour as has the palladium borax bead (Abstr., 1904, ii, 784) and Bredig's colloidal palladium solution, obtained by the disintegrating action of an electric discharge (Abstr., 1900, ii, 213). For

the preparation of the solution, conductivity water is less suitable than ordinary distilled water; when the reduction, which takes place more quickly than that of auric chloride, is complete, the conductivity of the solution becomes constant.

The filtrate obtained on precipitation of the metal with hydrochloric acid contains no palladium. Solutions containing 0.01 per cent. or more of palladium gradually deposit a part of the metal as a black precipitate; when evaporated, the solution darkens, and finally the metal is precipitated. The hydrochloric acid cannot be removed from the solution by dialysis; on prolonged dialysis, the palladium is partially precipitated, whereas the solution passes through a porous cell almost unchanged. The metal is precipitated also when the liquid hydrosol is shaken with animal charcoal or barium sulphate, or an electrolyte is added. These precipitations are diminished or prevented by the presence of a protecting agent, such as gum arabic or gelatin.

When an electric current is passed through the liquid hydrosol in a U-tube, the cathode limb becomes almost colourless, and has the conductivity only of highly purified water; the anode limb appears almost black, and a sharp line of demarcation between the two portions of the solution is observed. The hydrosol gradually dissolves at the anode, forming palladous chloride, when the metallic ion is deposited at the cathode.

G. Y.
