Inorganic Chemistry.

Rate of Solution of Hydrogen by Palladium. ALFRED HOLT (*Proc. Roy. Soc.*,1914, [*A*], **90**, 226—237. Compare A , 1913,ii,330,839). —Further experiments have been made to ascertain the connexion between the rate of solution of hydrogen in palladium at constant pressure and the concentration of the gas in the metal. The curves, which are obtained by plotting the rate of solution as a function of the quantity of gas which has been occluded by the metal, consist of two portions, which indicate the occurrence of two distinct processes. It is supposed that the platinum consists of two modifications of the element, which differ very considerably in respect of their activity towards hydrogen. The first portion of the velocity-concentration curve is probably determined by the dissolution of the hydrogen in the active or α-form, whilst the second part of the curve has reference to the dissolution of the gas in the inactive or β-modification. The fact that a smooth curve is obtained when platinum-black is used as the absorbing medium is supposed to show that this consists almost entirely of the active modification.

The phenomena observed when the heated metal is allowed to cool in contact with an atmosphere of hydrogen are shown to be capable of interpretation on the basis of the theory put forward.

H. M. D.

Partial and Intermittent Combustion of Gas. E. E. SOMERMEIER (*J. Ind. Eng. Chem.*, 1914, **6**, 374—378).—The author has investigated the influence of the volume of gas, of the method of ignition, and of the shape of the container, on the combustion of mixtures of hydrogen and air, and of natural gas and air.

With a high initial ignition temperature a reaction may start in a gas mixture which, as a whole, is incombustible, that is, the heat of combustion is insufficient to maintain the temperature at the kindling point. When the combustion is started from a source of very high temperature, more gas is burned in a large volume

of mixture than in a small volume, but the greater percentage of gas is burned in the mixture of smaller volume.

With a continuous source of high temperature, as with a white-hot wire, a lamp flame, or a running electric spark, the reaction produced may be intermittent. The gas immediately round the point of ignition burns and expands, combustion then ceasing until the expanded gas and products of combustion are replaced by another portion of the mixture of gas and air.

Full details are given of the way in which the limits of appreciable ignition or combustion vary with the volume of gas used, the source of ignition, and the shape of the container. The results indicate that a comparatively small excess of hydrogen above the theoretical requirement (compare this vol., ii, 356) is necessary to produce a vigorous reaction. Natural gas, or methane, on the other hand, ignites with such difficulty that, with ordinary methods of ignition, an appreciable reaction does not occur unless a very large excess of gas is present above that required by the thermal calculation.   T. S. P.

Preparation of Hydrogen Peroxide. HENCKELL & Co. (Swiss Patent 63359, 63360).—(I) A 1% solution of sulphuric acid is saturated with oxygen under a pressure of 100 atmospheres and electrolysed with the use of an amalgamated gold cathode. Solutions of hydrogen peroxide up to 3% concentration are obtained in this way. (II) Hydrogen peroxide is obtained by the action of oxygen under pressure in the presence of water on hydrogen passing through a porous tube impregnated with a catalyst such as palladium.   J. C. C.

Process for Increasing the Stability of Hydrogen Peroxide in Neutral Carriers of this Substance. E. MERCK (Swiss Patent 63361).—The stability of hydrogen peroxide can be greatly increased by the addition of acyl esters of aminohydroxycarboxylic acids; for example, (1) 1 part of β-dimethylamino-α-benzoyloxy*iso*butyric acid is added to 1000 parts of 3—30% hydrogen peroxide. (2) 600 parts of carbamide, 2500 parts of a 15% hydrogen peroxide solution, and 1 part of benzoyleneguanine are evaporated in a vacuum. The product (940 parts) contains about 36% of hydrogen peroxide; (3) 60 parts of ammonium sulphate and 75 parts of 30% hydrogen peroxide are stirred together, cooled, and the crystalline mass is separated, mixed with 0·05 part of α-benzoyl-β-piperidylpropionic acid, and dried in a vacuum. The product contains 20—22·2% of hydrogen peroxide.   J. C. C.

The Influence of Ocean Spindrift and Blown Spray on the Chlorine Content of Inland Waters. WILLIAM BARR (*J. Hygiene*, 1914, **14**, 119—128).—Chlorine in inland ground waters, except where beds of salt occur, is derived from the sea through the ocean spindrift and blown spray; the amount diminishes with the distance from the seaboard, but is affected by the configuration of the land, being greater where the land is continuously low, and

by the direction of prevailing winds. These statements are illus-
trated by charts of certain districts in Scotland, constructed from
the analyses of the inland waters there.   W. D. H.

Revision of the Density of Oxygen. ALBERT F. O. GERMANN
(*J. Chim. Phys.*, 1914, **12**, 66—108).—The methods employed in the
determination of the density of the air at Geneva (A., 1912, ii,
636) have been applied to oxygen. In order to obtain greater
accuracy in the measurement of the pressure of the gas at the
moment when the containing vessels (capacity 250 to 850 c.c.)
were closed, readings were taken on four barometers. The oxygen
was obtained by heating potassium permanganate, and afterwards
purified by fractional distillation.

The mean of fifteen determinations of the weight of a normal
litre ($0°$, 760 mm., sea-level, and a latitude of $45°$) is 1·42906 gram.
In combination with the values obtained by Morley and Rayleigh,
the most probable value is considered to be 1·42905 grams.

Two separate measurements made by the author gave for the
density of air 1·2927 and 1·2932.   H. M. D.

Occurrence of Ozone in the Upper Atmosphere. J. N. PRING
(*Proc. Roy. Soc.*, 1914, [*A*], **90**, 204—219. Compare T., 1910, **97**,
868).—It has been found that an aqueous solution of potassium
iodide may be used for the estimation of ozone in the air at
temperatures down to $-60°$. Below $-24°$, the reaction gives rise
to iodate, whatever the ozone concentration, but at higher tempera-
tures and at high dilutions (1 : 100,000) the products formed are
hypoiodite and free iodine. Since the oxides of nitrogen give the
iodate at all concentrations, and hydrogen peroxide can be dis-
tinguished by the titanium test, it has been found possible to
differentiate between these various substances, with the result that
atmospheric air has been found to contain definite quantities of
ozone, but no detectable quantities of hydrogen peroxide or the
oxides of nitrogen.

Observations made in this country indicate that the average
amount of ozone is 2·5 volumes per million volumes of air, and
that this amount varies very little with the altitude between 5
and 20 kilometres. In the Alps, a mean value of 2·5 volumes was
obtained at 2100 metres, and 4·7 volumes at 3580 metres. From
colorimetric observations, it would seem that ozone must be re-
garded as a contributing factor in determining the blue colour of
the sky.

According to experiments on the action of ultra-violet light on
air, ozone is formed to a limited extent. The rate of formation of
the gas is only slightly diminished in the presence of water vapour,
but decreases rapidly with falling pressure.   H. M. D.

Boiling Point of Sulphur on the Thermodynamic Scale. N.
EUMORFOPOULOS (*Proc. Roy. Soc.*, 1914, [*A*], **90**, 189—203).—The
results obtained in previous experiments (A., 1908, ii, 1029) could

not be regarded as final on account of the change in the volume of the glass bulb of the constant-pressure gas thermometer. In the experiments now described, the glass bulb was replaced by a bulb of fused silica. The new observations lead to 444·61° as the boiling point of sulphur on the thermodynamic scale, and to 273·13° as the melting point of ice.   H. M. D.

The Reducing Power of Sulphurous Acid. I. **Action of Sodium Hyposulphite on Tellurium and Selenium.** L. TSCHUGAEV and W. CHLOPIN (*Ber.*, 1914, **47**, 1269—1275).—Using an apparatus in which reactions can be carried out in an atmosphere of hydrogen, all oxygen being rigorously excluded, the authors find that tellurium (0·3—0·5 gram) dissolves in 10% sodium hydroxide (12—20 c.c.) containing sodium hyposulphite (1·2—2 grams) when the mixture is heated on the water-bath. The solution is at first violet, and then grows colourless; on cooling, colourless crystals separate, in which the ratio of sodium to tellurium agrees with that of a *sodium telluride*, Na_2Te; they are hydrated, but could not be obtained dry owing to their ready decomposition with separation of tellurium. The sodium telluride was further characterised by the formation from it of *benzyl telluride*, $(C_6H_5 \cdot CH_2)_2Te$, by heating it in aqueous alcoholic solution with benzyl chloride, or in aqueous solution with phenylbenzyldimethylammonium chloride (leucotrope), which also acts as a benzylating agent. Benzyl telluride crystallises in pale yellow needles, m. p. 53—53·5°, which readily decompose in the air, with separation of tellurium.

The mother liquor from the preparation of the sodium telluride contains chiefly sodium sulphite, together with varying quantities of sodium sulphide. The reaction is probably expressed by the equation: $Na_2S_2O_4 + Na_2Te_2 + 4NaOH = 2Na_2SO_3 + 2Na_2Te + 2H_2O$, the sodium telluride resulting from the tellurium and the sodium hydroxide. The sodium sulphide results from a secondary reaction between the sodium hyposulphite and the sodium hydroxide.

Sodium telluride is much more readily obtained when rongalite is used in place of sodium hyposulphite, formaldehyde being liberated; no sodium sulphide is formed. Sodium selenide can be obtained similarly from selenium, although the reaction does not go so readily; sulphur is attacked only to a very slight extent under the same conditions.   T. S. P.

The Sulphuric Acid Chamber Process. WALTHER HEMPEL (*Zeitsch. angew. Chem.*, 1914, **27**, 218—223).—An arrangement is described by means of which a mixture of sulphur dioxide, oxygen, and water vapour, in the proportions necessary to form sulphuric acid, could be introduced into a glass vessel containing nitrogen, oxygen, and oxides of nitrogen in known amounts. The mixture containing the sulphur dioxide was made by decomposing sulphuric acid by contact with a hot surface electrically heated. The glass vessel, which could be heated in a water-bath, contained a central

tube, through which a stream of cold water could be passed; there was also an exit tube for the sulphuric acid formed.

A prolonged series of experiments showed that the best yield of sulphuric acid was obtained when the gaseous mixture was obtained by the decomposition of sulphuric acid of D 1·5297, the glass vessel was heated at 60°, and cold water was run through the inner tube. Unless a temperature difference was maintained in the glass vessel, the yield of sulphuric acid was very small. Nitrous oxide was formed during the reaction in quantities greater than those observed in the manufacture by the chamber process. Further experiments also showed that when a mixture of nitric oxide, oxygen, and sulphur dioxide is absorbed by concentrated sulphuric acid, some nitrous oxide is formed.

The results obtained in the analyses of the chamber gases, etc., from various plants are given, and compared with those of Inglis (A., 1906, ii, 226; 1907, ii, 613).

By means of an appropriate arrangement, the velocity with which sulphur dioxide, oxygen, water vapour, and the various oxides of nitrogen react at different temperatures was determined. It was found that the velocity of formation of sulphuric acid is somewhat greater when nitrogen trioxide is used than with nitrogen tetroxide, this being in agreement with the formation of an intermediate product. The reaction proceeds best the more water and oxides of nitrogen there are present. With very high concentrations of oxides of nitrogen, the best temperature is 70°.

In the presence of a large excess of sulphurous acid and water, nitric oxide is almost completely reduced to nitrous oxide, only very small quantities of nitrogen being formed.   T. S. P.

Preparation of Persulphates from Sulphates or Bisulphates Without the Use of a Diaphragm. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 271642).—The electrolytic preparation of persulphates can be carried out without the addition of electrolytes or the use of a diaphragm if tin or aluminium cathodes are employed.   J. C. C.

The Formation of Dithionic Acid during the Preparation of Cuprous Sulphites. HENRY BAUBIGNY (*Ann. Chim.*, 1914, [ix], **1**, 201—239).—In the first part of the paper the author gives a brief review of the earlier work done on the formation of cuprous sulphites. The second part of the paper is a résumé of work already published (compare A., 1912, ii, 351, 447, 647).   W. G.

Hydrogen Telluride and the Atomic Weight of Tellurium. L. M. DENNIS and R. P. ANDERSON (*J. Amer. Chem. Soc.*, 1914, **36**, 882—909).—The work described in this paper was undertaken in order to determine the atomic weight of tellurium, and obtain evidence with regard to its alleged complexity.

Magnesium and aluminium tellurides were prepared, and hydrogen telluride was obtained by decomposing the latter compound with hydrochloric acid. The hydrogen telluride thus pre-

pared was fractionally distilled, and the atomic weight of tellurium in the fractions was determined by means of the ratio $Te : TeO_2$. As this method of preparing hydrogen telluride was not altogether satisfactory, a further quantity was obtained by electrolysis, using a tellurium cathode, a platinum anode, and a 50% solution of phosphoric acid as the electrolyte. The product was fractionally distilled, the twenty-one fractions were decomposed by passing the gas into nitric acid, and the solutions of tellurium dioxide and nitric acid thus obtained were evaporated to dryness, and the residues fused. The atomic weight of the tellurium in the various fractions was determined by titrating the resulting tellurium dioxide with potassium permanganate. The results support the view that tellurium is not complex, and that the atomic weight, 127·5, now assigned to it is the correct value.

Solid hydrogen telluride forms white crystals, and melts at $-57°$ to a very pale yellow liquid. Liquid hydrogen telluride boils at $0°$, and when freshly distilled is almost colourless; when left, however, the colour gradually becomes darker, owing to the presence of dissolved tellurium formed by decomposition. When hydrogen telluride is left in sealed tubes, it slowly dissociates, tellurium being deposited on the walls; this change seems to take place as rapidly in the dark as in the light. E. G.

The Active Modification of Nitrogen. II. H. B. BAKER and R. J. STRUTT (*Ber.*, 1914, **47**, 1049—1055. Compare this vol., ii, 357).—A reply to the second communication of Tiede and Domcke (this vol., ii, 196), in which the authors maintain the correctness of Strutt's previous experiments. They have also repeated the experiments of Tiede and Domcke, but cannot confirm their results. Special reference is made to Strutt's spectrographic investigations (A., 1912, ii, 214). T. S. P.

New Confirmation of the Nernst Theorem. M. TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), ii, 363—366).—Between the temperatures $140°$ and $320°$, the extent to which combination takes place between nitric oxide and chlorine is almost independent of the temperature, in spite of the fact that the heat of formation of nitrosyl chloride is 14,400 cal. (compare Briner and Pylkov, A., 1913, ii, 317). Also, the dissociation constants calculated from the equilibria obtained are less than those to be expected according to Nernst's theorem.

The above discrepancies are explained, according to the author, by the fact that the usually accepted equation, $2NO + Cl_2 = 2NOCl$, is wrong. The author's experiments show that between $-72°$ and $+40°$ nitric oxide and chlorine combine to a brown gas, which, at low temperatures, consists practically completely of $NOCl$. At higher temperatures it is mixed with a gas richer in nitric oxide, perhaps $(NO)_2Cl$ or $(NO)_3Cl$, and may be also with a gas richer in chlorine, perhaps $NOCl_2$. Assuming the existence of these other gases, the results obtained are in agreement with Nernst's theorem.
T. S. P.

Synthesis of Hydroxylamine*iso*monosulphonic (Amidopersulphuric) Acid. FRITZ SOMMER and HANS GEORG TEMPLIN (*Ber.*, 1914, **47**, 1221—1229).—*Hydroxylamine*iso*monosulphonic acid*, $NH_2 \cdot O \cdot SO_2 \cdot OH$, the existence of which was first indicated by Raschig (*Annalen*, 1887, **241**, 161) in the product formed by hydrolysing hydroxylamine*iso*disulphonic acid with hydrochloric acid, has now been obtained in almost pure condition by the action of chlorosulphonic acid on hydroxylamine hydrochloride at the ordinary temperature. It separates from a mixture of ether and methyl alcohol in the form of a microcrystalline powder, liberates iodine from potassium iodide, and is hydrolysed in acid solution to hydroxylamine.

A solution of the acid is also obtained by gently warming hydroxylamine sulphate with fuming sulphuric acid.   F. B.

The Formation of Red Phosphorus by the Oxidation of Phosphorus Vapour. V. KOHLSCHÜTTER and A. FRUMKIN (*Ber.*, 1914, **47**, 1088—1100. Compare this vol., ii, 267).—By means of an appropriate apparatus, the authors have been able to study the oxidation of phosphorus vapour at ordinary temperatures, oxygen being allowed to mix, in small portions at a time, with saturated phosphorus vapour. A dark red, homogeneous, and transparent product is formed, in which the ratio of phosphorus to oxygen increases as the rate of addition of oxygen to the vapour decreases. Within the limits of the experiments done, the increase does not stop at any simple atomic ratio of the elements. Nevertheless, the authors consider that the product is a definite compound, containing the ready-formed molecule of red phosphorus, $(P_2)x(P_4)y$ (compare Stock, A., 1913, ii, 1051), together with another part containing oxygen and phosphorus; by the splitting off of the latter part, red phosphorus is produced. The authors adduce evidence in support of their theory, the red product above-mentioned being considered to be analogous to the intermediate products which are formed in the transformation of white into red phosphorus by the catalytic action of phosphorus iodide and bromide. The analogy is not complete, however, and the differences are discussed in detail.

The authors' experiments again open the question of the existence of phosphorus suboxide, since their product cannot be a mixture of finely divided red phosphorus and solid phosphorus hydride, the presence of hydrogen being excluded by their method of experiment.   T. S. P.

Reductions and Reactions in Reversed Flames. II. Reduction of the Liquid, Anhydrous Chlorides of Groups 3—5 of the Periodic System, in the Reversed Chlorine-Hydrogen Flame. FRIEDRICH MEYER and HANS KERSTEIN (*Ber.*, 1914, **47**, 1036—1049).—The apparatus previously described (A., 1912, ii, 1051) for the study of reactions in reversed flames has been considerably improved by the authors, and a full description is given of the new apparatus.

The following are the results of experiments on the reduction of

various anhydrous chlorides in the reversed chlorine-hydrogen flame: boron trichloride and silicon tetrachloride are not affected. Carbon tetrachloride is reduced to finely divided, very voluminous carbon, which, however, still retains some hydrogen and chlorine; on oxidation with fuming nitric acid the carbon gives mellitic acid.

Titanium tetrachloride is readily reduced to the trichloride in the new apparatus, a yield of 70% being easily obtained. Since the reaction is reversible, the yield is improved by increasing the velocity of the current of hydrogen used. Stannic chloride gives a quantitative yield of stannous chloride (compare A., 1913, ii, 969).

Phosphorus pentachloride gives a red product, which is very similar to Schenk's phosphorus, and contains 92—94% of phosphorus, together with some of the chloride. Arsenic trichloride is reduced quantitatively to arsenic. Antimony pentachloride gives a greyish-black, loose powder, containing 93% of black antimony and 7% of antimony trichloride.

Vanadium tetrachloride gives a violet, very voluminous powder, consisting of 80% of the dichloride and 20% of the trichloride. If the velocity of reaction is increased by heating the tetrachloride more strongly, some of it is actually found in the reaction product. The relations are very complicated; in all probability the dichloride is first formed, and then combines to some extent with chlorine in the colder zone of the flame.　　　　　　　　　　　　T. S. P.

Water of Crystallisation. Compounds with $2H_2O$.　I. Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1914, **49**, 455—476).— The author's experiments show that it is not possible to state a dehydration temperature for a substance unless the conditions are specified. The dehydration should be effected in a thermostat in a dry atmosphere, or in a current of dry gas. The following dehydration temperatures were obtained for the salts mentioned under conditions of experiment described in the original: $CaSO_4,2Na_2SO_4,2H_2O$, about 180° (?); $Na_2WO_4,2H_2O$, 50°, 55°, and 60°; $Na_2Cr_2O_7,2H_2O$, 50° and 60°; $BaCl_2,2H_2O$, 50° and 60°; $SnCl_2,2H_2O$, 30°. Of these, the barium chloride loses the two molecules of water separately, the tin salt and the two sodium salts lose the two molecules simultaneously, but at different rates. The work of Rosenstiehl (A., 1911, ii, 270, 386) is adversely criticised.　　　　　　　　　　　　　　　　　　　R. V. S.

Preparation of Alkali Hydroxides. Julius Kersten (Austrian Patent 62281).—Alkali hydroxides can be obtained in a quantitative yield by the action of lead hydroxide on alkali chlorides according to the equation

$$2K(Na)Cl + 6Pb(OH)_2 = 2K(Na)OH + PbCl_2 + 5Pb(OH)_2.$$
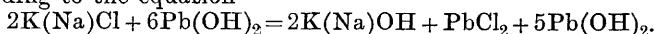
The lead hydroxide is suspended in a dilute, aqueous solution of the alkali chloride, and the mixture heated gradually to boiling. The basic lead chloride, after being separated from the alkali hydroxide, is dissolved in nitric acid, the solution evaporated to dryness, whereby the hydrogen chloride is evolved and is con-

densed, and the lead nitrate is dissolved in water and precipitated with ammonia.   J. C. C.

The Hydrothermal Formation of Silicates. M. SCHLAEPFER and P. NIGGLI (*Zeitsch. anorg. Chem.*, 1914, **87**, 52—80. Compare Niggli and Morey, A., 1913, ii, 1054).—When calcium chloride is used, it is necessary to line the autoclave with silver in order to avoid the introduction of iron. Starting from amorphous materials, α-quartz and tridymite have been identified, with corundum, orthoclase, and potassium-nepheline. Hieratite, K_2SiF_6, is identical with an artificially prepared mineral formerly wrongly identified as potassium-faujasite. Pyrophylite, and a mineral resembling zunyite, are doubtful. The products from a large number of experiments are described.

Tridymite must be unstable. It is only obtained in the absence of alkali, and is then probably only converted into the stable quartz. In the system $H_2O–Al_2O_3–K_2O–SiO_2$ at 470°, quartz, orthoclase, potassium-nepheline, corundum, and possibly pyrophylite are probably stable phases, according to the composition. Systems containing lime have very little tendency to crystallise. Iron facilitates the formation of anorthite. When iron is added, iron olivine is formed, and crystallises well.   C. H. D.

The Action of Hydrogen Sulphide on Sodium Hyposulphite. FRANK STURDY SINNATT (*J. Soc. Dyers*, 1914, **30**, 189—191).—Dry hydrogen sulphide has no action on dry sodium hyposulphite, but in the presence of water rapid reaction takes place quantitatively, according to the equation $Na_2S_2O_4 + H_2S = Na_2S_2O_3 + H_2O + S$. The sulphur is liberated in such a form that it can be readily collected and weighed, and the author suggests that the reaction may serve as a rapid method for the valuation of sodium hyposulphite.   T. S. P.

The Transformation Points of Sodium Tungstate. H. S. VAN KLOOSTER and H. C. GERMS (*Zeitsch. anorg. Chem.*, 1914, **86**, 369—372).—In the thermal determination of transformation points (this vol., ii, 167), only a single point, at 587°, was found for sodium tungstate. A second point was observed on the cooling curves, but not on the heating curves. By using a differential method, with potassium metaphosphate as comparison substance, the two transformation points are found to be 587° and 591°, the thermal effect at the latter temperature being very small.
C. H. D.

Purity of Fused Lithium Perchlorate and its Bearing on the Atomic Weight of Silver. THEODORE W. RICHARDS and MARSHALL W. COX (*J. Amer. Chem. Soc.*, 1914, **36**, 819—828).— Richards and Willard (A., 1910, ii, 292) have described a method for determining the atomic weight of silver which involved a study of the ratio LiCl : LiClO₄. An investigation has now been made with reference to the purity of the lithium perchlorate, and particularly as to its freedom from water.

In order to estimate traces of water in pure, fused lithium perchlorate, the salt may be decomposed, and the amount of water evolved with the products of decomposition determined. On decomposing the salt in this way, however, a portion of the solid in an exceedingly fine powder is carried along with the stream of gas. This source of error can be overcome by passing the gas through a porous porcelain dry filter or "dust-trap," the construction of which is fully described.

It has been found that lithium perchlorate, prepared entirely in contact with air filtered through the porcelain "dust-trap," is much less easily decomposed by heat than the salt which has been less carefully prepared. The purest lithium perchlorate decomposes slowly at 410—430°, and rapidly at 450°. The perchlorate, after being kept fused until of constant weight, does not yield a significant quantity of water even when the temperature is raised to 430° and most of the salt is decomposed.

The results of this work tend to justify the use of lithium perchlorate as a basis for determining the ratio of oxygen to silver, and confirm the value $Ag = 107 \cdot 81$ $[O = 16 \cdot 000]$ obtained by Richards and Willard (*loc. cit.*).   E. G.

Lithium Iridichloride and Iridochloride. MARCEL DELÉPINE (*Compt. rend.*, 1914, **158**, 1276—1278.* Compare A., 1908, ii, 702, 765; 1910, ii, 34; and Antony, A., 1893, ii, 380).—The author has prepared lithium iridichloride and iridochloride, and examined their properties. The former is obtained by adding the theoretical quantity of lithium carbonate to a solution of chloroiridic acid and evaporating to dryness in the cold over sulphuric acid. On recrystallisation from chlorine water the salt is obtained in large, black, exceedingly deliquescent crystals, $Li_2IrCl_6,6H_2O$. It is very soluble in both alcohol and water, and loses $4H_2O$ in dry air at 100°. On boiling its solution with a little alcohol, it is reduced, giving *trilithium iridochloride* and chloroiridous acid. This iridochloride is best prepared by reducing lithium iridichloride in aqueous solution with lithium oxalate. It crystallises from water in large, black, deliquescent rhombohedra, $Li_3IrCl_6,12H_2O$. It is very soluble in water and alcohol. A mixture of sodium and lithium iridichlorides left to crystallise deposits almost pure crystals of the former salt, containing only a trace of lithium. A solution of the iridochlorides at first also deposits the almost pure sodium salt, but on concentrating the solution further, hexagonal prisms of *disodium lithium iridochloride*, $Na_2LiIrCl_6,12H_2O$, are formed, and then hexagonal needles of *sodium dilithium iridochloride*, $NaLi_2IrCl_6,12H_2O$. These salts are only stable in solution in the presence of an excess of a salt richer in lithium.   W. G.

A New Theory of the Ammonia Soda Process. WILLIAM MASON (*Chem. Zeit.*, 1914, **38**, 513).—In the present-day ammonia soda process the ammoniacal sodium chloride is carbonated in two stages; in the first stage the treatment with carbon dioxide is continued until more than 80% of the ammonia has been transformed

* and *Bull. Soc. chim.*, 1914, [iv], **15**, 505—510.

into ammonium carbonate; in the second stage the solution from the first stage is further carbonated. At times the author has noticed a precipitate of sodium carbonate before all the ammonia has been changed into ammonium carbonate. From this and the results of various analyses of the products in the carbonating tower the author draws the conclusion that in the complete carbonation of the ammonia the following reaction takes place:

$$2NaCl + (NH_4)_2CO_3 = Na_2CO_3 + 2NH_4Cl.$$
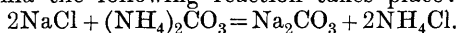
Part of the sodium carbonate precipitates as such, that remaining in solution being transformed into hydrogen carbonate and then precipitated.

The usual statement that the ammonia is first transformed into ammonium hydrogen carbonate, which then undergoes double decomposition with the sodium chloride, does not agree with the fact that ammonium hydrogen carbonate is just as insoluble as sodium hydrogen carbonate in the mother liquors; also such a reaction should be accompanied by absorption of heat, whereas actually heat is developed, in agreement with the known thermal effect of the action of carbon dioxide on a solution of sodium carbonate.   T. S. P.

The Distribution and Fate of Colloidal Silver in the Mammalian Body. I. The Characters of Colloidal Silver. J. VOIGT (*Biochem. Zeitsch.*, 1914, **62**, 280—294 ; **63**, 497).—An account is given of the ultramicroscopic analysis of various commercial preparations of colloidal silver, and the effect of different colloids in protecting them from aggregation on addition of salts.   S. B. S.

An Application of Calcium Carbide in the Formation of Alloys. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1914, **33**, 445—446).—A mixture of calcium carbide with borax or sodium chloride is a most efficient de-oxidising flux for copper and some copper alloys, such as bronzes, cupro-nickel, etc. A considerable number of metallic oxides are reduced to the metallic state by carbide, but unless the metal is very fusible, or a large amount of flux (borax, sodium, or magnesium or barium chloride) be employed, the infusible calcium oxide and any separated carbon or free carbide hold up the metal in shots or globules.   Much more satisfactory results are obtained when the haloid salts of the metals are used, the calcium haloid formed during the reaction acting as a flux.

The following alloys have been obtained : copper–manganese, copper–nickel, nickel–manganese, cobalt–manganese, copper alloys with tantalum, titanium, zirconium, etc.; manganese alloys with tin, bismuth, antimony, and lead.
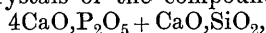
The manganese alloys with tin and bismuth, which contain more than 10% of manganese, show decided magnetic properties.

Where iron- and aluminium-free alloys are required, the carbide reduction is of value.   Only in the cases of nickel, cobalt, and iron alloys with manganese does any carbon appear to be taken up.

A convenient method for obtaining metallic chlorides in the

molten, anhydrous state is to drop a mixture of the metallic oxide
and ammonium chloride into a red-hot crucible, in small portions
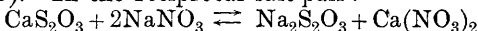at a time, using a slight excess of ammonium chloride.   T. S. P.

Constitution of Thomas Slag. H. BLOME (*Zeitsch. Kryst. Min.*,
1914, **53**, 568; from *Diss. Tech. Hochschule Berlin*, 1910, 1—21).—
Mixtures of lime, phosphoric oxide, and silica were fused, and the
solubilities of the products determined in 2% citric acid.   Tetra-
calcium phosphate melts at 1870°. When quickly cooled, the binary
system $4CaO,P_2O_5-2CaO,SiO_2$ shows maxima at the molecular ratios
1 : 1 and 1 : 4.   Slow cooling favours the crystallisation of a calcium
silico-phosphate, which is readily soluble in citric acid, and the
separation of free lime; the former is probably identical with the
blue ortho-rhombic crystals of the compound
$$4CaO,P_2O_5 + CaO,SiO_2,$$
described by Stead and Ridsdale in 1887.   L. J. S.

**The Formation of a Triple Salt from Aqueous Solutions
without the Simultaneous Formation of a Binary Double Salt.**
ROBERT KREMANN and HANS RODEMUND (*Zeitsch. anorg. Chem.*, 1914,
86, 373—379).—In the reciprocal salt-pair:
$$CaS_2O_3 + 2NaNO_3 \rightleftarrows Na_2S_2O_3 + Ca(NO_3)_2$$
a double salt is not formed, but a small region of stability exists
for a triple salt, $NaNO_3,CaS_2O_3,Na_2S_2O_3,11H_2O$, this region dimin-
ishing with rising temperature, but only single salts being formed.
The invariant transformation point is found by solubility deter-
minations to be 29°, and by thermal measurements to be 29·2°.
The determinations are tabulated, and the region is represented
graphically by Jänecke's method, in which a square diagram is
used.   C. H. D. ·

Fusions of Bisilicates with Sulphides and Haloids. A.
WOLOSKOV (*Zeitsch. Kryst. Min.*, 1914, **53**, 615; from *Ann. Inst.
Polytechn. St. Pétersbourg*, 1911, **15**, 421—442).—The systems
$MnSiO_3 + MnS$, $BaSiO_3 + BaS$, and $BaSiO_3 + BaCl_2$ were investi-
gated. Further, the solubilities of MnS and FeS in $BaSiO_3$ were
determined.   L. J. S.

Corrosion of Zincs of Different Compositions. EUG. PROST
Bull. Soc. chim. Belg., 1914, **28**, 94—99).—The author has studied
the action of solutions of sulphuric acid (0·5%), hydrochloric acid
(0·372%), and sodium chloride (5%) on specimens of commercial
zinc containing known quantities of impurities. In the cases of the
acid solutions, the zinc plate is allowed to remain in the solution
at the ordinary temperature for seven and a-half hours. With the
salt solutions the time of the experiment is prolonged to eighteen
days, and the solution agitated by a current of air on the tenth
and fifteenth day. In the latter case a white, flocculent precipitate
which contains zinc is formed in the solution, and the plates are
found to be covered with a greasy, adherent film of zinc hydroxide.
   The author is led to the following conclusions: The presence in
zinc of quantities of lead, cadmium, or iron greater than those

usually found in the refined product causes an increase in corrosion by acidic agents. Minute traces of arsenic, antimony, copper, or tin, in addition to the previously mentioned impurities, can considerably increase the tendency of zinc to corrode, and this influence is particularly marked in the cases of arsenic and antimony.

The action of sodium chloride solutions on zinc does not show any very striking features. The quantities of zinc dissolved are as great or even greater in the case of normal zincs as in that of zinc containing arsenic, antimony, copper, or tin. This result is possibly due to the protective action of the film of zinc hydroxide.

H. W.

The Freezing-point Diagram of the Lead–Arsenic Alloys and the Melting Point of Arsenic. W. HEIKE (*Intern. Zeitsch. Metallographie*, 1914, **6**, 49—57. Compare Friedrich, A., 1906, ii, 230).—When lead and arsenic are fused together in a sealed porcelain tube and thoroughly mixed, complete miscibility is found to occur. The freezing-point curve consists of only two branches, meeting in a eutectic point at 288° and 8·25 atomic % of arsenic. The curve has only been determined as far as 82·3 atomic % As, but extrapolation of the eutectic time curve indicates that solid solutions are not formed. The melting point of arsenic is found by extrapolation to be 852° (compare Goubau, this vol., ii, 189). C. H. D.

Red Lead. The Preparation of Pure Lead Orthoplumbate. JAROSLAV MILBAUER (*Chem. Zeit.*, 1914, **38**, 477—479, 559—560, 566—567, 587—588).—The author has investigated the various methods which have been proposed for the preparation of pure red lead.

Oxidation of lead oxide with oxygen or air at 470° and extraction of the resulting mass with a 10% solution of lead acetate, gives a pure product, but the process is tedious. Johnson's method, according to which lead oxide is heated with potassium nitrate, simply leads to an equilibrium, depending on the temperature, in accordance with the equation:

$$3PbO + KNO_3 \rightleftarrows Pb_3O_4 + KNO_2.$$
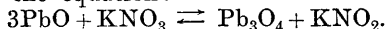
If, however, the product is then extracted with a solution of lead acetate, as proposed by Dumas, the lead oxide dissolves, and pure red lead is left. Lead nitrate cannot be used in place of lead acetate, as proposed by Löwe, since an insoluble basic lead nitrate is formed.

Oxidation of lead oxide with potassium chlorate is not satisfactory, since lead dioxide may be formed in addition to red lead; potassium bromate acts similarly to the chlorate, but potassium iodate gives no red lead. Also, lead nitrate cannot be used as the oxidising agent.

A new method, which gives very satisfactory results, is to heat a mixture of lead dioxide and potassium nitrate at 470°, reaction taking place according to the equation:

$$3PbO_2 + KNO_3 \longrightarrow Pb_3O_4 + KNO_3 + O_2.$$
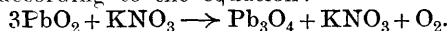
The resulting mass is then extracted either with a very concentrated solution of potassium hydroxide or with a solution of lead acetate. Other solvents were tried, but gave unsatisfactory results.

Extraction of calcium orthoplumbate with potassium hydroxide, or with solutions of sucrose, does not give good results. Levol's method (*Ann. Chim. Phys.*, 1854, **75**, 101), as given, is not satisfactory, as also that of Frémy (*ibid.*, 1840, **12**, 489), unless special precautions are taken. On the other hand, Brauner's method, in which the lead oxide of the composition $Pb_5O_7,3H_2O$ (compare Abegg's *Handb. anorg. Chem.*, Vol. III., Part 2, p. 570) is treated with concentrated potassium hydroxide, gives good resluts.

Investigation of the action of potassium hydroxide on lead dioxide and mixtures of lead oxide and lead dioxide, showed that a pure red lead is readily obtained by boiling a mixture of these oxides in the proportion of $3PbO : 2PbO_2$ with a strong solution of potassium hydroxide (150—200 grams in 100 c.c. of water).

T. S. P.

The Nature of Basic Lead Carbonate. EDWIN EUSTON (*J. Ind. Eng. Chem.*, 1914, **6**, 382—383. Compare this vol., ii, 366).—The author finds that normal lead carbonate withdraws lead hydroxide from basic lead acetate solution, with the formation of basic lead carbonate. Basic zinc carbonate, precipitated calcium carbonate, precipitated barium sulphate, and precipitated barium carbonate act in a similar manner, giving substances corresponding with the formulæ $ZnCO_3,Zn(OH)_2,3Pb(OH)_2$; $2CaCO_3,Pb(OH)_2$; $3BaSO_4,Pb(OH)_2$; and $3BaCO_3,2Pb(OH)_2$ respectively. The lead hydroxide portion of these compounds is soluble in ammonium chloride solution, but not in sucrose solution, as is also the case with basic lead carbonate. The barium carbonate and basic zinc carbonate compounds show the same characteristics as pigments as does white lead.

From the above results the author draws the conclusion that in basic lead carbonate the lead hydroxide is present neither in mechanical mixture nor in true chemical combination; basic lead carbonate is an adsorption compound of lead carbonate and lead hydroxide. T. S. P.

Action of Hydrogen Peroxide on Basic Lead Salts. V. ZOTIER (*Bull. Soc. chim.*, 1914, [iv], **15**, 402—408. Compare A., 1913, ii, 216). —Hydrogen peroxide reacts with basic lead acetates in two stages. In the first colloidal lead peroxide is formed, and in the second the lead peroxide reacts with the hydrogen peroxide. At the end of the reaction the liquid always contains some lead peroxide in solution. Basic lead formates and nitrates react similarly, except for the fact that dilute solutions of these salts only give colloidal lead peroxide The amount of residual lead peroxide is controlled by four factors. It is at its maximum when the hydrogen peroxide and the lead oxide of the basic salt are in equimolecular proportions. It diminishes with increase in the basicity of the lead salt,

and also with rise in temperature. For different basic acetates it is at its maximum when the salts have undergone the same molecular dilution.

The solution of lead peroxide obtained is exceedingly stable, being unaltered by prolonged boiling. On warming, the lead peroxide is reduced by formaldehyde, dextrose, and sulphites, but not by alcohol. In several of its reactions, such as the liberation of iodine from iodides, it resembles hydrogen peroxide. It presents the characteristic properties of colloidal suspensions. It has a distinct absorption spectrum, showing a broad band from the violet to the blue or green, according to the concentration and thickness of the liquid.   W. G.

The Hardness of Metals. J. H. ANDREW (*Intern. Zeitsch. Metallographie*, 1914, **6**, 30—43).—Alloys of copper and aluminium containing 10—11% of aluminium are harder when quenched than when slowly cooled, but alloys containing 12—13% Al are much harder when slowly cooled. With a pure β-alloy containing 12·5% Al, the hardness is independent of the temperature of quenching, between 570° and 1100°. With copper–tin alloys containing 20—28% Sn, the hardness is greater in the slowly-cooled condition, the difference increasing with the proportion of tin. Little difference is observed in the copper–zinc series, in which resolution of the β-constituent only takes place very slowly.

The hardness of quenched steels is attributed to a partial resolution of austenite into its components in the formation of martensite.   C. H. D.

Hardness and Modulus of Elasticity of Isomorphous Mixtures of Copper and Nickel. N. KURNAKOV and J. RAPKE (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 380—394).—Maxwell's relaxation theory leads to the expression $\eta = E \cdot T$, where η is the coefficient of internal friction and is proportional to the pressure of flow (compare Kurnakov and Shemtschushni, A., 1913, ii, 929), E the modulus of elasticity, and T the time of relaxation. Further, it has been found experimentally that the hardness, H, determined by Brinel's method, and the pressure of flow, are proportional to one another, so that η and H should also exhibit proportionality.

The authors have determined the hardness and modulus of elasticity of a series of alloys of nickel and copper in various proportions. Addition of nickel to copper is accompanied by a gradual increase of the hardness from 32 kilos. per sq. mm. to a maximum of 81·3 kilos. per sq. mm. for 47—50% Ni, beyond which the hardness falls regularly to 62·8, the value for nickel. On the other hand, the modulus of elasticity, in kilos. per sq. mm., increases linearly from 11,110 for copper to 20,100 for nickel.

Hence, the increase in the hardness and in the coefficient of internal friction for solid solutions showing a maximum of hardness does not depend on increase of the modulus of elasticity in the equation, $\eta = E \cdot T$, but is related to increased time of relaxation. This conclusion is confirmed by observations made on a

number of solid solutions of copper and of iron, in which increased hardness corresponds with diminution of the modulus of elasticity; this is the case with brass, bronze, steel, and other alloys of technical importance. Further, it seems that alteration of "relaxation" hardness proceeds parallel with that of brittleness.

A second typical case, theoretically possible, is that in which increased hardness results from increase of the modulus of elasticity. Such substances would be of great industrial interest, as they would be very hard without exhibiting increased brittleness. Whether manganese, nickel, and other special steels belong to this class must be determined by further experiment. T. H. P.

Action of Chloroform on the Metallic Sulphates. Method of Preparation of Anhydrous Chlorides. AUGUSTE CONDUCHÉ (*Compt. rend.*, 1914, **158**, 1180—1182).—Chloroform when passed over anhydrous copper sulphate at 250° gives a mixture of oxides and oxychlorides of carbon and sulphur. If the temperature rises to 280—300° the copper sulphate is soon completely converted into anhydrous cupric chloride. The reaction is more rapid the higher the temperature, but at 400° cuprous chloride begins to be formed, and the proportion of it increases rapidly with further rise in temperature. In the case of iron, whether ferrous or ferric sulphate is used, a mixture of ferrous and ferric chlorides is always obtained, the one which predominates corresponding with the sulphate used. Numerous other sulphates have been tried, and the minimum temperature at which the conversion into chloride occurs is given, being in the case of barium, calcium, and sodium sulphates 500°. At temperatures between 400° and 500° the chloroform itself begins to decompose, giving a carbonaceous deposit in the hot parts of the tube, and a crystalline deposit of carbon hexachloride in the cool parts. W. G.

Copper Peroxite. L. MOSER (*Zeitsch. anorg. Chem.*, 1914, **86**, 380—388).—The term "peroxite" has been proposed (Ebler and Krause, A., 1911, ii, 801) to denote the true salts of hydrogen peroxide. Copper peroxite, prepared from copper hydroxide and hydrogen peroxide (A., 1907, ii, 549), is always impure, owing to partial hydrolysis. By mixing solutions of cupric chloride and hydrogen peroxide, cooling to $-40°$ or $-50°$, and adding alcoholic potash, the pure peroxite, CuO_2, is obtained, and may be washed at $-50°$ with alcohol and ether. Gas is not evolved. The same product is obtained by the action of hydrogen peroxide at low temperatures on an alcoholic suspension of copper hydroxide. The mean ratio Cu : active oxygen is $1·05 : 1$. The peroxite may be obtained at about 0° by using ethereal hydrogen peroxide and very finely powdered copper hydroxide. The freshly prepared product may be almost quantitatively converted into hydrogen peroxide and a cupric salt by the action of dilute acids at about 0°

Several others methods of preparation have been tried without success. C. H. D.

Working Up Mercury Residues. H. J. TAVERNE (*Chem. Weekblad*, 1914, **11**, 448).—The author recommends reduction of mercury residues to the metal by iron and hydrochloric acid, any nitric acid present being previously eliminated by heating. The precipitated mercury is filtered, and distilled in a vacuum.

A. J. W.

Double Sulphites of the Alkalis and Mercury. HENRY BAUBIGNY (*Ann. Chim.*, 1914, [ix], **1**, 332—341).—Fuller experimental details are given of work already published (compare A., 1912, ii, 1175).   W. G.

Scandium Sulphate and Oxalate. F. WIRTH (*Zeitsch. anorg. Chem.*, 1914, **87**, 9—12).—Scandium sulphate is the most soluble of the sulphates of the rare earths, 100 c.c. of water dissolving 54·61 grams of the pentahydrate at 25°. The oxalate is the least soluble of the rare-earth oxalates in sulphuric acid, approaching thorium oxalate. Its solubility in sulphuric acid is greatly lessened by the presence of an excess of oxalic acid.   C. H. D.

Scandium Alkali Oxalates, Scandium-sulphuric Acid, and Scandium Sulphide. FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1914, **87**, 1—6).—The following salts are described: *sodium scandium oxalate*, $Sc_2(C_2O_4)_3,3Na_2C_2O_4,10H_2O$; the *potassium* and *ammonium* salts have the corresponding compositions. All are readily soluble in hot solutions of the alkali oxalates, and crystallise well on cooling. One of the ammonium salts shows a slight solubility in a cold saturated solution of the alkali oxalate. Hydrochloric acid precipitates crystalline scandium oxalate from the hot solutions. The compounds are to be regarded as salts of a complex acid, $[Sc(C_2O_4)_3]H_3$.

Scandium sulphate, $Sc_2(SO_4)_3,5H_2O$, dissolves in sulphuric acid (D 1·6), and a *compound*, $Sc_2(SO_4)_3,3H_2SO_4$, separates. This corresponds with similar compounds of the other rare earths.

Dry hydrogen sulphide converts the sulphate into *scandium sulphide*, Sc_2S_3, which is yellow, and stable in air at 100°.

C. H. D.

Action of Magnesium Salts on Complexes of Aluminium, Iron, and Bismuth with Organic Substances. A. QUARTAROLI (*Gazzetta*, 1914, **44**, i, 418—443).—The author has investigated the action of magnesium salts on ferric, aluminium, and bismuth hydroxides in absence and in presence of organic compounds, such as citric, tartaric, lactic, salicylic, and quinic acids, dextrose and mannitol, with which the above metals form complex compounds.

When ferric and aluminium hydroxides are precipitated in alkaline solution in presence of magnesium salts, the latter combine with the hydroxides to form insoluble ferrates and aluminates very rich in magnesium, five or six atoms of magnesium being sometimes present per atom of iron or aluminium. From solutions containing iron, aluminium or bismuth existing in combination with

hydroxy-acids or polyhydric alcohols in the form of complex ions, magnesium salts in moderate excess will precipitate these metals quantitatively. In some cases the precipitates consist of the same ferrates or aluminates as are formed in the absence of organic compounds, but in others the latter are also partly precipitated, probably owing to a molecular transformation of the complex salt into ordinary basic salt. Excess of the organic compound retards or limits the precipitation, unless a greatly increased proportion of magnesium salt is added. Deficit of the organic compound, if it is not such as to permit of immediate precipitation of ferric hydroxide by means of ammonia, causes the colloidal iron compounds generated to polymerise into so stable a form that they fix but little magnesium, and, unlike ferric hydroxide itself, retain their brick-red colour in presence of a very large excess of magnesium.

The author's results throw doubt on the trustworthiness of the method universally adopted as the official one for the estimation of phosphoric acid in superphosphates. It is found, indeed, that iron and aluminium retard the precipitation of magnesium ammonium phosphate in presence of ammonium citrate, and that, if filtration is protracted, precipitates of totally different character are obtained. This estimation is being investigated further.

The constitution of the complexes referred to above is discussed.

T. H. P.

The Chemical or Physical Nature of Colloidal Hydrous Aluminous Silicates. GEORG WIEGNER (*Centr. Min.*, 1914, 262—272); R. GANS (*Centr. Min.*, 1914, 273—279, 299—306).— Further discussion and replies bearing mainly on the constitution of "permutite" (compare this vol., ii, 55, 208). L. J. S.

Action of Salt Solutions on Aluminous Silicates. HANS SCHNEIDERHÖHN (*Jahrb. Min.*, 1914, i, *Ref.* 204—206; from *Zeitsch Deutsch. Geol. Ges.*, 1913, **65**, *Monatsber.* 349—354).—During the years 1872—1888, J. Lemberg made numerous experiments with salt solutions, acting for a period of a few days to a year and a-half, at 100° or 200°, on various minerals. The data he obtained, including some 600 analyses, are now discussed. With aluminous silicates of all types, the end-product of the reaction has the composition $R''O,Al_2O_3,nSiO_2,mH_2O$. Here $R''O$ represents the base of the salt solution which has replaced the base of the original mineral, this replacement being complete provided that the reaction has been continued for a sufficiently long period. When the solution contains an alkali hydroxide, carbonate, chloride, or sulphate, the silica molecules $n=2$, whilst with alkali silicate solutions $n=5$. L. J. S.

Action of Soluble Sulphates on Kaolin and Clays. R. RIEKE (*Zeitsch. Kryst. Min.*, 1914, **53**, 567—568; from *Sprechsaal für Keramik*, 1910, No. 48—51).—The addition of small amounts of soluble salts, particularly sulphates of calcium, zinc, copper, and

aluminium, to a paste of clay have the effect of increasing its toughness.   With alkali sulphates, the effect is only noticeable when very small quantities of the salt are present.   The sulphates are absorbed by the clay; and in the case of iron salts (the chloride as well as the sulphate) iron is extracted from the solution in the form of hydroxide.   L. J. S.

A Compound of Manganese Tribromide with Ethyl Ether. F. DUCELLIEZ and A. RAYNAUD (*Bull. Soc. chim.*, 1914, [iv], **15**, 408—413).—Fuller details are given of work already published (compare this vol., ii, 273).   W. G.

The Allotropic Transformations of Iron. ALBERT SAUVEUR (*J. Inst. Metals*, 1913, **88**, 171—190).—The view of Benedicks (A., 1913, ii, 599) that the $Ar2$ point is merely the termination of the $Ar3$ change is inconsistent with the facts that the points $Ar2$ and $Ac2$ are to be detected on the cooling and heating curves of electro-lytic iron, that $Ac2$ is given by steels containing less than 0·6% of carbon, and that the principal magnetic change occurs between 780° and 800°, and not at $Ac3$.   C. H. D.

The Structural Changes of Iron during Annealing. DONALD EWEN (*Intern. Zeitsch. Metallographie*, 1914, **6**, 1—17. Compare Kroll, A., 1910, ii, 1070).—A Swedish wrought iron containing 0·007% of carbon is heated in a vacuum.   Three distinct heat-relief patterns are obtained, corresponding with the original α-iron, γ-iron structure, and final α-iron structure.   The development of the α-iron relief on first heating is attributed to selective volatilisa-tion at the crystal boundaries, whilst the subsequent reliefs are due to changes of volume accompanying allotropic transformations. At high temperatures, within the γ-range, pitting is produced, especially when the metal is heated by the direct passage of a current (compare Kaye and Ewen, A., 1913, ii, 830).   C. H. D.

The Crystallising Properties of Electro-deposited Iron. J. E. STEAD and H. C. H. CARPENTER (*J. Iron Steel Inst.*, 1913, **88**, 119—170).—Specimens of electro-deposited iron, containing 0·008% of carbon, 0·009% of manganese, and 0·014% of silicon, in sheets 0·25 mm. thick, become very coarsely crystalline when heated above $Ac3$, and then cooled below $Ar3$.   This is the range within which ordinary specimens of iron and steel become more finely crystalline, whilst annealing between 700° and 800°, which leads to the formation of coarse crystals in mild steel, is without in-fluence on electro-deposited iron, even after cold-working.   A few seconds above 920° suffice to produce the coarse crystals, but very prolonged heating above that temperature, followed by slow cool-ing, is without effect.   The coarse structure, when once produced, is only destroyed by cold-working, by heating above $Ac3$ and quenching, or by heating for a long time above $Ac3$ and cooling slowly.   The results accord best with the view that at $Ar3$ iron changes directly from the γ- to the α-condition.

Thicker sheets of electro-deposited iron do not exhibit this behaviour, the upper limit of thickness being at about 0·26—0·30 mm., the most favourable thickness being 0·22—0·25 mm.

C. H. D.

A New Method for the Determination of the Critical Points *Ar*1, *Ac*1 [in Steel]. J. E. STEAD (*J. Iron Steel Inst.*, 1914, **88**, 399—415).—The point *Ac*1 in steel may be determined with an accuracy of 3° by quenching a rod in ice-cold water after heating in a muffle in such a way that the temperature gradient along the length of the rod is steady. The temperatures at different points are determined by inserting wires of silver, silver coated with sodium chloride, aluminium, and zinc, and measuring the lengths to which fusion takes place. The points 960°, 800°, 655°, and 420° are thus fixed, and intermediate temperatures are found by graphical interpolation. After quenching, the decarburised layer is removed from one surface of the bar by grinding, and the steel is then etched with dilute (20%) nitric acid. The boundary between the hardened portion (black) and the soft portion (grey) indicates the point *Ac*1, and is quite sharp.   C. H. D.

Corrosion by Dissolved Oxygen. J. W. COBB and G. DOUGILL (*J. Soc. Chem. Ind.*, 1914, **33**, 403—407).—The object of the authors' investigations was to determine the extent to which dissolved gases are responsible for extensive rusting in hot-water pipe systems. A sloping iron pipe, 180 cm. long and 2·5 cm. in diameter, heated by a furnace at the lower end, was fed with water under a constant head of pressure; the gaseous contents of the water were estimated before and after passage through the pipe, and the gases evolved from the water after passing through the pipe were also analysed.

It was found that a very large proportion of the dissolved oxygen in the water supply was not present in the water or gas leaving the pipe, but had been absorbed in the pipe. On collecting the evolved gases, by means of a special arrangement, just above the furnace, it was found that about half the loss of oxygen occurred in the first 30 cm. length of the pipe, that is, in the heater. The further loss of oxygen occurred in the 150 cm. of pipe beyond the heated length, and could be prevented if the expelled gases were collected at the end of the heated length.

In small-scale experiments on the rusting of pure iron foil when immersed in water, it was found that the expulsion of dissolved gas from the water by previous boiling was an effective method of preventing rusting. The rusting could also be almost prevented by treating the cold, air-saturated water with the quantity of sodium hydroxide and ferrous sulphate necessary to take up the dissolved oxygen.   T. S. P.

Glowing of Oxide Gels when Heated. K. ENDELL and R. RIEKE (*Centr. Min.*, 1914, 246—249).—The fact that certain metallic hydroxides emit a sudden glow when heated has long been known. Plotting the rise in temperature against the time, the heating

curves show a break (exothermic effect) at a point corresponding with the glow. Titanium dioxide precipitated from a cold solution glows and shows such a break at 670°; when, however, it is precipitated from a hot solution and dried at 110° (then containing $8·5\%$ H_2O), it shows the effect at about 400—500°. Ferric hydroxide precipitated from a hot solution of ferric chloride and dried at 160° (then containing 8% H_2O) glows and shows a break in the curve at 450°; but ferric oxide obtained by oxidising in the air the precipitate from a cold solution of a ferrous salt shows no such heating effect. Chromium oxide precipitated from a hot solution and dried at 160° ($4·5\%$ H_2O) shows the effect at 500—610°. In each case heat is developed, and the process is not reversible. The effect is due to an increase in the size of the particles and the giving up of surface energy, and is perhaps accompanied by the incipient crystallisation of the material.

L. J. S.

The Ferric Sulphates. F. WIRTH and BJARNE BAKKE (*Zeitsch. anorg. Chem.*, 1914, **87**, 13—46).—The "tetrasulphate,"

$$Fe_2(SO_4)_3,H_2SO_4,8H_2O,$$
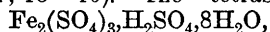
is prepared by dissolving the anhydrous sulphate in $10N$-sulphuric acid and drying the white, crystalline product. It loses $5H_2O$ very slowly over sulphuric acid, rapidly at 98°. It is sparingly soluble in alcohol, and is hydrolysed by steam.

Coquimbite, $Fe_2(SO_4)_3,9H_2O$, loses $5H_2O$ at 98°, and becomes anhydrous at 175°.

Yellow ferric sulphate, probably β-copiapite,

$$2Fe_2O_3,5SO_3,18H_2O,$$
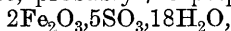
slowly breaks up in the solid state, yielding coquimbite.

The solubility relations in the system Fe_2O_3,SO_3,H_2O have been studied in detail at 25°, three to four weeks being allowed for the attainment of equilibrium. Crystallisation is very slow, and considerable supersaturation is necessary. Four solid phases are found: coquimbite, α-copiapite, β-copiapite, and the tetrasulphate. The solubility curve of the tetrasulphate may be followed far into the metastable region. α-Copiapite is $3Fe_2O_3,8SO_3,27H_2O$. The most concentrated solutions of ferric sulphate contain basic salts. The velocity of crystallisation increases with the acidity.

C. H. D.

The Reciprocal Influence on Solubility of Ferric Sulphate and Aluminium Sulphate. F. WIRTH and BJARNE BAKKE (*Zeitsch. anorg. Chem.*, 1914, **87**, 47—51. Compare Wirth, A., 1913, ii, 221).—The solubility of either ferric or aluminium sulphates in water at 25° is lowered by the addition of the other salt, the solubility curves meeting at the ratio Fe : Al $= 1 : 0·3831$. There is no evidence of the formation of a compound or of solid solutions.

C. H. D.

Higher Oxides of Cobalt. A. METZL (*Zeitsch. anorg. Chem.*, 1914, **86**, 358—368).—Cobalt peroxide, CoO_2, may be prepared

from cobalt sulphate, iodine, and alkali, washing by decantation, and filtering through asbestos in order to avoid reduction by filter paper. The ratio of cobalt to oxygen is then determined. The same compound is obtained by using silver nitrate and potassium hydroxide as the oxidising agent. Silver, which is precipitated at the same time, is removed by washing with a solution of potassium permanganate and nitric acid.

Oxidation with hydrogen peroxide and sodium hydrogen carbonate yields a green precipitate, which, analysed in the moist state, has the composition $CoCoO_3,CoCO_3$, thus consisting of cobalt carbonate and cobalt cobaltite. It is partly decomposed on washing with alcohol and ether. Copper sulphate, when similarly treated, yields a product, $Cu_2CuO_4,CuCO_3$. C. H. D.

Colour of Cobalt Salts in Solution. J. E. MARSH (*Chem. News*, 1914, **109**, 193. Compare this vol., ii, 373).—When a solution of sodium chloride (1 part by weight) and cobalt chloride hexahydrate (2 parts) in acetone (8 parts) and water (8 parts) is electrolysed, a light blue layer forms at the anode, the remainder of the solution retaining its pink colour. The experiment illustrates very well the electronegative character of the blue cobalt complex. In the absence of sodium chloride there is no separation into layers. T. S. P.

Determination of the Atomic Weight of Nickel. ŒCHSNER DE CONINCK and GÉRARD (*Compt. rend.*, 1914, **158**, 1345—1346).— A determination of the atomic weight of nickel from the ratio nickel oxalate, $NiC_2O_4,2H_2O : Ni$. The nickel oxalate was prepared pure as follows: An ingot of nickel was dissolved in nitric acid, hydrogen sulphide passed through, and then the iron oxidised and precipitated by ammonium hydroxide. The filtrate was treated with ammonium sulphide, the precipitate being washed with hydrochloric acid and then dissolved in aqua regia. The solution was evaporated to dryness, and the residue extracted with dilute hydrochloric acid. On addition of barium carbonate, followed by a current of chlorine, the cobalt was precipitated, and filtered off. The barium was precipitated, filtered off, and the filtrate evaporated to crystallisation. The crystals were dissolved in very dilute hydrochloric acid, and on the addition of a concentrated solution of oxalic acid the nickel was precipitated as nickel oxalate, $NiC_2O_4,2H_2O$, collected, washed and dried, and finally left over sulphuric acid for several weeks. A weighed quantity of the oxalate was heated in a current of hydrogen, the temperature being finally raised to 270—275°. The mean of five determinations gave the value 58·57 for the atomic weight. W. G.

Preparation of Nitrogen Compounds of Molybdenum. BADISCHE ANILIN- & SODA-FABRIK (Austrian Patent 62524. Compare A., 1912, ii, 946).—Pure precipitated molybdic acid is reduced by means of hydrogen at 700°, and nitrogen is then led over the product at the same temperature and under atmospheric pressure.

The temperature should not exceed 1000°, and molybdenum nitride is thus formed without operating under pressure, as in the process described previously (*loc. cit.*).　　　　　　　　J. C. C.

Binary Eutectics of Tin, Zinc, and Cadmium. A. M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 223—224).—The results obtained by Lorenz and Plumbridge (A., 1913, ii, 1056) confirm the law established by Flavicki (A., 1906, ii, 152) for eutectic alloys. For the zinc–tin eutectic, $q/p = 0.0892$, and for the cadmium–zinc eutectic, $q/r = 0.2163$. Hence, for the cadmium–tin eutectic, the value of $r : p$ should be $0.0892/0.2163 = 0.4123$, the actual value obtained being 0.4124.　　　　　　　T. H. P.

Experiments at High Temperatures. II. Preparation of Refractory Objects of Zirconium Dioxide. OTTO RUFF, H. SEIFERHELD, and O. BRUSCHKE (*Zeitsch. anorg. Chem.*, 1914, **86**, 389—400. Compare A., 1913, ii, 690).—Crucibles of zirconia may be used in a carbon tube resistance furnace at temperatures up to 2200°. It is advisable to mix the oxide with 1% of dry starch, which gives great mechanical strength when dried at 140°, and 3% of magnesia. The addition of magnesia causes considerable shrinkage in the first firing at 1450°, and there is then very little shrinkage at higher temperatures. The zirconia powder used for the original mixture must not have been ignited at a higher temperature than 1000°. Clay and colloidal oxides have not been found useful as binding material. Borax yields porous crucibles.

The dry mixture is just moistened with water, shaped in a press, and removed. The crucibles are dried for one hour at 100° and for three hours at 140°, and are fired, first at 1500° and then at 2200°. Natural zirconia (83.5%, with 11.5% SiO_2 and 4.7% Fe_2O_3) is more easily manipulated than the pure dioxide. The crucibles are only slightly porous, but it has not yet been found practicable to glaze them.　　　　　　　C. H. D.

Extraction of Germanium from the Waters at Vichy. JACQUES BARDET (*Compt. rend.*, 1914, **158**, 1278—1280).—Germanium having been detected spectrographically in Vichy mineral waters (compare A., 1913, ii, 785) the author has extracted it in the form of its oxide, separating it from the other metals present by a process of fractional precipitation with hydrogen sulphide and solution in acid alternately. The starting material is the deposit obtained on boiling off the carbon dioxide from the waters. Germanium is present to the extent of 1 part in 40,000,000 parts of water.　　　　　　　W. G.

Extraction of Vanadium by Treating its Ores with Acids and Oxidising Agents. BYRAMJI DORABJI SAKLATWALLA (D.R.-P. 270346).—The ore is boiled with dilute sulphuric acid (1:1), and to the solution is added ammonium persulphate. After prolonged boiling the vanadium separates as a red hydroxide, which on heating furnishes vanadium pentoxide in an almost pure condition.　　　　　　　J. C. C.

Chemical and Physico-chemical Observations in the Preparation of Colloidal Gold Solutions. WALTER HALLE and ERNST PRIBRAM (*Ber.*, 1914, **47**, 1398—1401).—Donau (*Vers. Deut. Naturforsch. Aerzte Wien.*, Sept. 1913) has shown that a colloidal solution of gold may be obtained by letting a hydrogen flame play on the surface of a very dilute solution of a gold salt, the formation of the colloidal solution being ascribed to the strong reducing action of the flame. The authors find, however, that such a solution contains nitrous acid, which is formed by the hydrogen flame burning in the air, and ascribe the formation of the colloidal gold to the reducing action of this acid. In confirmation of this they show that colloidal solutions are readily obtained by the action of nitrous acid (sodium nitrite and sulphuric acid) on a solution of gold chloride; as the concentration of the nitrous acid is reduced from $0 \cdot 00075$ to $0 \cdot 000452\%$, the colour of the gold solution changes from blue, through violet, to red.

This method of preparing colloidal gold solutions is important, because the gold particles are of uniform size.

The most convenient method of testing whether a glass vessel is suitable for preparing or containing a colloidal solution is to put into it 10 c.c. of water containing 2 drops of a $0 \cdot 2\%$ alcoholic solution of methyl-red; if the colour changes to yellow within twenty-four hours, owing to alkali dissolving from the glass, the glass is not suitable. T. S. P.

Alloys of Gold and Arsenic. A. P. SCHLEICHER (*Intern. Zeitsch. Metallographie*, 1914, **6**, 18—22).—Alloys containing from 0 to 25 atomic % of arsenic have been investigated thermally by melting an alloy rich in arsenic with gold. The freezing-point curve indicates a eutectic point in the neighbourhood of 46 atomic % As, the eutectic temperature being 665°. Only two micrographic constituents are visible, gold and the eutectic. Arsenic is evolved suddenly at the eutectic temperature on cooling. C. H. D.