

Inorganic Chemistry.

Affinities of Iodine in Solution. By H. GAUTIER and G. CHARPY (*Compt. rend.*, **111**, 645—647).—If mercury is agitated with any solution of iodine, a green precipitate of mercurous iodide is formed, but if the mercury contains another metal, the iodine combines with the latter in proportions depending on the nature of the solvent. In the case of an amalgam of lead, the difference in colour between lead and mercurous iodides enables the change to be followed.

Brown solutions of iodine (in alcohol, ether, acetone) yield with lead amalgam a yellow precipitate of lead iodide, even when the proportion of lead is very small, and no mercurous iodide is formed until all the lead has been converted into iodide.

On the other hand, violet solutions of iodine (in chloroform, carbon bisulphide) give green mercurous iodide, even in presence of considerable quantities of lead and when the iodine is in excess.

Solutions of intermediate tint give precipitates intermediate in colour between lead iodide and mercurous iodide, and it is found that if the solutions of iodine in various solvents are arranged in order according to their colour, and also according to the colour of the precipitate which they yield when agitated with lead amalgam, the two orders are the same. The colour of the precipitate is independent of the composition of the amalgam and the concentration of the iodine solution.

Careful examination of the reaction shows that brown solutions of iodine and pure mercury at first yield mercuric iodide, which passes into solution, whilst violet solutions of iodine at once form mercurous iodide, even whilst some free iodine remains. In presence of lead amalgam, brown solutions of iodine first form mercuric iodide, which attacks the lead, forming lead iodide and mercurous iodide, and the latter is again converted into mercuric iodide by the free iodine. No permanent precipitate of mercurous iodide is formed with brown solutions until all the lead has been converted into iodide.

It follows from these results that violet solutions of iodine contain the element in a more simple molecular condition, with a tendency to at once form mercurous iodide, this tendency being more marked, the simpler the condition of the iodine. The phenomena seem to belong to the same order as those to which Berthelot has given the name "tendency to conservation of type."

C. H. B.

Fluorspar from Quincié. By H. BECQUEREL and H. MOISSAN (*Compt. rend.*, **111**, 669—672).—It is well known that certain

specimens of fluorspar, when powdered, emit a peculiar odour, which has been attributed by different observers to free fluorine, hypochlorous acid, ozone, hydrocarbons, &c. The fluorspar examined by the authors was deep violet in colour, and came from Quincié, near Villefranche. It had the composition Ca , 36.14 ($= \text{CaF}_2$, 70.47); $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, 3.95; SiO_2 , 25.00; loss at a red heat 2.10 per cent; sp. gr. 3.117.

When powdered, it emitted an odour recalling that of ozone and likewise that of fluorine. Moissan has shown that fluorine decomposes water with liberation of ozone. The odour from the fluorspar is very similar to that emitted from the electrolytic cell in the isolation of fluorine, and even if the odour is due to ozone, the latter may be a product of the action of free fluorine on the moisture of the air.

Fluorspar from Quincié, when powdered in contact with moist air, evolves a gas which at once acts on ozone paper. If moistened with starch paste and potassium iodide solution, and powdered under a microscope, bubbles of gas are seen to escape, and an intense blue coloration is produced. When the fluorspar is powdered with sodium chloride or potassium bromide or iodide, free chlorine, bromine, or iodine is liberated. When heated above a red heat, the fluorspar decrepitates, loses its colour, and becomes ochreous, and afterwards gives no trace of ozone when powdered. If heated at 250° for an hour, which is quite sufficient to destroy all ozone, it still gives, when powdered, a strong reaction with ozone paper.

Small fragments of the mineral, when heated in a small glass tube, corrode its surface; when powdered with silicon, a pungent odour is emitted, and if the mixture is heated, silicon fluoride is evolved. If small fragments of the mineral are left in contact with water, the water becomes acid, and if the liquid is then evaporated in watch glasses, the latter are corroded.

No similar results were obtained with a white fluorspar from the Pyrenees, and although it is possible that the fluorine results from the dissociation of a perfluoride, the authors regard it as more probable that the free fluorine is occluded in the mineral.

C. H. B.

The Molecular Weight and Refractive Energy of Sulphur Dichloride. By T. COSTA (*Gazzetta*, 20, 367—372).—The existence of a definite compound of the composition SCl_2 has been repeatedly called in question (see this Journal, 1870, 455; 1871, 1163; Abstr., 1878, 553; 1886, 977); and the substance held by some to be sulphur dichloride has been variously regarded as a solution of chlorine in the monochloride, or as a compound in a state of partial dissociation. The author has determined cryoscopically the molecular weight of the reddish-brown liquid obtained by saturating the monochloride with chlorine below 0° , and then removing any excess of chlorine by passing in a current of carbonic anhydride, and the results of the determinations, both in benzene and acetic acid solution, agree with the molecular formula SCl_2 . This substance can, therefore, no longer be said to exist in a state of partial dissociation. Its density at 15.4° is 1.64819 and its molecular refractive energy $\mu_{\text{Na}} = 1.57169$, $\mu_{\text{Na}} = 1.57806$.

S. B. A. A.

Specific Gravity of Sulphuric Acid of Different Degrees of Concentration. By G. LUNGE and M. ISLER (*Zeit. ang. Chem.*, 1890, 129—136).—In consequence of the discovery of errors in Kolb's table, the authors have made fresh determinations with great care. The curve plotted from the results, whilst agreeing in many places closely with that of Kolb, is much smoother, and at the extremes, differs somewhat considerably. The table, of which the following is an abstract, was obtained by graphic interpolation; in the original, it is given for intervals of 0·005 (1° Twaddell) in the specific gravity:—

Sp. gr. at 15° 4° in vacuo.	Percentage of H ₂ SO ₄ .	Sp. gr. at 15° 4° in vacuo.	Percentage of H ₂ SO ₄ .	Sp. gr. at 15° 4° in vacuo.	Percentage of H ₂ SO ₄ .
1·000	0·09	1·400	50·11	1·800	86·90
1·020	3·03	1·420	52·15	1·820	90·05
1·040	5·96	1·440	54·07	1·824	90·80
1·060	8·77	1·460	55·97	1·826	91·25
1·080	11·60	1·480	57·83	1·828	91·70
1·100	14·35	1·500	59·70	1·830	92·10
1·120	17·01	1·520	61·59	1·832	92·52
1·140	19·61	1·540	63·43	1·834	93·05
1·160	22·19	1·560	65·08	1·836	93·80
1·180	24·76	1·580	66·71	1·838	94·60
1·200	27·32	1·600	68·51	1·840	95·60
1·220	29·84	1·620	70·32	1·8405	95·95
1·240	32·28	1·640	71·99	1·8410	97·00
1·260	34·57	1·660	73·64	1·8415	97·70
1·280	36·87	1·680	75·42	1·8410	98·20
1·300	39·19	1·700	77·17	1·8405	98·70
1·320	41·50	1·720	78·92	1·8400	99·20
1·340	43·74	1·740	80·68	1·8395	99·45
1·360	45·88	1·760	82·44	1·8390	99·70
1·380	48·00	1·780	84·50	1·8385	99·95

M. J. S.

Reduction of Oxygen Compounds with Sodium. By M. ROSENFELD (*Ber.*, 23, 3147—3149).—Sodium may be obtained in a finely-powdered condition by trituration with some other solid substance. Such a mixture of sodium and zinc oxide ignites spontaneously, and leaves a residue of metallic zinc. Ferric oxide and lead oxide react in a similar manner, whilst gypsum is reduced to calcium sulphide. Certain organic compounds, such as pyrogallol, wheat starch, or salicylic acid, inflame immediately on admixture with sodium, carbon being separated; other substances, such as milk sugar and cane sugar, after admixture with sodium, require to be exposed to moist air before reaction takes place. In the case of compounds which only contain carboxylic oxygen, the sodium salt of the acid is formed. Sodium benzoate and sodium oxalate are obtained from benzoic and oxalic acids respectively. The carbonaceous residue from rosaniline, toluidine, albumin, and other amido-compounds contains sodium cyanide; brucine, morphine, and strychnine yield a

porous mass of charcoal free from cyanogen. Both sodium cyanide and sodium cyanate were obtained from uric acid. "Saccharin" yields a residue containing sodium thiosulphate and sodium cyanide.
J. B. T.

Ammonium Pyrosulphite. By A. FOCK and K. KLÜSS (*Ber.*, **23**, 3149—3151).—Ammonium pyrosulphite, $(\text{NH}_4)_2\text{S}_2\text{O}_5$, is prepared by passing sulphurous anhydride into cold, concentrated, aqueous ammonia until the liquid becomes yellow; it is then allowed to evaporate spontaneously in a vacuum. The salt crystallises in large, thick, deliquescent plates, which belong to the rhombic system. Marignac has shown that the corresponding potassium salt crystallises in the monoclinic system.
J. B. T.

Properties of some Beryllium Salts and of the corresponding Aluminium Compounds. By F. SESTINI (*Gazzetta*, **20**, 313—319).—(1.) *Phosphates.* The phosphates were prepared in the gelatinous state by precipitating beryllium sulphate and potassium alum respectively with disodium phosphate, and washing the precipitate for 4 to 6 days; they are both sparingly soluble in distilled water, the beryllium salt being considerably the more soluble of the two. On igniting the moist beryllium phosphate, it left 6 per cent. of its weight of white anhydrous phosphate. A litre of a saturated solution of beryllium phosphate in 2 per cent. acetic acid contains 0.550 gram of the anhydrous salt (containing, however, 74.9 per cent. P_2O_5 instead of 74.2 per cent.). A similar solution of the aluminium salt, however, contains 0.375 gram of phosphate dissolved, containing 87.1 per cent. P_2O_5 (instead of 54.8 per cent.); this excess of acid is probably due to the formation of a little beryllium pyrophosphate and to the conversion of a portion of the aluminium phosphate by the acetic acid into a more soluble acid phosphate.

A litre of a saturated solution of the beryllium salt in 10 per cent. acetic acid contains 1.725 grams, and the corresponding aluminium solution 0.30 gram of the respective anhydrous phosphates. On gently heating the acetic acid solution of beryllium phosphate, it becomes turbid, and near the boiling point a white precipitate of a basic phosphate, of the formula $3\text{BeO}, \text{P}_2\text{O}_5, 3\text{H}_2\text{O} + \text{Aq.}$ is deposited; a solution of the aluminium salt at most becomes opalescent.

(2.) *Carbonates.*—100 c.c. of water saturated with carbonic anhydride at the ordinary pressure dissolves 0.185 gram of anhydrous beryllium oxide, and the solution becomes turbid on agitation or on boiling. Under the same conditions, only 0.001 gram of aluminium oxide passes into solution. The solubility of the beryllium oxide is due, according to the author, to the formation of an acid carbonate.

S. B. A. A.

Magnesium Lead Chloride. By R. OTTO and D. DREWES (*Arch. Pharm.*, **228**, 495—498).—A hot concentrated magnesium chloride solution dissolves a considerable amount of lead chloride and deposits, on cooling, a double chloride, $\text{PbCl}_2, 2\text{MgCl}_2 + 13\text{H}_2\text{O}$, in small, white, lustrous, indistinct crystals. The salt is exceedingly hygroscopic; moisture quickly converts it into a solution of magnesium

chloride, holding lead chloride in suspension. Calcium and lead chlorides appear to give a similar compound. J. T.

Electrolysis of Fused Aluminium Fluoride. By A. MINET (*Compt. rend.*, **111**, 603—606). The composition of the bath which gives the best results corresponds with the formula $12\text{NaCl} + \text{Al}_2\text{F}_6, 6\text{NaF}$; melting point 675° ; temperature at which vapours are evolved, 1035° ; sp. gr. at $820^\circ = 1.76$; coefficient of expansion 5×10^{-4} ; electrical conductivity at $870^\circ = 3.1$. The relation of the conductivity to the temperature is expressed by the equation $C_t = 3.1[1 + 0.0022(t - 870^\circ)]$. For a current of 1200 ampères, the mass of the bath is 20 kilos., the intensity of the current at the positive pole is 1 ampère, and the difference of potential between the electrodes is 5.5 volts. The composition of the bath is kept constant by the gradual addition of a mixture of aluminium hydroxide, $\text{Al}_2\text{O}_3(\text{OH})_2$, 416.4 parts, cryolite, 210.4 parts, and aluminium oxy-fluoride, $\text{Al}_2\text{F}_6, 3\text{Al}_2\text{O}_3$, 238.4 parts.

The difference of potential, ϵ , between the electrodes when the electromotive force is considerably below that required to produce decomposition is expressed by the equation $\epsilon = KI$, I being the intensity of the current, and the temperature being constant. As the point is approached at which the electromotive force of polarisation is equal to the electromotive force of decomposition of the electrolyte, the difference of potential cannot be calculated by means of any simple expression. At 870° , the maximum density of the current at the electrodes, corresponding with the first period of electrolysis of the bath specified, varies between 0.02 and 0.03 ampère.

During the second period of electrolysis, when the electromotive force is sufficient to produce decomposition, up to a density of 1 ampère at the positive electrode, the difference of potential is expressed by the equation $\epsilon = e + \rho I$, where e is the electromotive force of decomposition, and ρ is the resistance of the electrolyte. At 852° , $e = 2.15$ and $\rho = 0.01$; at 890° , $e = 2.40$ and $\rho = 0.0044$; at 980° , $e = 0.34$ and $\rho = 0.0033$. For densities of current higher than 1 ampère, the difference of potential cannot be calculated as a function of the intensity of the current by any simple expression; it rapidly attains a value similar to that existing in the electric arc.

In presence of salts of iron or silicon, within certain limits of density of current at the positive electrode, the salts decompose according to Sprague's law. At 810° , with salts of iron, $e = 0.75$ and $\rho = 0.0093$; at 840° , with silicon compounds, $e = 1.37$ and $\rho = 0.0089$; at 870° , with aluminium salts, $e = 2.15$ and $\rho = 0.0085$.

C. H. B

Preparation of Chromium from Potassium Chromium Chloride and Magnesium. By E. GLATZEL (*Ber.*, **23**, 3127—3130).—Chromium can be quickly prepared in an almost chemically pure condition in the following manner:—Potassium dichromate (100 grams) is dissolved in the least possible quantity of water, the solution mixed with hydrochloric acid of sp. gr. 1.124 (400 c.c.), and then 80 per cent. alcohol (100 c.c.) gradually added. The solution of potassium chromium chloride obtained in this way is treated

with potassium chloride (160 grams), the filtered solution evaporated to dryness, the residue heated until anhydrous, freed from the green portions, which are produced by the decomposition of the double salt, then powdered, and mixed with magnesium filings (50 grams). This mixture is heated, for about half an hour, to a bright-red heat, in a closed Hessian crucible in a wind-furnace, care being taken that the potassium chloride does not volatilise completely, otherwise the chromium is partially oxidised. The melt is separated from the superficial layer of chromium oxide, treated with water, and the finely divided metal freed from salts and unchanged magnesium by washing it with water, then boiling it with dilute nitric acid, and again washing with water, all the washing being done by decantation. The yield of the metal, dried at 100° , is about 27 grams.

Chromium, prepared in this way, is a light-grey, crystalline, non-magnetic powder of sp. gr. 6.7284 at 16° ; it can be melted in a Deville's furnace, but only with great difficulty, and after being melted it shows a silvery fracture. Two analyses of the powder showed that it contained 99.53 to 99.57 per cent. of chromium, and that it was free from silver and magnesium.

F. S. K.
