

## Inorganic Chemistry.

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**Distillation of Water.** By W. MAREK (*J. pr. Chem.*, 1899, [ii], 60, 582—584).—The apparatus described is for the preparation of moderately large quantities of specially pure distilled water; it consists of a copper still of some 36 litres capacity internally tinned and fitted with a tin head and worm. The various parts are joined by flanges which are ground into one another, so that no organic or inorganic cementing material is required. Ordinary distilled water (30 litres) is introduced and is boiled for several minutes before the worm is cooled, 0.3 gram of potassium permanganate in concentrated aqueous solution is introduced, and the distillation carried out in the ordinary manner; the first 3 litres are rejected and the following 18 litres collected in large glass bottles previously treated with nitric acid. The flame employed is small, and the whole operation requires some 15 hours. J. J. S.

**Nature of Water of Crystallisation.** By FRIEDRICH RINNE (*Jahrb. f. Min.*, 1899, i, 1—31).—The water of crystallisation of a salt behaves in many ways like ordinary free water; for example, it gradually evaporates, especially at a slightly elevated temperature,

and in some salts there are certain points analogous to the boiling point of ordinary water. Copper sulphate ( $\text{CuSO}_4 + 5\text{H}_2\text{O}$ ), when quickly heated, gradually rises in temperature to  $105^\circ$ , and remains at this temperature until  $2\text{H}_2\text{O}$  has been expelled; the temperature then again gradually rises to  $117^\circ$ , when the boiling point of the second  $2\text{H}_2\text{O}$  is reached; the boiling point of the last  $\text{H}_2\text{O}$  is  $258^\circ$ . A less sharply marked point is  $99^\circ$ , where  $\frac{1}{2}\text{H}_2\text{O}$  is lost. For barium chloride ( $\text{BaCl}_2 + 2\text{H}_2\text{O}$ ), the boiling point of each molecule of water is  $105^\circ$  and  $162^\circ$ . These boiling points vary with the atmospheric pressure.

Heulandite and stilbite are examples of another group of substances in which the water of crystallisation behaves in a different manner; here, there is nothing analogous to boiling point, the water being lost gradually and *pari passu* with the rise in temperature; at the same time, there is a gradual change in the optical orientation of the crystals (Abstr., 1896, ii, 368; 1897, ii, 327). The amount of water lost at any particular temperature is less the greater the atmospheric pressure and the greater the amount of moisture in the air.

In these two groups, the relation of the water of crystallisation to the salt can be considered to be, in the first case, that of a molecular compound, and, in the second, that of a solid solution. L. J. S.

**Action of Persulphates on Iodine.** By HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1898, 22, 388—390).—When solutions of potassium iodide and potassium persulphate are mixed and warmed, iodine is liberated; investigation shows that this iodine is oxidised to iodic acid by excess of persulphate. If iodine is digested in a loosely corked flask at a moderate temperature with a strong solution of ammonium persulphate, the iodine gradually dissolves, and crystalline ammonium hydrogen iodate is obtained. In Price's experiments on the reaction between potassium iodide and potassium persulphate (Abstr., 1899, ii, 147), there may have been catalytic action, the iodine being alternately oxidised by the persulphate, and reduced by hydriodic acid. J. C. P.

**Vapour Density of Sulphur.** By OTTO BLEIER and LEOPOLD KOHN (*Ber.*, 1900, 33, 50—51. Compare Biltz, Abstr., 1888, 1027; 1889, 340; Biltz and Meyer, 1889, 674; Krause and Meyer, 1890, 1365; Riecke, 1891, 381; Schall, 1889, 331.—The following results have been obtained with the aid of the apparatus previously described (Abstr., 1899, ii, 643):

<i>t</i> .....	$310^\circ$	$262^\circ$	$236^\circ$	$212^\circ$	$193^\circ$
<i>p</i> .....	42.6	15.0	9.4	4.2	2.1
$D(\text{O}_2 = 1)$	7.44	7.5	7.66	7.80	7.85

from which it follows that the undissociated sulphur molecule consists of eight atoms. J. J. S.

**Hyposulphurous Acid.** By AUGUST BERNTHSEN and MAX BAZLEN (*Ber.*, 1900, 33, 126—132. Compare Abstr., 1881, 508, 976).—By passing sulphur dioxide into a solution of sodium hydrogen sulphite in contact with zinc, it is converted quantitatively into the

hyposulphite according to the equation  $2\text{NaHSO}_3 + \text{SO}_2 + \text{Zn} = (\text{Na}_2\text{S}_2\text{O}_4 + \text{ZnSO}_3) + \text{H}_2\text{O}$ ; by adding chalk, the zinc sulphite can be removed, and a solution of sp. gr. 15—16° Bé. obtained, which will reduce a fifth of its weight of indigo. From this solution, the sodium hyposulphite separates in crystals on adding salt or sodium hydroxide, and when washed with aqueous, and then with dry acetone, has the composition  $\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$ , thus confirming the authors' earlier conclusions, and disproving the formula  $\text{NaHSO}_2$  given to the salt by Schützenberger [compare Nabl's zinc salt,  $\text{ZnS}_2\text{O}_4$  (this vol., ii, 13)]; Grossmann's acid salts (*J. Soc. Chem. Ind.*, 1898, 17, 1109; 1899, 18, 452—453) cannot be prepared from the pure material, as sodium hyposulphite solutions deposit sulphur on adding a single drop of acid. Sodium hyposulphite forms large, thin, glistening prisms, which are fairly stable, but gradually effloresce and oxidise to sodium pyrosulphite,  $\text{Na}_2\text{S}_2\text{O}_5$ ; the dry salt is more stable, but when heated to dull redness burns with a blue flame and liberates sulphur dioxide.

T. M. L.

**Oxidation of Hydroxylamine.** By GEORG VON KNORRE and KURT ARNDT (*Ber.*, 1900, 33, 30—42).—Either the acid hydroxylamine solution, or the oxidising solution, was boiled in a stout conical flask fitted with a funnel and a delivery tube until the air was expelled; the flask was then connected with a vessel filled with mercury, the second solution (freed from dissolved gas by boiling) was run in, and the gas evolved driven over by boiling into the vessel mentioned, transferred from this to a gas burette, and analysed. The oxidising agents tried were potassium nitrate and sulphuric or hydrochloric acid; hydrated manganese peroxide, potassium permanganate, potassium dichromate, vanadic acid, and potassium persulphate, all with sulphuric acid; alkaline copper sulphate and mercuric chloride; also hydrogen peroxide. Nitrous oxide is usually the main product, but nitric oxide is often mixed with it, and the solution nearly always contains nitric (or nitrous) acid. The relative amounts of the two oxides vary with the oxidising agent and with the concentration of the latter. With vanadic acid, the gas consists chiefly of nitrogen; with potassium persulphate, it is pure oxygen, and also with hydrogen peroxide, but in the last case only a small amount is formed.

C. F. B.

**Action of very dilute Nitric Acid [on Metals].** By A. VAN BIJLERT (*Zeit. physikal. Chem.*, 1899, 31, 103—113).—The products of the action of nitric acid on metals result from (1) the oxidising action of the non-dissociated portion of the acid, and (2) the reducing action brought about by the dissociated acid. The oxidising action is hence the greater the stronger the acid, and the reducing action is more evident when weaker acid is employed. For the metals magnesium, zinc, or cadmium the reaction,  $2\text{M} + 2\text{HNO}_3 \cdot \text{Aq} = 2\text{MNO}_3 \cdot \text{Aq} + \text{H}_2$ , is exothermic, and ammonium nitrate is among the products obtained; whilst, for copper, silver, or mercury, this decomposition absorbs heat, and in these cases no ammonium nitrate is found.

A series of experiments on the action of dilute nitric acid (*N*/20 to *N*/10) on zinc at about 25° shows that the amount of ammonia formed,

bears to the amount of zinc used, a ratio varying from 1 : 33 to 1 : 40, the ratio required by the equation  $4\text{Zn} + 10\text{HNO}_3 = 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$  being 1 : 15 or 16. This deviation is ascribed to the intermediate formation of the other reduction products, such as nitrous acid, nitric oxide, nitrogen, &c. No hydroxylamine was detected.

T. H. P.

**Spontaneous Combustion of Coal.** By RUD. GRIMM (*Zeit. angew. Chem.*, 1899, 1242).—A heap of slag containing furnace ashes mixed with a small proportion of unconsumed coal, became ignited internally on being left exposed to the air, probably owing to the presence in the interior of a small quantity of still glowing clinker; the outer crust of the heap was riven, and clouds of steam were evolved. In the rents so formed, large, rhombic crystals of sulphur and crusts of ammonium chloride were observed; the author explains the liberation of sulphur thus:  $\text{FeS} + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{FeO}$ ;  $2\text{H}_2\text{S} + \text{SO}_2$  (from  $\text{FeS}_2$ ) =  $3\text{S} + 2\text{H}_2\text{O}$ .

W. A. D.

**Solubility of Argon and Helium in Water.** By TADEUSZ ESTREICHER (*Zeit. physikal. Chem.*, 1899, 31, 176—187).—The absorption coefficient of argon is 0.05612 at 1°, and 0.02567 at 50°, falling regularly between those temperatures. The absorption coefficient of helium is 0.01487 at 0.5°, and 0.01404 at 50°, but at 25° it has a minimum value 0.01371; these values are about twice as large as that provisionally given by Ramsay, namely, 0.0073 at 18.2°. The minimum solubility of helium seems to be connected with the difficulty of liquefaction, for the solubility curve of hydrogen shows the same peculiarity (compare Abstr., 1892, 107); other gases with a higher critical temperature will probably be found to have a minimum solubility above 100°.

A full account is given of the apparatus and method employed.

J. C. P.

**Electrolysis of Potassium Chloride.** By ANDRÉ BROCHET (*Compt. rend.*, 1900, 130, 134—137).—A yield of over 70 per cent. of potassium chlorate is obtained when a neutral or slightly alkaline, 20 per cent. solution of potassium chloride, containing a small quantity of potassium dichromate is electrolysed with a current of 2 amperes, the temperature of the solution being maintained between 16° and 20°. If the solution is made more strongly alkaline, the yield of chlorate, and also of hypochlorite, is decreased, and if no potassium dichromate is present, the yield of potassium chlorate is never more than 35 per cent. (compare Foerster, *Zeit. Elektrochem.*, 1, 854).

H. R. LE S.

**New Explosive and Detonating Materials.** By UGO ALVISI (*Gazzetta*, 1899, 29, 478—490. Compare Abstr., 1899, ii, 414, 647, and 748).—The author gives the name *cremonites* to explosives composed of picric acid, or a picrate mixed with ammonium perchlorate. They keep well, require very powerful detonators, are more powerful than picric acid alone, and have a propulsive force nearly equal to that of the most powerful gelatin-dynamite.

*Cannel powder* is the name given to mixtures of coal and ammonium

perchlorate, 5 parts of the latter to 1 part of Scotch cannell giving the best results. It is simply prepared, has great resistance to shock, keeps well, is non-hygroscopic, and requires powerful detonators.

Ammonium perchlorate can be made on a commercial scale by the interaction of concentrated solutions of ammonium nitrate and sodium perchlorate.  
T. H. P.

**Crystalline Hydrates of Sodium Thiosulphate.** By W. W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1898, 22, 248—251).—Crystals of the composition  $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}$  may be obtained by driving off part of the water from the fused pentahydrate and allowing the solution to cool. The solubility curves of the pentahydrate and dihydrate intersect at  $50^\circ$ , which is accordingly the transition temperature of the two hydrates. To obtain the dihydrate in quantity, anhydrous thiosulphate is dissolved in fused pentahydrate and the solution kept at  $53^\circ$ . Crystallisation is induced by adding a few fragments of dihydrate, and the crystals formed are dried in an oven at  $53^\circ$ .

J. C. P.

**Preparation of Metallic Lithium.** By LOUIS KAHLENBERG (*J. Physical Chem.*, 1899, 3, 602—603).—Lithium may be obtained very readily by the electrolysis of solutions of lithium chloride in pyridine. A beaker with a concentrated solution of the salt in pyridine served as a cell, no diaphragm being used; a carbon pole was used as anode, and an iron plate as cathode; the E.M.F. was about 14 volts, the current density about 0.25 ampere per 100 sq. cm.; under these conditions, an adhering, silver-white deposit of metallic lithium was obtained.  
L. M. J.

**Action of Magnesium on Saline Solutions.** By HENRI MOURAOUR (*Compt. rend.*, 1900, 130, 140—141. Compare Abstr., 1899, ii, 656).—A rapid evolution of hydrogen takes place when magnesium powder is added to cold solutions of ammonium chloride, ammonium carbonate, ammonium oxalate, ammonium sulphide, sodium carbonate, borax, common alum, and chrome alum. With solutions of sodium phosphate, sodium acetate, sodium nitrite, sodium thiosulphate, potassium sodium tartrate, potassium chloride, potassium ferrocyanide, barium chloride, calcium chloride, and strontium chloride, the evolution of hydrogen is slow, and with a solution of ammonium fluoride, hydrogen is not evolved.  
H. R. LE S.

**Metallic Borates.** By LÉON OUVRARD (*Compt. rend.*, 1900, 130, 172—175).—The only well defined metallic salt of orthoboric acid is Ebelmen's magnesium borate,  $\text{Mg}_3(\text{BO}_3)_2$  (*Ann. Chim. Phys.*, 1851, [iii], 33, 50). The evidence in support of the tribasic character of the acid is derived chiefly from the study of its esters.

*Cadmium orthoborate*,  $\text{Cd}_3(\text{BO}_3)_2$ , prepared by adding cadmium oxide (1 mol.) to a fused mixture of potassium hydrogen fluoride (1 mol.) and boric oxide (1 mol.), and treating the cooled product with water, separates in the form of prismatic needles not affected by water, but readily soluble in dilute acids. The crystals produce a

marked effect on polarised light, the plane of extinction being inclined at  $9^\circ$  to the principal axis. G. T. M.

**Borates of Zinc, Manganese, Nickel, and Cobalt.** By LÉON OUVREAU (*Compt. rend.*, 1900, 130, 335—338).—The compound,  $3\text{ZnO} \cdot \text{B}_2\text{O}_3$ , obtained by fusing zinc oxide with molecular proportions of potassium hydrogen fluoride and boric oxide, forms flat prisms which belong to the orthorhombic system and have a marked action on polarised light; they are decomposed by hot water and are readily soluble in dilute acids.

The following compounds were prepared in a similar manner:  $3\text{MnO} \cdot \text{B}_2\text{O}_3$ , from manganese chloride, carbonate, or precipitated borate, forms light-brown, transparent needles, which are not decomposed by hot water but are very soluble in dilute acids;  $3\text{NiO} \cdot \text{B}_2\text{O}_3$ , from nickel chloride, carbonate, or amorphous borate, forms short, clear, green prisms which are not attacked by hot water but are soluble in acids. In the case of cobalt, the borate obtained had the formula  $2\text{CoO} \cdot \text{B}_2\text{O}_3$ ; if, however, less boric oxide is employed, then the compound  $3\text{CoO} \cdot \text{B}_2\text{O}_3$  is obtained as rose-coloured, rhombic crystals.

H. R. LE S.

**Behaviour of Zinc Oxide at High Temperatures.** By ROBERT C. SCHÜPPHAUS (*J. Soc. Chem. Ind.*, 1899, 18, 987—989).—In heating a mixture of zinc oxide and carbon under pressure, a powder of a permanent canary-yellow hue was obtained; this when analysed shows a higher percentage of zinc than is contained in zinc oxide. Similar compounds may also be obtained by heating zinc oxide in a current of pure nitrogen, or in a vacuum, or with zinc dust under pressure. In each case, the product must be allowed to cool off in contact with the air. L. DE K.

**Hydrolysis of Thallic Sulphate.** By HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1899, 22, 596—597).—A slightly acid solution of thallic sulphate gives a brown precipitate of hydroxide on dilution; the same precipitate is formed when the solution is warmed, probably owing to an increase of hydrolysis with temperature; ammonium sulphate seems to prevent the formation of the precipitate on warming, but it redissolves in any case on cooling. J. C. P.

**New Micro-chemical Reactions of Copper.** By Pozzi-Escot (*Compt. rend.*, 1900, 130, 90—91).—The iodide,  $\text{CuI}_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , is obtained in the form of small, blue tetrahedrons by adding ammonium iodide or sodium iodide to an ammoniacal solution of a cupric salt. An unstable compound, probably  $\text{CuI}_4 \cdot 4\text{NH}_3$ , is formed by adding ammonium iodide or sodium iodide to an ammoniacal solution of a cupric salt which is heated at  $40^\circ$  and contains sufficient ammonia to give a clear solution when hot. Under these conditions, the solution turns a yellowish-green colour, and deposits dark brown rhomboidal plates mixed with prismatic crystals of the same colour, and sometimes also with orange, orthorhombic plates. The colour and crystalline form of the deposit soon change, and after 10—40 minutes the deposit consists entirely of short, thick, flat prisms and triclinic

plates of a yellow colour and possessing a coppery lustre. When seen under the microscope, these changes are very characteristic.

H. R. LE S.

**Action of Bromine on Copper Salts in Presence of Alkali Hydroxides. A New Test for Copper Salts.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1899, ii, 990—991; from *Boll. Chim. Farm.*, 38, 665—668).—When copper salts are treated with an alkali hydroxide in presence of an excess of bromine water, a brown to black precipitate of the peroxide  $\text{CuO}_2$  is formed. Chlorine or iodine may be used instead of bromine, but the reaction then takes place much more slowly. The presence of 1/100000th part of copper in 1 c.c. of a solution of crystallised copper sulphate may be detected by the intense yellow coloration produced by evaporating the solution and treating the residue with potassium hydroxide solution and bromine water. By evaporating the solution to dryness, then adding a few drops of bromine water and again evaporating, a black residue of anhydrous copper bromide is left and by this method even 1/1000000th part of copper in 1 c.c. of a solution of the sulphate, may be detected. The black stain may be rendered more distinct by moistening the residue with concentrated sulphuric acid after evaporating with bromine water. By the action of alkali hydroxides and bromine on nickel and cobalt salts, the black hydroxides  $\text{Ni}_2(\text{OH})_6$  and  $\text{Co}_2(\text{OH})_6$  are formed. Platinum salts form the brown hydroxide  $\text{PtO}_2(?)$ . Manganese salts give a black and mercury salts a yellow precipitate. When bismuth oxide is treated with alkali and bromine water, the yellow hydroxide,  $\text{Bi}(\text{OH})_3$ , is first formed by the action of the alkali, and on heating is, by the action of the potassium hypobromite present, converted into a heavy brown powder of the oxide  $\text{Bi}_2\text{O}_4$ . Lead salts behave in a similar manner, the yellow precipitate of lead oxybromide, which is first formed, being converted into the dioxide on heating; this oxide, unlike that of bismuth, is insoluble in a small quantity of dilute nitric acid.

E. W. W.

**Action of Ammonia on Diammoniomeric Iodide.** By MAURICE FRANÇOIS (*Compt. rend.*, 1900, 130, 332—335. Compare *Abstr.*, 1899, ii, 657).—When a solution of ammonia of sp. gr. 0.923 is added to mercuric iodide, white diammoniomeric iodide is first formed. This, on the further addition of a large excess of ammonia, is converted into ammoniodimercuric iodide. The latter change is limited and also reversible, for on the addition of a solution of ammonia containing a large proportion of ammonium iodide to ammoniodimercuric iodide, the latter is partly converted into diammoniomeric iodide.

H. R. LE S.

**[Luminosity of Mixtures of Thoria and Ceria.]** By HERMANN THIELE (*Ber.*, 1900, 33, 183—187).—The luminosity of mantles prepared from mixtures of thoria and ceria and heated in the Wehnelt arc (*Ann. Phys. Chem.*, 68, 260), is not appreciably changed by increasing the amount of ceria from 0—5 per cent., but with larger amounts the luminosity decreases owing to the increased resistance thereby caused.



In the flame of the Wehnelt arc, however, as with the Bunsen flame, the luminosity is a maximum with mixtures containing from 1—2 per cent. of ceria. W. A. D.

**Separation of Gadolinite Earths and the Preparation of Pure Yttria.** By WILHELM MUTHMANN and R. BÖHM (*Ber.*, 1900, 33, 42—49. Compare this vol., ii, 18).—The normal chromates of the rare earths are all more soluble than the corresponding sulphates. They have the general formula  $M_2(\text{CrO}_4)_3 \cdot n\text{H}_2\text{O}$ , and as a rule  $n=8$ . Separations of the rare earths may be more rapidly effected by the aid of these chromates than by any other known method, the separation being best accomplished by fractionally precipitating solutions of the readily soluble dichromates with potassium chromate. In the separation of yttria earths, it is essential that (1) both solutions must be extremely dilute; (2) the liquid must be kept in rapid ebullition during the precipitation; (3) the precipitate must be in an extremely finely divided state, and must be kept in intimate contact with the liquid. Minute directions are given in the original for securing these conditions. By employing this method, the authors have succeeded in obtaining pure yttria from commercial yttrium oxide after six fractionations, the last fraction consisting of pure yttrium chromate in the form of minute, deep red prisms.

The atomic weight of yttrium, determined from this fraction by conversion into sulphate and then igniting for 15—20 hours to convert into oxide, was found to be 88.97. Cleve (*Abstr.*, 1883, 292) gives 89.92.

The specific gravities of the earths from the six different fractions were found to be 6.06, 5.62, 5.43, 4.87, 4.83 (pure yttria), and that of the original mixture 5.62. Cleve and Höglund give 5.028, Nilson and Pettersson (*Compt. rend.*, 1880, 91, 232) give 5.06, and Ekeberg (*Phil. Mag.*, 14, 346) 4.842 for pure yttria.

The other constituents of the crude oxide are erbia, which yields olive-coloured octahedra with potassium chromate, and an earth which yields a chromate in the form of small, golden needles. J. J. S.

**Gadolinium.** By CARL BENEDICKS (*Zeit. anorg. Chem.*, 1900, 22, 393—421).—Gadolinium is separated from the other rare earths by crystallising the nitrates from nitric acid (*Abstr.*, 1896, ii, 475), and when a fairly pure nitrate is obtained, this is subjected to partial precipitation with dilute ammonia (*Abstr.*, 1891, 17). A determination of the atomic weight, by conversion of the oxide into sulphate, gave  $\text{Gd} = 156.38$  (6 experiments:  $\text{O} = 16$ ). The following compounds are described. Gadolinium oxide,  $\text{Gd}_2\text{O}_3$ , is a white powder, easily soluble in acids, absorbs carbon dioxide from the air, is somewhat hygroscopic, and is not reduced by heating in a current of hydrogen. The *hydroxide* is a gelatinous precipitate, which rapidly absorbs carbon dioxide. The salts of gadolinium are mostly colourless, show no absorption spectrum, have a sweet, astringent taste, and are very similar to the salts of yttrium. The *chloride*,  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ , crystallises in thick, tabular, quadratic pyramids, and has a sp. gr. 2.424. The *bromide*, with  $6\text{H}_2\text{O}$ , crystallises in small,



pointed, rhombic tablets, of sp. gr. 2·844. The *platinichloride*,  $\text{GdCl}_3 \cdot \text{PtCl}_4 + 10\text{H}_2\text{O}$ , crystallises in orange-yellow, prismatic needles of sp. gr. 2·719. The *aurichloride* crystallises, with  $10\text{H}_2\text{O}$ , in yellow tablets of sp. gr. 2·706. *Gadolinium platinocyanide*,  $2\text{Gd}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_2 + 18\text{H}_2\text{O}$ , obtained by the action of the sulphate on barium platinocyanide, crystallises in long, pointed, and tabular, red crystals of the rhombic system, having a green metallic lustre, and is isomorphous with the corresponding yttrium and erbium salts; sp. gr. 2·563. The *nitrate*,  $\text{Gd}_3\text{NO}_3 + 6\frac{1}{2}\text{H}_2\text{O}$ , separates over sulphuric acid, or by evaporation in the air, in large, triclinic crystals of sp. gr. 2·332. It also crystallises with  $5\text{H}_2\text{O}$  from concentrated nitric acid in prisms of sp. gr. 2·406. The *double salt*, with ammonium nitrate,  $\text{Gd}_3\text{NO}_3 \cdot 2\text{NH}_4\text{NO}_3$ , crystallises in long, hair-like, deliquescent crystals. The *sulphate*,  $\text{Gd}_2\text{SO}_4 + 8\text{H}_2\text{O}$ , separates in small, lustrous, monoclinic crystals, and is isomorphous with yttrium sulphate; sp. gr. 3·007. The anhydrous salt has a sp. gr. 4·139. The *double salt*, with potassium sulphate,  $\text{Gd}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , has a sp. gr. 3·503. 100 c.c. of a saturated potassium sulphate solution will hold 0·87—0·77 gram  $\text{Gd}_2\text{O}_3$  in solution. The *selenate*,  $\text{Gd}_2\text{SeO}_4 + 10\text{H}_2\text{O}$ , crystallises at the ordinary temperature in large, colourless, rhombic prisms, is isomorphous with the yttrium and erbium selenates, and rapidly effloresces; sp. gr. 3·048. It separates, with  $8\text{H}_2\text{O}$ , at the temperature of the water-bath in nacreous crystals of sp. gr. 3·309. The anhydrous salt has a sp. gr. 4·175. The *double salt*, with potassium selenate,  $\text{Gd}_2\text{SeO}_4 \cdot 3\text{K}_2\text{SeO}_4 + 4\text{H}_2\text{O}$ , crystallises in slender, microscopic needles. *Gadolinium hydrogen selenite*,  $\text{Gd}_2\text{SeO}_3 \cdot \text{H}_2\text{SeO}_3 + 6\text{H}_2\text{O}$ , is an amorphous precipitate, which gradually forms aggregates of small needles. *Gadolinium ethyl sulphate*,  $\text{Gd}_3\text{EtSO}_4 + 9\text{H}_2\text{O}$ , obtained from the sulphate and barium ethyl sulphate, crystallises in large, transparent tablets belonging to the hexagonal system [ $a : c = 1 : 0\cdot5014$ ], is stable in the air, effloresces over sulphuric acid, and, when heated at  $115^\circ$ , loses  $3\text{EtOH} + 6\text{H}_2\text{O}$ ; sp. gr. = 1·923. The *vanadate*,  $\text{Gd}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 + 26\text{H}_2\text{O}$ , crystallises in the triclinic system [ $a : b : c = 1\cdot7083 : 1 : 0\cdot9894$ ;  $\alpha = 84^\circ 51'$ ,  $\beta = 94^\circ 51'$ ,  $\gamma = 82^\circ 13\cdot5'$ ]. The *basic carbonate*,  $\text{OH} \cdot \text{GdCO}_3 + \text{H}_2\text{O}$ , obtained by treating the hydroxide with carbon dioxide, crystallises in small, microscopic needles. The *normal carbonate*,  $\text{Gd}_2\text{CO}_3 + 13\text{H}_2\text{O}$  (?), is obtained by prolonged action of carbon dioxide on the hydroxide. The *oxalate*, with  $10\text{H}_2\text{O}$ , crystallises from concentrated nitric acid in large, monoclinic crystals; 1 gram of ammonium oxalate dissolved in 38 grams of water will hold 0·00083 gram of gadolinium oxide in solution. The *acetate* crystallises with  $4\text{H}_2\text{O}$  in sparingly soluble, colourless, triclinic crystals of sp. gr. 1·611. The *propionate* crystallises in a vacuum desiccator in crusts of large, rhombic tufts. E. C. R.

**Stable Hydrates of Manganese Chloride above  $0^\circ$ .** By HARRY M. DAWSON and P. WILLIAMS (*Zeit. physikal. Chem.*, 1899, **31**, 59—68).—Investigation with the dilatometer shows that the ordinary hydrate of manganese chloride,  $\text{MnCl}_2 + 4\text{H}_2\text{O}$ , is transformed into the dihydrate at  $57\cdot9^\circ$ , at which temperature also the vapour tension of the dry tetrahydrate becomes equal to the vapour pressure of the saturated

solution; at the same temperature, there is a corresponding discontinuity in the solubility curve and in the density of the saturated solution. When a manganese chloride solution crystallises at about  $70^{\circ}$ , large, well-formed crystals are obtained which, after draining, washing with alcohol, and drying between filter paper, are found to have the composition  $\text{MnCl}_2 + 2 \cdot 2\text{H}_2\text{O}$ , confirming the dilatometer result. A better method of preparing the dihydrate is to pass hydrogen chloride into an alcoholic solution of manganese chloride saturated at the ordinary temperature; the crystals of the dihydrate which separate are pink, but deeper in tint than the ordinary tetrahydrate. The dihydrate is stable from  $58$ — $198^{\circ}$ ; at the latter temperature, it is transformed into the anhydrous salt.

Marignac's  $\beta$ -tetrahydrate, obtained by crystallisation at  $0$ — $6^{\circ}$  of a solution saturated at a higher temperature, represents a labile form at all temperatures. J. C. P.

**Peroxides.** By SIMEON M. TANATAR (*Ber.*, 1900, 33, 205—208).—Peroxides are usually divided into two classes, the members of one of which yield hydrogen peroxide on treatment with acids, whilst those of the other do not. Piccini (*Abstr.*, 1897, ii, 9) further states that the true (hydrogen peroxide yielding) peroxides reduce certain compounds, such as manganese dioxide, lead dioxide, and potassium permanganate, in presence of acids, and that they are never produced by oxidation carried out with nitric or hypochlorous acid.

The author suggests that the two classes of peroxides may not differ in chemical constitution, but that the differences between their reactions may be accounted for by thermochemical considerations. The heat developed by the action of acids on the "false" peroxides is less than that required for the formation of hydrogen peroxide. Nickel peroxide, which acts in most respects as a false peroxide, develops, however, sufficient heat to render possible the formation of hydrogen peroxide, and the author has found that perceptible amounts of hydrogen peroxide are actually produced by the decomposition of nickel peroxide with sulphuric acid. The peroxides of nickel and cobalt, moreover, appear capable of converting barium hydroxide into the peroxide, for in their presence barium hydroxide brings about the reduction of potassium permanganate. Potassium permanganate is also slowly decolorised in the cold when it is mixed with solutions of sodium hypochlorite and barium hydroxide. A. H.

**Nature of the Change from Violet to Green in Solutions of Chromium Salts.** By WILLIS R. WHITNEY (*J. Amer. Chem. Soc.*, 1899, 21, 1075—1084. Compare *Abstr.*, 1896, ii, 525).—The author considers that the conclusions of Venable and Miller (*Abstr.*, 1898, ii, 592) are erroneous, and describes experiments which confirm the observations of Recoura (*Abstr.*, 1896, ii, 27) and of Favre and Valson (*Compt. rend.*, 1872, 74, 1032). [Compare also Dougal (*Trans.*, 1896, 69, 1526.)] E. G.

**A New Crystalline Molybdenum Sulphide.** By MARCEL GUICHARD (*Compt. rend.*, 1900, 130, 137—140).—When molybdenum disulphide is heated in the electric furnace, it is decomposed, and a

new compound, *molybdenum sesquisulphide*,  $\text{Mo}_2\text{S}_3$ , is formed; this crystallises in steel-grey needles of sp. gr. 5.9 at  $15^\circ$ . When slightly heated, it is readily decomposed by fluorine and chlorine, but only at a red heat by bromine, whilst iodine is without action on it, even at the higher temperature. When strongly heated in oxygen, molybdenum trioxide is formed, and in atmosphere of sulphur, it is converted into the disulphide. Hydrochloric and sulphuric acids have no action on it, but hot concentrated nitric acid and aqua regia readily dissolve it with formation of molybdic and sulphuric acids. If molybdenum sesquisulphide is heated to a temperature slightly higher than that at which it is formed, it is decomposed into metallic molybdenum, and, if carbon is present, the carbide  $\text{CMo}_2$  is formed. H. R. LE S.

**Enantiotropy of Tin. II.** By ERNST COHEN and C. VAN EIJK (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 149—153; *Zeit. physikal. Chem.*, 1899, 30, 601—622. Compare this vol., ii, 83).—The velocity of change of the white into the grey modification of tin has been determined, with the aid of a dilatometer, at various temperatures from  $0^\circ$  to  $-83^\circ$ , and has a maximum at about  $-48^\circ$ , which is accordingly the most favourable temperature for the conversion of white tin into grey tin.

Further qualitative investigation at a temperature of  $-4^\circ$  to  $-7^\circ$  shows that the change of dry white tin into grey tin takes place slowly, beginning at the edges. If the white tin has powdered grey tin in contact with it, the change is accelerated, and begins at the points of contact. White tin filings are much more rapidly converted than white block tin. J. C. P.

**Enantiotropy of Tin. III.** By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 281—286. Compare preceding abstract).—White tin can be inoculated with grey tin; a large block treated thus and kept at  $-5^\circ$  for 3 weeks was photographed and seen to be covered with grey nodules.

Previous investigation has shown that the velocity of change of white tin into grey tin is a maximum at  $-40^\circ$ , and zero at  $20^\circ$ . At the ordinary temperature, the velocity is small, and a very long time would be necessary for the transformation. This condition was regarded as fulfilled in the case of an antique vase dug up in Hampshire, and supposed to date from the fourth century; on examination, the vase was found to consist almost entirely of grey tin.

The velocity of the change of grey tin to white tin above  $20^\circ$  has been investigated with the aid of a dilatometer, and found to increase very rapidly, rendering measurement impossible at  $40^\circ$ . J. C. P.

**Bismuth Suboxide and Subsulphide.** By R. SCHNEIDER (*J. pr. Chem.*, 1899, [ii], 60, 524—543. Compare Abstr., 1899, ii, 227).—The following method for the preparation of bismuth suboxide,  $\text{Bi}_2\text{O}_3$ , is simpler, and yields better results, than the two methods previously described by the author. A solution of bismuth oxide,  $\text{Bi}_2\text{O}_3$ , in nitric acid, is poured slowly and with constant stirring into excess of dilute potassium hydroxide; the precipitate of bismuth hydroxide is washed by decantation, and then suspended in 2 per cent. potassium hydroxide in a

capacious flask; a solution of freshly prepared stannous chloride is slowly added, the flask completely filled with air-free water, tightly closed, and the contents well shaken. Bismuth suboxide is thus obtained as a light, perfectly homogeneous, black powder. If freely exposed to the air in a moist state, it is completely converted into ordinary bismuth hydroxide.

Bismuth subsulphide,  $\text{Bi}_2\text{S}_3$ , is conveniently prepared by heating bismuth suboxide in a stream of dry hydrogen sulphide. It forms a slate-grey, dense, entirely homogeneous powder. When moderately heated in absence of air, it remains unchanged; at a low red heat, it melts and decomposes into bismuth and the ordinary bismuth sulphide. If heated in a current of hydrogen, it is reduced to the metal; the reduction begins at the temperature of melting sulphur, and then proceeds smoothly and rapidly.

The author replies in detail to the criticisms of Vanino and Treubert (Abstr., 1899, ii, 428) on his previous communications, and adheres to his former conclusions. E. G.

**Isomorphous Compounds of Gold and Mercury.** By THEODOR H. BEHRENS (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 163).—The halogen salts of these metals have been found to yield complete series of compound crystals. These were prepared by adding chlorides or bromides of thallium, caesium, and rubidium to mixed solutions of the chlorides and bromides of gold and mercury. J. C. P.

**Preparation of Colloidal Metallic Solutions by the Disintegrating Action of an Electric Discharge.** By GEORG BREDIG (*Zeit. angew. Chem.*, 1898, 951—954).—Hitherto colloidal metallic solutions have been obtained by the action of chemical reducing agents. The author describes how an electric discharge between poles of gold, silver, and platinum, immersed in water, disintegrates the cathode, and gives a solution of the metal. In the case of gold, reddish-purple or dark blue solutions are thus obtained, which can be filtered without change and keep their colour for months; the gold may be precipitated from the solution by freezing or by the addition of electrolytes; non-electrolytes, on the other hand, are ineffective. When the colloidal solution is subjected to electrolysis, the metal is separated at the anode as a black slime.

Silver and platinum give clear, dark brown solutions, which even with a small metal concentration absorb light almost entirely and are generally similar in properties to the colloidal gold solution. The colloidal platinum solution behaves like platinum black in decomposing hydrogen peroxide with evolution of oxygen.

Careful microscopic investigation reveals no heterogeneity, but the author is nevertheless of opinion that these solutions are really heterogeneous systems of the very finest structure, the particles having probably about a thousand times the molecular dimensions. The colours observed are regarded as due to this state of fine division. J. C. P.

**Inorganic Ferments. I. Catalytic Action of Platinum, and the Chemical Dynamics of Hydrogen Peroxide.** By GEORG BREDIG and R. MÜLLER VON BERNECK (*Zeit. Physikal. Chem.*, 1899, 31, 258—353).—Close analogy exists between the decomposition of

hydrogen peroxide by organic ferments (Jacobson, Abstr., 1892, 899), and by colloidal platinum. The latter agent is formed by the action of an electric discharge between platinum wires immersed in water, and the dark brown solution so obtained (with a maximum possible concentration of 1 gram-atom of platinum in 1300 litres of water) behaves in numerous cases exactly like platinum black. As this colloidal platinum is precipitated by electrolytes, its action is advantageously studied on hydrogen peroxide, which is practically a non-conductor, and yields non-electrolytic decomposition products.

Solutions of hydrogen peroxide were prepared with the conductivity  $1.5 \times 10^{-5}$ — $3.7 \times 10^{-5}$ ; to a suitably diluted portion, some of the platinum solution was added, and the mixture was kept at a constant temperature (generally  $25^\circ$ ); portions extracted from time to time were titrated with permanganate solution, and the progress of the decomposition of hydrogen peroxide thus determined. Even a solution of 1 gram-atom of platinum in about 70 million litres of water markedly accelerates the decomposition of hydrogen peroxide. The authors have compared with this the catalytic action of the peroxides of manganese, cobalt, copper, and lead, in both acid and alkaline solution.

The decomposition of hydrogen peroxide in acid and neutral solution in presence of colloidal platinum of constant quantity and condition, proceeds strictly according to the unimolecular equation,  $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ . In alkaline solution, the catalytic action of colloidal platinum first increases, reaches a maximum, and then diminishes again, as the alkali concentration increases; this is exactly what happens in the action of organic ferments on hydrogen peroxide. The values for the velocity constant obtained in alkaline solution are not steady, probably owing to the partial combination of the hydrogen peroxide and the alkali, as indicated by freezing point and other experiments.

Colloidal platinum and organic ferments are both alike affected by the addition of electrolytes, but the analogy is perhaps most strikingly illustrated by the effect of certain poisons, such as hydrocyanic acid, hydrogen sulphide, and mercuric chloride; the colloidal platinum is, as it were, paralysed by these agents, but recovers itself after a certain time.

The catalytic action of the colloidal platinum solution increases with its concentration, although not proportionally, and is favoured by rise of temperature; the increase of the velocity constant in the latter case agrees well with Arrhenius' equation  $\log_e k_1/k_2 = A(T_1 - T_2)/(T_1 \cdot T_2)$ , where  $k_1$  and  $k_2$  are the velocity constants corresponding to the temperatures  $T_1$  and  $T_2$ , and  $A$  is a constant (Abstr., 1889, 1103). Light does not affect the catalytic action of the colloidal platinum.

The view that platinum acts on hydrogen peroxide as certain solids do on supersaturated gas solutions is not confirmed. The paper contains a review of various theories of catalytic action. J. C. P.

**Platinum Tetrachloride.** By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1900, 22, 445—465).—The electric conductivity of aqueous solutions of platinum tetrachloride is not constant, but alters with the

time, and the values are dependent on the dilution; the results are essentially those given by a weak acid, and are similar to those obtained with selenious acid. An aqueous solution of platinum tetrachloride, when titrated with sodium hydroxide, using phenolphthalein as indicator, is neutralised with two equivalents of alkali; and by determining the specific conductivity of solutions to which successive quantities of alkali are added, unmistakable evidence of the formation of an acid and a normal salt is obtained. This is more clearly shown when ammonia is used to neutralise the solution. It is therefore evident that a solution of platinum tetrachloride contains a dibasic acid. The silver salt,  $\text{Ag}_2\text{PtCl}_4(\text{OH})_2$ , has been known for some time. The author was unable to isolate the alkali salts from their solution. Copper, zinc, or cadmium hydroxides dissolve in the aqueous solution, but the resulting salts do not crystallise, and yellowish-brown gums are obtained, easily soluble in water and alcohol. The alcoholic solution, when precipitated with ether, yields yellow, gummy flocks, which solidify after a time, and these, on analysis, gave numbers agreeing fairly well with the formulæ  $\text{ZnPtCl}_4(\text{OH})_2 + 3\text{H}_2\text{O}$  and  $\text{CdPtCl}_4(\text{OH})_2$ . The *thallium* salt,  $\text{Tl}_3\text{Pt}_2\text{Cl}_8\text{H}_5\text{O}_4$ , obtained by precipitating an aqueous solution of the tetrachloride with a thallium salt, is a yellow, amorphous powder. The *lead* salt,  $\text{PbPtCl}_4(\text{OH})_2$ , is obtained as a yellow precipitate by adding a mixture of lead and sodium acetates to the aqueous solution; the *lead* salt,  $\text{PbPtCl}_4(\text{OH})_2, \text{Pb}(\text{OH})_2$ , obtained in alcoholic solutions, is a brownish powder. E. C. R.

**Nature of Palladium Hydrogen.** By JOHN SHIELDS (*Proc. Roy. Soc. Edin.*, 1898, 22, 169—186).—The E.M.F. of the combination—palladium containing a small quantity of hydrogen | dilute sulphuric acid | palladium containing a large quantity of hydrogen—is zero, or nearly so. Thus the cell does not behave like a true concentration cell, as would probably be the case were the absorption of hydrogen by palladium simply a process of solution. The view that a chemical compound is formed would agree better with the facts, for the E.M.F. in this case would be independent of the quantity of compound formed. The experiments are insufficient to determine whether the compound formed is  $\text{Pd}_3\text{H}_2$ , or whether it contains more hydrogen than corresponds with this formula. J. C. P.