

Inorganic Chemistry.

Reactions Occurring during the Discharge of the Oxygen-Hydrogen Cell. F. FISCHER and W. KRÖNIG (*Z. anorg. Chem.*, 1924, **135**, 169—176).—The yield of hydrogen peroxide produced by short-circuiting for 3 hours a Grove cell containing 2*N*-sulphuric acid and 1% titanium sulphate (the latter to stabilise the peroxide) was 17% referred to the current consumption. This yield was increased by enclosing the hydrogen electrode in a porous cell; by feeding the oxygen electrode with oxygen instead of air (cf. A., 1913, ii, 285) and by feeding it through two jets instead of one; by prolonged heating to redness of the platinised electrodes (*i.e.*, decreasing their surface); and by reducing the current, the time of the experiment, and the temperature. A 79% yield was obtained by electrolysing 0.5*N*-sulphuric acid containing titanium sulphate at 0°, using a current of 2 milliamp. It is concluded that, at the ordinary temperature at least, the *E.M.F.* of the Grove cell is mainly influenced by the combination of hydrogen and oxygen to form, not water, but hydrogen peroxide, which, under normal conditions, is catalytically decomposed. S. K. T.

Periodic Catalytic Decomposition of Hydrogen Peroxide. E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1924, **125**, 1282—1287).—The periodic decomposition of hydrogen peroxide by mercury is considered not to be due to the formation of a film of oxide (cf. this vol., ii, 325). Periodic catalytic decomposition of hydrogen peroxide solution at 35° is brought about by metals (*e.g.*, silver reduced by hydrazine or hydroxylamine sulphates; freshly prepared colloidal platinum, silver, and gold), alloys (*e.g.*, copper-aluminium, after previous melting in air; cf. *loc. cit.*), metallic couples (*e.g.*, magnesium-copper), amalgams (*e.g.*, magnesium), freshly precipitated metallic oxides (*e.g.*, barium peroxide), etc. Decomposition is steady with silver reduced with Rochelle salt, electrolytic copper, stale colloidal platinum, coconut charcoal, platinum black, manganese dioxide, silver amalgam, etc.

S. K. T.

Catalytic Decomposition of Hydrogen Peroxide Solutions by Blood Charcoal. J. B. FIRTH and F. S. WATSON (*Trans. Faraday Soc.*, 1924, **19**, 601—613).—Blood charcoal dried at 120° decomposes hydrogen peroxide solutions. Prolonged extraction with aqua regia and with bromine lowers the percentage of ash

(chiefly iron oxide) and gives an activity which decays less rapidly. Activation by heat treatment or by sorption and removal of iodine gives charcoals which decompose hydrogen peroxide much more vigorously. Two types of reaction are found with these activated charcoals, an α -activity which causes a rapid initial decomposition of the peroxide with appreciable rise in temperature, but decays in a few minutes, and a β -activity which produces a slower decomposition persisting for several hours. The amount of decomposition depends on the concentration of peroxide as well as on the activity of the charcoal. The activity of sugar charcoal is markedly increased by the incorporation of 9% of iron oxide and subsequent heat treatment whilst the ash alone from blood charcoal has very little action on the peroxide. S. S.

Landolt's Reaction: Its Acceleration by Bromide and Chloride. A. SKRABAL [in part with R. RIEDER] (*Z. Elektrochem.*, 1924, **30**, 109—124).—Together with the direct reduction of iodic acid by sulphurous acid, six further simultaneous reactions enter into the reduction, the rate of the reaction being represented by

$$-d[\text{IO}_3']/dt = k_1[\text{IO}_3'][\text{H}'][\text{SO}_3''] + k_2[\text{IO}_3'][\text{H}]^2[\text{I}']^2 + k_3[\text{IO}_3'][\text{H}]^2[\text{I}'][\text{Br}'] + k_4[\text{IO}_3'][\text{H}]^2[\text{I}'][\text{Cl}'] + k_5[\text{IO}_3'][\text{H}]^2[\text{Br}']^2 + k_6[\text{IO}_3'][\text{H}]^2[\text{Br}'][\text{Cl}'] + k_7[\text{IO}_3'][\text{H}]^2[\text{Cl}']^2.$$

Up to the reversal of the reaction these reaction products oxidise sulphurous acid practically instantaneously to sulphuric, so that the formula reaction is $\text{IO}_3' + 3\text{SO}_3'' = \text{I}' + 3\text{SO}_4''$. The values of k_3 , k_4 , k_5 , k_6 , and k_7 have been determined and the validity of the complete equation has been demonstrated. The kinetics of the halide-halogenate reaction can in general be represented by $-d[\text{IO}_3']/dt = k[\text{IO}_3'][\text{H}]^2[x][y']$, where x and y can be the same or different halogens. H. T.

Ultra-violet Emission Bands of Oxygen. R. C. JOHNSON.—(See ii, 510.)

Ozone in Flames. W. MANCHOT and E. BAUER (*Z. anorg. Chem.*, 1924, **133**, 341—360).—Ozone was detected by means of the silver test (A., 1909, ii, 993) in flames of hydrogen, hydrogen-oxygen mixture, carbon monoxide, coal gas, methane, ethylene, acetylene, and cyanogen, but not in the flame of an ordinary Bunsen burner. Elongated flames contain more ozone than thick, wide flames, and the quantity of ozone is affected by conditions such as the pressure of gases supplied to the burner, shape of the burner, etc. The ozone is chiefly confined to the hottest parts of the flame and is completely destroyed on diffusing through the cooler zones to the surrounding air. Ozone is almost instantaneously destroyed at 300°. The oxy-hydrogen flame contained about 0.1% of ozone at 1500—1600°, whilst the acetylene blowpipe flame contained about 1% at a higher temperature. These quantities are too high to be accounted for by purely thermal formation, according to Nernst's heat theorem, and experiment showed that, if oxygen is heated at 1600°, no detectable ozone is produced. The quantities of ozone in flames of carbon monoxide and cyanogen showed no diminution when the gases were dried over phosphorous pentoxide,

indicating that the ozone in flames is not produced from hydrogen peroxide as was suggested by Wartenburg (A., 1921, ii, 107). The formation of ozone is possibly due to the action of free electrons in the flame. The lowest temperature at which ozone was detected was 900°, and the temperature of its formation is estimated as about 1400°. Carbon monoxide when carefully dried over phosphorous pentoxide is still inflammable, but the flame is very sensitive to pressure variations (cf. Dixon, A., 1905, ii, 577). W. H.-R.

Structure of Selenium. H. COLLINS.—(See ii, 515.)

Tellurium Monoxide. J. J. DOOLAN and J. R. PARTINGTON (*J. Chem. Soc.*, 1924, **125**, 1402—1403).—Tellurium monoxide is obtained as a grey powder by heating tellurium sulphoxide, TeSO_3 (cf. Divers and Shimosé, T., 1883, 319; *Ber.*, 1883, **16**, 1004), in a vacuum at 180—225°, the product being washed with sodium carbonate solution, hot water, and finally alcohol. S. K. T.

Tellurous Acid as a Base. J. KASARNOWSKY (*Z. physikal. Chem.*, 1924, **109**, 287—301).—The concentrations of tellurous ions in solutions containing increasing amounts of hydrochloric acid have been determined by potential measurements with a tellurium electrode, and the total tellurium contents of the solutions have been determined chemically. It is found that the value of the concentration of the tellurium ions increases as the fourth power of that of the hydrogen ions, showing that tellurous acid acts as a weak base. Numerically, $[\text{Te}^{4+}][\text{OH}^-]^4/[\text{H}_2\text{TeO}_3]=1.5 \times 10^{-46}$. S. B.

Relationship between some Oxygen Compounds of Nitrogen. A. SANFOURCHE (*Ann. Chim.*, 1924, [x], **1**, 5—93).—An amplification of previously published work (A., 1922, ii, 454, 762; 1923, ii, 84). The rate of oxidation of nitric oxide was measured at temperatures ranging from 0° to 525°; the reaction appears to be of the second order. The fact that the temperature coefficient is less than unity is explained by the hypothesis that nitrous anhydride is first formed and then decomposed in part, the undecomposed portion undergoing further oxidation. The formation of nitric acid from nitrous fumes under the conditions which obtain in industry was studied; as the nitric acid first formed acts as an oxidising agent towards the less oxidised compounds, it is unusual to obtain in this manner acid of concentration greater than 50%. Nitric oxide reduces nitric acid, producing, with acid of 10% or lower concentration, nitrous acid only ($2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow 3\text{HNO}_2$); when the concentration of the nitric acid is in the neighbourhood of 20% a second reaction ($\text{NO} + 2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 3\text{NO}_2$) also occurs. The latter predominates with increasing concentration of the acid; with 70% acid the former ceases. Nitrous anhydride, or the gaseous mixture of the same composition which reacts as the anhydride, acts on water with production of nitrous acid, which decomposes, yielding two-thirds of the original nitrogen in the form of nitric oxide. Dilute nitric acid behaves towards the anhydride in a similar manner to water, but acid of

50% and greater concentration is reduced with formation of nitrogen peroxide, which dissolves in the acid. Both reactions take place simultaneously with acids of intermediate concentrations. Nitrogen peroxide originally forms with water or dilute nitric acid equimolecular quantities of nitrous and nitric acids; the subsequent decomposition of the nitrous acid thus formed is complete only when the concentration of the nitric acid does not exceed 20%; beyond this, the oxidising action of the nitric acid on the nitric oxide formed in the decomposition was observed, whilst with 70% nitric acid simple solution of the peroxide takes place. H. J. E.

Absorption of Nitric Oxide by Solutions of Ferrous Sulphate and Sodium Sulphite. L. MOSER and R. HERZNER (*Z. anal. Chem.*, 1924, **64**, 81—89).—An investigation of the absorptive power of solutions in the system ferrous sulphate-sulphuric acid-water for nitric oxide showed that the most efficient mixtures were a saturated neutral solution of ferrous sulphate and a solution containing 15% of ferrous sulphate, 20% of sulphuric acid, and 65% of water. In practice, however, the most satisfactory solution contains 15% by weight of anhydrous ferrous sulphate and 15% of 64% sulphuric acid. The relative absorption of nitric oxide by alkaline solutions of sodium sulphite in general increases with a decrease of concentration of sulphite and increases at first with the concentration of free alkali, then decreases when this exceeds a certain limit; the best mixture appears to consist of 11—15% of anhydrous sodium sulphite, 1% of sodium hydroxide, and 88—84% of water. A. R. P.

Silent Discharge involving Catalysis. F. O. ANDEREGG and E. H. BOWERS (*Proc. Indiana Acad. Sci.*, 1922, 181—186).—The yields of ozone and nitrogen pentoxide in air are much more dependent on the nature and extent of the surface than on the amount of inductive capacity of the various materials placed in the discharge space (cf. McEachron and George, *Bull. Purdue Univ.*, 1922, **6**, 1); glass wool is particularly active. Increase of voltage is accompanied by increased formation of ozone, followed by that of nitrogen pentoxide, a high concentration of which lowers the yield of ozone. Thus the concentration of the latter reaches a first, second, and sometimes a third maximum. Similar experiments were conducted with carbon monoxide. CHEMICAL ABSTRACTS.

Fog Formation in Air which has passed through a Silent Discharge. F. O. ANDEREGG and K. B. MCEACHRON (*Proc. Indiana Acad. Sci.*, 1922, 175—177; cf. Anderegg, McEachron, and others, *A.*, 1918, ii, 42; 1921, ii, 450; *Trans. Amer. Electrochem. Soc.*, 1920, **37**; and preceding abstract).—The fog formed when ozonised air is passed through an absorbent solution is due chiefly to hygroscopic nitrogen pentoxide. CHEMICAL ABSTRACTS.

Thermal Decomposition of Salts of Hydroxylamine and Hydrazine. K. A. HOFMANN and F. KROLL (*Ber.*, 1924, **57**, [B], 937—944).—The slow thermal decomposition of hydroxylamine

hydrochloride at about 150° , takes place in accordance with the equations: $3\text{NH}_2\cdot\text{OH}=\text{N}_2+\text{NH}_3+3\text{H}_2\text{O}$ and $4\text{NH}_2\cdot\text{OH}=\text{N}_2\text{O}+2\text{NH}_3+3\text{H}_2\text{O}$. The addition of basic substances represses the second in favour of the first change to an extent which is less than would be expected, whereas acidic substances displace the action in the contrary direction. Nitrous acid or nitrite is produced by the acid or alkaline fusion of hydroxylamine. It is therefore probable that hydroxyhydrazine is produced initially from 2 mols. of hydroxylamine and subsequently converted into the diamide of nitrous acid, $\text{OH}\cdot\text{N}(\text{NH}_2)_2$; this is hydrolysed to ammonia and nitrous acid (or nitrosyl acid in concentrated acid solution) which, with unchanged hydroxylamine, yields nitrous oxide. Confirmation of this hypothesis is found in the observation that nitrous oxide is not formed in the presence of sufficient alkali or of carbamide. In alkaline solution (cf. first equation) the diamide of nitrous acid suffers mainly intramolecular decomposition, $\text{OH}\cdot\text{N}(\text{NH}_2)_2=\text{N}_2+\text{NH}_3+\text{H}_2\text{O}$, accompanied by the subsidiary change: $\text{OH}\cdot\text{N}(\text{NH}_2)_2+\text{NaOH}=\text{NaNO}_2+2\text{NH}_3$.

Hydrazine hydrochloride decomposes above 200° into ammonium chloride, nitrogen, and hydrogen chloride. In the presence of hydroxylamine hydrochloride, reaction occurs at about 150° and, with suitable proportions of the reactants, follows the course: $2\text{NH}_2\cdot\text{OH}+\text{N}_2\text{H}_4\cdot 2\text{HCl}=2\text{NH}_4\text{Cl}+\text{N}_2+2\text{H}_2\text{O}$. The absence of nitrous oxide from the products indicates the quantitative participation of hydroxylamine in the change and the probable preliminary formation of a very unstable salt of diaminohydrazine.

The oxidising or reducing action of hydroxylamine depends largely on the conditions; in feebly acid solution hydroxylamine and ferric chloride give ferrous chloride and nitrous oxide, whereas in concentrated sulphuric or phosphoric acid solution hydroxylamine and ferrous sulphate yield ferric and ammonium sulphates. Hydroxylamine is oxidised by iodine in acetic acid but not in mineral acid solution; in concentrated hydrochloric acid solution hydroxylamine liberates iodine from hydrogen iodide. H. W.

Density of Graphite. E. RYSCHKEWITSCH and E. KÖSTER-MANN (*Z. Elektrochem.*, 1924, **30**, 86—88).—The density of graphite prepared by fusion and subsequent solidification, determined by the flotation method, is sharply defined at $d^{16} 2.232\pm 0.0013$. This value is in agreement, within the limits of experimental error, with that calculated from the lattice spacing by Debye and Scheerer. H. T.

Action of Permanganic Anhydride on the Varieties of Pure Carbon. J. F. DURAND (*Compt. rend.*, 1924, **178**, 1822—1824; cf. this vol., ii, 500).—Diamond, graphite, and acetylene black were treated with the green solution of permanganic anhydride in concentrated sulphuric acid. The action was rapid in the cold, all three being quantitatively converted into carbon dioxide, but the vigour of the reaction was unequal in the three cases. G. M. B.

Infra-red Absorption of Carbon Monoxide. E. F. LOWRY. —(See ii, 512.)

Ageing Phenomena in Silica Gels. R. SCHWARZ and F. STÖWENER (*Koll. Chem. Beihefte*, 1924, **19**, 171—202).—It has been shown previously (A., 1920, ii, 689, 690; 1921, ii, 260) that the ageing of silica gels is closely connected with the changes in conductivity of solutions of the gel in 3*N*-ammonia. For a number of gels the authors have determined the conductivity, and amounts of silica in solution in the colloidal and crystalloidal states after prolonged contact with 3*N*-ammonia. The results are expressed in terms of a "*Q* value" giving the ratio of the increase of conductivity to the amount of silica in a molecular state of dispersion. With normal ageing the *Q* value falls from 75×10^{-4} to about 25×10^{-4} . This behaviour is so well established that any anomalous conductivity can safely be referred to an anomalous behaviour of the gel. In this way it is found that gels prepared from silicon tetrachloride at either 0° or 100° and partially purified by dialysis show no alteration, but that normal ageing takes place when these gels are more carefully purified by repeated decantation and shaking with water. Gels from sodium silicate and acetic acid after dialysis show normal ageing, which is markedly retarded by small quantities of sodium chloride, carbamide, tartaric acid, or dextrose. Cases are recorded where normal ageing occurs in gels kept under water, so that the drying, which generally accompanies ageing, determines only the rate of the process. The authors conclude that the process of ageing consists of a dehydration of the primary particles which originally hold much water, and that it is probable that dehydration, in a strictly chemical sense, or polymerisation, also occurs. E. M. C.

Preparation of Potassium Antimonate. S. A. SCHOU (*Z. anorg. Chem.*, 1924, **133**, 404—410).—Grey antimony ore (Sb_2S_3) is boiled with potassium hydroxide solution, cupric oxide is added, and the whole stirred and boiled for $\frac{1}{2}$ hour, and then filtered. The filtrate (which should be quite free from sulphur and give a pure white precipitate with lead acetate solution) is evaporated to one-tenth of its original volume and treated with alcohol. The precipitated potassium antimonate is filtered off, washed with 50% alcohol, left for 24 hours, and then ground in a mortar and dried on filter paper. This method gives a yield of 90% of the theoretical, whilst a yield of 98% can be obtained if very finely divided antimony trisulphide, prepared by the careful ignition of the pentasulphide, is used instead of the ore. The antimony trisulphide and potassium hydroxide react to form a mixture of antimonite and thioantimonite, which are then oxidised by the cupric oxide with the formation of an intermediate oxysulphide, $\text{K}_3\text{SbO}_3\text{S}$, which cannot be isolated. The reactions may be expressed by the equations (1) $\text{Sb}_2\text{S}_3 + 6\text{KOH} = \text{K}_2\text{SbO}_3 + \text{K}_3\text{SbS}_3 + 3\text{H}_2\text{O}$; (2) $\text{K}_3\text{SbS}_3 + 3\text{CuO} = \text{K}_3\text{SbO}_3 + 3\text{CuS}$; (3) $\text{K}_3\text{SbO}_3 + 2\text{CuS} = \text{K}_3\text{SbO}_3\text{S} + \text{Cu}_2\text{S}$, (4) $\text{K}_3\text{SbO}_3\text{S} + \text{CuO} = \text{K}_3\text{SbO}_4 + \text{CuS}$. W. H. R.

Spectrum of Ionised Lithium. M. MORAND.—(See ii, 509.)

Formation of Double Salts in the Solid State in the System Lithium Chloride—Calcium Chloride. G. GRUBE and W. RÜDEL (*Z. anorg. Chem.*, 1924, **133**, 375—388).—The system lithium

chloride-calcium chloride has been investigated, in both the solid and liquid states, by thermal analysis. The two salts are totally miscible in the liquid state, the freezing-point curve being of the simple eutectic type, with an eutectic point at 496° and 38 mols. % of calcium chloride. The constituents separating from the liquid are solid solutions, the limits of solubility in the solid state at the eutectic temperature being 0—16 mols. % of calcium chloride, and 0—20 mols. % of lithium chloride. The limits of solid solubility decrease rapidly as the temperature is lowered. All binary mixtures on cooling show a thermal arrest in the solid state at 441° , due to the formation of the double salt $\text{LiCl}, \text{CaCl}_2$, the reaction $\text{LiCl} + \text{CaCl}_2 \rightleftharpoons \text{LiCl}, \text{CaCl}_2$ being reversible and exothermic from left to right. If finely powdered lithium and calcium chlorides are mixed and heated together, they react in the solid state to form the double salt, the action beginning at about 170° . The double salt is completely decomposed above 441° .
W. H.-R.

Molten Electrolytes, Born's Grating Forces, and the Constitution of Salts. W. BILTZ (*Z. anorg. Chem.*, 1924, **133**, 312—324).—The author's work on the electrolytic conductivity and other properties of fused salts is discussed and general conclusions are drawn with regard to fused chlorides. The majority of fused chlorides are either good conductors or very poor conductors. Out of 61 chlorides examined, 31 are good conductors in the fused state (κ of the order 0.1 to 1.0), 11 have κ of the order 10^{-6} , and 15 are non-conductors, leaving only 4 with moderate conductivity. These four are the chlorides of zinc, beryllium, and mercury, and the so-called tellurium dichloride. In any group or series of the periodic table, there is a sudden jump from an element of which the chloride is practically a non-conductor in the fused state to the next element of which the chloride is a good conductor. In group I this change occurs between hydrogen chloride and lithium chloride. In group II, the change is between beryllium and magnesium; in group III between aluminium and scandium; in group IV between titanium and zirconium; and in group V between antimony or tantalum and bismuth. In this way it is possible to divide the periodic table into halves corresponding with those elements of which the chlorides do and do not conduct electricity in the fused state; a few exceptions are, however, shown, particularly in group VIII. When an element forms two chlorides, the lower chloride is always the better conductor, whilst, generally speaking, a high m. p. corresponds with good conductivity and vice versa (cf. A., 1922, ii, 370). Chlorides which are good conductors are not found with a valency higher than four, all pentachlorides examined being non-conductors. These facts are then discussed in the light of Born's theory of the crystal grating (A., 1919, ii, 188, 424, 453) and the work of Kossel (A., 1916, ii, 243). Assuming that transference of electrons occurs in mono-, di-, tri-, and tetra-chlorides, the attraction between the oppositely charged ions will become greater as the charge on the metal atom increases, and the dissociation in the fused state will become correspondingly less, and the conductivity will decrease.

This accounts for the fact that lithium chloride is a good conductor and beryllium chloride a poor conductor in the fused state. At the same time, according to Born, a repulsion exists between two oppositely charged ions, owing to the action of the shells of electrons. This repulsion favours easy dissociation, and increases as the inner shells of electrons become greater. Thus in group I, the hydrogen ion possesses no shells of electrons and consequently the attractive forces prevail and hydrogen chloride is a non-conductor. In lithium chloride, however, the repulsive forces produced by the shells of electrons opposes the electrostatic attraction of the ions, and lithium chloride is a good conductor in the fused state. In group IV, where the metal ion has four charges, the electrostatic attraction is so much greater that it is only in the case of thorium chloride that the numerous shells of electrons produce a repulsive force sufficient to cause dissociation in the fused state. In this way, the opposing effects of (1) electrostatic attraction, and (2) the repulsion due to the shells of electrons, give an explanation of the conductivity of the fused chlorides of the different elements. W. H.-R.

Boiling Points and Heats of Evaporation of Salts. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **133**, 380—384).—The experimental results of Wartenburg (A., 1922, ii, 739) have been used to determine the molecular heat of evaporation λ , the boiling point T_b , and the Trouton ratio λ/T_b for the alkali halides, cuprous, thallos, and lead halides, and for silver chloride, tin tetrachloride, and sodium and potassium hydroxides. If the total heats of evaporation are taken, the Trouton ratio for the majority of these salts is of the order 20—23, whilst if the internal heat of evaporation (cf. Wartenburg, *loc. cit.*) is taken, the ratio is of the order 20—22 in the case of most of the alkali halides. Exceptions are presented by the cuprous halides for which the ratio λ/T_b is of the order 11—12, and by thallos fluoride (about 44). Slight irregularities are also shown by some of the lithium and sodium halides and by sodium hydroxide. The experimental values for the internal heat of evaporation of the different salts are higher than the value calculated by the equation of Nernst ("Lehrbuch," 7th ed., 294), and lower than those calculated from the equation of Gruneisen (A., 1912, ii, 534), whilst the equation of Wartenburg (*Z. Elektrochem.*, 1914, **20**, 444) gives results which are on both sides of the experimental values. The general agreement with all three equations is good except for the cases mentioned above. W. H.-R.

Orientation of Ammonium Iodide Crystals by Cleavage Planes of Micas. P. GAUBERT (*Compt. rend.*, 1924, **178**, 856—858).—The effect of different varieties of mica on the orientation of ammonium iodide crystals allowed to form in contact with them appears to depend on their composition, being related to the potassium content. When changes have taken place in mica involving loss or replacement of the potassium, the directing power with respect to deposited crystals is not apparent, although the optical properties may remain unchanged. Heating to redness, or

exposure to the action of hydrochloric acid, causes mica to lose the power of orientation. The author suggests that the potassium atoms exert a directing influence on the potassium atoms or ammonium groups in the iodides, and states that such action on these iodides affords a method of distinguishing micas from each other.

H. J. E.

Properties of Ammonium Nitrate. VIII. Analysis of Crystalline Deposits from Solution in Fused Ammonium Nitrate. E. P. PERMAN and D. R. DAWKINS (*J. Chem. Soc.*, 1924, 125, 1239—1244).—The deposits formed on cooling fused salts may be separated by filtration through a Gooch crucible, the residue being freed from mother liquor by repeated pressing in a special press. The method is applied to the reciprocal salt pairs previously investigated (cf. this vol., ii, 255), the results confirming the conclusions arrived at from a consideration of the m. p. curves.

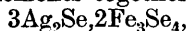
S. K. T.

Photochemical Decomposition of Silver Chloride. R. SCHWARZ and P. GROSS (*Z. anorg. Chem.*, 1924, 133, 389—403).—The action of panchromatic light on silver chloride has been investigated by a method similar to that used by the authors for silver bromide (A., 1923, ii, 815), the decomposition being measured by direct determination of the chlorine evolved. The silver chloride was prepared by precipitation of solutions of silver nitrate and sodium chloride in the presence of dilute nitric acid. Owing to adsorption the results are frequently affected by the presence of excess of silver salt or of chloride during the precipitation. In the moist state specimens prepared with excess of either salt show little difference. Drying over phosphorus pentoxide has little effect on specimens prepared with excess of chloride, but reduces the photochemical decomposition to about one-half in the case of specimens with excess of silver salt, this smaller decomposition being regarded as due to the masking of the surface chlorine atoms by the adsorbed positive silver ions. Colour tests indicated that dry silver chloride is darkened more strongly than dry silver bromide, and that, in both cases, specimens prepared with excess of halide are more sensitive than those with excess of silver salt. This is contrary to photographic practice in which excess of silver salt is always employed, indicating that "photographic sensitivity" (short exposures) is not identical with sensitivity to photochemical decomposition. Freshly-prepared dried silver chloride is slightly less sensitive to photochemical decomposition than specimens dried after keeping for some time under water, the sensitivity rising to a maximum after keeping for 50 hours, then decreasing slightly up to 150 hours, and then increasing again. Curves have been drawn representing the effect of light intensity and time on the decomposition of silver chloride.

W. H.-R.

Double Selenides. J. MEYER and H. BRATKE (*Z. anorg. Chem.*, 1924, 135, 289—312).—Double selenides containing two different

heavy metals could not be prepared; naturally occurring eucairite, $\text{Ag}_2\text{Se}, \text{Cu}_2\text{Se}$, is the only such selenide known with certainty. By fusing the appropriate elements together a substance,



was obtained, which may be either a double selenide or a mixture. The double *potassium iron selenide*, $\text{K}[\text{FeSe}_2]$, was obtained as dark violet crystals, fairly stable in air, by fusing together iron, selenium, and potassium carbonate. Replacement of the latter by potassium cyanide yielded a new *iron selenide*, Fe_3Se_4 , or $\text{Fe}[\text{FeSe}_2]_2$. New *selenides of cobalt*, Co_5Se_6 , or $\text{Co}_3[\text{CoSe}_3]_2$, and *nickel*, Ni_5Se_6 , or $\text{Ni}_3[\text{NiSe}_3]_2$, were prepared similarly, using potassium cyanide and carbonate, respectively, in the fusion mixture. Potassium manganese selenide was probably formed in a fusion of manganese, selenium, and potassium carbonate, but it was very unstable in air and towards water and acids. By using sulphur in place of selenium, crystals of uncertain composition were obtained, probably $\text{K}_2[\text{Mn}_3\text{S}_4]$. S. K. T.

Solubility of Calcium Carbonate in Water containing Carbon Dioxide under High Pressures. Properties of the Solutions obtained. O. HAEHNEL (*J. pr. Chem.*, 1924, [ii], 107, 165—176).—The solution obtained by treating an aqueous suspension of calcium carbonate with carbon dioxide under 56 atm. pressure at 18° contains 0.393% of calcium carbonate, corresponding with 0.637% of calcium hydrogen carbonate. This figure is considerably higher than any found by earlier investigators (cf. McCoy and Smith, A., 1911, ii, 380). Both prepared and natural (Iceland spar) calcium carbonate gave the same result. At first the experiments were carried out in an apparatus so fitted that after treatment the suspension could be filtered while still under pressure but later this was found to be unnecessary as the solutions obtained were fairly stable. Thus, even after standing exposed to the air at room temperature for 24 hours, the solution still contained 0.30% of calcium carbonate; it could be shaken, filtered through paper, or even gently warmed without appreciable precipitation taking place. A determination of the carbon dioxide evolved on boiling showed that calcium hydrogen carbonate was actually present. Attempts to isolate this compound in the solid form gave promising but unsatisfactory results. When the above solution was evaporated to dryness at 10° , anhydrous crystals of calcium carbonate were obtained, not the hexahydrate described by Johnstone and others (A., 1916, ii, 433). The solubility of calcium carbonate depends on the pressure of carbon dioxide to which the mixture is subjected. It reaches the above maximum at about 40 atm., not at 16 atm. as stated by McCoy and Smith (*loc. cit.*). The curve obtained by the author agreed well with that obtained for low pressures by Engel (A., 1886, 120). With rise in temperature (at 56 atm.), the solubility increases slightly, to 0.40% CaCO_3 at 25° , to fall off rapidly until it is 0.26% at 55° . The conductivity of the solution, saturated at 18° [0.64% $\text{Ca}(\text{HCO}_3)_2$] is $3605 \times 10^{-8} \text{ cm.}^{-1}\omega^{-1}$.

W. A. S.

21**

Reactions of Chromates at High Temperatures. I. Synthesis and Decomposition of Calcium, Sodium, and Magnesium Chromates in Air. M. R. NAYAR, H. E. WATSON, and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1924, 7, 53—70; cf. this vol., ii, 492).—Calcium and chromic oxides begin to interact in the presence of air to form calcium chromate at 650°; at 700° a 95% yield of chromate is obtained with mixtures containing 2 equivalents of calcium oxide to 1 of chromic oxide and a 60% yield when the ratio is 1 : 1. In the presence of excess of calcium oxide, equilibrium is attained at about 800°, although pure calcium chromate does not begin to decompose until 1000° is reached. No basic salts of definite composition are obtained by heating pure calcium chromate. Sodium carbonate and chromic oxide readily interact to form chromate at temperatures below 660°; the salt melts at 800° and remains undecomposed after prolonged heating at 1000°. Ferric oxide and, to a greater extent, calcium oxide accelerate the formation of chromate in mixtures of sodium carbonate and chromic oxide by preventing the mass from fusing and thus allowing better access of air. Magnesium chromate decomposes completely at 650° into a mixture of chromites from which $5\text{MgO} \cdot 4\text{Cr}_2\text{O}_3$ may be obtained as an insoluble residue after extraction of the mass with hydrochloric acid. Magnesium oxide and chromic oxide in equimolecular proportions give very little chromate below 600° and at higher temperatures yield only the chromite $6\text{MgO} \cdot 5\text{Cr}_2\text{O}_3$. A. R. P.

Electrolytic Conductivity of Molten Chlorides. A. VOIGT and W. BILTZ (*Z. anorg. Chem.*, 1924, 133, 277—305).—The conductivities of a number of molten chlorides have been determined with precautions to avoid the presence of moisture which greatly affects the results. The chlorides were prepared in glass or silica vessels and distilled into the conductivity apparatus. The following values (amongst others) were found for the specific conductivities at different temperatures. Beryllium chloride: 451°, 0.00319; 472°, 0.00868. Uranium tetrachloride: 570°, 0.34; 620°, 0.48. Thorium tetrachloride: 814°, 0.61; 866°, 0.71; 922°, 0.78. Lanthanum chloride: 950°, 1.30; 1000°, 1.42; 1025°, 1.49; 1075°, 1.63; 1135°, 1.77. Praseodymium chloride: 824°, 0.82; 875°, 0.97; 965°, 1.26. Neodymium chloride: 775°, 0.63; 827°, 0.765; 900°, 0.945. Bismuth trichloride: 266°, 0.442; 315°, 0.506; 350°, 0.555. Tellurium dichloride: 206°, 0.042; 230°, 0.0668; 271°, 0.114; 305°, 0.151. Tellurium tetrachloride: 236°, 0.1145; 277°, 0.161; 316°, 0.203. Molybdenum pentachloride: 216°, 1.8×10^{-6} ; 258°, 7.5×10^{-6} . Tungsten hexachloride: 280°, 1.98×10^{-6} ; 305°, 2.85×10^{-6} ; 330°, 6.94×10^{-6} . Tungsten pentachloride: 250°, 0.67×10^{-6} ; 275°, 1.35×10^{-6} ; 300°, 1.84×10^{-6} . It is doubtful if the salt described as tellurium dichloride has any definite existence, as the two different specimens used for the conductivity measurements both contained about 2% more chlorine than is required by the formula TeCl_2 . Lead tetrachloride, vanadium tetrachloride, phosphorus trichloride, phosphorus pentachloride, and selenium dichloride have electrolytic conduc-

tivities too small to be measured. The following values for the density of bismuth trichloride are abstracted: d^{250} 3.87, d^{300} 3.75, d^{350} 3.64. W. H.-R.

Dissociation Pressures of Hydrated Double Sulphates. II. Various Double Sulphates of the Type $M''SO_4.M'SO_4.6H_2O$.

R. M. CAVEN and J. FERGUSON (*J. Chem. Soc.*, 1924, **125**, 1307—1312).—The vapour pressures, p , of the double sulphates of the type $M''SO_4.M'SO_4.6H_2O$, where M'' is Mg, Zn, Cd, Mn, Fe'' , Co, or Ni, and M' is K, Rb, or Cs, may be expressed by the relation: $\log p = a + b/T - c/T^2$. When M'' is Cu, Cd, or Mn, p decreases in the order $M' = K, Rb, Cs$; for the remaining metals the order is K, Cs, Rb. The values of p for the ammonium double salts are very near, but are lower than, the values for the corresponding rubidium compounds. All the double sulphates examined form dihydrates on losing water, except when M'' is magnesium or ferrous iron, when tetrahydrates are formed (cf. A., 1917, ii, 534; T., 1922, **121**, 1406). S. K. T.

Active Agents in Luminescent Zinc Sulphides, Willemites, and Kunzites. T. TANAKA (*J. Opt. Soc. Amer.*, 1924, **8**, 659—667; cf. this vol., ii, 288).—The spectrum of the cathodoluminescence of 6 samples of zinc sulphide exhibited a series of bands attributed by the author (*loc. cit.*) to thallium, and also two series which had not been previously observed. It is concluded, from the wave-length intervals between the two series, and from other evidence, that these unknown bands are due to the presence of ytterbium. The luminescence of willemites and kunzites contained bands attributed to manganese, iron, thallium, and samarium, and also the two new series of bands. S. B.

Hardness of Lead-Cadmium and Lead-Tin Alloys. C. DI CAPUA and M. ARNONE (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 293—297).—If, as was indicated by thermal and conductivity measurements (A., 1922, ii, 576), lead and cadmium are completely immiscible in the solid state, the hardness diagram for their alloys should be rectilinear. This is, however, not the case, the hardness of lead being increased greatly by the presence of a very small proportion of cadmium and the curve changing its direction suddenly at about 1% of cadmium. Repetition of the thermal conductivity measurements shows a similar inflection at the same point, so that cadmium is soluble in lead in the solid state to the extent of about 1% at the ordinary temperature.

The alteration in the hardness curve produced by prolonged re-heating of the alloys is very small with lead-cadmium alloys, but with lead-tin alloys the character of the curve is entirely altered by such treatment. Tin dissolves 1—2% of lead and the latter about 10% of tin at the ordinary temperature. T. H. P.

Internal Friction of Molten Metals and Alloys. I. Lead-Bismuth Alloys. F. SAUERWALD (*Z. anorg. Chem.*, 1924, **135**, 255—264).—An apparatus is described in which the viscosity of molten metals and alloys may be measured at high temperatures

by a capillary method. Lead-bismuth alloys [%Pb=36.8, 43.5 (eutectic), 51.3] show a smaller viscosity than that calculated from the mixture rule; no maximum or minimum viscosity is observed for the eutectic alloy (cf. Plüss, A., 1916, ii, 294). S. K. T.

Dissolution of Lead in Alkaline Liquids by Alternating Currents. F. JIRSA and J. FABINGER (*Z. physikal. Chem.*, 1924, 109, 260—274).—In electrolysis by alternating currents, lead enters into solution as bivalent ions. The current required for dissolution is always greater than this statement would indicate owing to secondary reactions with hydroxyl ions, producing HPbO_2' and PbO_2'' ions, which may then be reduced by the cathodic component of the current. This effect increases with the concentration of the solutions. Potential experiments support the view that the lead electrode is completely active, and shows no mechanical anodic passivity. S. B.

Behaviour of Liquid Cuprous Sulphide, Ferrous Sulphide, Copper, and Iron. G. TAMMANN and H. BOHNER (*Z. anorg. Chem.*, 1924, 135, 161—168).—The quaternary equilibrium diagram for the system: $\text{Cu}_2\text{S} + \text{Fe} \rightleftharpoons \text{FeS} + 2\text{Cu}$ is discussed. Since at certain concentrations mixtures of liquid copper and cuprous sulphide and of iron and copper are immiscible, the diagram shows the existence of an area in which three layers are formed instead of two, one of sulphide and two metallic. The significance of this region is discussed, mainly on the basis of work by Baykoff (*Rev. Mét.*, 1909, 6, 536). When equivalent amounts of iron and cuprous sulphide are melted together, the copper and iron are practically equally divided between the two layers. This corresponds with the very small heat of the forward reaction in the above equation.

S. K. T.

Supposed Existence of Copper Carbonyl. E. MOND and C. HEBERLEIN (*J. Chem. Soc.*, 1924, 125, 1222—1223).—A repetition of Bertrand's experiments (this vol., ii, 47) does not support the existence of copper carbonyl. It is thought that the metallisation of insects can be explained by the adhesion and sintering of the copper oxide, which is shown to begin at 400°. S. K. T.

Structure of Crystalline Mercury. N. ALSÉN and G. AMINOFF (*Geol. Förening Stockholm Förhandl.*, 1922, 124—128; from *Chem. Zentr.*, 1924, i, 1754).—From X-ray analysis it is found that mercury has a hexagonal four-atom lattice with the following constants: $a=3.84 \text{ \AA.}$; $c=7.24 \text{ \AA.}$; $1:c=1:1.88$. The arrangement is similar to that found by Hull for zinc and cadmium.

G. W. R.

Has Pure Aluminium a Transformation Point? K. HONDA and I. IGARASI (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, 12, 305—308).—When commercial aluminium is heated, an abnormal expansion occurs in the temperature range 300—450°. The abnormal expansion increases as the silicon content increases to 1%, but then rapidly decreases. The author concludes that specimens entirely

free from silicon would show a normal expansion, and that no evidence for a transformation point exists. The effect of adding iron to aluminium which already contains traces of silicon, is very slightly to diminish the abnormal expansion. W. H.-R.

Colloid Chemical Characterisation of Technical Clays and Kaolins. I. W. OSTWALD and F. PIEKENBROCK (*Koll. Chem. Beihefte*, 1924, **19**, 138—170).—The authors consider the possibility of characterising clays and kaolins by measurements of the viscosity of suspensions of various concentrations. A number of factors, such as the concentration of the original suspension, ageing, the diameter of the capillary, and the mechanical treatment of the suspension, need to be controlled. Suspensions of clays and kaolin differ markedly in their behaviour on mechanical treatment. The viscosity of clay suspensions increases slowly and steadily with repeated squirtings through a capillary, whilst the viscosity of kaolin suspensions increases rapidly to a maximum. It is suggested that in kaolin suspensions the viscosity is a function of the size-distribution of the particles, but that in clays the principal factor is a stronger power of hydration and swelling. [Cf. *B.*, 1924, 597.] E. M. C.

Electro-deposition of Manganese. I. A. J. ALLMAND and A. N. CAMPBELL (*Trans. Faraday Soc.*, 1924, **19**, 559—573).—The electro-deposition of manganese from solutions of the chloride and sulphate has been studied and the influence of composition of electrolyte, current density, and temperature determined. Pure manganese in coherent form can be prepared in small amounts by using a catholyte containing 300 g. of manganous sulphate tetrahydrate, 100 g. of ammonium sulphate, and 2.5 g. of sulphuric acid per litre, the acidity being maintained by suitable additions of acid. Using a rotating cathode, current efficiencies of 50—60% were obtained. S. S.

Tervalent Manganese. V. J. MEYER and J. MAREK (*Z. anorg. Chem.*, 1924, **133**, 325—340; cf. *A.*, 1923, i, 12).—Oxidation of manganous salts in the presence of phosphoric acid gives a violet solution which gradually deposits a greyish-green precipitate of manganic orthophosphate (Christensen, *A.*, 1884, ii, 397). The violet colour is due to the presence of diphosphatomanganic acid $[\text{Mn}(\text{PO}_4)_2]\text{H}_3$, which has been prepared by the interaction of anhydrous manganic acetate and concentrated orthophosphoric acid at 100°. The reddish-violet crystals are very unstable and readily absorb moisture with the formation of the greyish-green manganic orthophosphate. The solution in concentrated phosphoric acid is, however, more stable, and, when this solution is electrolysed, the manganese goes to the anode, indicating that it is present as a complex anion. The trihydrated mono-sodium, mono-lithium, mono-potassium, and mono-ammonium diphosphatomanganates have been prepared. A similar pentahydrated sodium salt has been prepared, and an anhydrous guanidine salt, $[\text{Mn}(\text{PO}_4)_2]\text{H}_3 \cdot \text{CH}_5\text{N}_3$. These salts are probably monoclinic, dark red or violet in colour

(guanidine salt, dark yellow). This difference between the colours of the hydrated and anhydrous salts indicates that the water of hydration is not contained in the complex anion, but is simply water of crystallisation. The potassium salt is deliquescent but the others are stable in air. They are decomposed by hot water, yielding manganic hydroxide, whilst their solution in dilute phosphoric acid gradually deposits the greyish-green manganic orthophosphate. The violet colour given by manganese to the sodium metaphosphate bead in dry tests is probably due to the presence of a salt of diphosphatomanganic acid. W. H. R.

Pyrophoric Property of Metal Powders. G. TAMMANN and N. NIKITIN (*Z. anorg. Chem.*, 1924, **135**, 201—204).—The iron obtained by reducing ferrous oxalate in hydrogen loses its pyrophoric property at 530—536°, if the oxalate is not stirred during reduction, and at 370—400° if it is stirred. The corresponding temperatures for nickel oxalate are 370—390° and 330—365° (with less than 0.05 g. salt). The smaller the amount of salt used, the more vigorously and the longer it is stirred, the more certain is the product to be non-pyrophoric. Stirring favours the formation of large grains, *i.e.*, a small total surface. The experiments indicate, therefore, that pyrophoric power depends on the sizes of the metal particles. S. K. T.

High-temperature Density Measurements. V. Density and Expansion of Liquid and Solid Grey Pig-iron. F. SAUERWALD, H. ALLENDORF, and P. LANDSCHÜTZ (*Z. anorg. Chem.*, 1924, **135**, 327—332).—The specific volume of solid pig-iron, measured in a slightly modified apparatus from that previously described (*Z. Metallk.*, 1922, **14**, 457), showed a maximum value of 0.1484 at about 840°, which is attributed to the formation of mixed crystals of cementite and γ -iron. At the melting point the specific volume decreased abnormally, probably due to the formation of cementite. The value of dv/dT for the liquid phase was 0.32×10^4 over the range 1171—1315°. S. K. T.

Structural Constitution of Iron-Carbon-Silicon Alloys. K. HONDA and T. MURAKAMI (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **12**, 257—287).—Iron-carbon-silicon alloys, containing less than 30% of silicon and 4% of carbon, have been examined. In the primary crystallisation two types of crystals separate from the fused mass, namely, (1) a solid solution of iron, silicon, and carbon termed silico-austenite, and (2) a carbide or graphite. These form an eutectic if the carbon and silicon contents exceed a certain limit. As the silicon content increases from 0 to 21%, the eutectic temperature rises from 1130° to 1200°, and its carbon content falls from 4.3% to zero, *i.e.*, the solubility of carbon in molten iron decreases with rising silicon content. If the silicon content is less than 5.5%, the carbide mentioned above is pure cementite, Fe_3C , but with a greater silicon content its place is taken by a double compound or silico-carbide, of undetermined constitution, which is non-magnetic, readily decomposes with the formation of graphite,

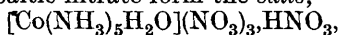
and forms no solid solution with cementite. On further cooling the solidified alloy, the silico-austenite deposits excess of silico-ferrite or of carbide, and at a certain temperature these form the eutectoid perlite. As the silicon content increases, the eutectoid temperature rises, and its carbon content decreases until, with more than 7% silicon, the change is no longer perceptible. If the silicon content exceeds 16%, the austenite on cooling deposits a compound, Fe_3Si_2 , in addition to the double carbide. As the silicon content increases, the A_3 and A_1 points rise in temperature but the A_2 point falls, so that the A_2 point may occur at a lower temperature than the A_1 point if the silicon content exceeds a certain amount. Graphite formation takes place very readily in these alloys owing to the instability of the double carbide, and to the fact that silicon lowers the solubility of carbon in the fused mass or in austenite. Graphitisation is favoured by increasing silicon content and also by slow cooling, so that rapidly cooled specimens which contain no graphite may produce graphite when annealed. The graphite in this system is usually not a primary product, but is produced by the decomposition of the double carbide. W. H.-R.

Reversible Colloid of Iron. A. F. G. CADENHEAD and W. H. VINING (*Can. Chem. Met.*, 1924, **8**, 65).—A substance resembling ferric hydroxide gel and hydrosol was isolated during the preparation of manganese acetate (cf. this vol., i, 826). CHEMICAL ABSTRACTS.

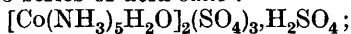
Titration of Ferric Chloride with Sodium Hydroxide, using the Oxygen Electrode. R. B. SMITH and P. M. GIESY (*J. Amer. Pharm. Assoc.*, 1923, **12**, 855—856).—Continuous curves were obtained, showing that ferric oxychloride does not exist.

CHEMICAL ABSTRACTS.

Neutral and Acid Salts of Cobaltammines. A. BENRATH and H. WÜRZBURGER (*Z. anorg. Chem.*, 1924, **135**, 226—232).—The formation of acid salts when neutral complex cobaltammines are treated with acid solutions of varying concentration is detected by analysis or by solubility curves. Aquopentamminecobaltic nitrate and hexamminecobaltic nitrate form the salts,



and $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3, \text{HNO}_3$, respectively. The corresponding sulphates form two series of acid salts:



$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3, \text{H}_2\text{SO}_4$, and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{SO}_4)_3, 2\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_3, 2\text{H}_2\text{SO}_4$, respectively; the second of these salts has been previously described (A., 1898, ii, 592). The salt described by Klobb (A., 1902, ii, 143) does not appear to exist. The cobalt in these compounds has a co-ordination number of four. S. K. T.

Evolution of the Molecule of Nickel Hydroxide in Contact with Water. (MLLE.) S. VEIL (*Compt. rend.*, 1924, **178**, 842—844; cf. A., 1923, ii, 122, 373; this vol., ii, 183).—Nickel hydroxide was precipitated by the action of sodium hydroxide on a nickel salt. The precipitate was dissolved and reprecipitated several times, specimens of the oxide being prepared from each precipitate by

heating. The molecular coefficient of magnetisation of the hydroxide decreases with each successive precipitation; in the case of the oxides the value reaches a maximum and thence decreases.

H. J. E.

Monocrystalline Tungsten. A. E. VAN ARKEL (*Physica*, 1923, **3**, 76—87; from *Chem. Zentr.*, 1924, i, 1651—1652).—The deposition of tungsten on a filament of monocrystalline tungsten in an atmosphere of dissociating tungsten hexachloride was studied. The effect of different conditions of experiment on the deposition of tungsten is discussed. The inclination of the crystal axis to the axis of the filament exerts an effect. Deposition takes place most readily on the 110 and 111 faces. The tendency to the formation of polycrystalline aggregates is greatest on the cube faces. The deposited tungsten is soft and pliable. After the filament has been subjected to mechanical treatment, the monocrystalline structure is lost and any further deposition takes place in the form of polycrystalline tungsten. X-Ray analysis shows that the filaments have a well-marked reticulate lamination perpendicular to the axis of the filament.

G. W. R.

Crystal Structure of White Tin. A. E. VAN ARKEL (*Proc. K. Akad. Wetensch.*, 1924, **27**, 97—104).—In continuation of the work of Burger (*Physica*, 1922, **2**, 56) on the properties of single crystal wires of tin, the author has taken röntgenograms to determine the orientation of the crystals in relation to the axis of the filament. The results are not in agreement with Bijl and Kolkmeijer's conclusions (A., 1919, ii, 108, 161), which do not explain the absence of a number of lines, exhibit divergencies in position and intensity for some of the lines, and do not explain satisfactorily the axial ratios given by Miller (*Ann. Phys. Chem.*, 1843, **58**, 660). White tin is calculated to have eight atoms per structure element and a tetragonal diamond structure, in agreement with that derived by Mark and Póányi (A., 1923, ii, 768).

T. H. P.

Arc Spectrum of Titanium. C. C. KIESS and H. K. KIESS.—(See ii, 510.)

Tervalent Vanadium. I. J. MEYER and R. BACKA (*Z. anorg. Chem.*, 1924, **135**, 177—193).—Anhydrous vanadium trichloride is prepared by passing carbon dioxide through vanadium tetrachloride at 140—150°. The latter chloride is obtained by passing chlorine over ferro-vanadium at dull red heat. Hydrogen chloride reacts at 300—400° with vanadium to give the trichloride, and with ferro-vanadium to give the dichloride. Anhydrous vanadium tribromide is best prepared by direct combination of the elements. The anhydrous tri-iodide could not be prepared.

Hexaminevanadium trichloride $[V(NH_2)_6]Cl_3$, and the corresponding bromide, are obtained by pouring liquid ammonia on to the appropriate halide; on moistening with concentrated nitric acid, both these compounds are converted to the nitrate, $[V(NH_3)_6](NO_3)_3$. All three compounds are decomposed by water: $[V(NH_3)_6]Cl_3 + 3H_2O = V(OH)_3 + 3NH_3 + 3NH_4Cl$; they are unstable in air: $[V(NH_3)_6]Cl_3 + O + 2H_2O = NH_4VO_3 + 3NH_4Cl + 2NH_3$, and in moist

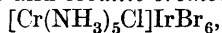
air they form the insoluble aquo-compound, $[V(H_2O)_6]Cl_3$. These compounds resemble the corresponding compounds of iron and aluminium rather than those of chromium and cobalt.

A *silicide*, VSi_2 , is prepared by heating together vanadium pentoxide, silicon, and fluorspar. The action of chlorine compounds (e.g., carbonyl, thionyl, sulphuryl, and sulphur chlorides) at 600° on vanadium (which may be prepared in 93.5% purity by the Goldschmidt process) yields vanadium tetrachloride; carbon monoxide at $500\text{--}800^\circ$ forms a carbide, the finely divided metal catalysing the reaction: $2CO=CO_2+C$. S. K. T.

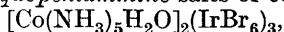
Bivalent Bismuth. E. NEUSSER (*Z. anorg. Chem.*, 1924, **135**, 313—326).—It is extremely improbable, theoretically, that bismuth can enter into combination as a bivalent element and the suboxide, BiO , is re-investigated from this point of view. The oxide, prepared by heating the basic oxalate or by reducing the hydroxide, is of variable composition, its bismuth content never reaching the theoretical value. This is not due to absorption of moisture, carbon dioxide, or oxygen; it is probably caused by the presence of hydroxide in the oxide. Metallic bismuth can be extracted from the substance by shaking with mercury. When heated for 16 to 18 hours in dry hydrogen sulphide, the suboxide behaves as a mixture of metal, trioxide, and hydroxide, each of which is attacked by the gas at a different rate. The presence of hydroxide explains the variable composition of the suboxide and also the low density (7.16 at 22° when freshly prepared) compared with that calculated for a mixture of bismuth metal and trioxide. Tanatar's thermochemical results, supporting the existence of the suboxide, are criticised (A., 1901, ii, 553). S. K. T.

Bromoiridates of Complex Metal Bases and Chloro- and Bromo-iridates of Organic Bases of High Molecular Weight.

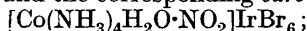
A. BENRATH [with W. BÜCHER, A. WOLBER, and J. ZEUTZIUS] (*Z. anorg. Chem.*, 1924, **135**, 233—254).—Fairly pure potassium bromoiridate is obtained in almost quantitative yield by warming together saturated solutions of potassium bromide and sodium chloroiridate, in presence of a little bromine, which is constantly renewed. The following new compounds are described: *hexammine-chromic nitrate bromoiridate*, $[Cr(NH_3)_6]NO_3IrBr_6$, and the *sulphate*, together with the corresponding *cobalt* compounds; *hexammine-chromic bromoiridate*, $[Cr(NH_3)_6]_2(IrBr_6)_3$, and the *cobalt* analogue; *chloropentamminechromic* and *cobaltic bromoiridates*,



etc.; the following *aquopentammine* salts of cobalt:



$[Co(NH_3)_5H_2O]Cl(IrBr_6)$ and the *sulphate*, $[Co(NH_3)_5H_2O]_2Cl_4IrBr_6$ and the *sulphate*, and $[Co(NH_3)_5H_2O]_4(SO_4)_3(IrBr_6)_3$; two *pentammine sulphates*, $[Co(NH_3)_5SO_4]_2IrBr_6$, $[Co(NH_3)_5SO_4]_4SO_4IrBr_6$; and the following *tetrammines*: $[Co(NH_3)_4(NO_2)_2]_2IrBr_6$ (*cis*- and *trans*-modifications) and the corresponding *carbonate*;



$[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}(\text{OH})_2]\text{SO}_4\text{IrBr}_6$ and the *hydroxide*;

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2\text{SO}_4(\text{IrBr}_6)_2$,

and the corresponding *disulphate*. The number of ammine groups has no influence on the colour. The accumulation of acid residues in either sphere tends to deepen the colour, whilst their replacement by hydroxyl groups lightens it. The individual nature of the groups has a large influence.

The *chloro-* and *bromo-iridates* of the following complex bases are also prepared ($x=1$ and 2 ; $X=\text{Cl}$ and Br): *quinine*,

$(\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2)_x\text{H}_2\text{IrX}_6$;

cinchonine, $(\text{C}_{19}\text{H}_{22}\text{ON}_2)_x\text{H}_2\text{IrX}_6$; *cinchonidine*,

$(\text{C}_{19}\text{H}_{22}\text{ON}_2)_x\text{H}_2\text{IrX}_6$;

strychnine, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_2\text{H}_2\text{IrX}_6$; *brucine*, $(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2)_2\text{H}_2\text{IrX}_6$;

"*nitron*," $(\text{C}_{20}\text{H}_{16}\text{N}_4)_2\text{H}_2\text{IrBr}_6$, the chloride having been previously prepared (A., 1922, ii, 515). These are nearly all obtained by mixing neutral or acid solutions of the base with a solution of sodium chloro- or bromo-iridate. The solubilities of most of the compounds described are measured by the conductivity method, since they are sparingly soluble. The chloroiridates are more soluble than the corresponding bromo-compounds, and the mono-alkaloidal salts are more soluble than the analogous dialkaloidal salts.

S. K. T.