

INORGANIC CHEMISTRY.

THE study of radioactivity, isotopy, and atomic constitution has assumed such importance that a separate Report is now devoted to these developments of inorganic chemistry, and atomic constitution is here discussed solely from the stand-point of valency and the ordinary chemistry of the elements. Nevertheless, the bulk of orthodox inorganic chemical work, including as such those cases in which the application of physical methods is of interest for the results attained rather than for the methods employed, is so great that the Report can only be kept within the prescribed limits by ruthless economy of words and omission of much interesting material. An effort has been made, however, to report precisely, rather than to comment on, as much as possible of the work deemed to be of general interest to chemists.

Atomic Theory.

Langmuir has deduced the types of valency, and its numerical values, for most elements by a method simpler than that formerly employed,¹ and, on the basis of the electron theory of chemistry, Sir J. J. Thomson² has attributed structures to the unit cells of elements according to their valency, and has calculated therefrom values for bulk-modulus, critical frequency, and dielectric constant which agree with experimental values. It has been found³ that carbon dioxide and nitrous oxide have identical viscosities over the range 0—100°, and it is inferred that their molecular dimensions are the same, in agreement with Langmuir's view that both molecules have the same arrangement of the outer electrons.

The principle of induced alternate polarity of atoms, previously applied to explain many properties of organic compounds, has now been derived simultaneously and independently by Lapworth⁴ and by Kermack and Robinson,⁵ as a necessary consequence of the electron theory. It is perhaps important to observe that in both

¹ I. Langmuir, *Science*, 1921, **54**, 59; *A.*, ii, 137.

² Sir J. J. Thomson, *Phil. Mag.*, 1922, [vi], **43**, 721; *A.*, ii, 355.

³ C. J. Smith, *Proc. Physical Soc.*, 1922, **34**, 155; *A.*, ii, 549.

⁴ A. Lapworth, *T.*, 1922, **121**, 416.

⁵ W. O. Kermack and R. Robinson, *ibid.*, 427.

cases it is found desirable to postulate union of atoms, not only by the normal "single" or "double" bond, consisting in the sharing by adjacent atoms of two or four electrons, respectively, but also by the sharing of one or three electrons. A bond of three electrons has already been proposed as affording the most rational expression of the constitution of benzene, and a single electron bond has been supposed probable,⁶ so that there is no special difficulty in accepting the variation of the Lewis-Langmuir hypothesis. Thus among the elements of the First Period this theory continues to prove adequate.

Difficulties begin with sodium and increase among the heavier elements, where it becomes evident that the usual hypothesis is at best no more than a first approximation to the truth about atomic constitution, accounting well enough for the broad similarities within and differences between the various groups, but failing to give, for example, as any hypothesis pretending to finality must give, a theoretical basis for the detailed differences observed within each group. Reviewing such differences, one cannot escape the conclusion that chemical properties are determined, not by the outer electrons alone, but by the atomic constitution as a whole; and if this is so, the assumption, now general, that the chemical properties of isotopes are identical, whilst probably true or very nearly true for the heavier elements, may not hold for the lighter elements. It is thus important to consider the several attempts which have been made to amend the original hypothesis.

From a consideration of emission spectra, Bohr has developed a dynamic theory of the structure of the heavier elements, postulating eccentric orbits for certain electrons (which thus belong, in a sense, to more than one level in the atom), and irreconcilable with any conception of sharply separated shells of electrons,⁷ which accounts for the colour (in compounds), paramagnetism, and relative complexity of spectra of the elements and is strongly supported by recent work upon the X-ray spectra.⁸ Measurements of the intensity of reflection of X-rays per unit volume of the units constituting crystalline sodium chloride⁹ may be interpreted as showing the existence in successive shells, counting outwardly, of 7 and 3 electrons in the sodium atom, and of 10, 5, and 3 electrons in the chlorine atom; or, alternatively, give for the variation of electron density with distance from the centre of each atom values which agree well with those calculated for an atom of the type proposed by

⁶ Sir J. J. Thomson, *Phil. Mag.*, 1921, [vi], **41**, 538; *A.*, ii, 279.

⁷ N. Bohr, *Z. Physik*, 1922, **9**, 1; *Nature*, 1921, **108**, 208; *A.*, ii, 363, 277.

⁸ D. Coster, *Phil. Mag.*, 1922, [vi], **43**, 1070; **44**, 546; *A.*, ii, 491, 677.

⁹ W. L. Bragg, R. W. James, and C. H. Bosanquet, *ibid.*, 1922, **44**, 433; *A.*, ii, 703.

Bohr; but appear to show clearly that there is not in either atom of sodium chloride a shell of eight electrons.

From the chemical point of view come attempts to bring the static hypothesis into closer accord with the facts by modifying Langmuir's fourth postulate. Bury's modification¹⁰ reads: "The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus successive layers can contain 2, 8, 18, and 32 electrons. Groups of 8 and 18 electrons in a layer are stable, even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18 or from 18 to 32, there occurs a transition series of elements which can have more than one structure." This leaves unchanged the structures assigned by Langmuir to the elements of the First Period, but gives to all succeeding elements new structures which are in better accord with Bragg's atomic diameters and satisfactorily explain many chemical properties, for example, the similarities and differences in the triplets of Group VIII and the existence and characters of the rare earths. It seems significant, too, that Bury's structures for the inert gases are similar to those deduced by Bohr from the emission spectra. The argument of the paper cannot be reproduced in abstract and those interested will find that the original paper repays careful study. It has since been shown¹¹ that Bury's structures afford probabilities of complexity of spectra in general agreement with the observed numbers of lines for many elements.

Another alternative disposition of electrons (2 : 8 : 18 : 32 : 18 : 8 instead of Langmuir's 2 : 8 : 8 : 18 : 18 : 32) has been suggested by Dauvillier,¹² as a result of investigations of the *L*- and *K*-series lines in the *X*-ray spectra of a number of the heavier metals; and he too supposes that chemical properties are in part dependent on the internal electrons, and that inner electron shells may be incomplete. Regarding the "atomic radius" as the distance from the centre to an electron group in the valency shell, it has been shown that the distance between atomic centres is often less than the sum of the atomic radii: a number of causes may be adduced to explain the fact, among which the conception of bonds of more than one electron and the possibility of more than one arrangement of electrons within the atomic sphere¹³ are of interest, as they have already been

¹⁰ C. R. Bury, *J. Amer. Chem. Soc.*, 1921, **43**, 1602; *A.*, ii, 43.

¹¹ H. S. King, *ibid.*, 1922, **44**, 323; *A.*, ii, 277.

¹² A. Dauvillier, *J. Phys. Radium*, 1922, [vi], **3**, 154, 221; *Compt. rend.*, 1921, **173**, 1077; *A.*, ii, 559, 678, 43.

¹³ M. L. Huggins, *Physical Rev.*, 1922, **19**, 346; *A.*, ii, 634.

supposed, on quite other grounds, to be possible. The suggestion is made that, in the second and third shells, the fifth and subsequent electrons pair with the first four to give a tetrahedral arrangement of pairs, and that the forces causing pairing result, in the case of the heavier elements, in the formation of triplets of electrons in the inner shells.¹⁴

This stimulating clash of theories evidently arises in part because chemical phenomena can best be interpreted by a static conception of the atom whilst physical evidence demands a dynamic conception. Therefore special interest attaches to the suggestion made by Sir Oliver Lodge¹⁵ that these views might be reconciled were chemical union attributed, not to electrical attraction between the atoms, but to interlacing of the stationary magnetic fields which must accompany rapidly revolving electrons. Theories of magnetism clearly tend to assume a form favourable to such an hypothesis;¹⁶ and to the connexion between chemical constitution and magnetic properties in compounds, developed chiefly by Pascal (whose recent work confirms the usual view of the constitution of the acids of sulphur, phosphorus, and arsenic),¹⁷ is given new significance by experiments showing that ferro-magnetism is increased in iron and actually imparted to manganese by fusion in hydrogen, whilst the magnetic susceptibility of palladium is reduced by the adsorption of hydrogen. These phenomena may be explained by the assumption that the entry of hydrogen into the electron system of the metal produces a new system corresponding with the element of next higher atomic number, in the case of manganese, iron; in that of palladium, silver.¹⁸

Atomic Weights.

Glucinum.—Basic glucinum acetate, prepared from the technical carbonate, was recrystallised from glacial acetic acid until free from iron, sublimed, and converted into nitrate, which was dissolved in ammonium carbonate. Glucinum carbonate precipitated from this solution was calcined to oxide, and this, by ignition with carbon in a current of chlorine, gave the pure chloride, which was collected and weighed with exclusion of water. The ratios $\text{GCl}_2 : 2\text{Ag}$ and

¹⁴ M. L. Huggins, *Science*, 1922, **55**, 459; *J. Amer. Chem. Soc.*, 1922, **44**, 1841; *A.*, ii, 632, 744.

¹⁵ Sir O. Lodge, *Nature*, 1922, **110**, 341; see also W. Hughes, *ibid.*, 1922, **110**, 37; *A.*, ii, 701, 632.

¹⁶ For a useful summary, see A. E. Oxley, *Nature*, 1923, **111**, 54.

¹⁷ P. Pascal, *Compt. rend.*, 1921, **173**, 712; 1922, **174**, 457, 1608; *A.*, 1921, ii, 692; 1922, ii, 285, 564.

¹⁸ A. E. Oxley, *Proc. Roy. Soc.*, 1922, [A], **101**, 264; *A.*, ii, 469.

$\text{GICl}_2 : 2\text{AgCl}$ were determined in the usual manner, the mean result of all analyses being the value $\text{G} = 9.018$,¹⁹ appreciably lower than the accepted value $\text{G} = 9.1$.

Boron.—By the methods used in the foregoing determination, the same authors²⁰ have measured the ratios $\text{BCl}_3 : 3\text{Ag}$ and $\text{BCl}_3 : 3\text{AgCl}$, three samples of purified boron trichloride giving the mean values $\text{B} = 10.840$, 10.818 , and 10.825 , respectively. The first value is rejected for discordance and the rounded mean of the latter two values, $\text{B} = 10.82$, is taken.

Baxter and Scott²¹ reduced boric oxide with excess of magnesium, extracted with hydrochloric or hydrobromic acid, and treated the resulting boron at 700° with chlorine or with argon saturated with bromine vapour. The samples of chloride or bromide thus prepared were freed from excess of halogen and repeatedly distilled through Hempel fractionating columns in evacuated glass apparatus. Each then gave, when compared with silver in the usual way, the value $\text{B} = 10.83 \pm 0.01$. These results, differing by no more than 1 part in a thousand, are a great improvement on those formerly available, and accord much better with the isotope ratio determined by Aston than, for example, the value $\text{B} = 10.900$ found by Smith and van Haagen.²²

Yttrium.—Yttria, prepared from Norwegian gadolinite and purified by a rigorous and prolonged process of fractional crystallisation (as bromate) and fractional precipitation, converted into chloride and titrated with weighed silver in the usual way gave, as the mean of twenty-one values varying from 88.97 to 89.08 , the value $\text{Yt} = 89.03$.²³

Lanthanum.—The low value, $\text{La} = 138.91$, found by Baxter, Tani, and Chapin,²⁴ has been confirmed by determination of the ratio $\text{LaCl}_3 : 3\text{Ag}$ using spectroscopically pure lanthanum chloride. Ten experiments gave for the atomic weight extreme values of 138.84 and 138.97 , with a mean $\text{La} = 138.89$.²⁵ It seems clear, therefore, that the international figure, $\text{La} = 139.0$, is too high.

Some work has been recorded on measurement of atomic weights

¹⁹ O. Hönigschmid and L. Birkenbach, *Ber.*, 1922, **55**, [B], 4; *A.*, ii, 214.

²⁰ *Anal. Fis. Quím.*, 1922, **20**, 167; *A.*, ii, 641.

²¹ G. P. Baxter and A. F. Scott, *Science*, 1921, **54**, 524; *A.*, ii, 285.

²² E. F. Smith and W. K. van Haagen, *Carnegie Inst. Pub.*, 1918, **267**, 1; *A.*, 1920, ii, 247.

²³ H. C. Fogg and C. James, *J. Amer. Chem. Soc.*, 1922, **44**, 307; *A.*, ii, 297.

²⁴ G. P. Baxter, M. Tani, and H. C. Chapin, *ibid.*, 1921, **43**, 1080; *A.*, 1921, ii, 454.

²⁵ B. S. Hopkins and F. H. Driggs, *ibid.*, 1922, **44**, 1927; *A.* ii, 770.

by physical methods. Forty-five determinations gave a mean value of 1.42897 ± 0.00007 grams for the weight of the litre of oxygen at 0° and 760 mm. in latitude 45° , in close agreement with other recent work on this constant but less by 0.00008 gram than the accepted value.²⁶ Recalculation from the known density of hydrogen bromide, using the new value for oxygen, gives $\text{Br} = 79.927$.²⁷

Determinations of the normal density and compressibility of carbon dioxide and ethylene²⁸ give values for the atomic weight of carbon, 11.998 and 12.000, respectively, appreciably lower than the international value, $\text{C} = 12.05$, but in better accord with atomic theory; and the gravimetric determinations of Richards and Hoover have been criticised.²⁹ On the other hand, a strong protest has been entered³⁰ against such use of atomic weights derived from gas densities in criticism of "chemical" atomic weights, and supported by proof³¹ that the proportion of impurities in atomic weight silver and iodine is very much smaller than has been alleged.³²

Chemical Reaction.

Before proceeding to deal with individual elements in Group order, consideration must be given to certain results which cannot be placed in any definite category (unless we invoke the hard-pressed word catalysis) and yet are clearly of fundamental significance.

Baker has extended the experiments previously reported.³³ Pure liquids were sealed up in Jena-glass flasks with pure phosphoric oxide and after lapse of time were opened to atmospheric pressure through dry mercury and gradually heated, precaution being taken to avoid superheating: the temperature of steady ebullition was taken as the boiling point with the results given in the table: ³⁴

²⁶ E. Moles, *J. Chim. physique*, 1921, **19**, 100; E. Moles and F. González, *Anal. Fis. Quím.*, 1922, **20**, 72; E. Moles and M. Crespi, *ibid.*, 190; *A.*, ii, 141, 497, 636.

²⁷ E. Moles, *J. Chim. physique*, 1921, **19**, 135; *A.*, ii, 140.

²⁸ Ph. A. Guye and T. Batuecas, *Helv. Chim. Acta*, 1922, **5**, 532; T. Batuecas, *ibid.*, 544; *A.*, ii, 617, 618.

²⁹ E. Moles, *Anal. Fis. Quím.*, 1921, **19**, 255; *A.*, ii, 51.

³⁰ G. P. Baxter, *J. Amer. Chem. Soc.*, 1922, **44**, 595; *A.*, ii, 370.

³¹ G. P. Baxter and L. W. Parsons, *ibid.*, 577; G. P. Baxter, *ibid.*, 1922, **44**, 591; *A.*, ii, 376, 377.

³² P. A. Guye and F. E. E. Germann, *Compt. rend.*, 1914, **159**, 225; *A.*, 1914, ii, 727.

³³ H. B. Baker and Muriel Baker, *T.*, 1912, **101**, 2339.

³⁴ H. B. Baker, *ibid.*, 1922, **121**, 568.

| | Period of drying (years). | Original boiling point. | New boiling point. | Rise in boiling point. |
|-----------------------|---------------------------------|-------------------------------|--------------------------|------------------------------|
| Bromine | 8 | 63° | 118° | 55° |
| Mercury | 9 | 358 | 420—425 | 62 |
| Hexane | 8½ | 68.4 | 82 | 14 |
| Benzene | 8½ | 80 | 106 | 26 |
| Carbon disulphide ... | 1+27 | 49.5 | 80 | 30 |
| " tetrachloride... | 9 | 78 | 112+ | 34 |
| Ethyl ether | 9 | 35 | 83 | 48 |
| Methyl alcohol | 9 | 66 | 120+ | 54 |
| Ethyl alcohol | 9 | 78.5 | 138 | 60 |
| Propyl alcohol | 9 | 95 | 134 | 39 |

These large differences of boiling point are undoubtedly real. The mercury maintained at 360° for thirty minutes did not boil and gave only a trace of condensate above the liquid: the hexane was transferred to another flask, not specially dried, and still boiled at 81°: water could be boiled through the benzene with only slow evaporation of the latter: and the ether at 20° had a vapour pressure of 374 mm. only, as against the normal value of 442 mm. The liquids recover their normal boiling points on exposure, even to air dried with sulphuric acid and phosphoric oxide; benzene slowly, ethyl ether and the three alcohols very rapidly.

Comparative experiments with dried and undried bromine, benzene, hexane, and nitrogen tetroxide showed that the capillary rise increased steadily during drying to a value which indicates an increase of molecular weight to 1.5—3.0 times that for the normal liquids. These results clearly support the earlier hypothesis that drying shifts the equilibrium between normal and associated molecules; possibly because absence of water hinders or inhibits dissociation, as it is known to do in the case of certain vapours, and has no effect or a smaller effect on the opposing association. If, as is usually supposed, the degree of association of a liquid is increased by lowering of temperature, information as to whether association is stopped or merely hindered might be obtained by ascertaining the ultimate effect of drying different specimens of the same liquid maintained at widely different temperatures throughout the whole period of drying. It has been shown, rather unexpectedly, that in benzene, carbon tetrachloride, carbon disulphide, ether, bromine, sulphur dioxide, and nitrogen trioxide, drying produces no change in volume as great as 1 part in 10,000.

Thermometers suspended in the vapour from dry hexane and benzene, boiling at 82° and 106°, respectively, showed temperatures of 68.4° and 80°, the boiling points of the normal liquids; a very curious result. Smits had previously suggested³⁵ that, supposing internal change to be inhibited by drying, fractional distillation

³⁵ A. Smits, *Z. physikal. Chem.*, 1922, **100**, 477; *A.*, ii, 358.

should result in a separation of the normal and associated liquids, and later experiments³⁶ have shown that if a specimen of dried benzene is distilled over completely, the temperature of a thermometer suspended in the vapour shows a steady rise, indicating that fractional distillation does, in fact, occur.

Apparently, similar changes may take place in the solid state, preliminary experiments having shown that the melting points of sulphur and iodine, originally 112.5° and 114° , are, after nine years' drying, 117.5° and 116° , respectively.

It has been found³⁷ that the reactivity of ammonia, measured by the expansion at constant temperature resulting from its partial dissociation in contact with an activated platinum wire heated by a definite current for a definite time, is the same for ammonia obtained by slow escape from a commercial cylinder of liquid ammonia, by heating aqueous ammonia and drying the gas with quicklime, or by liquefying either preparation and allowing it to evaporate isothermally at its boiling point. Under the same conditions, ammonia allowed to escape very rapidly from a cylinder had a much lower reactivity, and it is concluded that an "inactive" phase of ammonia has thus been obtained which contains more molecules of the type characteristic of liquid ammonia³⁸ than are normally present in the "active" phase, and that the existence of such active and inactive phases explains the chemical inactivity of dried gases and supports the radiation theory of chemical reactivity.³⁹

It may be suggested, however, that the experimental results will bear a simpler, if less significant, interpretation. It is known that ordinary commercial ammonia, dried over lime, contains about 1 per cent. of water,⁴⁰ and that rapid, irreversible distillation such as may occur by free discharge of gas from a cylinder of liquid is a very effective means of separating the constituents even of a constant-boiling mixture,⁴¹ so that the gas thus obtained may well be considerably drier than that in real equilibrium with the cylinder liquid. Baly has found that addition of water vapour to ordinary ammonia increases its reactivity, drying certainly decreases its reactivity, and so the greater dryness of the "inactive" form would appear to be capable of explaining the whole of the observations, including the "recovery" of the gas in cylinders on standing (by

³⁶ H. B. Baker, private communication.

³⁷ E. C. C. Baly and H. M. Duncan, *T.*, 1922, **121**, 1008.

³⁸ The "liquidogen" molecules of Traube, *Ann. Physik*, 1902, [iv], **8**,

³⁹ E. C. C. Baly, *Phil. Mag.*, 1920, [vi], **40**, 15; *Trans. Faraday Soc.*, 1922, **17**, 588; *A.*, ii, 628.

⁴⁰ See, e.g., A. G. White, *T.*, 1922, **121**, 1688.

⁴¹ See, e.g., R. S. Mulliken, *J. Amer. Chem. Soc.*, 1922, **44**, 2389; *A.*, 1923, ii, 31.

acquisition of the equilibrium content of water vapour), identity of slowly released cylinder gas with laboratory preparations dried by lime, recovery of "inactive" gas in the experimental tube when the wire is heated at 200° (release of adsorbed water from the wire or walls), and the increase in reactivity of "inactive" ammonia with increase of temperature of the wire (the five pairs of figures given show that twenty seconds' heating with currents of 4.00, 4.10, 4.25, 4.35, and 4.50 amps. produces decomposition in the ratios active/inactive = 2.18, 1.76, 1.60, 1.46, and 1.35, respectively).

The "activation" of chlorine by light, a subject of much past controversy, has been reaffirmed. A rigid series of experiments ⁴² proves that when chlorine is exposed to sunlight or intense ultra-violet light and mixed with hydrogen in the dark, reaction occurs immediately on exposure of the mixture to the light of two 100-watt tungsten lamps, whilst with chlorine not so insulated reaction is delayed by the known "induction period" of about two minutes. The effect of insolation persists in the dark for three hours, but is diminished after twenty-four hours and disappears after several days. An equally rigorous series of experiments shows that chlorine exposed to the light of a 3000-watt Bovie quartz mercury lamp or to a high tension discharge will not react with hydrogen in the dark even when the interval between insolation and mixing is only 0.01 second, so that any explanation of activation in terms of the formation of a triatomic or other active form of chlorine seems improbable.

A globule of fused calcium chloride between two copper wires shows great decrease in resistance in presence of a trace of moisture, and use of this device as a "detector" has shown ⁴³ that pure hydrogen reacts with copper oxide at a definite and reproducible temperature, which is lowered some 20° if the hydrogen first passes over platinised asbestos. Similar results were obtained with hydrogen and sulphur, formation of hydrogen sulphide (detected by lead acetate paper) occurring at a lower temperature if the hydrogen first passed over palladium black. The activated hydrogen was found to be ionised, but only to an extent considered altogether insufficient to explain reaction; and the persistence of the phenomenon when glass wool was interposed between the platinised asbestos and copper oxide and the absence of any change in refractive index by activation or increase of volume on decay seem to show that the observed effects cannot be attributed to monatomic or triatomic hydrogen. The explanation advanced is that the internal

⁴² G. L. Wendt, R. S. Landauer, and W. W. Ewing, *J. Amer. Chem. Soc.*, 1922, **44**, 2377; *A.*, 1923, ii, 22.

⁴³ P. Anderson, *T.*, 1922, **121**, 1153; see also, R. N. Pease and H. S. Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179; *A.*, ii, 148.

energy of the hydrogen molecules is increased by contact with the platinum or palladium : this should result, presumably, in a lowering of the temperature of the metal, and the explanation might thus be tested experimentally.

Lastly, reference may be made to the mysterious variation observed ⁴⁴ in the rate of decomposition of mercuric fulminate in a vacuum at 80°, which seems to bear some resemblance to the foregoing unexplained phenomena.

The Inert Gases.

A spectrophotometric method has been developed for the estimation of krypton and xenon in admixtures with argon.⁴⁵ Positive-ray analysis of the residues from a thousand tons of liquid air has given evidence of new constituents of the atmosphere with molecular weights 163 and 260 ; but the observed lines may be due to diatomic molecules of xenon and krypton.⁴⁶

Precise determinations show that the solubility of helium has not, as was supposed, a minimum at 20°.⁴⁷ A detailed account of the distribution, sources, and chemical composition of helium-bearing natural gases has been published.⁴⁸

Anderson has shown ⁴⁹ that in the explosion of metallic wires by heavy condenser discharges a temperature of some 20,000° is attained in the wire in 1/300,000 second. It is now reported that thin tungsten wires exploded in this way yield gas which when obtained in a vacuum shows the helium spectrum, and if obtained in an atmosphere of pure carbon dioxide and measured after absorption of the latter in alkali has, as the mean of twenty-one experiments, a volume which corresponds to an amount of helium about 25 per cent. of the weight of tungsten taken.⁵⁰ This result, if confirmed, would appear to be the first case of atomic decomposition by artificial means.

Group I.

Active hydrogen ⁵¹ has been prepared in the Siemens ozoniser, using both induction coil discharge and a Tesla discharge of much higher frequency and voltage, and also by passing pure hydrogen

⁴⁴ R. C. Farmer, *T.*, 1922, **121**, 174.

⁴⁵ C. Moureu and A. Lepape, *Compt. rend.*, 1922, **174**, 908; *A.*, ii, 394.

⁴⁶ Sir J. J. Thomson, *Proc. Roy. Soc.*, 1922, [A], **101**, 290; *A.*, ii, 565.

⁴⁷ H. P. Cady, H. M. Elsey, and E. V. Berger, *J. Amer. Chem. Soc.*, 1922, **44**, 1456; *A.*, ii, 642.

⁴⁸ G. S. Rogers, *U.S. Geol. Survey, Prof. Paper*, 1921, No. **121**.

⁴⁹ J. A. Anderson, *Astrophys. J.*, 1920, **51**, 37.

⁵⁰ G. L. Wendt and C. E. Irion, *J. Amer. Chem. Soc.*, 1922, **44**, 1887; *A.*, ii, 773.

⁵¹ *Ann. Reports*, 1920, **17**, 37.

over a platinum wire heated electrically at 800° , the effect in this case being probably due to the emission of positive ions. It is decomposed by contact with certain metals (Pt, Ni, Cu, Pb, Sb, Cd) and unchanged by others (Ag, Hg, Sn, Bi, Mo, Zn, Al). Definite proof was obtained that hydrogen contracts when activated and recovers its original volume on standing, and that the active form condenses to a liquid at or slightly above -180° . A relatively slow progressive change is observed in the spectrum produced by the discharge during the activation at -180° ,⁵² the Balmer series giving way to the secondary line spectrum. These results, especially the evident smallness of the energy change involved in its therm-ionic production, support the original view that this active hydrogen is in fact triatomic hydrogen, H_3 (named *hyzone*, by analogy with ozone), rather than the isotope of hydrogen, *isohydrogen*, of atomic weight 3 (containing a *single* atomic nucleus of three protons) postulated by Harkins as a unit of atomic structure and, rather unfortunately, symbolised by him as H_3 .

Wood has observed⁵³ that long vacuum tubes containing hydrogen give, in the central portion, mainly the Balmer series spectrum and at the ends mainly the secondary spectrum. On closing the switch, a momentary flash of the secondary spectrum, lasting about 1/50 sec., is seen throughout the tube, provided that 1/5 sec. or more has elapsed since the previous discharge. With dry hydrogen, no Balmer series is seen unless a momentary heavy condenser discharge is passed. Gas drawn by a pump from the central portion of the tube and caused to impinge upon fractured glass surfaces (or some metals, oxides, and other substances), raises them to incandescence.⁵⁴ The explanation advanced is that molecular hydrogen (to which the secondary spectrum is attributed) is dissociated by the discharge to form atomic hydrogen (believed to be the source of the Balmer spectrum), the incandescence of solids being due to their acting as catalysts for the exothermic recombination of the atoms.

Clearly the phenomena observed by Wendt and by Wood are very intimately related, but further experiment is necessary to decide finally which interpretation is correct, although Wendt's seems more probable. There is a concurrence of opinion that the "clean-up" of hydrogen and nitrogen in discharge tubes is due to chemical changes.⁵⁵ Evidence has been obtained that active

⁵² G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510; *A.*, ii, 369.

⁵³ R. W. Wood, *Phil. Mag.*, 1921, [vi], **42**, 729; *A.*, 1921, ii, 665.

⁵⁴ R. W. Wood, *Proc. Roy. Soc.*, 1922, [A], **102**, 1; *A.*, ii, 759.

⁵⁵ F. H. Newman, *Phil. Mag.*, 1922, [vi], **44**, 215; *Nature*, 1922, **109**, 749; G. L. Wendt, *ibid.*, 749; *A.*, ii, 546, 639, 639.

modifications of hydrogen and nitrogen are produced also by the action of α -rays.⁵⁶

Measurement of the dissociation tensions has shown that lithium hydride is the most stable of all the alkali and alkaline-earth hydrides, those of calcium, strontium, and barium decreasing in stability in the order named.⁵⁷ X-Ray photographs of lithium hydride show a structure similar to that of sodium chloride, with positive lithium-ions and negative hydrogen-ions,⁵⁸ and the view that metallic hydrides are true salts, in which hydrogen acts as a halogen, is vindicated also by very ingenious and skilful experiments proving that electrolysis of a solution of calcium hydride in a fused eutectic mixture of potassium and lithium chlorides gives hydrogen at the anode in the quantity required by Faraday's law.⁵⁹

Pure hydrogen peroxide is diamagnetic to a greater extent than water and therefore does not appear to contain the molecular linking characteristic of molecular oxygen: its solubility in alcohol is 18 per cent. and in ether 1 per cent.; it is insoluble in pure dry benzene. Curves of solubility for sodium chloride, sodium nitrate, and sugar in hydrogen peroxide are generally similar to those for the same substances in water and indicate a similar degree of ionisation of the salts. The curve for sodium sulphate in hydrogen peroxide differs materially from that in water, owing to the formation of the compound $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$. The halogen hydrides are apparently insoluble in the peroxide, but are oxidised thereby; and the halogens are much less soluble than in water. Investigation of the freezing-point curve for the system $\text{NH}_3\text{--H}_2\text{O}_2$ up to a concentration of 60 per cent. of ammonia shows the existence of one compound only, $\text{NH}_3 \cdot \text{H}_2\text{O}_2$, m. p. 24.5° , which can be prepared also by the action of ammonia on the peroxide in anhydrous ether. Hydrogen peroxide is quite stable in the absence of water, but its decomposition is, of course, autocatalytic.⁶⁰

Lithium nitrate, with a little water, is a good absorbent for ammonia, and the resulting liquid, unlike those produced with ammonium nitrate or thiocyanate, has no corrosive action on steel or iron.⁶¹

Fused caustic soda contains about 1.1 per cent. of water, which can only be removed by heating at 500° in a vacuum. The action

⁵⁶ F. H. Newman, *Phil. Mag.*, 1922, [vi], **43**, 455; *A.*, ii, 279.

⁵⁷ F. Ephraim and E. Michel, *Helv. Chim. Acta*, 1921, **4**, 900; *A.*, ii, 58.

⁵⁸ J. M. Bijvoet and A. Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 26; *A.*, ii, 569.

⁵⁹ D. C. Bardwell, *J. Amer. Chem. Soc.*, 1922, **44**, 2499; *A.*, 1923, ii, 20.

⁶⁰ O. Maass and W. H. Hatcher, *ibid.*, 2472; *A.*, 1923, ii, 21.

⁶¹ R. O. E. Davis, L. B. Olmstead, and F. O. Landstrum, *ibid.*, 1921, **43**, 1575, 1580; *A.*, ii, 56, 49.

upon iron, nickel, and copper of fused caustic soda, with and without the addition of 5—10 per cent. of sodium peroxide, has been studied at 350—720°; the results are very complex and interesting, many definite crystalline products having been obtained. That obtained from iron forms transparent red hexagonal crystals, stable to boiling water or aqueous caustic soda and to cold dilute mineral acids, but apparently decomposing when kept; analysis gave the composition $\text{Na}_2\text{Fe}_3\text{O}_6$, and there is some evidence that a similar compound is formed with nickel.⁶²

Sodium sulphate tetrahydrate, $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, otherwise unknown, has been shown to exist in mixed crystals with sodium chromate.⁶³

Experience gained in the preparation of free tetraethylammonium has led to the preparation of free ammonium in about a 50 per cent. yield by the addition of a 1.8 per cent. solution of potassium in liquid ammonia to a 1 per cent. ammonia solution of ammonium chloride at -70° .⁶⁴

Rubidium bromate, prepared from the pure carbonate and bromic acid and recrystallised, forms, like caesium bromate, small hexagonal crystals resembling cubes, m. p. 430° , and sparingly soluble in water.⁶⁵

Measurement over a range of temperatures of the dissociation pressures of hydrated cupric alkali sulphates, of the type $\text{CuSO}_4 \cdot \text{M}'_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, showed the stability at any given temperature to increase in the order K, Rb, Tl, NH_4 , Cs; and it is inferred that the basicity of the corresponding hydroxides increases in the same order.⁶⁶

Excess of hydrogen peroxide gives with cold solutions of sodium copper carbonate a gelatinous, yellowish-brown precipitate having an oxygen : copper ratio between Cu : $1\frac{1}{2}\text{O}$ and Cu : 2O, thus affording fresh evidence for the existence of an unstable peroxide, CuO_2 .⁶⁷ The action of potassium persulphate on cuprous hydroxide in presence of barium hydroxide below 0° is said to give the oxide Cu_2O_3 which, whilst an oxidising agent, is apparently not peroxidic.⁶⁸

Cuprous sulphide is formed by the action of sulphur on cuprous chloride.⁶⁹ Cupric sulphide on oxidation by air yields free sulphur

⁶² T. Wallace and A. Fleck, *T.*, 1921, **119**, 1839.

⁶³ T. W. Richards and W. B. Meldrum, *J. Amer. Chem. Soc.*, 1921, **43**, 1543; *A.*, ii, 54.

⁶⁴ H. H. Schlubach and F. Ballauf, *Ber.*, 1921, **54**, [B], 2825; *A.*, ii, 55.

⁶⁵ H. D. Buell and C. R. McCrosky, *J. Amer. Chem. Soc.*, 1921, **43**, 2031; *A.*, ii, 146.

⁶⁶ R. M. Caven and J. Ferguson, *T.*, 1922, **121**, 1406.

⁶⁷ J. Aldridge and M. P. Applebey, *ibid.*, 238.

⁶⁸ G. Scagliarini and G. Torelli, *Gazzetta*, 1921, **51**, ii, 225; *A.*, ii, 68.

⁶⁹ F. W. Pinkard and W. Wardlaw, *T.*, 1922, **121**, 1300.

if freshly precipitated, but only cupric sulphate and thiosulphate if preserved for some hours before exposure to oxygen; the existence of two modifications, formulated as $\text{Cu}^{\text{II}}\text{S}$ and $\text{Cu}^{\text{I}}\text{S}_2$, is inferred.⁷⁰

The corrosion of copper by ammonium nitrate and ammonia has been found to yield cupric tetrammine nitrate and nitrite, and the preparation of the latter compound from basic cupric nitrite and ammonia is described. Dry cupric tetrammine nitrate is remarkably stable, retaining its ammonia at 120° in a vacuum, but exploding at 212° : the nitrite loses ammonia at $95\text{--}100^\circ$ in air, forming the diammine nitrite, $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$.⁷¹

A strong solution of sodium persulphate (preferable to the potassium salt because of its greater solubility) acts on finely divided crystalline silver or concentrated aqueous silver nitrate to give a black peroxide which, in the latter case, gave an atomic ratio O/Ag as high as 1.295 and therefore was possibly impure Ag_3O_4 .⁷²

In sharp contrast with a number of doubtful or negative results,⁷³ Hartung, using a Steele and Grant type B quartz micro-balance⁷⁴ carrying 43 mg. and sensitive to 2×10^{-5} mg., has shown that films of silver chloride, bromide, or iodide, formed by direct halogenation of silver films, deposited from a tartrate silvering solution on thin silica supports, are darkened on exposure to light and lose weight, in some experiments with the chloride to the extent of more than 80 per cent. of the halogen present in the salt. Decomposition was accelerated in a vacuum or by presence of ozone, and rehalogenation restored the original weight and colour.⁷⁵ It seems clear, therefore, that neither oxygen nor water is essential to light action on the silver halides, and that their decomposition yields metal and halogen, and not a sub-halide.

Adsorption of iodine from aqueous or alcoholic solution does not occur with pure silver iodide,⁷⁶ and Carey Lea's observation to the contrary was probably due to the presence of silver nitrate as an

⁷⁰ W. Gluud, *Ber.*, 1922, **55**, [B], 952, 1760; *A.*, ii, 446, 572.

⁷¹ H. Bassett and R. G. Durrant, *T.*, 1922, **121**, 2630.

⁷² G. I. Higson, *ibid.*, 1921, **119**, 2048.

⁷³ A. G. Rabinovich, *J. Physical Chem.*, 1922, **26**, 577; C. Tubandt and G. Eschenhagen, *Z. physikal. Chem.*, 1922, **100**, 489; J. Eggert and W. Noddack, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 631; F. Weigert and W. Schöller, *ibid.*, 1921, 641; P. P. Koch and F. Schrader, *Z. Physik*, 1921, **6**, 127; *A.*, ii, 605, 346, 9, 10, 183.

⁷⁴ E. J. Hartung, *Phil. Mag.*, 1922, [vi], **43**, 1056; *A.*, ii, 495.

⁷⁵ *Idem.*, *T.*, 1922, **121**, 682.

⁷⁶ F. E. E. Germann and R. N. Traxler, *J. Amer. Chem. Soc.*, 1922, **44**, 460; *A.*, ii, 371.

impurity in his silver iodide. Silver perchlorate is extremely soluble in water and moderately soluble in benzene, and the three components form a remarkable system which has been studied up to the melting point of silver nitrate; silver perchlorate and water have the lowest eutectic point known for a true salt and water, -50.2° ; and a hydrate, $\text{AgClO}_4 \cdot \text{H}_2\text{O}$, and a compound, $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$, have been isolated.⁷⁷ Silver bromate is dimorphous, forming tetragonal crystals below and hair-like crystals above the transition point, 98.5° ; the dry salt melts at $308-310^{\circ}$ and is stable to light; it may advantageously be substituted for arsenious oxide as a standard in iodometry.⁷⁸ The existence of colourless and yellow forms of alkali silver thiosulphates is confirmed, and several new compounds of this type are described.⁷⁹

A number of new, complex gold chlorides containing ammonium, rubidium, and caesium have also been prepared.⁸⁰ Anodic oxidation of gold in dilute sulphuric acid is shown to yield auric hydroxide.⁸¹ Hydrogen sulphide in excess reacts with very dilute aqueous chloroauric acid to give pure auric sulphide, but the sulphides Au_2S and Au_2S_2 could not be obtained.⁸²

The existence of reaction limits in gold alloys previously reported⁸³ has been confirmed by electrochemical investigations,⁸⁴ and Tammann's explanation, although subject to criticism, still appears the most probable.⁸⁵

Group II.

A comparison of the band spectrum of glucinum with that of aluminium confirms the close similarity of atomic structure for these metals which would be anticipated from their chemical relationship.⁸⁶

Glucinum hydroxide precipitated from the sulphate by ammonia is found always to contain much ammonium sulphate, which cannot

⁷⁷ A. E. Hill, *J. Amer. Chem. Soc.*, 1922, **44**, 1163; *A.*, ii, 555.

⁷⁸ J. H. Reedy, *ibid.*, 1921, **43**, 1440; *A.*, ii, 56.

⁷⁹ E. Jonsson, *Ber.*, 1921, **54**, [B], 2556; *A.*, ii, 57.

⁸⁰ E. Suschnig, *Monatsh.*, 1921, **42**, 399; *A.*, ii, 514; H. L. Wells, *Amer. J. Sci.*, 1922, **3**, [v], 257, 315, 414; *A.*, ii, 449, 449, 514.

⁸¹ F. Jirsa and O. Buryánek, *Chem. Listy*, 1922, **16**, 189; *A.*, ii, 713.

⁸² A. Gutbier and E. Dürrwächter, *Z. anorg. Chem.*, 1922, **121**, 266; *A.*, ii, 513.

⁸³ *Ann. Reports*, 1919, **16**, 198.

⁸⁴ G. Tammann, *Z. anorg. Chem.*, 1921, **118**, 48, 93; 1922, **121**, 193; R. Lorenz, W. Fraenkel, and M. Wormser, *ibid.*, 1921, **118**, 231; *A.*, ii, 75, 380, 63, 21.

⁸⁵ G. Masing, *Z. anorg. Chem.*, 1921, **118**, 293; W. H. Creutzfeldt, *ibid.*, 1922, **121**, 25; W. Jenge, *ibid.*, 1921, **118**, 36; G. Tammann, *Z. Elektrochem.*, 1922, **28**, 36; *A.*, ii, 37, 347, 64, 255.

⁸⁶ L. C. Glaser, *Ann. Physik*, 1922, [iv], **68**, 73; *A.*, ii, 675.

be washed out unless the hydroxide is first dried and powdered; when thus purified and dried, it approximates closely to the composition $\text{Gl}(\text{OH})_2$.

The form of the 25°-isotherm for the system $\text{GlSO}_4-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$ shows that over the range 27—30 per cent. of GlSO_4 and 28—37 per cent. of $(\text{NH}_4)_2\text{SO}_4$, the solid phase is the double salt, $\text{GlSO}_4, (\text{NH}_4)_2\text{SO}_4, 2\text{H}_2\text{O}$; ⁸⁷ and solubility determinations for glucinum sulphate in water indicate that $\text{GlSO}_4, 4\text{H}_2\text{O}$ is the only solid phase, and that the hexahydrate previously reported is not formed. ⁸⁸

Dilute magnesium amalgam absorbs ammonia with separation of a solid solution of magnesium hexammoniate, $\text{Mg}(\text{NH}_3)_6$, in mercury; ⁸⁹ and thermal analysis of the system magnesium-mercury shows the existence of the compounds MgHg_2 , with transition at 170° to MgHg , m. p. 625°; Mg_3Hg_2 , m. p. 562°; and Mg_2Hg , m. p. 580°. ⁹⁰

Magnesium perchlorate has been found to form a trihydrate as well as the hexahydrate previously described: it is completely dehydrated without decomposition at 250°, and the anhydrous salt has a remarkable avidity for water and has been proved to be an excellent neutral drying agent, rather slower in action than phosphoric oxide but as efficient as the latter at the ordinary temperature, capable of absorbing a greater quantity of water per unit weight, and easily regenerated by heating. ⁹¹ Evidence is adduced for the existence of magnesium sulphate octahydrate, having a transition point to the heptahydrate at 48.2°. ⁹²

An improved method is given for the electrolytic preparation of dilute calcium amalgam. ⁹³ Metallic calcium gives a vapour pressure curve which, by extrapolation, indicates a boiling point of 1240°; but the metal used contained nearly 3 per cent. of impurity, including 1.62 per cent. of magnesium, ⁹⁴ and it seems appropriate to repeat the protest entered in a previous Report against the use of impure or indefinite material in exact determinations. Pure calcium is found to be almost passive toward nitrogen, but the presence of more electropositive metals (K, Ba) or, better, calcium nitride favours reaction. ⁹⁵

⁸⁷ H. T. S. Britton, *T.*, 1922, **121**, 2612.

⁸⁸ *Idem.*, *ibid.*, 1921, **119**, 1967.

⁸⁹ A. G. Loomis, *J. Amer. Chem. Soc.*, 1922, **44**, 8; *A.*, ii, 294.

⁹⁰ R. P. Beck, *Rec. trav. chim.*, 1922, **41**, 353; *A.*, ii, 545.

⁹¹ H. H. Willard and G. F. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2255; *A.*, ii, 850.

⁹² S. Takegami, *J. Chem. Soc. Japan*, 1921, **42**, 441; *A.*, 1921, ii, 698.

⁹³ B. S. Neuhausen, *J. Amer. Chem. Soc.*, 1922, **44**, 1445; *A.*, ii, 643.

⁹⁴ N. B. Pilling, *Physical Rev.*, 1921, **18**, 362; *A.*, ii, 291.

⁹⁵ O. Ruff and H. Hartmann, *Z. anorg. Chem.*, 1922, **121**, 167; O. Ruff, *Z. physikal. Chem.*, 1922, **100**, 419; *A.*, ii, 377, 363.

The existence of solid calcium-ammonium at -15° to $+30^{\circ}$ is confirmed;⁹⁶ and new compounds of calcium chloride with 1 mol. of ammonia and of calcium bromide and iodide with 1, 2, and 8 molecules of ammonia have been prepared, and the vapour tensions of these and the known ammines determined.⁹⁷ The second calcium silicide previously reported and variously formulated by different workers, is now shown to be calcium monosilicide, CaSi or Ca_2Si_2 .⁹⁸

Strontium is completely insoluble in solid lead, but forms one compound, Pb_3Sr , m. p. 676° , which is said to form with lead a eutectic melting at the same temperature as lead.¹

Reaction between nitrogen in excess and compressed mixtures of barium carbonate with wood-charcoal or graphite attains a practicable velocity at 1300 — 1400° : in fifteen to thirty minutes at this temperature, formation of cyanide reaches a maximum of 65 per cent., which is not increased at 1600° . The primary change produces barium carbide, which then reacts with nitrogen to form cyanide; cyanamide formation is due to a secondary reaction which is facilitated by higher temperature.²

Barium sulphate dissolves in 98 per cent. sulphuric acid at 25° to the extent of 14.9 grams/100 c.c., and the solution contains barium sulphuric acid, $\text{H}_2[\text{Ba}(\text{SO}_4)_2]$, which can be accumulated and crystallised in the anode compartment by electrolytic transport. Barium selenic acid can be prepared in a similar manner or by crystallisation from a saturated solution of barium selenate in selenic acid.³

Thermal analysis shows the zinc-arsenic alloys to comprise two brittle compounds, Zn_3As_2 , m. p. 1015° , and ZnAs_2 , m. p. 771° ; ⁴ and indicates that magnesium and cadmium form one compound, CdMg , soluble in all proportions in either metal.⁵

Cadmium dissolves in aqueous ammonium nitrate quietly and without evolution of gas, and it has thus been proved that impurities in the metal form a net-like structure between the crystallites.⁶

Tests of the method previously described ⁷ for the purification of mercury by air at 150° showed that it removed lead completely

⁹⁶ E. Botolfsen, *Bull. Soc. chim.*, 1922, [iv], **31**, 561; *A.*, ii, 570.

⁹⁷ G. F. Hüttig, *Z. anorg. Chem.*, 1922, **123**, 31; *A.*, ii, 849.

⁹⁸ L. Wöhler and F. Müller, *ibid.*, 1921, **120**, 49; *A.*, ii, 293.

¹ E. Piwowarsky, *Z. Metallk.*, 1922, **14**, 300; *A.*, ii, 644.

² P. Askenasy and F. Grude, *Z. Elektrochem.*, 1922, **28**, 130; *A.*, ii, 445.

³ J. Meyer and W. Friedrich, *Z. physikal. Chem.*, 1922, **101**, 498; *A.*, ii, 644.

⁴ W. Heike, *Z. anorg. Chem.*, 1921, **118**, 264; *A.*, ii, 60.

⁵ L. Guillet, *Rev. Met.*, 1922, **19**, 359; *A.*, ii, 570.

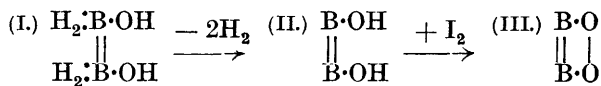
⁶ G. Tammann, *Z. anorg. Chem.*, 1922, **121**, 275; *A.*, ii, 502.

⁷ *Ann. Reports*, 1921, **18**, 45.

with a loss of 2 per cent. of mercury as against a loss of 3.7 per cent. when purification was effected in the usual way with nitric acid (d 1.175), but that tin was not completely eliminated by fifteen hours' air treatment (loss 1.4 per cent.) or by three passages through nitric acid (loss 9.2 per cent.).⁸ A study of the equilibrium between mercuric chloride, yellow mercuric oxide, and water at 35° shows the existence of two oxychlorides of mercury; $\text{HgCl}_2 \cdot 2\text{HgO}$, forming purplish-scarlet needles, and $\text{HgCl}_2 \cdot 4\text{HgO}$, a brownish-yellow amorphous substance which appears to form a solid solution with mercuric oxide.⁹

Group III.

The potassium salt of hexahydrodioxidyboron has been isolated. Magnesium boride is extracted with dilute aqueous potassium hydroxide, the extract is concentrated in a vacuum, separated from potassium metaborate and magnesium hydroxide and further concentrated, and the residue is washed with methyl alcohol and recrystallised two or three times in a vacuum from water free from carbon dioxide. It forms slightly deliquescent, colourless crystals, easily soluble in water. The solution has an alkaline reaction, is a powerful reducing agent, and yields hydrogen when acidified and even, slowly, on exposure to atmospheric carbon dioxide; concentrated nitric acid acts upon the solid salt so vigorously that the hydrogen evolved takes fire. The salt in solution evolves 2.95 per cent. of its weight of hydrogen; the residual solution can further absorb 1 atom of iodine for each two atoms of hydrogen previously evolved; and measurements of equivalent conductivity indicate that the molecular formula is $\text{K}_2\text{O}_2\text{B}_2\text{H}_4$.¹⁰ The properties of the salt thus confirm the earlier view¹¹ that aqueous extracts of magnesium boride contain the acid $\text{H}_6\text{B}_2\text{O}_2$, to which the structural formula (I) is attributed because it best represents the loss of hydrogen to form (II) and the subsequent interaction with iodine (III).



In the course of attempts to prepare complex polyborates, the pentaborates of potassium, rubidium, and thallium, $\text{M}^1_2\text{O}_5\text{B}_5\text{O}_{13}$, crystallising with 8, 10, and $8\text{H}_2\text{O}$, respectively, have been prepared.¹²

Crystalline aluminium hydroxide, identical under *X*-ray examination with the mineral *gibbsite*, begins to decompose only at 145° and

⁸ C. Harries and F. Evers, *Z. angew. Chem.*, 1921, **34**, 541; *A.*, 1921, ii, 698.

⁹ S. Toda, *J. Chem. Soc. Japan*, 1922, **43**, 312; *A.*, ii, 769.

¹⁰ R. C. Rây, *T.*, 1922, **121**, 1088.

¹¹ Of Travers, Rây, and Gupta.

¹² A. Rosenheim and F. Leyser, *Z. anorg. Chem.*, 1921, **119**, 1; *A.*, ii, 50.

at 200° still retains 8 per cent. of water, which is completely removed only at much higher temperatures. The product of dehydration at 275° adsorbs water, but does not combine with it. Alumina prepared by dehydration at 325° gives an X-ray pattern which indicates a structure, crystalline, but different from that of diaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or corundum; the product of calcination above 1000° gives the pattern of corundum.¹³

Aluminium chlorosulphoxide, $\text{AlCl}_3 \cdot \text{SO}_2$, is obtained by agitating powdered aluminium chloride with sulphuryl chloride for eight hours at 0–30° with rigid exclusion of water; when treated with sulphur or sulphur monochloride in sulphuryl chloride solution, it yields a crystalline precipitate of the compound $\text{Al}_2\text{Cl}_6 \cdot \text{S}_2\text{Cl}_2$. Both compounds are violently decomposed by water, in the latter case with separation of free sulphur, and are extremely active agents for the chlorination of organic compounds.¹⁴

It has been found that hydrochloric and sulphuric acids do not, as has been supposed, reduce thallic oxide, but dissolve it to form the corresponding thallic salts. The existence of an acid (or mixed) sulphate, with a ratio $\text{Ti} : \text{SO}_4 = 1 : 2$, has been confirmed; and the reduction of thallic salts by hydroxylamine, ferrous sulphate, and sodium arsenite has been found to proceed according to the equations $\text{Ti}_2\text{O}_3 + 2\text{NH}_2 \cdot \text{OH} \rightarrow \text{Ti}_2\text{O} + 3\text{H}_2\text{O} + \text{N}_2\text{O}$; $\text{Ti}_2(\text{SO}_4)_3 + 4\text{FeSO}_4 \rightarrow 2\text{Ti}_2\text{SO}_4 + 2\text{Fe}_2(\text{SO}_4)_3$; $\text{Ti}_2\text{O}_3 + \text{As}_2\text{O}_3 \rightarrow \text{Ti}_2\text{O} + \text{As}_2\text{O}_5$.¹⁵ There is reason to believe that Ti_2SO_4 , $\text{Ti}_2(\text{SO}_4)_3$ and $5\text{Ti}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3$ are the only thallic-sulphates which exist.¹⁶

Thermal analysis of the system $\text{Ti}_2\text{O}-\text{B}_2\text{O}_3$ indicates the existence of thallic ortho-, meta-, and pyro-borates, the first melting at 370° with decomposition and the others melting at about 474° and 434°, respectively.¹⁷ Double halides of thallium and bismuth, $2\text{TlBr} \cdot \text{BiBr}_3$ and $2\text{TlI} \cdot \text{BiI}_3$, precipitated by potassium bromide or iodide from nitric acid solutions of the constituent metals, form respectively lemon-yellow and red hexagonal crystals, readily hydrolysed to thallic halide, bismuth oxyhalide, and free halogen;¹⁸ and some double thiosulphates of thallium and arsenic, antimony, or bismuth, of the type $\text{Ti}_3\text{M}(\text{S}_2\text{O}_3)_3$,¹⁹ and complex or

¹³ L. H. Milligan, *J. Physical Chem.*, 1922, **26**, 247; *A.*, ii, 447.

¹⁴ O. Silberrad, *T.*, 1922, **121**, 1015.

¹⁵ A. J. Berry, *ibid.*, 394.

¹⁶ A. Benrath and H. Espenschied, *Z. anorg. Chem.*, 1922, **121**, 361; *A.*, ii, 504.

¹⁷ G. Canneri and R. Morelli, *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 109; *A.*, ii, 571.

¹⁸ G. Canneri and G. Perina, *Gazzetta*, 1922, **52**, i, 241; *A.*, ii, 512.

¹⁹ G. Canneri, *ibid.*, 37; *A.*, ii, 378.

²⁰ V. Cuttica and A. Paciello, *ibid.*, 141; *A.*, ii, 377.

double nitrites of thallium with copper, nickel, barium, or lead, $\text{Ti}_3[\text{Cu}(\text{NO}_2)_5]$; $\text{Ti}_4[\text{Ni}(\text{NO}_2)_6]$; $\text{TiNO}_2 \cdot 2\text{Ba}(\text{NO}_2)_2$; $2\text{TiNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ have been described.²⁰

A careful redetermination has been made of the densities of the oxides of six rare-earth metals (La, Pr, Nd, Sm, Eu, Gd),²¹ and a good deal of work, which cannot usefully be summarised here, has been done on the separation of the rare-earths by basic precipitation and kindred methods,²² and on the extraction of scandium from thorveitite and its purification.²³

Group IV.

The fusion of carbon at atmospheric pressure by resistance heating of carbon rods is reported: the solidified drops of carbon and the points from which they are detached are said to consist of pure graphite.²⁴ The observation that diamond is unchanged when heated at 1100° in carbon dioxide but becomes covered with amorphous carbon²⁵ would, if correct, seem to afford a possible means of preparing pure carbon without possibility of contamination with hydrogen, an attempt to obtain this by decomposition of carbon monoxide at 450° in presence of ferric oxide having failed.²⁶

When aqueous carbon dioxide is added to a large excess of ammonia, the anhydrous carbon dioxide immediately forms ammonium carbamate, which is sufficiently stable to permit the precipitation of the carbonate carbon dioxide as barium carbonate. This method has been applied to a study of the hydration of carbon dioxide in solutions of sodium hydroxide and sodium carbonate.²⁷

Iron pentacarbonyl is best obtained from iron and carbon monoxide at 200° and 300 atm. pressure; molybdenum carbonyl, formerly supposed to be $\text{Mo}(\text{CO})_6$, is now found to have a Mo : CO ratio 1 : 5.2, best represented by $\text{Mo}_5(\text{CO})_{26}$ or a similar complex formula. Two ruthenium carbonyls are obtained at 300—400 atm. pressure: one a crystalline solid of unknown composition, soluble in benzene but insoluble in alcohol or water; the other a chocolate-brown, amorphous solid, $\text{Ru}(\text{CO})_2$, insoluble in benzene, but soluble in

²¹ W. Prandtl, *Ber.*, 1922, **55**, [B], 692; *A.*, ii, 379.

²² W. Prandtl and J. Rauchenberger, *Z. anorg. Chem.*, 1921, **120**, 120, 311; W. Prandtl and J. Lösch, *ibid.*, 1922, **122**, 159; P. H. M.-P. Brinton and C. James, *J. Amer. Chem. Soc.*, 1921, **43**, 1397, 1446; *A.*, ii, 298, 770, 769, 62, 39.

²³ P. Urbain and G. Urbain, *Compt. rend.*, 1922, **174**, 1310; *A.*, ii, 504.

²⁴ E. Ryschkewitsch, *Z. Elektrochem.*, 1921, **27**, 445; 1922, **28**, 185; compare F. Sauerwald, *ibid.*, 1922, **28**, 183; *A.*, 1921, ii, 696; 1922, ii, 443.

²⁵ A. Foix, *Bull. Soc. chim.*, 1922, [iv], **33**, 678; *A.*, ii, 641.

²⁶ J. P. Wibaut, *Rec. trav. chim.*, 1922, **41**, 400; *A.*, ii, 565.

²⁷ C. Faurholt, *Z. anorg. Chem.*, 1921, **120**, 85; *A.*, ii, 272.

alcohol or water without decomposition.²⁸ The action of nitric oxide on cobalt tetracarbonyl causes evolution of carbon monoxide and yields a cherry-red liquid which has been definitely characterised as $\text{Co}(\text{CO})_3\text{NO}$, $d^{14} = 1.5126$; m. p. -1.05° ; b. p. 78.6° at 760 mm. Mol. wt. (from V.D.) = 171.7 (calc. $M = 173$); it decomposes slowly above 66° . Similar actions take place with nitric oxide and nickel pentacarbonyl or diferro nonacarbonyl, but the yields were too small to enable the composition of the products to be established.²⁹

Pure sugar charcoal, heated with sulphur at $400\text{--}1000^\circ$ at low pressures, yields a coke-like solid containing 2.0—3.5 per cent. of sulphur which is not extracted by toluene and is only partly oxidised by bromine water or removed by heating at 750° in hydrogen: this affords further evidence of the existence of stable solid sulphides of carbon.³⁰

Investigations of the solubility in hydrofluoric acid of the varieties of silicon obtained by crystallisation from solution in molten aluminium, silver, and copper lead to the conclusion that they differ mainly in degree of subdivision and are not really allotropic forms;³¹ a view confirmed by X-ray evidence that the structures of amorphous, graphitic, and crystalline silicon are identical.³²

Sodium metasilicate is found to yield three hydrates only: $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, rhombic, m. p. 47° ; $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$, monoclinic, m. p. 63.5° ; and $\text{Na}_2\text{SiO}_3 \cdot 4\text{H}_2\text{O}$, hexagonal, m. p. $83\text{--}85^\circ$, other hydrates mentioned in the literature being probably mixtures of these.³³

Much interesting work has been done on germanium, our previous knowledge of which was due very largely to Winkler, whose investigations were limited by lack of material. Germanium has been extracted from zinc residues containing about 0.2 per cent. of Ge by processes, described in detail in the original,³⁴ dependent on the volatility of the chloride with steam; in this way relatively large amounts of this very rare element have been obtained and are being utilised in a reinvestigation of its compounds.

Germanium dioxide is largely, but not wholly, reduced to metal by hydrogen at $550\text{--}900^\circ$; the metal reacts with pure bromine,

²⁸ R. L. Mond and A. E. Wallis, *T.*, 1922, **121**, 29.

²⁹ *Idem.*, *ibid.*, 32.

³⁰ J. P. Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 92; *Rec. trav. chim.*, 1922, **41**, 153; *A.*, ii, 52, 373.

³¹ W. Manchot, *Ber.*, 1921, **54**, [B], 3107; W. Manchot and H. Funk, *Z. anorg. Chem.*, 1922, **120**, 277; **122**, 22; *A.*, ii, 144, 286, 764.

³² W. Gerlach, *Physikal. Z.*, 1922, **23**, 114; *A.*, ii, 265.

³³ A. Erdenbrecher, *Mikrokosmos*, 1921, **15**, 55; *A.*, ii, 444.

³⁴ L. M. Dennis and J. Papish, *J. Amer. Chem. Soc.*, 1921, **43**, 2131; *A.*, ii, 150.

superficially at the ordinary temperature, completely at 220° , to form the tetrabromide, which is best purified by fractional distillation and then forms a white solid crystallising in regular octahedra, m. p. 26.1° , b. p. (corr.) 185.9° . The liquid can be supercooled to -18° and has $n_D^{25} = 1.6269$, $d_{25}^{25} = 3.1315$, and specific conductivity <0.000078 mhos. The tetrachloride, similarly prepared, and freed from chlorine by prolonged passage of a current of air, is a colourless liquid, b. p. 86.5° (corr.), m. p. -49.5° , $n_D^{25} = 1.3606$, $d_{25}^{25} = 1.874$. Both compounds fume in air and are slowly decomposed by water with a characteristic crackling sound, but are unchanged by strong sulphuric acid.³⁵

As an outcome of general investigations³⁶ on the preparation of gaseous metallic hydrides by the spark discharge and from alloys and solutions germanium hydride has been shown to have the composition GeH_4 and to be free from any considerable amount of other hydrides.³⁷ By a modified form of the Marsh test, the formation and decomposition of the hydride may be used as an extremely delicate test for germanium; and it may be estimated gravimetrically by precipitation as magnesium orthogermanate, MgGeO_4 .³⁸

Stannous hydroxide, prepared by precipitating aqueous stannous chloride with sodium hydroxide or ammonia, is stable in air, wet or dry, up to 110° , dissolves in acetic acid to form stannous acetate, $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$, has probably the formula $3\text{SnO}_2 \cdot 2\text{H}_2\text{O}$, and by keeping under water is converted into dark grey, crystalline stannous oxide, which is dispersed to a yellow, colloidal solution by excess of water.³⁹

The change of α -stannic acid to β -stannic acid is explained as due to the combination of stannic hydroxide (functioning as a base) with itself (functioning as an acid), and the theory receives support from measurements of the relative strength of the hydroxide as acid and as base considered in conjunction with the solubility of the α - and β -forms in hydrochloric acid and caustic alkali, as to which new facts are adduced.⁴⁰

The existence of lead monoxide in two forms, recently denied,⁴¹ has been conclusively proven. By slow cooling, solutions of lead oxide in aqueous caustic potash yield, according to the concentration of alkali, relatively large crystals of either the stable red tetragonal

³⁵ L. M. Dennis and F. E. Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299; *A.*, ii, 302.

³⁶ F. Paneth *et al.*, *Ber.*, 1922, **55**, [B], 769, 775; *A.*, ii, 383.

³⁷ F. Paneth and E. Schmidt-Hebbel, *ibid.*, 2615; *A.*, ii, 776.

³⁸ J. H. Müller and N. H. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909; *A.*, ii, 775; J. H. Müller, *ibid.*, 2493; *A.*, 1923, ii, 43.

³⁹ F. W. Bury and J. R. Partington, *T.*, 1922, **121**, 1998.

⁴⁰ G. E. Collins and J. K. Wood, *ibid.*, 441, 1122, 2760.

⁴¹ S. Glasstone, *ibid.*, 1921, **119**, 1914.

form or the metastable yellow rhombic bipyramidal form; and these forms differ in density, in solubility, and in *E.M.F.* against lead in normal caustic soda.⁴² There is some evidence that these forms are enantiotropic; but this point is in doubt, and further investigation is required to establish their relationship. Further physical investigation of the oxides of lead confirms the view of red lead as plumbous orthoplumbate and indicates the probable existence of a higher oxide in electrolytically deposited lead dioxide.⁴³

Examination of the *X*-ray spectra of rare-earth oxides has identified Urbain's celtium as the element of atomic number 72, intermediate between lutecium, 175, and tantalum, 181.5, and a member of this group.⁴⁴

Group V.

Formation of ammonia in good yield from hydrogen and excess of nitrogen in electron tubes occurs with applied electromotive forces equal to or greater than the ionisation potential of nitrogen; ⁴⁵ which is held to show that ionisation of nitrogen is the first step in this synthesis.

Decomposition of ammonium nitrate proceeds normally at 210–260°, yielding 98 per cent. nitrous oxide, but the presence of even 0.1 per cent. of ammonium or sodium chloride, or the over-heating of the pure nitrate, gives impure gas containing 30–50 per cent. of nitrogen; with the pure salt, the subsidiary reactions are probably $\text{NH}_4\text{NO}_3 \rightleftharpoons \text{NH}_3 + \text{HNO}_3$ and $5\text{NH}_3 + 3\text{HNO}_3 \longrightarrow 9\text{H}_2\text{O} + \text{N}_2$, and the explosive decomposition at 300° may be represented as $8\text{NH}_4\text{NO}_3 \longrightarrow 16\text{H}_2\text{O} + 2\text{NO}_2 + 4\text{NO} + 5\text{N}_2$.⁴⁶ Ammonium chlorate is perfectly stable in cold saturated aqueous solutions, but if solid salt is present progressive decomposition occurs which finally becomes explosive; the solid decomposes, rapidly if enclosed, slowly if exposed, the residue being ammonium nitrate free from chloride. These phenomena are due to autoxidation, catalysed by the products of decomposition.⁴⁷

A simple method has been described for the preparation of crystalline hydroxylamine by interaction of equivalent quantities of the hydrochloride and sodium ethoxide in absolute alcohol;

⁴² M. P. Applebey and R. D. Reid, *T.*, 1922, **121**, 2129; see also F. M. Jaeger and H. C. Germs, *Z. anorg. Chem.*, 1921, **119**, 145; *A.*, ii, 65.

⁴³ S. Glasstone, *T.*, 1922, **121**, 58, 1456, 1469, 2091.

⁴⁴ A. Dauvillier, *Compt. rend.*, 1922, **174**, 1347; *A.*, ii, 463; G. Urbain, *ibid.*, 1349; *A.*, ii, 505.

⁴⁵ E. B. Andersen, *Z. Physik*, 1922, **10**, 54; E. Hiedmann, *Chem. Ztg.*, 1921, **45**, 1073; *A.*, ii, 562; *A.*, 1921, ii, 694.

⁴⁶ H. L. Saunders, *T.*, 1922, **121**, 698.

⁴⁷ F. Fairbrother, *J. Amer. Chem. Soc.*, 1922, **44**, 2419; *A.*, 1923, ii, 27.

the product differs from the purest hydroxylamine hitherto obtained only in being rather less stable.⁴⁸

The mechanism of absorption of oxides of nitrogen by alkali is still in doubt; further evidence supports the view that oxidation of nitric oxide to nitrogen tetroxide proceeds without intermediate formation of nitrous anhydride; yet the absorption of a gaseous system NO-NO₂ by alkali hydroxide proceeds in a manner which can best be explained by assuming the presence of nitrous anhydride in small concentrations.⁴⁹ The fact that nitrogen pentoxide has unusual stability in presence of traces of ozone⁵⁰ is best explained by the assumption that its decomposition is catalysed by the products (which are reconverted immediately to pentoxide by ozone), as has been shown to be the case in the photochemical decomposition of nitrogen pentoxide and in the thermal decomposition of its solutions in carbon tetrachloride and chloroform.⁵¹

Evidence of the existence of an active form of hypophosphorous acid is again obtained from a study of its rate of reaction with cupric chloride; but any purely physical explanation⁵² is rejected in favour of the idea that there may exist an equilibrium between the ordinary acid and its tervalent form, HP(OH)₂, which would be expected to be very reactive.⁵³

Two interesting methods are described for the purification of phosphoric oxide, hitherto a very tedious and wasteful operation, very necessary in precise work, but often omitted. In one the oxide is dropped into a rapid current of oxygen in an iron tube at 600—700°, the sublimate being condensed in a long wide glass continuation tube; 50 grams of pure oxide can thus be prepared from 100 grams of crude material in an hour.⁵⁴ The second method is ingenious and very simple: commercial phosphoric oxide is heated at 175—220° in ozonised air until fully oxidised: the product still contains, of course, any non-volatile impurity originally present, but it is free from lower oxides and is no more liable than the resublimed oxide to yield gas in high vacua. Evidence was obtained that the phosphorous oxide present in commercial phosphoric oxide reacts

⁴⁸ H. Lecher and J. Hofmann, *Ber.*, 1922, **55**, [B], 912; *A.*, ii, 442.

⁴⁹ E. Briner, S. Niewiazski, and J. Wiswald, *Helv. Chim. Acta*, 1922, **5**, 432; *A.*, ii, 563; F. Foerster, *Ber.*, 1922, **55**, [B], 490; *A.*, ii, 284; A. Sanfourche, *Compt. rend.*, 1922, **175**, 469; *A.*, ii, 762.

⁵⁰ F. Daniels, O. R. Wulf, and S. Karrer, *J. Amer. Chem. Soc.*, 1922, **44**, 2402; *A.*, 1923, ii, 24.

⁵¹ Daniels and Johnston, *ibid.*, 1921, **43**, 53; R. H. Lueck, *ibid.*, 1922, **44**, 757; *A.*, ii, 433.

⁵² *Ann. Reports*, 1921, **18**, 41.

⁵³ A. D. Mitchell, *T.*, 1922, **121**, 1624.

⁵⁴ G. I. Finch and R. H. K. Peto, *ibid.*, 692.

with water to form phosphine which, under the influence of electrical discharges (for example, produced by friction between mercury and glass), reacts with mercury to form the phosphide (Hg_3P_2 ?) and hydrogen.⁵⁵

Phosphine, with but little hydrogen, is best prepared by the action of 10 per cent. sulphuric acid on aluminium phosphide.⁵⁶

A review of the past evidence and consideration of new experiments on the heat evolved by arsenic in cooling from various high temperatures confirm the transition point to yellow arsenic at about 750° , but indicates that whilst brown or "amorphous" arsenic may be, as has been supposed, a distinct monotropic modification, "grey" arsenic is probably not an allotropic form, but merely an intermediate stage in the conversion of colloidal arsenic to the crystalline state.⁵⁷ This is clearly a case in which X-ray analysis might give important information.

Arsenic combines with aluminium at 750° to give a brown, amorphous compound, Al_3As_2 , infusible and undissociated at temperatures up to 1600° , but apparently dissociating at the ordinary temperature, as old specimens slowly deposit yellow arsenic and leave a residue of black arsenic on solution in hydrochloric acid, whereas the freshly prepared substance is completely soluble in acid.⁵⁸

Bismuth subiodide, BiI_2 , has been obtained in red, orthorhombic needles, which dissolve in aqueous potassium iodide to an orange solution, act as a strong reducing agent, and decompose to the tri-iodide and bismuth at 400° .⁵⁹

It has been stated that tantalum pentachloride is a good conductor whilst columbium pentachloride is an insulator, but measurements with the anhydrous chlorides show that the conductivities are about the same and extremely small, about 0.25×10^{-6} mhos.⁶⁰

Group VI.

Liquid ozone and oxygen are only partly miscible, and are readily separated by fractional distillation. Pure ozone so obtained has been employed for a redetermination of physical constants (m. p. -249.7° ; b. p. -112.4° ; T_k -5° ; P_k 64.8 atm.; d^{-182° 1.71),⁶¹ and for an ingenious and skilful determination of vapour density

⁵⁵ J. J. Manley, *T.*, 1922, **121**, 331.

⁵⁶ L. Moser and A. Brukl, *Z. anorg. Chem.*, 1921, **121**, 73; *A.*, ii, 393.

⁵⁷ P. N. Laschtschenko, *T.*, 1922, **121**, 972.

⁵⁸ Q. A. Mansuri, *ibid.*, 2272.

⁵⁹ H. G. Denham, *J. Amer. Chem. Soc.*, 1921, **43**, 2367; *A.*, ii, 218.

⁶⁰ W. Biltz and A. Voigt, *Z. anorg. Chem.*, 1921, **120**, 71; *A.*, ii, 302.

⁶¹ E. H. Riesenfeld and G. M. Schwab, *Ber.*, 1922, **55**, [B], 2088; *A.*, ii, 637; *Z. Physik*, 1922, **11**, 12; *A.*, ii, 761.

by direct weighing of a bulb filled with ozone, the pressure at the time of filling being extrapolated from the observed growth of pressure in the bulb after weighing. The molecular weight found confirms the formula O_3 ,⁶² and neither investigation affords any evidence whatever of the existence of higher polymerides of oxygen.

Ozone oxidises nitrogen tetroxide instantly to the pentoxide, the completion of the quantitative reaction $N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$ being sharply indicated by disappearance of colour, so that a true *titration* can thus be performed in the gaseous phase.⁶³

Sulphur dioxide partly oxidises cuprous chloride in concentrated hydrochloric acid according to the equation (i) $2Cu_2Cl_2 + SO_2 + 4HCl \rightleftharpoons 4CuCl_2 + 2H_2O + S$; but the reverse change is obscured by a secondary action, (ii) $6CuCl_2 + S + 4H_2O \rightarrow 3Cu_2Cl_2 + 6HCl + H_2SO_4$. With increasing acid concentration, first cuprous sulphide, then mixtures of the sulphide and sulphur, and finally sulphur only are precipitated. A reaction analogous to (i) occurs with mercurous chloride in hydrochloric acid concentrations from 8*N* to 2*N*, whilst further reduction occurs (*a*) to mercurous chloride and mercury at 2*N* – 0.16*N*, and (*b*) to mercury only at acid concentrations less than 0.02*N*.⁶⁴

Sodium sulphite or bisulphite, dropped into warm dilute aqueous sulphuric acid, yields hydrogen sulphide, probably by the reaction $4H_2SO_3 \rightarrow H_2S + 3H_2SO_4$, which may well be an intermediate stage in the known reaction $3H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + S$; ⁶⁵ and there is evidence that hydrated sodium sulphite, excluded from air, undergoes autoxidation to sulphate.⁶⁶

Freshly prepared solutions of bisulphites show an absorption band characteristic of metabisulphites and therefore probably contain a small proportion of the latter in equilibrium; they are stable in light if oxygen is excluded, but in its presence are oxidised with formation of sulphate and develop an absorption band characteristic of hydrated sulphur dioxide.⁶⁷

Measurements of viscosity, conductivity, and contraction on mixing show that a complex, $H_2SO_4 \cdot H_2O \cdot (C_2H_5)_2O$, is present in systems of sulphuric acid, water, and ether.⁶⁸

Aluminium selenide, Al_2Se_3 , easily prepared from its elements

⁶² S. Karrer and O. R. Wulf, *J. Amer. Chem. Soc.*, 1922, **44**, 2391.

⁶³ O. R. Wulf, F. Daniels, and S. Karrer, *ibid.*, 2398; *A.*, 1923, ii, 23.

⁶⁴ W. Wardlaw and F. W. Pinkard, *T.*, 1921, **121**, 210; L. M. Stewart and W. Wardlaw, *ibid.*, 1481.

⁶⁵ G. M. Bennett, *ibid.*, 1922, **121**, 1794.

⁶⁶ S. L. Shenefield, F. C. Vilbrandt, and J. R. Withrow, *Chem. and Met. Eng.*, 1921, **25**, 953; *A.*, ii, 45.

⁶⁷ E. C. C. Baly and R. A. Bailey, *T.*, 1922, **121**, 1813.

⁶⁸ J. R. Pound, *ibid.*, 941.

as a light brown powder, unstable in air, affords, by reaction with acids, a convenient source of hydrogen selenide, which can be purified by liquefaction at -80° and re-evaporation. The dry gas is stable in ordinary daylight and unaffected by dry oxygen.⁶⁹ Hydrogen telluride has been prepared in a similar way and resembles the selenide except in its lesser stability to light and oxidation.⁷⁰ Further work is recorded on the properties of selenium oxychloride,⁷¹ and the oxybromide has been obtained, by the action of bromine on a mixture of selenium and selenium dioxide at 0° , as a reddish-yellow solid, m. p. 41.5° , b. p. $217^{\circ}/740$ mm. with much decomposition, $d_{20}^{25} 3.38$, which generally resembles the oxychloride in its remarkable chemical activity.⁷²

A convenient method is described for the preparation of selenium dioxide by combustion of selenium in oxygen containing nitrous fumes;⁷³ and it has been shown that it forms only one hydrate, $\text{SeO}_2 \cdot \text{H}_2\text{O}$.⁷⁴ Nitrosylselenic acid, $\text{NO} \cdot \text{O} \cdot \text{SeO}_2 \cdot \text{OH}$, obtained by the action of liquid nitrogen trioxide on anhydrous selenic acid, is a colourless, crystalline solid melting at 80° with decomposition and unstable even at the ordinary temperature.⁷⁵

Tellurium, purified by distillation and crystallised by solidification or sublimation, has $d 6.310$, which is unchanged by long heating at various temperatures. It is probable, therefore, that tellurium does not exhibit the dynamic allotropy which has been attributed to it.⁷⁶ Oxidation of tellurium tetrachloride with chlorine is a convenient method of obtaining pure telluric acid in almost theoretical yield.⁷⁷

A study of the solubility of chromium trioxide in sulphuric acid⁷⁸ shows that when the concentration of the latter is 85—95 per cent. the solid phase is brown, minutely crystalline $\text{CrO}_3 \cdot \text{SO}_3$; whilst in stronger acid the solid phase is probably the chromisulphuric acid, $\text{CrO}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$, described by Gay-Lussac and recently prepared, together with the corresponding chromiselenic acid and certain salts of these acids.⁷⁹

⁶⁹ L. Moser and E. Doctor, *Z. anorg. Chem.*, 1921, **118**, 284; *A.*, ii, 46.

⁷⁰ L. Moser and K. Ertl, *ibid.*, 269; *A.*, ii, 48.

⁷¹ V. Lenher, *J. Amer. Chem. Soc.*, 1922, **44**, 1664; *A.*, ii, 706; compare *Ann. Reports*, 1921, **18**, 53.

⁷² *Idem.*, *ibid.*, 1668; *A.*, ii, 707.

⁷³ J. Meyer, *Ber.*, 1922, **55**, [B], 2082; *A.*, ii, 639.

⁷⁴ W. Manchot and K. Ortnier, *Z. anorg. Chem.*, 1922, **120**, 300; *A.*, ii, 283.

⁷⁵ J. Meyer and W. Wagner, *Ber.*, 1922, **55**, [B], 690; *A.*, ii, 372.

⁷⁶ A. Damiens, *Compt. rend.*, 1922, **174**, 1344, 1548; *A.*, ii, 498, 562.

⁷⁷ J. Meyer and H. Moldenhauer, *Z. anorg. Chem.*, 1921, **119**, 132; *A.*, ii, 49.

⁷⁸ L. F. Gilbert, H. Buckley, and I. Masson, *T.*, 1922, **121**, 1934.

⁷⁹ J. Meyer and V. Stateczny, *Z. anorg. Chem.*, 1922, **122**, 1; *A.*, ii, 773.

The dichlorides of molybdenum, tungsten, and tantalum have been prepared, in some cases by new methods, and have been shown uniformly to be represented by the formula $\text{HM}_3\text{Cl}_{7.4}\text{H}_2\text{O}$ and not by the complex formulæ hitherto given to them.⁸⁰

Metallic tungsten acts slowly on thoria at 2400° in a vacuum and in argon, nitrogen, or hydrogen to form thorium and tungsten trioxide, the latter appearing in part to react with tungsten to form a grey, metallic, crystalline substance, very stable to acids and alkalis, which may be a "bronze" of the type $\text{Th}(\text{WO}_3)_n$, where $n = 3 - 10$.⁸¹

The green colour sometimes observed in tungsten trioxide is due to surface reduction to lower oxides,⁸² and X-ray examination of the hydrated oxides shows the existence of H_2WO_4 and H_4WO_5 as distinct compounds,⁸³ the former being confirmed also by the form of the vapour pressure-composition curve.⁸⁴ Evidence has been obtained that the sodium tungstate, $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$, is really an acid salt, $4(\text{Na}_2\text{WO}_4) \cdot 6(\text{H}_2\text{WO}_4) \cdot 17\text{H}_2\text{O}$, and corresponding salts of other bases, differing, however, in water content, have been isolated.⁸⁵

An icositetrahydrate of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, is found to exist at temperatures below -20° .⁸⁶

Group VIII.

The photography of the spectrum of fluorine, excited by the discharge between gold electrodes, deserves mention because of the attendant experimental difficulties.⁸⁷ A simple method for the preparation of pure ammonium hydrogen fluoride consists in treating aqueous hydrofluosilicic acid with excess of ammonia, filtering, concentrating in platinum, and subliming the product.⁸⁸

The existence of HClBr_2 , deduced by Berthelot from the heat of solution of bromine in hydrochloric acid, is confirmed and that of HClI_2 and HBrI_2 evidenced by measurements of the distribution of free halogen between aqueous halogen acids and an immiscible solvent.⁸⁹

The normal chlorites of sodium, lithium, calcium, strontium,

⁸⁰ K. Lindner *et al.*, *Ber.*, 1922, **55**, [B], 1458; *A.*, ii, 509.

⁸¹ C. J. Smithells, *T.*, 1922, **121**, 2236; compare E. Wedekind, *Edel-Erden und -Erze*, 1922, **3**, 109.

⁸² J. A. M. van Liempt, *Z. anorg. Chem.*, 1921, **119**, 310; *A.*, ii, 73.

⁸³ H. C. Burger, *ibid.*, 1922, **121**, 240; *A.*, ii, 508.

⁸⁴ G. F. Hüttig and B. Kurre, *ibid.*, 1922, **122**, 44; *A.*, ii, 773.

⁸⁵ E. F. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027; *A.*, ii, 774.

⁸⁶ F. E. E. Germann, *ibid.*, 1466; *A.*, ii, 649.

⁸⁷ W. R. Smythe, *Astrophys. J.*, 1921, **54**, 133; *A.*, ii, 99.

⁸⁸ M. Ikawa, *J. Chem. Soc. Japan*, 1921, **42**, 768.

⁸⁹ P. Rây and P. V. Sarkar, *T.*, 1922, **121**, 1449.

and univalent thallium have been prepared and are found to be unstable substances, exploding when dry by percussion and decomposed by heat, in the case of the sodium salt according to the equation $3\text{NaClO}_2 \rightarrow 2\text{NaClO}_3 + \text{NaCl}$.⁹⁰

An examination of the mineral fluocerite by means of the X-ray spectrograph has given indications⁹¹ that it may contain the element of atomic number 61, a member of this group.

Group VIII.

The amount of electrolytic iron foil dissolved by aqueous sulphuric acid (in thirty-four hours at 15°) has been found to vary with acid concentration in a remarkable manner, rising steadily with 0.5*N*- to 2*N*-acid, then falling with 3*N*-acid, and again increasing to progressively higher values with 4*N*- and 5*N*-acid. Another series of experiments shows that when a disk of pure iron is rotated for thirty minutes in acids of concentrations *N*/5, *N*/10, *N*/50, and *N*/100, the amount of iron dissolved depends only on the velocity of rotation, with which it increases linearly up to a peripheral speed of 35 m.p.h., in marked contrast to the corrosion of iron in aerated water, which ceases at a speed of 5 m.p.h.⁹²

Samples of ferric oxide prepared by twenty-seven different methods have been found to give identical X-ray spectra, which affords strong evidence that, despite their outward differences, they are really the same form of the compound.⁹³ A peculiar iron salt, $\text{FeSO}_4\text{Cl}\cdot 6\text{H}_2\text{O}$, has been obtained by treating a concentrated solution of ferrous sulphate with chlorine, and by other methods.⁹⁴

It is satisfactory to record the publication of a study of the general equilibrium in the system $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ from 50—200° which resolves in a convincing fashion the doubt and complexity associated with the hydrates and sulphates of ferric oxide. The components in suitable proportions were heated together in sealed tubes for times so prolonged as to ensure the attainment of equilibrium (its non-attainment being the probable cause of uncertain and conflicting results in many previous investigations of the system), and the liquid and wet solids were separated and analysed. Determination of the composition of the dry solid phase was effected by Schreinemakers's "residue" method, controlled by microscopic observations, especially of refractive index and dispersion. The results, embodied

⁹⁰ G. R. Levi, *Gazzetta*, 1922, **52**, i, 417; *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 212, 370; *A.*, ii, 567.

⁹¹ A. Hadding, *Z. anorg. Chem.*, 1922, **122**, 195; *A.*, ii, 780.

⁹² J. A. Newton Friend and J. H. Dennett, *T.*, 1922, **121**, 41.

⁹³ J. A. Hedvall, *Z. anorg. Chem.*, 1922, **120**, 327; **121**, 217; *A.*, ii, 300, 381.

⁹⁴ O. Röhm, *Collegium*, 1921, No. **614**, 282; *A.*, ii, 648.

in a series of triangular diagrams and a solid model, indicate that the only solid phases existing within the range studied are : ⁹⁵ Fe_2O_3 ; $\text{Fe}_2\text{O}_3, \text{H}_2\text{O}$; $3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 5\text{H}_2\text{O}$; $2\text{Fe}_2\text{O}_3, 5\text{SO}_3, 17\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3, 3\text{SO}_3$ (two forms : rhombohedral and orthorhombic); $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 6\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 7\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 3\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$. Other investigations confirm the existence, as phases stable in part of the system at 18° and 25° , of $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 7\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$.⁹⁶ The colourless form of iron alum occasionally encountered is shown to be due to the presence of ferric hydroxide as an impurity.⁹⁷

In the course of further studies on the properties of subsidiary valency groups, the trihydrate and tri- and hexa-ammines of cobaltous fluoride have been prepared.⁹⁸

Aqueous solutions of ruthenium tetroxide conduct electricity, have a weak acid reaction, and form salts with alkalis; but of these only the ammonium salt, $(\text{NH}_4)_2\text{RuO}_5$, could be obtained in a pure state.⁹⁹

⁹⁵ E. Posnjak and H. E. Merwin, *J. Amer. Chem. Soc.*, 1922, **44**, 1965; *A.*, ii, 772.

⁹⁶ M. P. Appleby and S. H. Wilkes, *T.*, 1922, **121**, 337.

⁹⁷ J. Bonnell and E. P. Perman, *T.*, 1921, **119**, 1994.

⁹⁸ G. L. Clark and H. K. Buckner, *J. Amer. Chem. Soc.*, 1922, **44**, 230; *A.*, ii, 300.

⁹⁹ F. Krauss, *Z. anorg. Chem.*, 1921, **119**, 217; *A.*, ii, 75.

H. V. A. BRISCOE.