

## Inorganic Chemistry.

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**Preparation of Chlorine in a Kipp's Apparatus.** By J. THIELE (*Annalen*, **253**, 239—242).—Chlorine may be conveniently prepared in a Kipp's apparatus by the action of hydrochloric acid on bleaching powder. By means of a handpress, the bleaching powder is compressed into a hard cake; this is broken into small lumps and used in this form.  
W. C. W.

**Automatic Apparatus for Evolving Gases from Liquids.** By J. THIELE (*Annalen*, **253**, 242—246).—A convenient apparatus for preparing hydrogen chloride from commercial hydrochloric acid or sulphurous anhydride from a concentrated solution of sodium hydrogen sulphite may be made from a three-necked Wolff's bottle. This is provided with—(1) a delivery tube fitted with a stop-cock; (2) a small stoppered separating funnel with the stem drawn out to a fine point; and (3) a safety funnel with some mercury in the bend and a loose plug of cotton wool in the funnel. The Wolff's bottle is half filled with the solution of sodium hydrogen sulphite, for example, and the sulphuric acid is slowly introduced through the separating funnel.  
W. C. W.

**Reciprocal Displacement of Oxygen and the Halogens.** By BERTHELOT (*Compt. rend.*, **109**, 546—548 and 590—597).—The author summarises his previous work on the reciprocal displacement of oxygen and chlorine and describes some later results.

Pure concentrated fuming hydrochloric acid is not decomposed by oxygen in presence of sunlight, but if some manganous chloride is present the liquid acquires a deep-brown colour, the atmosphere in the flask becomes charged with chlorine, and the liquid has bleaching properties. Oxygen is absorbed and hydrochlorides of manganese perchloride are formed. If the liberated chlorine is removed and hydrogen chloride and oxygen are introduced into the flask, a further quantity of chlorine is set free, and this process may be repeated several times. The decomposition ceases when the hydrates of the hydrochloric acid contain the maximum amount of water; dilute non-fuming hydrochloric acid is not decomposed even after long exposure in presence of manganese chloride. Ferric chloride behaves in the same manner as manganous chloride, but the phenomena are very much less distinct.

The heat of formation of dissolved hydrobromic acid is almost identical with that of water, and hence in presence of water, but under these conditions only, reciprocal decomposition may take place. In presence of excess of water, oxygen readily decomposes hydrogen bromide under the influence of light. Similar decomposition takes place at the ordinary temperature in the case of a fuming solution of hydrobromic acid, that is, hydrates of the free acid not saturated with water, but is arrested almost immediately by the formation of hydrogen perbrom-

ide,  $\text{HBr}_3$ ;  $\text{HBr}$  conc. soln. +  $\text{Br}_2$  gas =  $\text{HBr}_3$  diss. develops +9.2 Cals., the total heat of formation, +43.5 Cals., being greater than the heat of formation of water. Oxygen does not decompose dilute hydrobromic acid, that is, the saturated hydrates of the acid, nor a solution of potassium bromide acidified with hydrochloric acid.

The formation of hydrogen perbromide explains the decomposition of water by bromine, but this change is limited by the dissociation of the perbromide in presence of water.

Dilute solutions of hydriodic acid are readily decomposed by oxygen under the influence of light at the ordinary temperature, the change corresponding with the liberation of 15.9 Cals. for each atom of gaseous iodine.

The heats of formation of dissolved potassium iodide and hydroxide are practically the same, and slight variations in the conditions serve to turn the reaction in one direction or the other. The combination of iodine with potassium iodide in concentrated solution to form potassium triiodide liberates +5.0 Cals. for each atom of gaseous iodine; the action of iodine on dissolved potassium hydroxide with formation of hypoiodite or iodate liberates +4.1 Cals. and +5.4 Cals. respectively for each atom of gaseous iodine. It follows that oxygen will not displace iodine from potassium iodide except under conditions in which potassium triiodide is stable, that is, in very concentrated solutions. Experiment showed that dilute solutions of potassium iodide remain quite colourless when exposed to light for a long time in presence of pure air; very concentrated solutions soon become orange and the colour deepens with prolonged exposure. The liquid then gives a blue coloration with starch and has an alkaline reaction; if, however, it is diluted, it rapidly becomes colourless, owing to dissociation of the potassium triiodide and the action of the liberated iodine on the potassium hydroxide which has been formed.

It is well known that even dilute potassium iodide solutions become yellow when exposed to ordinary air. This is due to the fact that the carbonic anhydride of the air takes part in the reaction. Carbonic acid does not displace hydriodic acid, but the simultaneous action of oxygen and carbonic anhydride on a dilute solution of potassium iodide produces potassium hydrogen carbonate and free iodine, the change being accompanied by the liberation of +13.5 Cals. for each atom of gaseous iodine. The colour of the liquid becomes deeper if the quantity of carbonic anhydride in the atmosphere above it is increased. The action of the oxygen is still greater in presence of acetic or hydrochloric acid, but in these cases the result is in part due to the displacement of some hydriodic acid. Acetic acid liberates very little hydriodic acid, but the action of the oxygen depends on the successive liberation of small quantities. Hydrochloric acid liberates more hydriodic acid and in this case the action of the oxygen is more marked. In presence of a large excess of air, a solution of potassium iodide acidified with hydrochloric acid is completely decomposed by the action of light in a few days.

If manganous chloride is added to a highly concentrated solution of

potassium iodide and the mixture exposed to light, a higher oxide of manganese is precipitated and iodine is liberated; dilute solutions show the same phenomena in a lower degree.

All the reciprocal displacements of oxygen and the halogens under the influence of light are in agreement with the thermochemical determinations.

C. H. B.

### Simultaneous Synthesis of Water and Hydrogen Chloride.

By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **109**, 641—644).

—Mixtures which contained oxygen and hydrogen in the proportion required to form water, with varying proportions of chlorine; and mixtures of hydrogen and chlorine in the proportions to form hydrogen chloride, with varying quantities of oxygen, were exploded by means of a spark, and the residual chlorine was determined by means of standard sodium arsenite. If  $p$  represents the total hydrogen which enters into combination, and  $p'$  the quantity which combines with oxygen,  $\frac{p - p'}{p'}$  gives the ratio of the hydrogen converted into water to the hydrogen which forms hydrogen chloride. This ratio is independent of the initial pressure, and of the nature of the spark. It is always less than unity if the proportion of chlorine is more than half the volume of the hydrogen, and it varies with every alteration in the proportion of chlorine. When the volume of chlorine present is double the volume of the hydrogen, the quantity of water formed becomes inappreciable. It is evident that the results do not agree with Bunsen's law.

With equal volumes of hydrogen and chlorine and varying proportions of oxygen, the ratio  $\frac{p - p'}{p}$  is always less than unity and does not vary greatly when the ratio of oxygen to hydrogen varies from 0.25 to 3. With equal volumes of the three gases the change is represented by the equation  $5\text{Cl}_2 + 5\text{H}_2 + 5\text{O}_2 = 8\text{HCl} + \text{H}_2\text{O} + \text{Cl}_2 + 4\text{O}_2$ .

C. H. B.

**Equilibrium between Hydrogen, Chlorine, and Oxygen.** By H. LE CHATELIER (*Compt. rend.*, **109**, 664—667).—The author discusses the results of Hautefeuille and Margottet (preceding Abstract) from the point of view of his own laws of chemical equilibrium. The agreement between the observed and calculated numbers is very close. He points out that the degree of moisture of the gases, which is very important, is not specified. The formula shows that a reduction of initial pressure should be accompanied by a reduction in the proportion of water formed, and the fact that this is not observed indicates that the chlorine is partially dissociated. The varying effects of chlorine and oxygen depend solely on their relative volumes and not on their chemical properties.

C. H. B.

**Preparation of Oxygen in a Kipp's Apparatus.** By J. VOLHARD (*Annalen*, **253**, 246—248).—Small quantities of oxygen can be conveniently prepared in a Kipp's apparatus by the action of hydrogen

peroxide on bleaching powder. Nitric acid is added in sufficient quantity to neutralise the lime in the bleaching powder. The oxygen contains a small quantity of chlorine. W. C. W.

**Action of Sulphur on Solutions of Metallic Salts.** By G. VORTMANN and C. PADBERG (*Ber.*, **22**, 2642—2644).—The authors find that with many proto-salts when their aqueous solutions are boiled with flowers of sulphur, about half the metal present is precipitated as sulphide, the remainder being oxidised to the per-salt. When a strongly acid solution of stannous chloride was employed, no stannous sulphide was precipitated, but hydrogen sulphide was evolved, and the whole of the tin oxidised to stannic chloride. With an aqueous solution of stannous chloride, and with an acid solution of cuprous chloride, rather less than half the tin was precipitated as sulphide, a little being oxidised in the same manner as with the strongly acid solution of tin. With mercurous nitrate, almost exactly half of the mercury was precipitated as sulphide.

Solutions of manganese, iron, nickel, zinc, and cadmium sulphates, and acid solutions of bismuth and antimonious chlorides, and of arsenious and arsenic acids, are not altered when boiled with sulphur. L. T. T.

**Preparation of Nitric Oxide.** By J. THIELE (*Annalen*, **253**, 246).—Nitric oxide is prepared in the apparatus previously described (this vol., p. 6) by adding a strong solution of sodium nitrite to a solution of ferrous chloride or sulphate in hydrochloric acid. If the sodium nitrite contains carbonate, it may be removed by precipitation with calcium chloride. W. C. W.

**Phosphonium Sulphate.** By A. BESSON (*Compt. rend.*, **109**, 644—645).—When hydrogen phosphide is passed into sulphuric acid at the ordinary temperature, there is considerable development of heat, sulphur separates, and sulphurous acid is formed. If the acid is previously cooled by means of ice and salt, the gas is somewhat largely absorbed, and the liquid remains limpid. After a time, however, it begins to decompose in the manner indicated, the temperature rises, and decomposition becomes very rapid. If the acid is cooled to  $-20^{\circ}$  or  $-25^{\circ}$  by the rapid evaporation of methyl chloride, a syrupy liquid is obtained, from which a white, crystalline, highly deliquescent, solid separates; this seems to be phosphonium sulphate. When thrown into water at the ordinary temperature, it dissolves with a strident noise, and hydrogen phosphide is evolved, but the sulphuric acid is not reduced. When exposed to air at the ordinary temperature, the phosphorus is oxidised to phosphoric, phosphorous, and hypophosphorous acids, whilst the sulphuric acid is reduced to sulphurous acid and sulphur, with a small quantity of hydrogen sulphide. The crystals may be dissolved in dilute sulphuric acid, and if the solution is electrolysed at  $-25^{\circ}$  or  $-40^{\circ}$  with a mercury cathode, there is only a very slight intumescence of the mercury, and hence, if phosphonium amalgam exists, it is very unstable even at the freezing point of mercury. The solution has a high resistance, and if the

current is too strong the compound is decomposed with great rapidity in the manner already described.

Hydrogen phosphide has no action on nitric acid at  $-25^{\circ}$ .

C. H. B.

**Behaviour of Sodium Thiosulphate towards Acids and Metallic Salts.** By W. VAUBEL (*Ber.*, **22**, 2703—2704).—A reply to Vortman (*Abstr.*, 1889, 1107) upholding the author's previous views (*ibid.*, p. 943).

**Direct Production of Crystalline Sodium Carbonate and Chlorine from Sodium Chloride.** By W. HEMPEL (*Ber.*, **22**, 2475—2478).—In the electrolysis of metallic chlorides, which give readily soluble decomposition-products, the latter are further decomposed as soon as the quantity produced reaches a certain limit. When, however, the compound produced is only sparingly soluble, this secondary decomposition does not take place, and the whole strength of the current is utilised. Potassium chloride and sodium chloride, for example, can be converted into the corresponding chlorate; calcium chloride and magnesium chloride can be decomposed into chlorine and a solid hydroxide, by employing a diaphragm.

Marx (*D. R.-P.*, No. 46318) has shown that alkaline chlorides can be directly converted into chlorine and an alkaline hydrogen carbonate, by passing carbonic anhydride through the solution during electrolysis, metal and liquid diaphragms being employed.

The author, who has been engaged independently in making similar experiments, describes, with the aid of diagrams, an apparatus in which sodium chloride can be directly converted into chlorine and crystalline carbonate. The cathode is a perforated iron disc, the anode a perforated carbon disc, the perforations being about 4 mm. in diameter, and bored in an upward direction to allow the gas to escape freely. A disc of ordinary asbestos-paper, placed immediately between the carbon and iron discs, serves as a diaphragm. The three discs are placed in the centre of a vessel made of porcelain and glass, which is thus divided into two chambers, each of which is provided with a conducting tube, in one case for carbonic anhydride, in the other for chlorine. If sodium chloride is added from time to time through a suitable aperture, and the water which is removed with the crystalline carbonate is replaced, the apparatus can be worked continuously, sodium carbonate and almost chemically pure chlorine being obtained.

A tension of 3.2 volts is required for decomposing the sodium chloride, and a tension of 2.5 volts to overcome the polarisation current; but the latter has only a slight tension when both electrodes are made of carbon. With a current of 1.73 ampères 0.93 gram of chlorine per hour was produced, so that if a dynamo were employed it should give 64.5 grams of chlorine and 259.8 grams of  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$  per horse-power-hour.

F. S. K.

**Preparation of Crystalline Normal Lithium Phosphate and Arsenate.** By A. DE SCHULTEN (*Bull. Soc. Chim.* [3], **1**, 479—480).—Fused lithium chloride dissolves the amorphous, normal phosphate, and on cooling and washing the melt, rhomboidal, tabular crystals of

normal lithium phosphate, which have a sp. gr. 2·41 at 15°, and are infusible at a white heat, are obtained.

The normal arsenate is similarly prepared; it corresponds with the phosphate physically, and is of sp. gr. 3·07 at 15°. T. G. N.

**Cadmium Phosphates and Arsenates.** By A. DE SCHULTEN (*Bull. Soc. Chim.* [3], 1, 473—479).—The normal orthophosphate,  $\text{Cd}_3(\text{PO}_4)_2$ , falls as a voluminous, amorphous precipitate when normal sodium phosphate is added to the solution of a cadmium salt.

Hydrogen disodium phosphate throws down from a hot solution of cadmium chloride or sulphate an amorphous precipitate which quickly becomes crystalline. After purification by dissolution in phosphoric acid and cautious reprecipitation by alkaline hydroxides, it forms small, prismatic hexagons of sp. gr. 3·98 at 15°, having the composition  $\text{H}_2\text{Cd}_3(\text{PO}_4)_4 + 4\text{H}_2\text{O}$ ; these, when dissolved in cold phosphoric acid (sp. gr. 1·1), are reprecipitated unaltered on warming or on heating in sealed tubes to 250°, but redissolve on cooling; as thus produced, their sp. gr. is 4·12 at 15°. This phosphate loses its water at a red heat, and fuses at a white heat; it is probably the compound described by Stromeyer as the normal phosphate.

Monocadmium phosphate,  $\text{H}_4\text{Cd}(\text{PO}_4)_2 + 2\text{H}_2\text{O}$ , crystallises out after slow evaporation of a saturated solution of the previous salt in cold dilute phosphoric acid at the normal temperature. It exists as large clino-rhombic prisms of sp. gr. 2·742 at 15°, which lose their water of crystallisation at 100°, and are decomposed by water to form a flocculent phosphate,  $\text{H}_2\text{Cd}_3(\text{PO}_4)_4 + 4\text{H}_2\text{O}$ .

Cadmium chlorapatite.—Normal cadmium orthophosphate and the second phosphate described above dissolve in fused cadmium chloride, and on slowly cooling the melt, long, hexagonal prisms of the salt,  $3\text{Cd}_3(\text{PO}_4)_2, \text{CdCl}_2$ , of sp. gr. 5·46 at 15°, separate.

A cadmium bromapatite,  $3\text{Cd}_3(\text{PO}_4)_2, \text{CdBr}_2$ , may be similarly prepared, but is always contaminated with cadmium pyrophosphate, from which it may be separated by cold, dilute nitric acid, which dissolves only the bromapatite; the cadmium pyrophosphate,  $\text{Cd}_2\text{P}_2\text{O}_7$ , exists as flattened oblique lamellæ of sp. gr. 4·965 at 15°.

Cadmium arsenates.—When the amorphous powder,  $\text{H}_2\text{Cd}_3(\text{AsO}_4)_4 + 4\text{H}_2\text{O}$ , which is precipitated on the addition of hydrogen disodium arsenate to the solution of a cadmium salt, is dissolved to saturation in a cold solution of arsenic acid of sp. gr. 1·3, and, subjected to heat, crystals of the salt  $\text{HCdAsO}_4 + \text{H}_2\text{O}$ , having a sp. gr. of 4·164 at 15° are deposited.

Monocadmium arsenate,  $\text{H}_4\text{Cd}(\text{AsO}_4)_2 + 2\text{H}_2\text{O}$ , crystallises out when a saturated solution of the compound  $\text{H}_2\text{Cd}_3(\text{PO}_4)_4 + 4\text{H}_2\text{O}$ , in arsenic acid solution (sp. gr. 1·3), is allowed to evaporate at the ordinary temperature. It forms large, clino-rhombic prisms of sp. gr. 3·241 at 15°, which are isomorphous with those of the corresponding phosphate. At 70—80°, they lose their water of hydration, and are partly decomposed; with excess of water, they form a flocculent substance,  $\text{H}_2\text{Cd}_3(\text{AsO}_4)_4 + 4\text{H}_2\text{O}$ .

Cadmium chlorarsenoapatite,  $3\text{Cd}_3(\text{AsO}_4)_2, \text{CdCl}_2$ , is produced by fusing either normal ammonium arsenate or the salt  $\text{H}_2\text{Cd}_3(\text{AsO}_4)_4 +$

$4\text{H}_2\text{O}$ , with excess of cadmium chloride. Its sp. gr. is 5.865 at  $15^\circ$ , and its physical properties correspond with those of the chlorapatite.

Cadmium bromarsenioapatite,  $3\text{Cd}_3(\text{AsO}_4)_2, \text{CdBr}_2$ , is similarly prepared, and exists as long yellow prisms of sp. gr. 6.017.

Cadmium pyroarsenate,  $\text{Cd}_2\text{As}_2\text{O}_7$ , is prepared by fusing a mixture of cadmium bromide (22 parts) with potassium bromide (5 parts), and adding to the fused mass normal ammonium arsenate (9 parts); after washing the melt, the colourless crystals of the pyroarsenate are separated from the yellow bromarsenioapatite by treatment with dilute nitric acid, which dissolves the latter compound only. This pyroarsenate forms crystals of sp. gr. 5.474 at  $15^\circ$ , corresponding in physical properties with the pyrophosphate. T. G. N.

**Action of Sodium Thiosulphate on Metallic Salts.** By G. VORTMANN and C. PADBERG (*Ber.*, 22, 2637—2641).—The authors have extended Vortmann's work on copper salts (*Abstr.*, 1888, 787) to other metallic salts.

When a concentrated solution of sodium thiosulphate is added to a strong solution of lead acetate until the lead thiosulphate first precipitated has been just redissolved, and alcohol is then added, an oily liquid separates, which when rubbed with absolute alcohol solidifies to a crystalline mass of the formula  $\text{PbS}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3 + 12\text{H}_2\text{O}$ .

Thallous sulphate under similar treatment yields small needles of the formula  $\text{Tl}_2\text{S}_2\text{O}_3, 2\text{Na}_2\text{S}_2\text{O}_3 + 8\text{H}_2\text{O}$ .

When molecular proportions of cadmium sulphate and barium thiosulphate are rubbed together with a little water, the insoluble barium sulphate formed filtered off, and alcohol added to the filtrate, *cadmium thiosulphate*,  $\text{CdS}_2\text{O}_3 + 2\text{H}_2\text{O}$ , separates as an oil, which gradually solidifies to a yellowish-white, crystalline mass. When equal molecular proportions of sodium thiosulphate and cadmium nitrate in aqueous solution are mixed together and alcohol added, yellowish-white needles of the formula  $2\text{CdS}_2\text{O}_3, \text{Na}_2\text{S}_2\text{O}_3 + 7\text{H}_2\text{O}$  are formed. If a large excess of the thiosulphate is used, the compound  $\text{CdS}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O}$  separates as an oil. This gradually solidifies to small, yellow scales, which lose 4 mols.  $\text{H}_2\text{O}$  over sulphuric acid.

On mixing strong solutions of zinc iodide and sodium thiosulphate and adding alcohol, an oil separates, which after long exposure over sulphuric acid solidifies to a gum-like mass of the formula  $2\text{ZnS}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3 + 10\text{H}_2\text{O}$ . It is deliquescent, and decomposes gradually with formation of zinc sulphide.

*Ferrous thiosulphate*,  $\text{FeS}_2\text{O}_3 + 5\text{H}_2\text{O}$ , forms green crystals easily soluble in water. A double salt,  $\text{FeS}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3 + 8\text{H}_2\text{O}$ , was obtained by precipitating a mixed solution of ferrous iodide and sodium thiosulphate with alcohol. It forms bright-green crystals, soluble in water.

Manganese thiosulphate,  $\text{MnS}_2\text{O}_3 + 5\text{H}_2\text{O}$ , is crystalline but unstable. A pale, rose-coloured double salt,  $\text{MnS}_2\text{O}_3, 2\text{Na}_2\text{S}_2\text{O}_3 + 16\text{H}_2\text{O}$ , was obtained.

The cobalt double salt,  $\text{CoS}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O}$ , forms a blue,



gum-like mass, soluble in water. No corresponding nickel salt could be prepared, though a crystalline salt,  $\text{NiSi}_2\text{O}_3 \cdot 6\text{NH}_3 \cdot 3\text{H}_2\text{O}$ , was obtained.  
L. T. T.

### New Method of Preparing Anhydrous Aluminium Chloride.

By C. F. MABERY (*Ber.*, **22**, 2658).—The author finds that dry hydrogen chloride extracts the whole of the aluminium from an alloy of copper and aluminium without attacking the copper. The reaction is most energetic a little below a red heat. The alloys containing 15 to 40 per cent. of aluminium are best powdered, mixed with powdered charcoal (to prevent the fusion of the remaining copper), put into a graphite retort, and when heated just below a red heat a current of hydrogen chloride is passed through. The aluminium chloride distils over, and may be condensed in suitable vessels, the liberated hydrogen passing on.  
L. T. T.

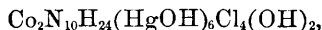
**Alkali Aluminium Silicates.** By A. GORGEU *Zeit. Kryst. Min.*, **15**, 646, from *Bull. soc. fran. min.*, **10**, 278).—On melting kaolin with alkali haloid salts in the presence of moist air, silicates are formed, having the composition  $\text{AlR}'\text{SiO}_4$ . By melting kaolin with potassium carbonate or caustic potash at a dull-red heat, an amorphous salt,  $\text{AlKSiO}_4$ , is obtained, whilst at a more intense heat octahedra are obtained, having the composition  $\text{Al}_2\text{K}_2\text{SiO}_6$ , or else a more basic silicate also crystallising in the regular system. The sodium-compounds prepared in a similar way are always basic, and form doubly refracting crystals.  
B. H. B.

**Mercuricobaltammonium Salts.** By G. VORTMANN and E. MORGULIS (*Ber.*, **22**, 2644—2648).—When solutions of the mercuric double salts of cobaltammonium chlorides are treated with potash or soda, red precipitates are formed, which appear to be cobalt-ammonium chlorides, in which part of the hydrogen is replaced by varying proportions of the univalent radicles ( $\text{HgCl}$ ) or ( $\text{HgOH}$ ).

**Luteocobalt salts.** A solution of the salt  $\text{Co}_2(\text{NH}_3)_{12}\text{Cl}_6 \cdot 6\text{HgCl}_2$ , or a mixture of one part by weight of luteocobalt chloride and three parts of mercuric chloride, when treated with 6 mols. of soda yields the salt  $\text{Co}_2\text{N}_{12}\text{H}_{28}(\text{HgCl})_6(\text{HgOH})_2\text{Cl}_6$ ; or with excess of soda, the salt  $\text{Co}_2\text{N}_{12}\text{H}_{28}(\text{HgOH})_8\text{Cl}_6$ . Both compounds are bright-red, and decompose quickly when moist, slowly when dry. Equal weights of luteocobalt chloride and mercuric chloride with excess of soda yield a slightly more stable, red salt,  $\text{Co}_2\text{N}_{12}\text{H}_{32}(\text{HgOH})_4\text{Cl}_6$ .

**Purpureocobaltdecamine salts.**—1 mol. of purpureocobalt chloride, 6 mols. of mercuric chloride, and 6 mols. of soda yield a dark-red, flocculent salt,  $\text{Co}_2\text{N}_{10}\text{H}_{22}(\text{HgCl})_6(\text{HgOH})_2\text{Cl}_6$ ; with excess of soda, the salt  $\text{Co}_2\text{N}_{10}\text{H}_{22}(\text{HgOH})_8\text{Cl}_6$  is formed.

**Roseocobaltdecamine salts.**—1 mol. of roseocobalt chloride, 6 mols. of mercuric chloride, and 6 mols. of soda yield a violet-red precipitate,  $\text{Co}_2\text{N}_{10}\text{H}_{24}(\text{HgOH})_6\text{Cl}_6$ ; with excess of soda, a salt,



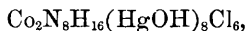
is formed. Both salts are very unstable.



*Purpureocobaltoctamine salts*.—1 mol. of purpureocobaltoctamine chloride, 6 mols. of mercuric chloride, and 6 mols. of soda yield the salt,  $\text{Co}_2\text{N}_8\text{H}_{16}(\text{HgCl})_4(\text{HgOH})_4\text{Cl}_6$ ; with excess of soda, the salt  $\text{Co}_2\text{N}_8\text{H}_{16}(\text{HgOH})_8\text{Cl}_6$  is formed.

Equal weights of the cobalt and mercuric salts with excess of soda yield the salt  $\text{Co}_2\text{N}_8\text{H}_{16}(\text{HgOH})_8\text{Cl}_4(\text{OH})_2$ .

*Roseocobaltoctamine salts*.—Under like conditions as with the purpureo-salts, the three salts,  $\text{Co}_2\text{N}_8\text{H}_{16}(\text{HgCl})_6(\text{HgOH})_2\text{Cl}_6$ ,



and  $\text{Co}_2\text{N}_8\text{H}_{16}(\text{HgOH})_8\text{Cl}_4(\text{OH})_2$ , are formed. All three are violet-red, and decompose at ordinary atmospheric temperature, as do also the corresponding purpureo-compounds. L. T. T.

**Cobaltoctamine Salts.** By G. VORTMANN and O. BLASBERG (*Ber.*, **22**, 2648—2655).—When cobalt nitrate, sulphate, or chloride is dissolved in a small quantity of water and added to a mixture of ammonia and ammonium carbonate, violet-red solutions are formed. If these are oxidised by a current of air, decamine salts are formed, but on evaporation these are decomposed, octamine salts crystallising out. The following salts are described:—

|   |                               |
|---|-------------------------------|
| $\text{Co}_2(\text{NH}_3)_{10}(\text{NO}_3)_2(\text{CO}_3)_2, 2\text{H}_2\text{O}$ .....      | Crystalline.                  |
| $\text{Co}_2(\text{NH}_3)_{10}(\text{SO}_4)_2\text{CO}_3, 4\text{H}_2\text{O}$ .....          | Crystalline.                  |
| $\text{Co}_2(\text{NH}_3)_8(\text{NO}_3)_2(\text{CO}_3)_2, \text{H}_2\text{O}$ .....          | Cherry red crystals.          |
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_4)_2\text{CO}_3, 4\text{H}_2\text{O}$ .....             | Long, thin needles.           |
| $\text{Co}_2(\text{NH}_3)_8\text{SO}_4(\text{CO}_3)_2, 3\text{H}_2\text{O}$ .....             | Dark red, prismatic crystals. |
| $\text{Co}_2(\text{NH}_3)_8\text{Cl}_4\text{CO}_3, 2\text{H}_2\text{O}$ .....                 | Crystalline.                  |
| $\text{Co}_2(\text{NH}_3)_8\text{Cl}_2(\text{CO}_3)_2, \text{H}_2\text{O}$ .....              | "                             |
| $\text{Co}_2(\text{NH}_3)_8(\text{NO}_3)_2(\text{SO}_4)_2, 2\text{H}_2\text{O}$ .....         | "                             |
| $\text{Co}_2(\text{NH}_3)_8(\text{NO}_3)_6, 2\text{H}_2\text{O}$ .....                        | "                             |
| $\text{Co}_2(\text{NH}_3)_8(\text{NO}_3)_2\text{Cl}_4, 4\text{H}_2\text{O}$ .....             | "                             |
| $\text{Co}_2(\text{NH}_3)_8(\text{NO}_3)_2\text{I}_4, 2\text{H}_2\text{O}$ .....              | "                             |
| $\text{Co}_2(\text{NH}_3)_8\text{Br}_2(\text{SO}_4)_2$ .....                                  | "                             |
| $\text{Co}_2(\text{NH}_3)_8\text{I}_2(\text{SO}_4)_2$ .....                                   | "                             |
| $\text{Co}_2(\text{NH}_3)_8\text{I}_2\text{Cl}_4, 2\text{H}_2\text{O}$ .....                  | Brown scales.                 |
| $\text{Co}_2(\text{NH}_3)_8(\text{OH})_2\text{Cl}_4, 2\text{H}_2\text{O}$ .....               | Dark green powder.            |
| $\text{Co}_2(\text{NH}_3)_8(\text{OH})_2\text{Cl}_4, 2\text{HgCl}_2$ .....                    |                               |
| $\text{Co}_2(\text{NH}_3)_8(\text{OH})_2\text{Cl}_4, \text{PtCl}_4, \text{H}_2\text{O}$ ..... |                               |

L. T. T.

**Action of Sulphurous Acid on Cobaltammonium Salts.** By G. VORTMANN and G. MAGDEBURG (*Ber.*, **22**, 2630—2637).—The authors have obtained the following compounds:—

|  |                          |
|--|--------------------------|
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3\text{Am})_6, 10\text{H}_2\text{O}$ .....               | Yellowish-brown needles. |
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3)_6\text{Ba}_3, 7\text{H}_2\text{O}$ .....              | Golden-yellow scales.    |
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3)_6\text{Ba}_2\text{Am}_2, 7\text{H}_2\text{O}$ .....   | Golden-yellow scales.    |
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3)_6\text{Co}_2^{\text{VI}}, 36\text{H}_2\text{O}$ ..... | Orange crystals.         |
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3)_6\text{Co}_2^{\text{VI}}, 24\text{H}_2\text{O}$ ..... | Orange crystals.         |

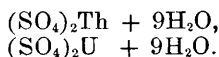
|  |                            |
|--|----------------------------|
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3)_6(\text{NH}_3)_{12}\text{Co}^{\text{vi}}.8\text{H}_2\text{O}$ | Orange powder.             |
| $\text{Co}_2(\text{NH}_3)_8(\text{SO}_3)_2(\text{SO}_3\text{Am})_2.4\text{H}_2\text{O}$                | Yellowish-brown needles.   |
| $\text{Co}_2(\text{NH}_3)_8\text{SO}_4(\text{SO}_3)_4\text{Co}^{\text{vi}}.24\text{H}_2\text{O}$       | Yellow crystalline powder. |
| $\text{Co}_2(\text{NH}_3)(\text{NH}_3)_6(\text{SO}_3)_2\text{Cl}_2.4\text{H}_2\text{O}$                | Dark brown crystals.       |
| $\text{Co}_2(\text{NH}_3)_{10}(\text{SO}_3\text{Na})_6.2\text{H}_2\text{O}$                            | Light brown crystals.      |
| * $\text{Co}_2(\text{NH}_3)_{10}(\text{SO}_3)_6\text{Co}^{\text{vi}}.8\text{H}_2\text{O}$              | Brownish-yellow powder.    |
| $\text{Co}_2(\text{NH}_3)_{10}(\text{SO}_3)_3.3\text{H}_2\text{O}$                                     |                            |
| $\text{Co}_2(\text{NH}_3)_{10}(\text{SO}_3)_2\text{Cl}_2$  | Brown crystalline powder.  |
| $\text{Co}_2(\text{NH}_3)_{12}(\text{SO}_3)_2\text{Cl}_2.6\text{H}_2\text{O}$                          | Yellow needles.            |

The authors consider that these salts show the existence of four series of salts.

1.  $\text{Co}_2(\text{NH}_3)_{6-12}(\text{SO}_3)_3$ .
2.  $\text{Co}_2(\text{NH}_3)_{6-12}(\text{SO}_3)_2(\text{SO}_2\text{R})_2$ .
3.  $\text{Co}_2(\text{NH}_3)_{6-12}(\text{SO}_3)(\text{SO}_3\text{R})_4$ .
4.  $\text{Co}_2(\text{NH}_3)_{6-12}(\text{SO}_3\text{R})_6$ .

L. T. T.

**New case of Isomorphism of Uranium and Thorium.** By C. RAMMELSBERG (*Zeit. Kryst. Min.*, **15**, 640—641; from *Sitzber. preuss. Akad. Wiss.*, 1886, 603).—The author shows that the thorium sulphate described by Nordenskiöld and others, and the uranium sulphate hitherto regarded as rhombic, have a similar composition, namely:—



The crystals of the latter are only seemingly rhombic in consequence of twin-formation; in reality they are monosymmetric, like the thorium sulphate. The axial ratios of the two minerals are: uranium sulphate,  $a : b : c = 0.597 : 1 : 0.6555$ ,  $\beta = 82^\circ 11'$ ; thorium sulphate,  $a : b : c = 0.598 : 1 : 0.658$ ,  $\beta = 81^\circ 50'$ . B. H. B.

**Fluorine-compounds of Vanadium and its Analogues.** By E. PETERSEN (*J. pr. Chem.* [2], **40**, 271—296; compare *Abstr.*, 1889, 107).—The following double salts of vanadium oxyfluorides and potassium fluoride have been obtained:—

$2\text{KF} \cdot \text{VOF}_3$ , a white, crystalline precipitate, is obtained by adding a solution of potassium fluoride to one of vanadic acid in hydrofluoric acid; when dried over sulphuric acid, it becomes reddish-brown, and has the above formula.

$4\text{KF} \cdot \text{VF}_5 \cdot \text{VOF}_3$  separates as a white precipitate from the mother-liquor of the above salt.

$\text{HF} \cdot 3\text{KF} \cdot 2\text{VOF}_3$  crystallises from a hot solution of either of the preceding salts in hydrofluoric acid in beautiful, colourless prisms, which lose very little weight at  $100^\circ$ .

$3\text{KF} \cdot \text{VOF}_3 \cdot \text{VO}_2\text{F}$  is the white, crystalline residue left when the precipitate obtained by adding a solution of vanadium pentoxide in hydrofluoric acid to a solution of potassium fluoride is treated with water at the ordinary temperature; if hot water is used and the solution is poured into a hot solution of potassium fluoride, a crystalline precipitate is obtained, of uncertain composition, but approaching

\* Probably Künzel's pentaminedicobaltic sulphite.

the formula  $4\text{KF}, \text{VOF}_3, \text{VO}_2\text{F}$ ; or if the first-mentioned precipitate is heated with water for some minutes, a salt having nearly the composition  $\text{VOF}_3, \text{VO}_2\text{F}$  is obtained.

$2\text{KF}, \text{VO}_2\text{F}$  separates from a warm solution of vanadium pentoxide in hydrofluoric acid when it is nearly neutralised with potassium hydroxide. It crystallises in yellow, six-sided, truncated prisms. When recrystallised from water, it yields the salt  $3\text{KF}, 2\text{VO}_2\text{F}$ .

$3\text{HF}, 9\text{NH}_4\text{F}, 5\text{VOF}_3$ , obtained by adding ammonium fluoride in slight excess to the solution of vanadium pentoxide in hydrofluoric acid, crystallises in large, colourless, four-sided prisms.

$3\text{NH}_4\text{F}, \text{VO}_2\text{F}$  crystallises from a solution of vanadium pentoxide in hydrofluoric acid when it is nearly neutralised with ammonia. The crystallography of the salt is given.

$\text{HF}, 7\text{NH}_4\text{F}, 4\text{VO}_2\text{F}$  separates in white crystals from the solution of the last-named salt in warm water.

$2\text{Nb}_2\text{O}_5, 3\text{KF}, 5\text{H}_2\text{O}$  is obtained by melting niobium pentoxide (1 part) with potassium fluoride (3.25 parts) and treating the melt with water, when the salt remains undissolved as a crystalline powder.

$\text{Nb}_2\text{O}_5, \text{KF}, 3\text{H}_2\text{O}$  is a prismatic, crystalline powder, obtained by fusing niobium pentoxide (1 part) with potassium fluoride (1.3–1.5 parts).

The author reviews the work already done on the vanadium double fluorides, and concludes his paper with the following directions for extracting vanadic acid from the finery slag of Taberg:—300 grams of the finely-powdered slag is mixed with 400 c.c. of hydrochloric acid (sp. gr. 1.18) and shaken. After 24 hours, water is added to make the bulk up to  $1\frac{1}{2}$  litres, and the whole filtered through linen. Iron is then added, and, after the evolution of hydrogen has ceased, sodium acetate until the liquid is reddish-brown; finally, acetic acid and sodium phosphate are added until all iron, chromium, aluminium, and vanadium are precipitated as phosphates. The precipitate is mixed with sodium carbonate (0.5 part) and heated on an iron plate for  $\frac{1}{2}$ — $\frac{3}{4}$  hour; the mass is treated with water, hydrochloric acid added to nearly neutralise the solution, which is then heated, filtered, and made acid with acetic acid; solid ammonium chloride is now added, when a red, crystalline ammonium vanadate,  $(\text{NH}_4)_2\text{O}, 2\text{V}_2\text{O}_5, 4\text{H}_2\text{O}$ , separates; this is heated and the residual vanadium oxide treated with hot nitric acid at  $110$ — $120^\circ$ , and converted into ammonium metavanadate by evaporating off the nitric acid, dissolving in ammonia, and crystallising; pure vanadic acid is obtained from this salt by igniting and repeating the nitric acid treatment. A. G. B.

**Vapour-density of Antimony Pentachloride.** By R. ANSCHÜTZ and N. P. EVANS (*Annalen*, **253**, 95—105).—By means of a modification of La Coste's apparatus, the authors have attempted to determine the density of the vapour of antimony pentachloride under reduced pressure. As antimony trichloride boils at  $143$ — $144^\circ$  under 70 mm. pressure and antimony pentachloride boils at  $102$ — $103^\circ$  under 68 mm. pressure, the determinations were made under 58 mm. pressure at a temperature of  $218^\circ$ . The mean of four determinations gave the value 10, the theoretical density being 10.33. It was impossible to

exclude all traces of moisture from the apparatus and avoid the formation of minute quantities of the monohydrate of antimony pentachloride.  
W. C. W.

**Atomic Weight of Palladium.** By E. H. KEISER (*Amer. Chem. J.*, **11**, 398—403).—Attempts were at first made to use the double chlorides of palladium with ammonium and with sodium, but they had to be abandoned, as these compounds contain water, from which it is almost impossible to completely free them; moreover, the dried salts are very hygroscopic, and absorb water rapidly while being weighed.

Finally, the yellow, crystalline palladodiammonium chloride,  $\text{PdN}_2\text{H}_6\text{Cl}_2$ , was used; this is formed whenever hydrochloric acid is added to a solution of palladium chloride in excess of ammonia; it is a stable compound, and can be obtained very pure. It contains no water of crystallisation, can be dried completely, and is not hygroscopic. When heated in a current of pure hydrogen, the colour changes from yellow to black, hydrogen being absorbed, and metallic palladium and ammonium chloride formed. On raising the temperature, the ammonium chloride volatilises, and spongy palladium is left behind; this is cooled below a red heat in a current of hydrogen, and then the hydrogen is displaced by air; in this way the occlusion of hydrogen is prevented. The weight of palladium obtained from a known weight of the chloride is thus ascertained, and from this the atomic weight of palladium is calculated, assuming  $\text{N} = 14\cdot01$ ,  $\text{H} = 1$ ,  $\text{Cl} = 35\cdot37$ . Two series of experiments were made; the palladammonium chloride used in the second series was prepared from the metallic palladium obtained in the first. The results give as mean value  $\text{Pd} = 106\cdot35$  :—

| Series. | Experiments. | Atomic weight. |          |          |
|---------|--------------|----------------|----------|----------|
|         |              | Mean.          | Maximum. | Minimum. |
| I.      | 11           | 106·352        | 106·459  | 106·292  |
| II.     | 8            | 106·350        | 106·455  | 106·286  |

C. F. B.

**Ruthenium Potassium Nitrites.** By A. JOLY and M. VÈZES (*Compt. rend.*, **109**, 667—670; compare *Abstr.*, 1889, p. 352).—If ruthenium chloride is added to a boiling solution of potassium nitrite until the precipitate which forms at first is redissolved, and the liquid is concentrated and allowed to cool, it deposits dichroic, orange-red, monoclinic prisms of  $90^\circ 10'$ . They are very soluble in water, can be purified by repeated recrystallisation without undergoing alteration, and have the composition  $\text{Ru}_2\text{O}_3(\text{N}_2\text{O}_3)_4, 4\text{KNO}_2$  or  $\text{Ru}_2\text{O}_3(\text{NO})_2, (\text{N}_2\text{O}_3)_2, 4\text{KNO}_2$ .

When the potassium nitrite is in excess, and prolonged ebullition is avoided, a pale-yellow, crystalline precipitate is obtained of the composition  $\text{Ru}_2\text{O}_3, (\text{N}_2\text{O}_3)_2, 8\text{KNO}_2$  or  $\text{Ru}_2\text{O}_3(\text{NO})_2, \text{N}_2\text{O}_3, 8\text{KNO}_2$ . Separation of the ruthenium is never complete, and the mother-liquor, on concentration, yields crystals of the first compound. The second salt is converted into the first by prolonged ebullition with water, and the reverse change is effected by the addition of potassium nitrite. At a

low temperature, the second salt crystallises with 2 mols.  $\text{H}_2\text{O}$ . Other double nitrites seem to be formed, but are relatively very unstable.

If the double nitrites are heated with ammonium chloride and hydrochloric acid, only part of the nitrogen is evolved and one atom of the nitrogen remains in combination with each atom of ruthenium. The solution when concentrated yields the potassium ruthenium nitrosochloride previously described (*loc. cit.*).

No compound was obtained corresponding with that to which Claus attributes the formula  $\text{Ru}(\text{NO}_2)_3, 3\text{KNO}_2$ . C. H. B.

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