

Inorganic Chemistry.

Place of Hydrogen in the Periodic System. By BOHUSLAV BRAUNER (*Chem. News*, 1901, 84, 233—234).—A theoretical paper dealing mainly with the question as to whether hydrogen should be regarded as the first member of the halogen group, or whether the old view that it should stand at the head of the first group is still most in accordance with facts. D. A. L.

Positive and Negative Halogen Ions. By JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1901, 23, 797—799).—Attention is drawn to

the existence of positive chlorine ions in aqueous solutions of chlorine and hypochlorous acid, experimental proof of which is furnished by the work of Jakowkin (Abstr., 1899, ii, 736). E. G.

Formation of Ozone. By ALBERT LADENBURG (*Ber.*, 1901, **34**, 3849—3851).—In preparing ozone by means of the 'silent discharge,' the proportion of ozone reaches a maximum for intermediate values of the current strength, but increases progressively with falling temperature. The maximum percentage recorded is 10.79. T. M. L.

Production of Ozone. By A. CHASSY (*Compt. rend.*, 1901, **133**, 789—791).—The quantity of ozone formed in a Berthelot's apparatus at 20° increases with the time, according to a law which is independent of the intensity of the discharge. The curve representing the rate of increase is asymptotic to a line parallel with the axis of time, and the quantity of ozone formed tends towards a limit which depends on the temperature and is independent of the intensity of the discharge. The formation of a given quantity of ozone requires less expenditure of energy in the form of electric discharge when the percentage of ozone is low than when it is high. C. H. B.

Decomposition of Potassium Iodide Solutions by Ozone. By KARL GARZAROLLI-THURNLACKH (*Monatsh.*, 1901, **22**, 955—975. Compare Brunck, Abstr., 1900, ii, 572; Péchard, Abstr., 1900, ii, 536).—In the product obtained by the action of ozone on solutions of potassium iodide, the amount of iodine which could be extracted by carbon disulphide was determined by titration with potassium arsenite; the iodine present as hypoiodite or other compound and the total iodine were also estimated. When a concentrated solution of potassium iodide has been exposed to the action of ozone for five minutes, the solution contains iodine, hypoiodite, iodate, periodate, and potassium hydroxide. Further changes then take place, the quantity of hypoiodite and periodate gradually decreases, the former ultimately disappearing, whilst the amounts of iodine, potassium hydroxide, and iodate increase. Conditions more favourable for the formation of periodate, but less favourable for that of hypoiodite, are obtained by passing the ozone into the solution of the iodide. Attempts to obtain direct evidence of the presence of potassium peroxide or hydrogen peroxide failed, however. The fume which is formed when ozone acts on potassium iodide contains an iodine oxide which is attacked by potassium arsenite.

By the action of ozone on a solution of potassium bromide, hypobromite and bromate are formed together with some bromine.

E. W. W.

Pure Tellurium and its Atomic Weight. By PAUL KÖTHNER (*Annalen*, 1901, **319**, 1—58).—The communication contains a bibliography of the subject and a discussion of the relationship of tellurium to its neighbouring elements in the periodic classification. Tellurium may be separated from its common impurities (copper, silver, gold,

bismuth, antimony, arsenic, and selenium) by dissolving the crude substance in hydrochloric acid containing a little nitric acid, evaporating off the excess of the latter reagent, diluting the cooled solution with water until the deep yellow colour of tellurium tetrachloride disappears, filtering from the precipitate of silver chloride and the oxychlorides of antimony and bismuth, and treating the warm filtrate with sulphur dioxide. The precipitated metalloid is again subjected to the foregoing treatment and fractionally precipitated by the reducing agent. Three fractions are employed, and after repeating the operation two or three times the middle fraction consists of pure tellurium; the first portions contain arsenic, whilst the third fraction shows traces of copper and gold. The element may be obtained in a crystalline form by passing sulphur dioxide into a hot solution of the tetrachloride in concentrated hydrochloric acid (20.3 per cent.); the crystals being opaque with a silvery lustre.

Telluric acid, prepared by Staudenmaier's method (Abstr., 1896, ii, 96), even after repeated crystallisation, exhibits, in its spectrum, lines characteristic of silver, copper, and antimony.

The basic nitrate, $\text{OH} \cdot \text{TeO} \cdot \text{O} \cdot \text{TeO} \cdot \text{ONO}_2$, employed by Norris, Fay, and Ederly (Abstr., 1900, ii, 272), is conveniently prepared by dissolving small quantities of tellurium in a slight excess of nitric acid and evaporating the solution obtained from several experiments. In this way, the separation of tellurium is reduced to a minimum. This salt, however, even after repeated crystallisation, still contains traces of silver and copper.

Tellurium can be separated from all other elements except antimony by distillation in a vacuum, and since this element is removed in purifying the basic nitrate, it follows that a combination of the two processes should lead to the production of pure tellurium. The product obtained by reducing the recrystallised nitrate with sulphur dioxide is distilled under 9—12 mm. pressure in a tube divided into segments by asbestos partitions. After repeated distillation through three or four of these compartments, a specimen is obtained which is quite free from impurities. The spectrum of this product agrees in every respect with that of the element prepared from diphenyl telluride (Steiner, Abstr., 1901, ii, 235, 236).

The foregoing method is more readily carried out and is far less wasteful than that based on fractional precipitation with sulphur dioxide.

Telluric acid, $\text{Te}(\text{OH})_6$, the basic sulphate, $2\text{TeO}_2 \cdot \text{SO}_3$, and the double chlorides with ammonium and rubidium are not suitable for the atomic weight determination, the compound finally selected being the recrystallised basic nitrate. The atomic proportions of tellurium and nitrogen were determined by decomposing the basic nitrate in a modified Dumas apparatus and estimating the nitrogen, water, and residual tellurium dioxide. In this way, three experiments gave a mean atomic weight of 126.8; the method, however, is open to objection, owing to the errors incidental to the absolute method of estimating nitrogen.

The atomic weight was finally obtained with greater accuracy by heating the pure salt and weighing the dioxide. The results of seven

determinations which were very concordant showed that tellurium, obtained by the author's process, has an atomic weight of 126.7 ($H=1$) or 127.88 ($O=16$). The ultra-violet spectrum seems to be the best criterion of the purity of the tellurium, and photographs of the spectra of different preparations are included in the communication.

G. T. M.

Experiments on the Atomic Weight of Tellurium. By GIOVANNI PELLINI (*Ber.*, 1901, **34**, 3807—3810).—To purify the tellurium, diphenyl telluride was repeatedly fractionated under diminished pressure and then converted into the dibromide, which was purified by recrystallisation from benzene and then oxidised to telluric acid. The tellurium obtained from the acid was distilled in a vacuum. For the atomic weight determinations, tellurium was in one series oxidised by nitric acid to dioxide; in another series, the dioxide was reduced to tellurium in a current of hydrogen. The mean value of six determinations in the first series was 127.65 (maximum 128.05, minimum 127.41); in the second series, the mean value of three determinations was 127.62 (maximum 128.02, minimum 127.30) when $O=16$.

K. J. P. O.

Preparation of Nitrogen from Ammonium Nitrate. By JUL. MAI (*Ber.*, 1901, **34**, 3805—3806).—On heating a mixture of glycerol (2 parts) and ammonium nitrate (1 part) at 190° , a reaction begins, which continues without further application of heat until the temperature has fallen to 150° . The gas evolved is mainly nitrogen mixed with a small quantity of carbon dioxide. The reaction begins at a lower temperature, and the gas is evolved more regularly if 2 or 3 drops of concentrated sulphuric acid are added to the mixture. The glycerol is oxidised to glyceric acid and at the same time a very small amount of pyridine bases is formed. From 10 grams of ammonium nitrate, 2690 c.c. of nitrogen were obtained instead of 2775 c.c. theoretically possible (at *N.T.P.*).

K. J. P. O.

The Condition Diagram for Phosphonium Chloride. By GUSTAV TAMMANN (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 244—256).—The melting curve of phosphonium chloride is given by the equation: $t = 28.5 + 0.0329(p - 50) - 0.00000366(p - 50)^2$ up to a pressure of 1550 kilos., and above this by $t = 28.5 + 0.0295(p - 50) - 0.00000159(p - 50)^2$. The change of volume on fusion was determined by the method already described (*Abstr.*, 1900, ii, 714); at the triple point, the change in volume amounts to 0.87 c.c. per gram, that is five times greater than the greatest (naphthalene) known up to the present. The calculated heat of fusion, 180 cal. per gram, is more than double that of water, and the high value is probably due to the fact that phosphonium chloride does not melt without dissociation. Phosphonium chloride exists at low temperatures as a white (amorphous?) mass; at higher temperatures, in clear crystals. The transition point is near -41° and the crystals (supercooled) have the higher vapour pressure. Phosphonium chloride can be obtained in the hypercritical condition, which was found to be impossible in the case of carbon dioxide (*Abstr.*, 1899, ii, 635).

J. McC.

Oxidation of Boron to Silica and Reduction of Boric Acid to Silicic Acid. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 929—930).—It is claimed that when amorphous boron is oxidised with barium peroxide, with potassium chlorate and sulphuric acid, or with other oxidising agents, considerable amounts of silica are formed, and also that when boric acid is reduced by the addition of sodium to a solution of boric acid in strong alkali or by the aid of zinc dust, silicic acid is formed. It is suggested that $B_4 = SiO$. J. J. S.

The Supposed Conversion of Boron into Silica and of Boric Acid into Silicic Acid. By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1901, 25, 977—978).—A criticism on Fittica's communication (preceding abstract). J. J. S.

Oxidation of Boron and Reduction of Boric Acid to Silicon Compounds. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 978).—A reply to Councler (preceding abstract). J. J. S.

Influence of High Temperature on the Texture of the Hydrogel of Silicic Acid. By JACOBUS M. VAN BEMMELN (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 607—624. Compare Abstr., 1897, ii, 137; 1899, ii, 12, 84).—The hydrogel of silicic acid when ignited loses its power of absorbing water. Ignition for a short time causes only partial loss of this power, and the water which is then absorbed merely fills up the spaces in the network of the silica. Prolonged ignition causes the complete disappearance of these spaces, with consequent contraction of the whole mass.

The sp. gr. after ignition is 2.2; the sp. gr. of the material forming the network of the hydrogel is higher than this (2.5—3.0), which indicates that the substance expands when dehydrated. J. McC.

Direct Conversion of Gas Carbon into Diamond. By ALBERT LUDWIG (*Chem. Zeit.*, 1901, 25, 979—980).—Diamond crystals are formed when an electric current is passed through an iron spiral embedded in powdered gas carbon and surrounded by an atmosphere of hydrogen under great pressure. The same transformation occurs in the absence of iron, but a much higher temperature is required.

J. J. S.

Decomposition of the Chlorides of Alkali Metals. By C. W. VOLNEY (*J. Amer. Chem. Soc.*, 1901, 23, 820—824).—When sodium chloride (1 mol.) is treated at 18° with sulphuric acid (1 mol.) of sp. gr. 1.84, the following reaction takes place without any development of heat: $2NaCl + 2H_2SO_4 = NaHSO_4 + H_2SO_4 + HCl + NaCl$. On heating the residue to 120°, a further quantity of hydrogen chloride is evolved, in accordance with the equation: $NaHSO_4 + H_2SO_4 + NaCl = 2NaHSO_4 + HCl$. When potassium chloride is treated with concentrated sulphuric acid at 17—18°, the temperature rises to 30° and then gradually falls to 17°, whilst in the case of ammonium chloride under the same conditions the temperature rapidly falls from 18° to 1°.

E. G.

Electrolysis of Ammonium Chloride [and Ammonium Iodide] in Solution in Liquefied Ammonia. By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 713—714. Compare Abstr., 1899, i, 410; ii, 152).—The electrolysis of ammonium chloride, bromide, and iodide in solution in carefully dried liquefied ammonia was carried out in a U-tube of glass, platinum electrodes being used (compare Ruff, Abstr., 1901, ii, 653). At -50° , the iodide was very soluble, the bromide moderately, the chloride little, soluble, and ammonium fluoride nearly insoluble in liquefied ammonia.

Liquefied ammonia, prepared with care, is practically a non-conductor (Frenzel, Abstr., 1900, ii, 474). When ammonium chloride is dissolved in it, chlorine is evolved at the anode, and at -60° to -80° is free from nitrogen; at the same time, the liquid becomes yellow from the presence of dissolved chlorine; no chloride of nitrogen is produced. Pure hydrogen is evolved continuously at the cathode. In the case of a solution of ammonium iodide, iodine is deposited at the anode, and does not react with, or dissolve in, the liquid ammonia at -70° , even after 24 hours. If the temperature is allowed to rise, the iodine crystals disappear and a very heavy, dark-coloured liquid is formed, which falls to the bottom of the tube (compare Hugot, Abstr., 1900, ii, 274).

K. J. P. O.

Study of Ammonium Amalgam. By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 803—808).—The previous work on the existence of ammonium amalgam is discussed, and it is pointed out that the first problem is the accurate measurement of the ammonia and hydrogen evolved in the decomposition of the amalgam. To solve this problem, the author prepares the amalgam by acting on sodium amalgam with a solution of ammonium chloride (or ammonium iodide) in liquefied ammonia at -35° ; sodium chloride (or iodide) and a metallic mass are rapidly formed; no gas is evolved. The liquid ammonia is poured off from the metal and the latter washed with liquid ammonia and finally with dry ether, saturated with hydrogen, and cooled to -80° . At -80° , the metal becomes very hard; at -40° , it begins to liquefy, and at -30° to increase in volume; at $+15^{\circ}$, the volume has increased twenty-five or thirty fold, and a characteristic pasty mass is formed. In the decomposition accompanying this increase in volume, heat is developed, and the temperature is raised $5-6^{\circ}$ above the surroundings.

In order to measure the gases evolved in the decomposition, a portion of the metal, which was cooled to -80° , was placed in a glass tube, which was then exhausted whilst the temperature was maintained between -80° and -90° . At this temperature, no decomposition took place during the exhaustion. The temperature was allowed to rise, and after twelve or fifteen hours, decomposition was complete. In all the experiments, the gas evolved consisted accurately of two volumes of ammonia and one of hydrogen. In some of the experiments, the cooled metal was washed with sulphuric acid or ether saturated with hydrogen chloride; although part of the amalgam was destroyed, the remainder gave up the same proportion of ammonia and hydrogen. The author, however, believes that the radicle ammonium is not present in the metal, but that an ammoniacal hydride is formed, for when an aqueous solution

of ammonia is caused to act on pasty sodium amalgam, hydrogen is slowly evolved, whilst if the amalgam contains sodium hydride, the metal immediately swells up and forms a pasty mass.

When hydrogen is passed over sodium heated at 320° , the gas is rapidly absorbed and a transparent, crystalline, hygroscopic hydride, Na_2H , is formed, which, as a powder, takes fire in air or oxygen, and in chlorine (Troost and Hautefeuille, *Abstr.*, 1874, 767). When heated in a vacuum, the hydride decomposes into sodium and hydrogen. The hydride can be readily separated from excess of metallic sodium by treating the mixture with dry liquid ammonia, when the sodium dissolves as sodium-ammonium, leaving the pure hydride. K. J. P. O.

Decomposition of Calcium-Ammonium and of Lithium-Ammonium by Ammonium Chloride. By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 715—717. Compare *Abstr.*, 1901, ii, 600, 653).—In order to ascertain if ammonium is capable of existing at about -100° , the author has caused calcium-ammonium ($\text{Ca}[\text{NH}_3]_4$) to interact with ammonium chloride in the presence of liquefied ammonia. Pure, dry ammonia was led over a known weight of calcium contained in a U-tube, one of the arms of which was constricted. A crystal of dry ammonium chloride was placed in the constriction. On cooling the tube until the ammonia liquefied, calcium-ammonium was formed and dissolved in the excess of liquid ammonia. As more ammonia liquefied, the ammonium chloride became immersed in and dissolved by the liquid. The reddish-brown colour of the calcium-ammonium then rapidly disappeared, hydrogen gas was evolved, and collected in a special apparatus connected with the U-tube. After the evaporation of the ammonia, a compound of calcium chloride and ammonia remained in the U-tube. The volume of the hydrogen obtained showed that at the temperature used (-80°) ammonium does not exist. Exactly similar results were obtained when lithium was employed instead of calcium. K. J. P. O.

Ammonium: Action of Hydrogen Sulphide on Metallo-ammonium. By HENRI MOISSAN (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 490—496; and *Compt. rend.*, 1901, 33, 771—774).—After tracing the history of the searches after ammonium, the author shows that when liquid hydrogen sulphide acts on a known weight of lithium-ammonium or calcium-ammonium at between -75° and -70° , the sulphide of the metal is produced along with free ammonia and hydrogen, according to the equations $(\text{LiNH}_3)_2 + \text{H}_2\text{S} = \text{Li}_2\text{S} + 2\text{NH}_3 + \text{H}_2$, and $\text{Ca}(\text{NH}_3)_4 \cdot 2\text{NH}_3 + \text{H}_2\text{S} = \text{CaS} + 6\text{NH}_3 + \text{H}_2$. There is therefore no evidence of the existence of ammonium at this low temperature. Ruff's results (*Abstr.*, 1901, ii, 653) have been confirmed. J. McC.

Solubility of Silver Bromide and Iodide in Water. By FRIEDRICH KOHLRAUSCH and F. DOLEZALEK (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018—1023).—The determination of solubility is based on the increase in the conductivity of water shaken up with these compounds (compare Kohlrausch and Rose, *Abstr.*, 1894, ii, 7). It is found that saturated solutions of silver bromide and iodide

(at 21°) contain, respectively, 0.107 mg. and 0.0035 mg. of the salt per litre. These values are smaller than those previously obtained (*loc. cit.*), owing probably to the precautions taken, but agree fairly well with the values based on the potential differences between a silver electrode and the saturated solutions referred to (compare Danneel, *Abstr.*, 1900, ii, 467). J. C. P.

Silver Subhaloids. By KOLOMAN EMSZT (*Zeit. anorg. Chem.*, 1901, 28, 346—354).—Vogel claims to have prepared silver subhaloids by the action of cuprous chloride, bromide, and iodide on silver nitrate, and concludes that these are not mixtures of silver and silver haloid. Analysis leads to the formula Ag_4Cl_2 for the subchloride; when the substance is treated with nitric acid, however, 2 mols. of silver are dissolved and 2 mols. of silver chloride are left, whilst ammonia or sodium thiosulphate extracts 2 mols. of silver chloride and leaves 2 mols. of silver. On continued shaking with mercury, silver is extracted. By elutriation, the composition is changed.

Light is supposed to produce on the photographic plate a subhaloid of silver which is acted on by the developer. The substances prepared from cuprous salts are themselves acted on by light and are not affected by developers. The author concludes that these supposed subhaloids are merely mixtures of silver and silver haloid produced by the reaction: $\text{Cu}_2\text{Cl}_2 + 4\text{AgNO}_3 = 2\text{Ag} + 2\text{AgCl} + 2\text{Cu}(\text{NO}_3)_2$. J. McC.

The so-called Silver Peroxynitrate. By SIMEON L. TANATAR (*Zeit. anorg. Chem.*, 1901, 28, 331—336).—The “silver peroxynitrate” was obtained by electrolysis of a 25 per cent. solution of silver nitrate between platinum electrodes at 0°, the anode and cathode being separated by a porous cylinder. The substance is deposited at the anode in dark green crystals with a metallic lustre (with 10 dichromate cells, 5 grams can be obtained in an hour). Different preparations had the same composition; the crystals are free from water (Mulder, *Abstr.*, 1896, ii, 561; 1897, ii, 260; Šulc, *Abstr.*, 1897, ii, 99) and contain 8.09 per cent. of peroxide oxygen, 79.44 of total silver, and 18.13 of silver nitrate—amounts corresponding with those required for the formula $\text{Ag}_2\text{NO}_{11}$. With potassium iodide, the crystals give iodine and potassium iodate.

Electrolysis of other nitrates in neutral and alkaline solutions gives nothing indicating the formation of pernitrites and there is no evidence of the production of pernitrites by the action of hydrogen peroxide on the nitrates of the alkali or alkaline earth metals.

By the electrolysis of silver fluoride, a product is obtained which very closely resembles “silver peroxynitrate.” The product, on being heated, evolves oxygen violently; it contains more peroxide oxygen than silver oxide (Ag_2O_2). Analysis (8.3 per cent. of peroxide oxygen) leads to the formula $\text{Ag}_{15}\text{F}_3\text{O}_{16}$. It is highly improbable that in this compound oxygen is directly united to fluorine, and since the ratio of silver to oxygen is not 1 : 1, it is to be assumed that silver forms another peroxide besides Ag_2O_2 and the salt may be a molecular compound, $4\text{Ag}_3\text{O}_4 \cdot 3\text{AgF}$. Analogously, “silver peroxynitrate” is $2\text{Ag}_3\text{O}_4 \cdot \text{AgNO}_3$.

$\text{Ag}_{15}\text{F}_3\text{O}_{16}$, when digested on the water-bath, and washed with hot water gives the compound $2\text{Ag}_3\text{O}_4 \cdot \text{AgF}$ (of the same type as the nitrate) with 8.94 per cent. of peroxide oxygen. J. McC.

Solubility of Silver Sulphate and Mercurous Sulphate. By KARL DRUCKER (*Zeit. anorg. Chem.*, 1901, **28**, 361—363).—The solubility of these sulphates in water, sulphuric acid, and potassium sulphate solutions at 25° are as follows, the solubility being expressed in grammols. per litre, and c being the concentration of the acid or salt solution used :

Mercurous sulphate.

	c .	Solubility.
H ₂ O.....	—	11.71×10^{-4}
$\frac{1}{2}$ H ₂ SO ₄	0.0400	8.31×10^{-4}
$\frac{1}{2}$ H ₂ SO ₄	0.1000	8.78×10^{-4}
$\frac{1}{2}$ H ₂ SO ₄	0.2000	8.04×10^{-4}
$\frac{1}{2}$ K ₂ SO ₄	0.2000	9.05×10^{-4}

Silver sulphate.

H ₂ O.....	—	2.57×10^{-2}
$\frac{1}{2}$ H ₂ SO ₄	0.0200	2.60×10^{-2}
$\frac{1}{2}$ H ₂ SO ₄	0.0400	2.64×10^{-2}
$\frac{1}{2}$ H ₂ SO ₄	0.1000	2.71×10^{-2}
$\frac{1}{2}$ H ₂ SO ₄	0.2000	2.75×10^{-2}
$\frac{1}{2}$ K ₂ SO ₄	0.0200	2.46×10^{-2}
$\frac{1}{2}$ K ₂ SO ₄	0.0400	2.36×10^{-2}
$\frac{1}{2}$ K ₂ SO ₄	0.1000	2.31×10^{-2}
$\frac{1}{2}$ K ₂ SO ₄	0.2000	2.32×10^{-2}

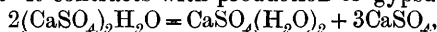
In the case of silver sulphate, the increase of solubility with increasing concentration for sulphuric acid indicates the existence of a new salt the solubility of which more than compensates for the normal isohydric depression.

J. McC.

The Formation of Natural Anhydrite and the Rôle of Time in Chemical Transformations. By JACOBUS H. VAN'T HOFF [with FREDERICK G. DONNAN, EDWARD F. ARMSTRONG, WILLY HINRICHSSEN, and FRITZ WEIGERT] (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 471—489. Compare Abstr., 1900, ii, 531; 1901, ii, 506).—Gypsum is only very slowly transformed into the hemihydrate or into anhydrite at the transition temperature. The tension of water vapour from gypsum attains the value of one atmosphere with formation of the hemihydrate, (CaSO₄)₂.H₂O, at 101.45°; this point has been found by noting the rise of temperature produced by the addition of common salt to a mixture of gypsum and water, and then by adding water to a mixture of higher boiling point, the temperature remaining constant until, in the first case, the gypsum was completely converted into the hemihydrate, and in the second case until the hemihydrate was completely transformed into gypsum. The transition is greatly accelerated by the presence of solvent liquids; in a tensimeter containing a mixture of precipitated gypsum and the hemihydrate moistened with a solution of magnesium chloride, the tension at 50° became constant at 49.5 mm. after 7 days. At 25°, the tension is 9.1 mm. and 4.99 mm. at 17°. The connection between tension and temperature is given by the equation $\log p = \log p' + 1.493 - 567.7/(t + 273)$, where p is the ten-

sion of gypsum, p' that of water, both at the temperature t . When $p = p'$ (970 mm.), $t = 107.2^\circ$; this would indicate that $2\text{CaSO}_4(\text{H}_2\text{O})_2 \rightleftharpoons (\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$ takes place at this temperature, and in a dilatometer, containing moist gypsum and using mercury as indicating liquid, a change of volume has been observed at about 107° . In presence of a solution containing 20 per cent. of sodium chloride, gypsum commences to dehydrate at 93° .

For the transformation of gypsum into soluble anhydrite, neither natural nor precipitated gypsum is suitable, but gypsum obtained by treating plaster of paris with much water gave good results. The vapour tension of gypsum in forming anhydrite is higher than that when the hemihydrate is produced: $\log p = \log p' + 1.41 - 518.8/(t + 273)$. The transition temperature (at which $p = p'$) corresponding with the reaction $\text{CaSO}_4(\text{H}_2\text{O})_2 = \text{CaSO}_4 + 2\text{H}_2\text{O}$ is 95° . The hemihydrate is unstable and at 90° it contracts with production of gypsum,



then expands slowly owing to formation of anhydrite, $\text{CaSO}_4(\text{H}_2\text{O})_2 = \text{CaSO}_4 + 2\text{H}_2\text{O}$.

The formation of natural anhydrite takes place extremely slowly, but has been observed at 37° . The temperature of formation is depressed by the presence of sodium chloride or other salts, and in this way the natural deposits may be accounted for without assuming a high temperature at the time of formation.

Transitions, such as those referred to above, take place at very different speeds. In the case of salts, double salts, and their hydrates, if the acid is monobasic and the metal monatomic, the transformation is rapid. If the acid is dibasic or the metal diatomic, it is slower (compare supersaturation of sodium sulphate and carbonate, calcium chloride, &c.), and if the acid is dibasic and the metal di- or tri-atomic, hours, or even days, may be required for the change to take place completely (compare the very slow deposition of ferric chloride from its supersaturated solution). In the case of the non-metals, the resistance to transformation increases with the molecular magnitude (ozone and oxygen, plastic and ordinary sulphur, white and red phosphorus, the various modifications of carbon). The idea of "false equilibrium" may be in some measure accounted for by this influence of time on reaction. J. McC.

Solubility of Gypsum in Aqueous Solutions of Sodium Chloride. By FRANK K. CAMERON (*J. Physical Chem.*, 1901, 5, 556—576).—The solubility of gypsum is greatly increased by the addition of sodium chloride, thus, at 26° , the solubility per 100 grams of water is 0.2126 gram, but by the addition of 15.2 grams of sodium chloride it is increased to 0.76 gram. Below 37.5° , a maximum of solubility is obtained when the quantity of sodium chloride present is about 135—140 grams per litre; at higher temperatures, the existence of this maximum is doubtful. The transition temperature of the gypsum to the hemihydrate is shown to be dependent on the medium with which it is in contact; in paraffin, change does not occur until about 145° , although in presence of a strong sodium chloride solution it occurs at 101.45° . The rate of dissolution of gypsum in pure water is exceedingly slow, a fact which probably accounts for the diverse numbers which

have been given for its solubility; the author's results are, at 26°, about 1 part of gypsum in 372 parts pure water. The theoretical explanation is not fully discussed, but the author considers that the maximum point of the solubility cannot be accounted for by our present hypotheses regarding solutions.

L. M. J.

Density and Expansion by Heat of Solutions of Magnesium Chloride. By GUSTAV J. W. BREMER (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 455—470).—The densities of solutions of magnesium chloride of different concentrations have been determined at various temperatures; for the solutions examined, the density at any particular temperature can be ascertained by means of the formula $d_t = d_0 (1 - at - bt^2)$, the values of d_0 , a , and b being:

Grams of magnesium chloride per 100 c.c. of solution.	d_0 .	a .	b .
20·0004	1·160503	$2·2738 \times 10^{-4}$	$1·3443 \times 10^{-6}$
13·3111	1·11055	$2·0072 \times 10^{-4}$	$1·7534 \times 10^{-6}$
9·9506	1·08451	$1·8587 \times 10^{-4}$	$2·0482 \times 10^{-6}$
6·7158	1·059117	$1·7208 \times 10^{-4}$	$2·2884 \times 10^{-6}$

The density at 0°, d_0 , expressed as a function of the weight of magnesium chloride, p , in 100 c.c. of solution, is $d_0 = 1 + (9·1729 \times 10^{-3} \times p) - (5·507 \times 10^{-5} \times p^2)$. The coefficient of expansion, a , increases with the concentration, whilst b diminishes, which indicates that the expansion is the more regular the higher the concentration. The curves representing the expansion of the four solutions intersect near 60°.

J. McC.

Formation of Tachyhydrite. By JACOBUS H. VAN'T HOFF, F. B. KENRICK, and HARRY M. DAWSON (*Zeit. physikal. Chem.*, 1901, 39, 27—63).—The solubility relations of magnesium chloride and calcium chloride were investigated and the saturation fields obtained for the compounds $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, and tachyhydrite. Equilibrium between tachyhydrite and the two hexachlorides occurs at 22·39°, at which temperature the double salt is first deposited; at 29·4°, the hexahydrate of calcium chloride passes into the tetrahydrate, but the temperature is lowered by the addition of magnesium chloride, so that the equilibrium temperature of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, and tachyhydrite is only 25°. A diagram is given representing the solubilities between 16·7° and 32°. Increase of pressure causes a rise of temperature of formation of tachyhydrite and by direct determination with a manocryometer the temperature coefficient was found to be +0·0162° per atmosphere. The value may be calculated by the expression $dT/dP = 1033·3T(v_2 - v_1)/42500r$, where v_2 and v_1 are respectively the specific volumes of the tachyhydrite with its saturated solution and the equivalent simple hydrates, and r is the thermal value of the change. Direct determination led to $v_2 - v_1 = 0·06342$ c.c.; the densities were found to be, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} = 1·5907$; $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} = 1·7182$; tachyhydrite = 1·6655, saturated solution 1·4477, and hence $v_2 - v_1 = 0·06323$ c.c. The value of r , obtained indirectly from the

heats of solution of the various compounds, is 33·82 cal., and from these numbers, the result $dT/dP = 0\cdot0135^\circ$ per atmosphere is obtained, a value which agrees well with the direct determinations (see Abstr., 1900, ii, 12).
L. M. J.

Hydroxides of Zinc and Lead. By W. HERZ (*Zeit. anorg. Chem.*, 1901, 28, 474–476).—Zinc hydroxide, precipitated from a solution of zinc sulphate by dilute potassium hydroxide, readily dissolves in excess of potassium hydroxide and is completely dissolved when for 1 Zn there are 6 OH groups. If, however, the zinc hydroxide is previously dried at 60–70° in a vacuum desiccator, it becomes comparatively difficult to dissolve, and is completely dissolved when for 1 Zn there are 35·8 OH groups in the solution. Lead hydroxide, on the other hand, is not altered in solubility by drying at 60–70°. It is completely dissolved when for 1 Pb there are 8·5 to 8·8 OH groups in the solution.
E. C. R.

Action of Water on Lead. By STANISLAV RŮŽIČKA (*Arch. Hygiene*, 1901, 41, 23–45).—The action of water and solutions of salts on bright metallic lead was examined by placing the lead in cylinders containing the various liquids, inserting the stopper so that the cylinder contained no air, leaving the whole for 24 hours, and then estimating the amount of lead contained in the liquid. The nitrates, chlorides, sulphates, and carbonates of potassium, sodium, calcium, magnesium, and ammonium were employed, and it was found that the influence of these salts is independent of the base and that whilst nitrates increase the action of the water, or in certain concentrations leave it unaltered, chlorides, sulphates, and carbonates diminish the action, the effect increasing in the order named. When the different salts are present together, they preserve this mode of action. Thus the addition of a nitrate increases the action of solutions of chlorides, sulphates, or carbonates; the addition of a carbonate diminishes the action of solutions of nitrates, chlorides, or sulphates; the addition of a sulphate diminishes the action of solutions of nitrates or chlorides, but has no effect on those of carbonates; finally, the addition of a chloride diminishes the action of solutions of sulphates and nitrates, and either increases or leaves unaltered those of carbonates. When the same piece of lead is exposed to the action of fresh solutions containing carbonate, the amount of lead taken up diminishes very greatly and the surface of the lead becomes covered with a thin film which cannot easily be removed by rubbing.

The same diminution occurs even in the presence of nitrates and free oxygen, provided that the carbonate be present in sufficient proportion (more than half the equivalent of the nitrate). Free carbon dioxide also greatly diminishes the action of water and salt solutions on lead, both when present as a saturated solution at the commencement of the experiment, and when a current of the gas is passed through the liquid throughout the experiment. The presence of air in all cases greatly increases the solvent action.

The action of various organic substances was also examined, and it was found that infusions of grass leaves and of radish leaves diminished the action of water, whilst infusion of peat greatly increased it

The action of the salts is ascribed to the varying solubility of the lead salts of the corresponding acids, the nitrate being the most soluble and the sulphate and carbonate the least.

A. H.

Radioactive Substances. By FRITZ GIESEL (*Ber.*, 1901, 34, 3772—3776. Compare Abstr., 1901, ii, 99).—The assumption that radioactive lead contains a new active element is scarcely justifiable unless it can be shown that this material possesses properties differing from those of the known radioactive elements (compare Abstr., 1901, ii, 19, 159, 216, and 655).

The activity of radioactive lead sulphate, indicated either by its effect on the electroscope or by its photographic action, is not diminished on keeping, neither is it increased by the action of the cathode rays. The photographic action of the sulphate is also exhibited by the carbonate, chloride, and sulphide. The author has noticed the phosphorescence of radioactive lead sulphate, but the action is so slight that an experienced eye is required to detect it.

A sample of radioactive lead sulphate, wrapped in black paper and laid on the glass of a photographic plate, did not produce any effect even after fifteen hours; an impression was obtained, however, when the specimen was enclosed in transparent paper. This result is obtained with the sulphate and not with the corresponding chloride or sulphide.

A feebly active radium preparation enclosed in black paper affects a photographic plate when placed directly on the film; the radioactive lead sulphate enveloped in tracing paper produces an appreciable effect, even through the glass of the plate. In the former case, the Becquerel rays are operative, whilst in the latter the action is due to light rays. An artificial mixture of inactive lead and radium, containing so little of the latter substance that its presence cannot be detected by chemical means, is nevertheless distinctly radioactive, this property being noticeable in the lead sulphide and also in the iodide prepared from it.

The new product obtained by the author from the radium mother liquors (Abstr., 1901, ii, 99) resembles actinium and radium in retaining its radioactivity for a year. Polonium preparations, when preserved for a similar period, exhibit a marked diminution of activity.

The rare earths of the cerium group, containing cerium, lanthanum, and didymium as the chief constituents, give photographic impressions after 5 hours' exposure. The precipitate obtained from a thorium nitrate solution by the action of hydrogen peroxide is also strongly radioactive. In all these cases, the activity, however, rapidly diminishes, this result indicating the absence of actinium.

The water distilled off from crystallised radium-barium chloride is strongly radioactive, at first even more so than the residual chloride. That this activity is not due to any radium which might have been mechanically carried over into the distillate is shown from the fact that the action diminishes in the course of a few days.

G. T. M.

Radioactive Substances. By KARL A. HOFMANN and EDUARD STRAUSS (*Ber.*, 1901, 34, 3970—3973. Compare Abstr., 1901, ii, 655).—A reply to Giesel (preceding abstract). Further experiments are

described which tend to prove that the radioactive lead sulphate is free from radium, actinium, and polonium. L. L. S.

Action of Carbon Dioxide and Alkali Salts on Metallic Oxides and the Relative Strength of Hydrochloric and Nitric Acids. By OTTO KUHNING (*Ber.*, 1901, **34**, 3941—3945. See Abstr., 1901, ii, 656).—From a consideration of the previous experiments (*loc. cit.*), it would appear that nitric acid is a stronger acid than hydrochloric acid. Experiments are now described in which the copper oxide is replaced by mercuric oxide and lead oxide. Mercuric oxide, in the presence of sodium chloride and carbon dioxide, is slowly converted into the oxychloride, $2\text{HgCl}_2, \text{HgO}$, but, if the sodium chloride is replaced by sodium nitrate, the oxide is not attacked. Similar results, although not so definite, were obtained with lead oxide. R. H. P.

Identity of the Red and Yellow Oxides of Mercury. By J. KOSTER and S. J. STORK (*Rec. Trav. Chim.*, 1901, [ii], **20**, 394—397).—When the red oxide is finely powdered for 2 hours in an agate mortar, it is almost as easily acted on by aqueous oxalic acid as the yellow oxide, although the different action of this acid on the two oxides has hitherto been used as a pharmaceutical distinction. Obviously, as maintained by Ostwald (*Zeit. physikal. Chem.*, 1895, **18**, 159; Abstr., 1900, ii, 712), the oxides are identical and not isomeric (compare Cohen. Abstr., 1900, ii, 184, 381). W. A. D.

Thallium Chlorobromides of the Type Ti_4X_6 . By VICTOR THOMAS (*Compt. rend.*, 1901, **133**, 735—737. Compare Abstr., 1901, ii, 159).—Cushman (Abstr., 1900, ii, 725) obtained two isomeric compounds of the formula $\text{Ti}_4\text{Cl}_3\text{Br}_3$, crystallising in characteristically different forms (orange plates and blood-red crystals). The author finds that the chlorobromide, $\text{Ti}_4\text{Cl}_3\text{Br}_3$ (*loc. cit.*), crystallises usually in a mixture of needles and plates, which appear to belong to the same crystalline system. The one form readily passes into the other. Both forms, when heated alone or in presence of the solution from which they have been deposited, become blood-red; on cooling, they regain their original orange colour. K. J. P. O.

Place of the Rare Earth Metals among the Elements. By BERTRAM D. STEELE (*Chem. News*, 1901, **84**, 245—247).—Arguments are advanced in favour of regarding the rare earth metals as an inter-periodic group between groups IV and V of a modified periodic system with seven elements each in groups I and II, and seventeen elements in each of the groups III and IV. D. A. L.

Metals of the Cerium Group. By THEODOR H. BEHRENS (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 67—91).—The metals of this group, lanthanum, cerium, praseodymium, neodymium, and samarium, can be separated from the metals accompanying them in minerals by precipitation as formates in slightly acid solution. If the quantity of cerium metals is small, the other metals should first be removed,

thorium as oxalate, metals of the yttrium group by precipitation with sodium sulphate, ammonium carbonate or ammonium lactate, and zirconium as lactate.

The formates of the metals of the cerium group are sparingly soluble and crystallise in the pentagonal dodecahedron form. Lanthanum and praseodymium formates are the least soluble and consequently can be separated by addition of formic acid in insufficient quantity.

The acetates are easily soluble and difficult to obtain crystallised. On boiling the solutions, basic acetates are formed. Basic lanthanum acetate with iodine turns red, then violet, and finally blue.

The oxalates are precipitated as monoclinic crystals sparingly soluble in water, but easily so in concentrated hydrochloric acid or nitric acid.

Ammonium succinate precipitates the metals of the cerium group either in spheroidal aggregates or prismatic crystals depending on the substances present in the solution. Solutions in which cerium and praseodymium nitrates predominate give flocculent masses which appear bluish in reflected light, neodymium and thorium nitrates give smooth, brown plates and spheroids. Prismatic crystals are precipitated from solutions containing much lanthanum nitrate; the crystals show brilliant polarisation colours of the second and even of the third order, and the lanthanum succinate can always be recognised amongst the other succinates. After being warmed with ammonia, cerium succinate, when moistened with hydrogen peroxide, turns brown, and can thus be distinguished from the other succinates, which remain colourless.

The metals of the cerium group can also be distinguished by conversion into benzoates or salicylates.

It is possible to obtain cerium pure by repeated crystallisation of the ammonium double nitrates; pure neodymium can only be prepared in this way with the aid of some precipitant, and on account of the isomorphous nature of the double nitrates it is not possible to separate pure praseodymium. No separation of lanthanum and praseodymium can be attained by crystallisation of the acetates.

A pure solution of lanthanum can be obtained by extracting the mixed "cerite" oxide with nitric acid of sp. gr. 1.2 for 10 minutes; even better results are obtained with dilute sulphuric acid.

When cerium is precipitated with an oxidising agent (sodium hypochlorite, hydrogen peroxide, potassium permanganate) in presence of sodium acetate, lanthanum is constantly carried down with it, and if persulphuric acid is used, the cerium precipitate is further contaminated with double sulphates of calcium and the metals of the cerium group.

By the addition of ammonia, samarium is first precipitated, then neodymium, praseodymium, and lanthanum, but no satisfactory separation can be made on this basis. Cerium nitrate, when boiled with much water, is precipitated as basic nitrate, but the precipitate constantly contains very appreciable quantities of lanthanum, samarium, and neodymium. In the same way, basic cerium sulphate can be obtained, and if care be taken that some free sulphuric acid is present, so that the cerium is not completely removed in the precipitate, an almost pure cerium salt is obtained.

Mosander's method of separating lanthanum, neodymium, and praseodymium as normal sulphates does not lead to pure products, neither does Delafontaine's modification in which the solution is shaken with alcohol.

The author does not regard it as yet possible to give a satisfactory method of separating the metals of this group in a pure form.

J. McC.

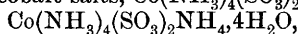
Mechanism of Action of Hydrogen Peroxide on Permanganic Acid. By A. BACH (*Ber.*, 1901, **34**, 3851—3855).—Traube has suggested that the reduction of permanganic acid by hydrogen peroxide is due to the readiness with which the hydrogen of the peroxide is oxidised; Berthelot, on the other hand, has suggested that the peroxide first becomes oxidised to the higher oxide, H_2O_3 , which then decomposes into water and oxygen. In order to test these views, the behaviour of ethyl hydrogen peroxide towards permanganic acid and of 'Caro's acid' towards permanganic oxide were studied; it is suggested that on Traube's hypothesis these compounds should only reduce half as much oxygen as the equivalent of hydrogen peroxide, whilst on Berthelot's hypothesis the reducing power should be the same. Actually, the ethyl hydrogen peroxide behaves exactly like hydrogen peroxide, whilst Caro's acid shows a somewhat lower reducing power, and this is regarded as affording support to Berthelot's hypothesis.

T. M. L.

Passive Iron. By ALEXIS FINKELSTEIN (*Zeit. physikal. Chem.*, 1901, **39**, 91—110).—Determinations of the polarisation capacity and resistance of passive iron indicate that it cannot be covered by a coating of badly conducting oxide, and the numbers are very nearly equal to those obtained for platinum. Passive iron does not behave as an iron electrode, but as an oxygen electrode of variable oxygen concentration. The *E.M.F.* of iron electrodes against various solutions were determined; addition of potassium cyanide to the solutions greatly lowers the *E.M.F.*, and in solutions of mixed ferrous and ferric salts the *E.M.F.* decreases as the ferrous salt becomes replaced by ferric. The polarisation curves were investigated, and the non-existence of an oxide layer again indicated. The author discusses the cause of the passivity, and shows that it may be accounted for by the assumption that the surface of passive iron consists solely of tervalent iron, the formation of passive iron by oxidising agents and electrolysis being due to the replacement of the bivalent by tervalent iron.

L. M. J.

Isomerism in the Cobalt-tetrammine Series. By KARL A. HOFMANN and A. JENNY (*Ber.*, 1901, **34**, 3855—3873).—Two isomeric disulphitetetramminecobalt salts, $Co(NH_3)_4(SO_3)_2NH_4 \cdot 3H_2O$ and



result from the action of sulphurous acid on the carbonatotetrammine chloride, or on a solution, oxidised by exposure to air, of ammoniacal cobalt acetate. The first of these has already been described (Hofmann and Reinsch, *Abstr.*, 1898, ii, 377), but it has since been found that all the water can be driven off without destroying the compound, and its formula must therefore be written in the form given above.

It forms brown, birefringent prisms belonging to the monoclinic system [$a : b : c = 0.859 : 1 : 0.534$; $\beta = 111^\circ 23'$]; it affords no coloration with ammoniacal sodium nitroprusside, and no precipitate with mercurous nitrate, but slowly gives a flocculent precipitate with thallium nitrate; in aqueous solution, it has half the normal mol. weight and is regarded as dissociating into the ions NH_4 and $\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2$. When dissolved in sulphuric acid, hydrochloric acid precipitates the praseo-chloride, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}, \text{H}_2\text{O}$.

The second salt crystallises from water in reddish-yellow prisms which are fairly stable in air but rapidly effloresce in a vacuum; like the preceding salt, it is readily converted into the praseo-chloride, and behaves in a similar manner with thallium nitrate, mercurous nitrate, and ammoniacal nitroprusside.

These two isomeric salts cannot be regarded as merely polymorphous forms of one salt, as they give different colour reactions with sulphuric acid and are not converted into one another by recrystallisation.

The two corresponding sodium salts usually crystallise with $2\text{H}_2\text{O}$ and $4\text{H}_2\text{O}$ respectively. The first salt is brown in colour and has already been described (Hofmann and Reinsch, *loc. cit.*; Werner and Gröger, Abstr., 1898, ii, 379); it forms square tablets, probably belonging to the monoclinic system, and is precipitated unchanged from a concentrated aqueous solution on adding alcohol, but separates from a dilute solution in reddish-brown, orthorhombic needles with $3\text{H}_2\text{O}$; in aqueous solution, it shows half the normal mol. weight.

The isomeric sodium salt forms golden-yellow needles of the formula $\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2\text{Na}, 4\text{H}_2\text{O}$, readily effloresces, and loses all its water in a vacuum.

The salt $\text{Co}_2(\text{NH}_3)_4(\text{SO}_3)_3, 6\text{H}_2\text{O}$ is prepared from a bye-product obtained in making the ammonium salts described above; it forms birefringent prisms, and is completely dehydrated at 85° ; when dissolved in sulphuric acid and mixed with hydrochloric acid, it gives chloropentamminocobalt chloride (purpureo-chloride), $\text{CoCl}(\text{NH}_3)_5\text{Cl}_2$, and is therefore regarded as a double salt of a pentammine sulphite with a triammine sulphite.

Complex salts of the formulae $\text{Co}_3(\text{NH}_3)_8(\text{SO}_3)_6\text{Na}_3, 6\text{H}_2\text{O}$ and $\text{Co}_3(\text{NH}_3)_6(\text{SO}_3)_6\text{Na}_2, 6\text{H}_2\text{O}$ are described.

The acid sulphite, $\text{Co}(\text{NH}_3)_4(\text{CO}_3) \cdot \text{SO}_3\text{H}$, forms violet-red crystals, and is shown to be a true tetrammine by its conversion into the praseo-chloride.

Three sulphito-compounds containing $\frac{3}{2}$ mols. of NH_3 are described: a dark-brown salt, $\text{Co}_2(\text{NH}_3)_6(\text{SO}_3)_3, 3\text{H}_2\text{O}$, crystallising in prisms; a dark-brown salt, $\text{Co}(\text{NH}_3)_3(\text{SO}_3)_2, \text{H}_2\text{H}_2\text{O}$, crystallising in hexagonal tablets, and a dark-brown sodium salt, $\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{SO}_3)_2\text{Na}, 2\text{H}_2\text{O}$, which will only part with $2\text{H}_2\text{O}$ without decomposition. T. M. L.

Some Allotropic Modifications of Inorganic Compounds. By W. HERZ (*Zeit. anorg. Chem.*, 1901, 28, 342—345. Compare Abstr., 1900, ii, 728; 1901, ii, 513).—Nickel sulphide, precipitated with ammonium sulphide, shows the same phenomena as cobalt sulphide. The nickel sulphide, exposed to the air, oxidises very readily to sulphate.

Chromium hydroxide, precipitated by alkali, is easily soluble in excess of the reagent; after being dried in a vacuum, however, the hydroxide is insoluble in alkalis. In these cases, the less stable form is first produced and gradually changes to the more stable form.

Zinc oxide heated to 250° shows a faint yellow colour and if the yellow (hot) and the white (cold) oxide were allotropic forms it would be expected that on prolonged heating at this temperature the change to the yellow modification would be complete. The intensity of the colour does not, however, increase, indicating that there is no transition and that the two forms cannot be considered as allotropic modifications.

J. McC.

Chromium Halogen Compounds with Alcohol. By IWAN KOPPEL (*Zeit. anorg. Chem.*, 1901, **28**, 461—473).—The salt $\text{CrCl}_3 \cdot 3\text{EtOH}$ is obtained by treating metallic chromium with a concentrated solution of dry hydrogen chloride in absolute alcohol. It crystallises in deep red needles, is fairly stable in dry air, in damp air is quickly converted into green chromium trichloride hexahydrate, and when heated yields alcohol and ethyl chloride. It dissolves in water to a red solution which quickly turns green, the same colour phenomenon taking place more slowly in alcohol, chloroform, or acetone solution. An examination of the electrical conductivity of the solution in absolute alcohol shows that this colour change is due to causes similar to that observed by Werner and Gubser (*Abstr.*, 1901, ii, 453) in the case of the green chromium chloride, the change of colour from red into green being accompanied by an increase in the electrical conductivity. This salt is also obtained by heating the violet chromium chloride with absolute alcohol and a stick of metallic zinc.

The corresponding chromium bromide salt, obtained in a similar manner, crystallises in dark reddish-brown crystals which give brown solutions that quickly turn green. It was not, however, obtained in a pure state.

E. C. R.

Silicomolybdates. By WLADISLAW ASCH (*Zeit. anorg. Chem.*, 1901, **28**, 273—313).—Molybdic acid, when added to a boiling solution of sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) dissolves readily at first and some gelatinous silicic acid is separated. By further addition of molybdic acid to the saturation point, the silicic acid redissolves and the solution (which becomes intensely yellow) when evaporated at 45° deposits yellow crystals of sodium silicomolybdate, $2\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 21\text{H}_2\text{O}$. This salt is dimorphous. Attempts to obtain any other sodium silicomolybdate proved futile. Solutions of sodium silicomolybdate with solutions of salts of potassium, ammonium, rubidium, cesium, thallium, barium, strontium, calcium, nickel, cobalt, cadmium, aniline, pyridine, and quinoline give corresponding silicomolybdates. Of these, only the following have been analysed: $2\text{K}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 16\text{H}_2\text{O}$; $2\text{MgO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 30\text{H}_2\text{O}$; $2\text{BaO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$, and $2\text{CaO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$. With a dilute solution of silver nitrate, sodium silicomolybdate gives a small quantity of ruby crystals and a yellow salt having the composition $2\text{Ag}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$.

With concentrated silver nitrate, a yellow precipitate of $4\text{Ag}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 15\text{H}_2\text{O}$ is obtained.

By treating the sodium or potassium salt (1 mol.) with hydrochloric acid (4 to 8 mols.) compounds of the formulæ $1\frac{1}{2}\text{Na}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 17\text{H}_2\text{O}$ and $1\frac{1}{2}\text{K}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 14\text{H}_2\text{O}$ are formed, and these salts can also be prepared by adding the calculated quantity of alkali to the free acid. This potassium salt gives, with silver nitrate, yellow crystals of $1\frac{1}{2}\text{Ag}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 11\text{H}_2\text{O}$, as well as ruby crystals which have not been analysed. With alkali or sodium carbonate, sodium silicomolybdate (with $1\frac{1}{2}\text{Na}_2\text{O}$) gives only sodium trimolybdate. Silicomolybdic acid, $\text{SiO}_2, 12\text{MoO}_3, 32\text{H}_2\text{O}$ (or $2\text{H}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 30\text{H}_2\text{O}$), was obtained by decomposing the sodium salt with dilute sulphuric acid and extracting with ether.

By dialysing a 5 percent. solution of the salt $2\text{K}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 16\text{H}_2\text{O}$ it was found that the ratio of $\text{K}_2\text{O} : \text{SiO}_2 : \text{MoO}_3$ was the same in the diffused solution as in the original, indicating that the silicic and molybdic acids form a complex ion. The conductivities and densities of solutions of the acid and of the potassium salt have been determined at 10° , 20° , 30° , and 40° . The results indicate that the silicomolybdates are fairly stable and only suffer decomposition at high dilution, and that this decomposition is increased by rise of temperature.

By measuring the depression of the freezing point of Glauber's salt (Lowenherz, Abstr., 1896, ii, 149), caused by the addition of the sodium salt, it was found that the mol. weight corresponds with that required for the formula $\text{Na}_4\text{SiMo}_{12}\text{O}_{40}$. The salts $2\text{R}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, \text{aq}$ are to be regarded as normal salts of tetrabasic silicomolybdic acid, whilst the salts $1\frac{1}{2}\text{R}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, \text{aq}$ are acid salts of the same acid ($\frac{1}{2}\text{R}_2\text{O}$ being replaced by $\frac{1}{2}\text{H}_2\text{O}$).

At 100° , $2\text{Na}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 21\text{H}_2\text{O}$ loses $17\frac{1}{2}$ mols. of water, and $1\frac{1}{2}\text{Na}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 17\text{H}_2\text{O}$ loses 13 mols.; that is, the normal salt has $3\frac{1}{2}$ mols. of water of constitution and the acid salt has 4.

In the analysis of the compounds the silica was determined after removing the molybdic acid by heating to a high temperature in a current of hydrogen chloride. J. McC.

Uranous Sulphate. By WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1901, 483—485).—The sp. gr. of aqueous solutions of uranous sulphate as well as of solutions in sulphuric acid and hydrochloric acid have been determined. A 1 per cent. solution in water has a sp. gr. 1.0058, a 10 per cent. solution 1.0539. A 1 per cent. solution in sulphuric acid of sp. gr. 1.14 has a sp. gr. 1.1442, a 5 per cent. solution 1.1626. In solution in hydrochloric acid of sp. gr. 1.046, a 1 per cent. solution has a sp. gr. 1.0525, a 5 per cent. solution 1.0744. Water acts on uranous sulphate, producing a basic salt and a substance of the formula $2\text{USO}_4, 3\text{UO}, 4\text{H}_2\text{O}$ has been isolated.

J. McC.

Tin-Aluminium Alloys. By LÉON GUILLET (*Compt. rend.*, 1901, 133, 935—937).—The action of stannic oxide on aluminium is very energetic, but the limit of inflammation is reached with a mixture corresponding with Al_4Sn . The product from this mixture, when

treated with dilute hydrochloric acid, yields lamellar and filiform crystals of the compound Al_4Sn . Similarly, mixtures corresponding with Sn_4Al , SnAl , and SnAl_2 yield lamellar and filiform crystals of the compound AlSn .
C. H. B.

New Element associated with Thorium. By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1901, 23, 761—774. Compare Brauner, *Proc.*, 1901, 17, 67).—Freshly precipitated thorium hydroxide was dissolved in hydrochloric acid; the solution was neutralised with ammonia and saturated with sulphur dioxide. A basic sulphite separated, and on addition of ammonia to the filtrate a further precipitate was obtained. Each of these precipitates was carefully ignited; the resulting oxides had the sp. gr. 9·38 and 10·367 respectively.

On heating a solution of thorium hydroxide in saturated citric acid solution, a white, amorphous precipitate of the hydrated citrate of real thorium was obtained, which yielded specimens of the oxide of sp. gr. varying from 9·188 to 9·253, whilst the citrate obtained by concentrating the filtrate furnished an oxide of sp. gr. 10·50. After the removal of the insoluble citrate from a large quantity of the saturated citrate solution, the filtrate slowly deposited a small quantity of heavy crystals which, on ignition, yielded 31·61 per cent. of oxide of sp. gr. 8·47—8·77; the author suggests this may be the oxide of the new metal discovered by Hofmann and Prandtl (*Abstr.*, 1901, ii, 387) in euxenite; on evaporation of the filtrate, several fractions of the crystalline citrate were obtained, the oxide from which had a sp. gr. 10·14—11·26.

The radioactivity of the oxide (sp. gr. 9·25) obtained from the insoluble citrate is very slight, whilst the oxides of high specific gravity are quite active, the activity increasing with the sp. gr.

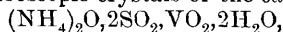
These experiments indicate the presence of a new element, the oxide of which has a high sp. gr.; its atomic weight (calculated for a quadrivalent element) appears to lie between 260 and 280. The author proposes for this metal the name *carolinium*.

The atomic weight of thorium, obtained by analysis of the tetrachloride, was found as the mean of two experiments to be 222—223·3.

E. G.

Sulphites and Sulphates of Quadrivalent Vanadium. By IWAN KOPPEL and E. C. BEHRENDT (*Ber.*, 1901, 34, 3929—3936).—Vanadyl sulphite forms two series of double salts with the sulphites of the alkalis, the salts of one series being blue, and having the empirical formula, $\text{R}'_2\text{O}, 2\text{SO}_2, 3\text{VO}_2, \text{aq}$, those of the other being green, with the formula $\text{R}'_2\text{O}, 2\text{SO}_2, \text{VO}_2, \text{aq}$.

The *salt*, $(\text{NH}_4)_2\text{O}, 2\text{SO}_2, 3\text{VO}_2, \text{H}_2\text{O}$, obtained when a solution of ammonium metavanadate (1 mol.) and ammonia (1 mol.) is saturated with sulphur dioxide and evaporated in the presence of the same gas, crystallises in long, blue, rectangular tablets, which are quite stable in air. When a saturated solution of ammonium metavanadate is mixed with a large excess of a neutral solution of ammonium sulphite and evaporated, green, microscopic crystals of the *salt*,



are obtained.

The corresponding potassium and sodium salts are obtained by analogous methods. The blue *potassium* salt crystallises in microscopic tablets, which dissolve in water without decomposition; the green *potassium* salt crystallises, with $5\frac{1}{2}\text{H}_2\text{O}$, from water in rectangular tablets, and is stable in air. The blue *sodium* salt was obtained in long, prismatic crystals with $4\text{H}_2\text{O}$, and the green *sodium* salt with $5\text{H}_2\text{O}$ as a microcrystalline powder, both, however, decomposing when kept in air.

When barium metavanadate suspended in water is reduced with sulphur dioxide, a solution is obtained which, when evaporated in the presence of sulphur dioxide, deposits a dark brown, microcrystalline powder having the composition $3\text{VO}_2, 2\text{SO}_2, 4\frac{1}{2}\text{H}_2\text{O}$; this may be either vanadyl sulphite or vanadyl sulphurous acid. Double sulphates of the alkalis and vanadyl can be obtained by crystallisation of the mixed sulphates at 100° or above from solutions containing sulphuric acid. *Ammonium vanadyl sulphate*, $2\text{VOSO}_4, (\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{O}$, *potassium vanadyl sulphate*, $2\text{VOSO}_4, \text{K}_2\text{SO}_4$, and *sodium vanadyl sulphate*, $2\text{VOSO}_4, \text{Na}_2\text{SO}_4, 2\frac{1}{2}\text{H}_2\text{O}$,

were obtained as extremely hygroscopic, microcrystalline tablets. An *ammonium vanadyl sulphate* of the composition $(\text{NH}_4)_2\text{SO}_4, \text{VOSO}_4, 3\frac{1}{2}\text{H}_2\text{O}$, was also prepared.

R. H. P.

Compounds of Gold and Chlorine. By FERNAND MEYER (*Compt. rend.*, 1901, 133, 815—818).—If gold is treated with liquid chlorine in a sealed tube at the ordinary temperature, the metal is superficially attacked and converted into a crystalline, red mass. When the tubes containing the gold and chlorine are heated intermittently at 100° , the gold entirely dissolves, forming a deep yellow solution, and, on cooling, auric chloride separates in wine-red, very hygroscopic crystals.

The dissociation of auric chloride has been studied in a specially constructed apparatus. At 150° , the dissociation becomes marked, and a greyish-green solid (a mixture of aurous chloride and gold) and chlorine are formed. The dissociation pressure was measured up to 205° , when the system ceases to have only one variable, as the auric chloride begins to volatilise. If at a given temperature, t , the chlorine (which was at a given pressure, p) was slowly removed from the apparatus, until all the auric chloride had disappeared, the pressure assumed a new value, p' , which remained constant until only gold was left in the tube. Auric chloride, therefore, dissociates into aurous chloride and chlorine. Aurous chloride is sensibly dissociated at 170° ; the dissociation pressure was measured up to 240° . These experiments show that there is only one compound of gold and chlorine, namely, aurous chloride, containing less chlorine than auric chloride.

K. J. P. O.

Ruthenium. IV. The Chlorides. By JAS. LEWIS HOWE (*J. Amer. Chem. Soc.*, 1901, 23, 775—788).—*Cæsium* and *rubidium ruthenichlorides*, Cs_2RuCl_6 and Rb_2RuCl_6 , crystallise in black, almost opaque, regular octahedra and are slightly soluble in water. The *oxyruthenichlorides*, $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ and $\text{Rb}_2\text{RuO}_2\text{Cl}_4$, form dark purple, cubic crystals, and are instantly decomposed by water with production of a black precipitate. *Cæsium* and *rubidium chlorides* unite with

ruthenium trichloride to form the *double* salts, $\text{Cs}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$ and $\text{Rb}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$, which are dark brown powders fairly soluble in water.

When a slightly acid solution of caesium ruthenichloride is heated with water and alcohol, a rose-coloured *salt*, $2\text{CsCl}\cdot\text{Ru}(\text{OH}_2)\text{Cl}_3$, is produced, which crystallises in prisms and is very slightly soluble in water. By electrolytic reduction of ruthenium trichloride and addition of caesium chloride to the product, a bluish-green *substance*, $3\text{CsCl}\cdot 2\text{RuCl}_2\cdot\text{H}_2\text{O}$, is precipitated which rapidly oxidises in the air.

E. G.
