variety and were identified as *Sirex Gigas*. The damage consisted of small holes through the bottom of a new sulphuric acid chamber. It was proposed to coat the timbers before covering with lead, with a thick mixture of gas-tar and creosote oil.—Conroy, (*Ibid.*, 1011), reviews the chemical trade of England as compared with that of Germany. The conclusions arrived at, are that as regards general chemicals and medicines, England's position is satisfactory, and that she holds her own as to volume of trade. But there appears evidence of a lag behind the times; the trade in fine chemicals, organic and inorganic and synthetic alkaloids, perfumes, etc., is not adequately represented in England. Many tables of imports and exports of Germany and the United Kingdom, are given. Thorne and Jeffers, (*Analyst.*, **31**, 101), have devised a method for purifying zinc from arsenic. The zinc is fused and treated with sodium.—about 1 gram per pound of zinc. The mixture is well mixed by pouring from one crucible into another, and then heated to just above the melting point of zinc, with exclusion of air, at first, and later with the crucible open. A crust forms, which is broken through and the metal poured off and heated considerably above its melting point, and after skimming, it is granulated. Arsenic can be removed from hydrochloric acid by the use of a copper-tin couple. —Baxter, (Eng. Pat. 5,209, (1905)), proposes to impregnate wood, textile fabrics, paper or other material, with a solution containing ammonium phosphate and boric acid, to render them less combustible and more resistent to water.

REVIEW OF INORGANIC CHEMISTRY.

JAS. LEWIS HOWE.

In this review the order of the Periodic System will be followed. Material which has already been treated in the *Review of American Chemical Research* in *this Journal* will be omitted, as well as most of the phenomena of radioactivity.

Group I. A new determination of the boiling points of the metals of the alkalies has been made by Ruff and Johannsen (*Ber.*, **38**, 3601), not less than 25 grams of each metal being boiled in a wrought iron retort, and the temperature measured by a platinum—platinum-rhodium thermoelement. Experiment showed that at the temperatures used, the metals did not attack the iron vessels. The results were: cesium, 670°; rubidium, 696°; potassium, 757.5°; sodium, 877.5°. Lithium did not volatilize at the temperature at which the retort melted, so that its boiling point is at least above 1400°. No simple mathematical formula could be found to express the boiling points as a function of the atomic weight. The lithium used in the experiments was prepared by the electrolysis of a mixture of lithium and potassium chlorides, but the same authors find (*Z. Elektrochem.*, **12**, 186) a better electrolyte in a mixture of lithium bromide with 10-15 per cent. lithium chloride. In a graphite retort with a thick iron wire as kathode and a current of 100 amperes at 10 volts the output is 80 per cent. of the theoretical. The metal obtained contained only a trace of sodium as impurity, and fused at 180°.

It has been found by Hofmann and Hiendlmaier (*Ber.*, **39**, 3184) that the burning of potassium to K_2O_4 is a powerful oxidizing agency. Most

metals are strongly attacked, platinum and gold being oxidized to potassium aurate and platinate, respectively. Copper, iron, nickel and cobalt are also oxidized, the latter two with the formation of crystalline compounds. In these the potassium is replaced by hydrogen on hydrolyzing with water. The nickel compound formed, $NiO_2.NiO.2H_2O$, is itself a strong oxidizing agent, attacking even cellulose.

In preparing sodium hydroxide by the useful method of Küster (allowing clean metallic sodium to deliquesce under a bell jar in a nickel gauze funnel over water), Harpf and Fleissner suffered from a terrific explosion (*Z. chem. Apparatenkunde,* 1, 534). Küster attributes this (*Ibid.,* 535) to the use of a shallow nickel gauze dish instead of a funnel. Some sodium hydroxide could collect on the crust left when impure sodium was used, and becoming diluted by absorption of water, would cause local heating when the metallic sodium happened to come in contact with it. Sodium seems often to contain some explosive compound, possibly a carbide, which explodes when heated. All danger can be obviated in this preparation if the funnel used is large and steeply inclined. As this method of preparing sodium hydroxide has come into quite extensive use, it is well that attention has been called to possibility of accident.

The blue color of many specimens of rock salt has been variously attributed to organic inclusions, to the presence of metallic sodium, and to a subchloride. A number of investigations along this line have been made the past year. Wöhler and Kasarnowski (*Z. anorg. Chem.,* 47, 353) have particularly studied the coloration of the alkali and alkaline earth halides by metallic vapors. The natural colorations can be in many cases nearly reproduced, but the artificially colored crystals show some decided differences from those naturally colored, particularly in the fact that much higher temperatures are necessary for decolorization. The authors seem inclined to favor the subhalide theory. Siedentopf (*Physik. Z.,* 6, 855) has studied the colored crystals under the ultramicroscope, and concludes that the color is due to the presence of minute crystals of the metal, perhaps so protected by films of the halide that even chlorine has no decolorizing effect. The particles of metal he estimates as smaller than 0.4μ. If a subhalide were the cause it must appear in many modifications and have substantially the same properties as the metal itself. Since sodium chloride absorbs strongly the Becquerel rays, the color of the natural mineral might be caused by the cumulative action of weak rays. Pieszczek (*Pharm. Ztg.,* 51, 700) shows by analysis that colored rock salt invariably contains 0.4 per cent less chlorine than pure salt, but he inclines to the theory that a subchloride is present, especially as the color of the blue salt is not affected by boiling with alcohol, or heating with mercury, however finely ground it may be. On the other hand the color seems to disappear in time, indicating the absence of any such protecting film of halide as is suggested by Siedentopf.

The work of Joannis on the alkali metals, which has appeared from time to time in the *Comptes Rendus,* has been collected in a paper in the *Annales de Chimie et de Physique* ((8) 7, 5). He finds, contrary to the results of Ruff and Geisel, later spoken of (p. 390), that the molecule of sodium-ammonium in liquid ammonia solution is $(NaNH_3)_2$ and that of potassium-ammonium is analogous. Potassium-ammonium dissolves metallic sodium at zero, and on allowing the ammonia to evaporate at ordinary temperatures, a liquid potassium-sodium alloy is left. An ex-

cess of lead reacts with sodium-ammonium forming $Pb_2Na.2NH_3$, which decomposes similarly. If the sodium-ammonium is in excess, sodamide is formed and a compound, Na_2Pb, which oxidizes with great rapidity in the air. Joannis also finds that when carbon dioxide comes in contact with sodium trioxide, Na_2O_3, sodium carbonate is formed and a quantity of oxygen liberated equal to the amount of carbon dioxide used. He therefore suggests the use of this oxide of sodium for the purification of air in submarine boats and other confined spaces, where men must remain for considerable lengths of time. Potassium carbonyl is decomposed with the formation of the carbonate and oxide and free carbon. The decomposition of sodium carbonyl is similar.

According to Rengade (*Compt. rend.*, **142**, 1149) perfectly dry oxygen acts energetically upon metallic cesium at ordinary temperatures, and more slowly at lower temperatures. The only oxide which seems to be formed is Cs_2O_4, analogous to the oxides of potassium and rubidium, but for the complete conversion of the metal into the oxide, it is necessary to heat it in an excess of oxygen for considerable time at above 300°. Dry carbon dioxide is without action upon this oxide at ordinary temperature. In the absence of moisture aluminum reacts neither with the oxide nor with the pure metal.

In a later paper (*Ibid.* **143**, 592) Rengade describes the normal oxide Cs_2O, which he prepared by the oxidation of excess of cesium, this excess being afterwards distilled off in a vacuum. The oxide forms orangered crystals which darken on heating, and absorb water and carbon dioxide from the air. The oxide is appreciably volatile at 200°, melts at 450° to 500°, and decomposes into the metal and an oxide Cs_2O_2.

In the electric furnace Moissan (*Ibid.*, **141**, 853, 977), has distilled copper, using a stream of 300 amperes at 110 volts. The vapor condenses on a cold copper tube in a felty mass of copper threads, which show all the properties of metallic copper. At its boiling point copper absorbs graphite, which crystallizes out when the copper cools. Gold distils easily at a temperature somewhat above that of copper, but below the volatilization point of lime. The condensed vapors are in part minutely crystalline. When gold-copper alloys are distilled, the copper passes off before the gold. Tin likewise vaporizes first in gold-tin alloys, and in this case it is possible to obtain purple of Cassius in the dry way. Different purples may be obtained by using different oxides, such as SiO_2, ZrO_2, Al_2O_3, etc. Like copper, gold absorbs graphite and gives it up in crystalline form on cooling. The boiling point of gold at 760 mm. is about 2530°. The molecular weight of silver vapor has been determined by von Wartenberg (*Ber.*, **39**, 381) by Nernst's method and found to be between 107 and 111. The molecule is therefore monatomic. As the iridium flask used was rapidly attacked by silver vapor, it was found necessary to coat its interior with zirconia and ceria. This was accomplished by repeatedly rinsing it with a nitrate solution of the earths and heating. In this manner it became coated in the interior with a glaze of the oxides.

Silver dioxide, Ag_2O_2, is found by Kempf (*Ibid.*, **38**, 3963, 3966) to be an energetic oxidizing agent, indeed the best for use in acid solutions. He prepares it by mixing silver nitrate with potassium persulphate. As the silver dioxide is continually regenerated, it is only necessary to have an excess of the persulphate present. The oxidation of oxalic acid to carbon dioxide by this mixture forms an excellent lecture experiment to illustrate

catalytic action. The reaction is quantitative. Benzene is instantly oxidized to benzoquinone, and this further into maleic acid, carbon dioxide, carbon monoxide and formic acid. Ammonia in ammonium salts is oxidized quantitatively into nitric acid, while its oxidation by the persulphate alone is never complete. The reaction with oxalic acid is useful for the determination of persulphates. Watson (*Pr. Chem. Soc.*, **21**, 297) finds that silver dioxide is stable at 100°, and soluble in nitric acid with the formation of a brown solution, which probably contains either $Ag_4(NO_3)_8$ or $Ag_2(NO_4)_2$. The black crystalline peroxide, formed at the anode on electrolyzing a solution of silver nitrate is not the dioxide, but a peroxide-nitrate, $Ag_7O_{11}N$. This is much more active than the dioxide and is decomposed by water and by organic substances, such as filter paper.

A long paper by Eder has appeared in the *Sitzungsberichte* of the Vienna Academy (*Math.-Nat. Kl.*, **114**, IIa), on the latent photographic image. His investigations show that the image is composed of a subbromide of silver of varying composition, according to the length of exposure to the light. The various stages of the action of the light are fully discussed.

Moir (*Pr. Chem. Soc.*, **22**, 105, 165) finds that gold leaf is readily soluble in an acid solution of thiocarbamide in the presence of oxidizing agents. The gold is present in a complex ion, and two crystalline salts containing this ion have been prepared, but the constitution of the salts is merely conjectural. A series of finely crystalline double acetates of gold with bivalent metals has been prepared by Weigand (*Z. angew. Chem.*, **19**, 139). The salts are soluble in water with neutral reaction and the solutions are fairly stable. The crystals are stable in the air and the author suggests that they would be suitable salts for atomic weight determinations of gold. They are prepared by precipitating gold with barium or other hydroxide and dissolving the precipitate in hot acetic acid. Barium meta-aurate, $Ba(AuO_2)_2.5H_2O$, a slightly soluble salt was also prepared.

Group II. Tests of refractory apparatus of magnesia are described by Arndt (*Chem.-Ztg.*, **30**, 211) and Wedekind (*Ibid.*, 329). The apparatus which comes in the form of crucibles, tubes, boats, etc., is more refractory than lime or alumina, having a melting point of about 2500°. It is about as resistant as porcelain and is not attacked by hydrochloric acid. Magnesia vessels are particularly to be recommended for use in the electric furnace. A very complete study of the carbonates of magnesium by Davis has appeared in the *Journal of the Society of Chemical Industry* (**25**, 788). The conclusion is reached that the compound which separates from a solution of magnesium hydrogen carbonate is not a hydrated normal carbonate but a mixed acid-basic carbonate of the formula, $HO.MgCO_3H.2H_2O$, formed by the partial hydrolysis of the magnesium bicarbonate.

A compound has been put upon the market by Jaubert under the name of hydrolith, for the generation of hydrogen. It is claimed to be of great value in military ballooning, since it is easily transported and on treatment with water generates 1000 liters of hydrogen per kilo. Hydrolith has been examined by Krull (*Z. angew. Chem.*, **19**, 1233) and found to be a compound of calcium and hydrogen, and is prepared by the action of calcium on a "metallic salt," but what salt is not stated. It has for some

time been known that the rapidity of evolution of hydrogen from water by metallic calcium can be very materially accelerated by previously heating the calcium in hydrogen. Guntz and Bassett (*Bull. soc. chim.,* [3] **35,** 404) have tried to prepare basic salts of calcium, by heating the metal with various salts in a vacuum and also in atmospheres of hydrogen, methane and argon. No evidence of basic salts was found, but it appeared that by the action of moisture on metallic calcium there is formed an equimolecular mixture of calcium oxide and calcium hydride. Guntz (*Compt. rend.,* **141,** 1240) has prepared pure barium by heating an amalgam of barium in hydrogen and then decomposing the hydride in a vacuum, condensing the barium in crystals on a cooled steel tube. Strontium was prepared in a similar manner (*Ibid.,* **142,** 200) and the thermochemical values of both metals determined. A full account of the properties of strontium amalgam and hydride, and of the pure metal is given in later papers (*Bull. soc. chim.,* [3] **35,** 494, 503).

While the subject of radioactivity is outside the scope of this review, a few points, especially regarding the occurrence of radium, may be noted. During the past year there has been much work done in determining the radioactivity of mineral springs. In connection with their examination of the Austrian hot springs, Mache and Meyer (*Physik. Z.,* **6,** 692) find in the mineral reissacherite, a highly hydrated wad from Gastein, the greatest known natural concentration of radium, and call attention to the fact that the mineral does not contain uranium, nor is uranium found in any mineral in the vicinity of Gastein. Schmidt and Kurz (*Ibid.,* **7,** 209), studying the springs of Hesse, draw the conclusion that practically all spring waters are radioactive, and that almost without exception all carry radium. They could trace no connection between the strength of emanation and the depth, temperature or chemical composition of the springs. In general, springs in eruptive rocks are much more active than those in sedimentary rocks. The least activity is in springs from limestone. Not all medicinal springs are active, but the most active of the hundred examined by the authors were of this class. Dienert (*Compt. rend.,* **142,** 449, 883) concludes that there is no connection between radioactivity and geological formation, but where the soils are richest in clay the radioactivity seems to be strongest. In no case is radium present in the water. The springs which have the highest activity are freest from bacteria. Sarasin (*Physik. Z.,* **6,** 708) found the air from the blowing well at Meyrin, near Geneva, ten times as radioactive as that of the surrounding atmosphere. As a demonstration of the evolution of helium from radium, Sir William Crookes (*Chem. News,* **94,** 144) fuses radium bromide on both electrodes of a vacuum tube and exhausts while the current is passing, until all the carbon dioxide has disappeared, and seals. No spectrum of helium is present, but after three months both the yellow and the green helium lines are visible. No sign of neon was found.

In investigating the phosphorescence of various sulphides, Jorissen and Ringer (*Congrès de Chim. pharm. de Liège,* 1905) confirm previous observations that pure calcium and barium sulphide do not phosphoresce, but the phenomenon is induced by minute traces of foreign substances, especially by bismuth. The same is true of zinc sulphide. Here, even in the absence of all heavy metals, small quantities of sodium, potassium or magnesium chloride induce phosphorescence, while large quantities of magnesium chloride inhibit it. If the phosphorescence is induced by

sodium or potassium chloride, manganese compounds increase it, copper lessens it, while platinum and silver completely suppress it. Treatment with hot water does not affect the phenomenon. The foreign salts appear to be present in solid solution. Similar results are found regarding the phosphorescence of barium sulphide, in an extended paper by Mourelo (*An. Soc. espagn. fis. et quim.*, **2**, 335, 374).

A new resemblance of cadmium to magnesium and the metals of the alkaline earths has been found by Manchot (*Ber.*, **39**, 1170). When cadmium burns, the monoxide is not exclusively formed, but small quantities of the peroxide. This can be shown by burning cadmium at the lowest possible temperature in order to avoid the volatilization of the metal, and condensing the fumes in a beaker moistened with an acidified solution of potassium iodide. Iodine is immediately set free by the condensed peroxide.

A number of papers have appeared (*Compt. rend.*, **141**, 1015; **142**, 395, 573, 887, 1338; **143**, 313) by Duboin on the iodo-mercurates. The most common type is $M''HgI_4$, the sodium salt forming a tetrahydrate, the lithium a hexa- and an octohydrate, the calcium an octohydrate, barium a pentahydrate, and magnesium a nonohydrate. Barium forms the compound, $BaHg_5I_{12}.8H_2O$, and strontium gives the same type. Calcium, barium, magnesium and manganese also give other types. The specific gravity of all the salts was determined. All crystallized from concentrated solutions over sulphuric acid and all are instantly decomposed by water. They are generally soluble in most organic solvents. Foote and Levy (*Am. Ch. J.*, **35**, 236) have recently described a number of sodium, potassium, rubidium and cesium chloro-mercurates, but none of them belong to any of the types found by Duboin for the iodo-mercurates. Mascarelli (*Atti accad. Lincei, Roma*, [5] **15**, ii, 192) has investigated the question of the modifications of mercuric iodide which form on crystallization. While from solutions in the nitro aromatic derivatives at low concentrations the red form separates, at somewhat higher concentrations both forms, and at high concentrations only the yellow form, he nevertheless concludes that in reality it is in all cases only the yellow metastable form which crystallizes out, and the different results are due solely to the velocity of transition to the stable red form. This crystallization would then be in accordance with the general rule that the metastable form should be at first formed.

Group III. An investigation of the manganese borides, MnB and MnB_2, prepared by Wedekind, shows that they are magnetic substances (*Z. Elektrochem.*, **11**, 850). The antimonide is somewhat less magnetic and the arsenide when prepared is not magnetic, but becomes so on heating in the air. The bismuthide, phosphide, carbide, and sulphide are also magnetic, but the silicide is not. The magnetism in these cases appears to be a property of the molecule, while the magnetism of iron, cobalt and nickel is a property of the atom. The sulphide of boron is, according to Hoffmann, (*Z. angew. Chem.*, **19**, 1362) readily prepared by heating the boride of iron in a stream of dry hydrogen sulphide. It sublimes in the colder portion of the tube, in part in fine white brilliant crystals, and in part as an amorphous powder. It can be freed from the small amount of accompanying sulphur by washing with carbon bisulphide. This method is a great improvement upon the old process of Wöhler and Deville, using amorphous boron.

The past year has been one of considerable activity among the workers on the rare earths. After daily fractioning for several years, Urbain has isolated some 50 grams of dysprosium and determined its atomic weight as 162.49. It forms a white oxide and yellowish green salts. It gives every sign of uniformity, and Urbain (*Compt. rend.*, **142**, 785) identifies it with Zγ and Zα of deBoisbaudran, Δ of Demarçay, X₂, of Exner and Gδ of Crookes. Urbain also (*Ibid.*, **141**, 954) discusses the phosphorescence spectra of the rare earths from the standpoint of mixtures of large masses of one element excited by traces of another, and draws the conclusion that Crookes' victorium is in reality a mixture which contains gadolinium. Urbain further (*J. chim. phys.*, **4**, 31) sums up his papers for the past seven years with some general conclusions, including the theory of fractionation. He says: The rare earths can be classified with reference to their solubility in a fixed order, viz., lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium. This order holds for many physicochemical properties, and is in the opinion of the author a good guide in the separation of the earths. There are a few exceptions, as in the solubility of the nitrates and the ethyl-sulphates, and in the atomic weight of cerium. In a later paper (*Ibid.*, 321) Urbain positively identifies gadolinium with Crookes' victorium. Matignon (*Compt. rend.*, **141**, 1230; **142**, 83; *Ann. chim. phys.*, [8] **8**, 364, 386, 402, 417, 426, 440) has studied particularly the chlorides of the rare earths. Among the chlorides of samarium he finds a type, new among the rare earths. When samarium chloride, $SmCl_3$ is heated in hydrogen or ammonia or with the calculated quantity of aluminum powder, it is reduced to the dichloride, $SmCl_2$, which is soluble in water, but not in alcohol and other organic solvents. It oxidizes very readily. He thinks it probable that the didymiums form similar compounds, but has not yet been able to prepare them. Feit and Przibylla (*Z. anorg. Chem.*, **50**, 249) have determined the atomic weights of a number of the rare earths volumetrically, by dissolving the oxides in $N/2$ sulphuric acid and titrating back the excess of acid with $N/10$ sodium hydroxide. They ascribe the discordant results of other workers, not to the imperfect separations of their material, but to defects in the ordinary analytical method, that of changing the sulphate into the oxide by heat. Holmberg (*Chem. Centrbl.*, **1906**, II 1595) in a paper from the Upsala laboratory on didymium, claims that all the previous neodymium preparations have been impure and hence the atomic weights found have been discordant. By using metabenzene sulphonate, he has prepared pure neodymium, and finds the atomic weight 144.08. He advocates the use of the salts of organic acids for the separations of the rare earths, and especially the use of the sulphonic acid salts. He gives the composition and solubility of a large number of organic salts of the rare earths.

Group IV. The problem of the genesis of the diamond has been attacked by Koenig (*Z. Elektrochem.*, **12**, 441) from the standpoint of physical chemistry. Above 1000° graphite is the stable form of carbon. It is as yet uncertain whether at a lower temperature there is a transition-point between diamond and graphite, or whether the diamond is at all temperatures a metastable form. Since the specific volume of the diamond is less than that of graphite, the transition-point should rise with increasing pressure. At low temperatures, however, even at high pressures, the formation of the diamond from graphite is improbable, owing

to the low velocity of the transition. At high temperatures it can only occur when the formation of the metastable form is accelerated. Possible methods of diamond crystallization are (1) from fusion, (2) from sublimation, and (3) from solution. The last method has thus far promised the best results, but the proper solvent seems not yet to have been found. The author has experimented with the deposition of carbon formed by the decomposition of carbonic oxide at 1000° on a glazed porcelain tube, but although he has placed a pure diamond crystal in the condensing gas, the only result has been to obtain a ring of black coal. Kahn (*Compt. rend.*, **143**, 49) finds that it is possible by continued heating to obtain a calcium carbide with an excess of carbon, up to 5 per cent. As the carbide begins to decompose by further heating the carbon is precipitated as graphite. The author attributes the phenomenon to the solution of graphite in fused carbide.

During the year considerable study has been put upon the compounds of silicon and many new silicides have been prepared. Vigouroux has worked (*Ibid.*, **141**, 951; **142**, 87) on the compounds of silicon with aluminum and copper. Pure aluminum does not unite with pure silicon, but if a third metal is present, well defined crystalline compounds are formed. Such were prepared with fourteen metals, as iron, chromium, vanadium, lead and antimony. They can be prepared by fusing the three elements together in a hydrogen atmosphere in a furnace, by the thermite process, or by the reduction of potassium fluosilicate with aluminum in the presence of the other metal or its oxide or sulphide. The aluminosilicides are all metallic in appearance, hard, and rather brittle, attacked by alkalies, but generally resistant to acids except hydrofluoric. The author calls attention to the fact that clay crucibles should be avoided in operations which could give rise to these compounds. While copper unites readily with silicon, the amount which it can take up by direct fusion with excess of silicon is about 10 per cent. When this mass is again heated with a large excess of silicon there remains after treatment with dilute alkali the compound, Cu_4Si. This copper silicide is metallic, hard and brittle, silver white when prepared, but becoming red or yellow in a short time. It is little attacked by alkalies and dilute acids except nitric, and is completely dissolved by a mixture of nitric and hydrofluoric acids. Lebeau (*Ibid.*, **141**, 889; **142**, 154) finds that this silicide fuses at about 800°. He also notes that the amount of silicon which remains in combination with copper is very considerably influenced by the rapidity of cooling. When the rate is slow, a much larger quantity of free silicon separates out. Hönigschmid (*Ibid.*, **142**, 157; **143**, 224) has prepared the silicides of thorium, zirconium and titanium. Thorium silicide is prepared by the action of aluminum on a mixture of potassium fluothorate and fluosilicate, and has the formula, $ThSi_2$. The silicides of zirconium and titanium are similarly prepared and have analogous formulas. The first is resistant to solutions of alkalies and to nitric acid, and the other two are resistant to all acids except hydrofluoric, as well as to alkalies. Guertler and Tammann have investigated (*Z. anorg. Chem.*, **49**, 93) the nickel silicides by physicochemical methods and find in the fusion curves two maxima corresponding to the compounds, Ni_2Si and $NiSi$. By slow cooling of the nickel-silicon mixtures they find evidence of the further compounds, Ni_3Si and Ni_3Si_2. In a similar investigation (*Ibid.*, **50**, 117) on the manganese-silicon mixtures, Doerinckel finds Mn_2Si and $MnSi$.

Jordis finds (*Z. Elektrochem.*, **11**, 835) that when a pure silica hydrogel is put into a solution of an electrolyte decided quantities of the salt are adsorbed or absorbed. Such a hydrogel which contains an electrolyte, when immersed in pure water gives up salt, but a portion is in any case retained. When washed with cold water there is a steady decrease of the salt in the wash water until at last no more salt is removed from the hydrogel. On the other hand, when warm water is used the removal of the salt is irregular and seems to undergo periodic variations. From this Jordis concludes that the adsorption of salts by hydrogels is a complex phenomenon, whose nature is not understood.

Biron has contributed several papers in continuation of his work on the chlorostannates. These papers (*J. russ. phys. chem. Ges.*, **37**, 963, 994, 1036) deal with the hydrolysis of stannic chloride, especially as influenced by the presence of other chlorides. From the inhibition of the hydrolysis he obtains the relative tendency to form chlorostannates. The highest results are found for lithium chloride, while potassium chloride gives values about half as great. The chlorides of the bivalent metals lie between these two, with the exception of zinc and cadmium chlorides, which show very low figures. Pélabon (*Compt. rend.*, **142**, 889, 928) has determined the solidification point curves for mixtures of tin with sulphur, selenium and tellurium. The addition of sulphur to tin raises the solidification temperature very rapidly at first and then more slowly until a maximum is reached when the composition is SnS. Beyond this point the curve begins to fall but it can be followed only a short distance, as the mixture loses sulphur when heated. The tin-selenium curve is analogous to the tin-sulphur curve up to its maximum at $SnSe$. It then falls slowly and regularly until the proportion of tin is insignificant. Sn_2Se_3 does not exist in the liquid state as a compound, for the mixture with this composition shows two solidification points. The mixture which corresponds to the composition, $SnSe_2$, however, has a single solidification point, but the curve shows no irregularity at this point. The tin-tellurium curve is very similar to that of tin-selenium. The maximum is at the composition, $SnTe$. The curve shows no peculiarities at the points corresponding to Sn_2Te_3 and $SnTe_2$.

In his work on the distillation of metals in the electric furnace, elsewhere noticed in this review, Moissan finds (*Ibid.*, **142**, 673) that titanium distils very slowly, but regularly. The distilled metal shows the same properties as the ordinary fused metal. From the fact that the maximum temperature of the electric furnace is according to Violle not far from 3500°, and in the electric arc all known elements and compounds can be volatilized, it follows that the temperature of the sun need not be above 3500° in order to give its spectrum. Owing to higher pressures, however, on the sun, and the consequent raising of the volatilization point, it is possible that the temperature of the sun should actually somewhat exceed this, but it probably lies nearer Violle's temperature of 2000°-3000°, than that proposed by Wilson of 6590°.

An interesting preparation of thorium hydroxide in hydrosol form is described (*Ber.*, **39**, 2857) by Müller. He peptonizes the freshly precipitated gelatinous hydroxide by a small amount of thorium nitrate solution. This hydrosol can be preserved a long time and even be boiled without gelatinizing. It can also be evaporated to a varnish, which upon the

addition of water goes slowly into a colloidal solution. It is precipitated by acids and alkalies, but not by neutral salts.

Group V. A number of experiments with liquid nitrogen are described by Erdmann in the *Berichte,* (39, 1207), the nitrogen being condensed in an apparatus devised by the author from compressed nitrogen, which is a commercial article in Germany. Liquid nitrogen, having a lower boiling point than oxygen, furnishes a convenient means of getting very low temperatures. It is also an excellent solvent, and Erdmann suggests its use for the determination of the molecular weight of ozone in solution. While an ignited magnesium wire is extinguished in liquid nitrogen, if the liquid is mixed with filings of metallic calcium, the mass can be ignited by the Goldschmidt mixture, and the calcium burns to the nitride. Other experiments are described in the paper. Guntz and Bassett (*Bull. soc. chim.,* [3] 35, 201) find that the best method of preparing copper nitride is to heat freshly precipitated and dried cuprous oxide in a dry ammonia stream at 265°. No nitride is produced when lithium nitride reacts with cuprous chloride, and but little by the action of ammonia on crystallized cuprous or cupric oxide. Copper nitride has the formula, Cu_3N; it is dark green, and is easily acted on by acids and slowly by alkalies with the production of ammonia. With concentrated nitric acid, one-half of the nitrogen is oxidized, only half being given off as ammonia.

By the hydrolysis of hydroxylamine-trisulphonates, Haga (*J. Chem. Soc.,* 89, 240) has obtained a new series of disulphonates, which he designates as α-β-sulphonates in distinction from the β-β-sulphonates which were first prepared by Frémy. The formulas of the two series are respectively $KSO_3.ONH.SO_3K$ and $HO.N(SO_3K)_2$, and this is considered by Haga to be the first undoubted instance of structural isomerism in inorganic chemistry.

A very considerable amount of work has been done the past year upon metal ammoniums and the metal-amines. Ruff and Geisel (*Ber.,* 39, 828) have taken up anew the question whether the so-called metal ammoniums of the alkalies have a real existence, and answer the question in the negative. When a metal of the alkalies or of the alkaline earths is dissolved in liquid ammonia, on evaporation of the ammonia, a red mass is left which has long been considered to be a metal ammonia, or a metal-ammonium, according to the way a formula like $NaNH_3$ is to be interpreted. The authors find that this red mass is really a mixture of the metal with a saturated solution of the metal in ammonia. By using a linen filter and pressure at a very low temperature, they succeeded in filtering off the solution and leaving the metal in a more or less compact state. The authors made a complete study of the solubility of the metals in question in liquid ammonia, and found no evidence of the formation of any compound. The possibility that on solution there was the formation of a metal amine and a metal hydride which could react upon each other with the formation of the metal and ammonia, was negatived by studying the behavior of both these classes of compounds, alone and in conjunction. In the light of their paper, the conclusion that the solution of these metals in ammonia does not contain such compounds as $NaNH_3$ seems well justified. Working on a solution of strontium in ammonia, Roederer (*Bull. soc. chim.,* [3] 35, 715) finds that on evaporation in a vacuum strontium amide, $Sr(NH_2)_2$, is formed. When oxygen acts at a low temperature on the

solution, the result is the formation of a mixture of the oxide and the peroxide. Carbon monoxide forms strontium carbonyl, $Sr(CO)_2$, and nitric oxide forms a precipitate of strontium hyponitrite, $Sr(NO)_2$. If strontium is heated at 200° in a stream of ammonia, it is partially converted into the amide, and at 800° a mixture of strontium nitride and hydride results.

By the action of liquid ammonia on anhydrides of the fifth and sixth groups, Rosenheim and Jacobsohn (*Z. anorg. Chem.*, **50**, 297) have prepared an interesting series of salts, which seem to be imino-acid salts. Chromium trioxide with ammonia gives a brown compound, easily soluble in water, and readily losing ammonia, which has the composition $CrO_3.4NH_3$. When treated with lead iodide this gives a heavy powder, whose composition approaches the formula $(NH_3)_4(CrO_3)_2Pb$. This the authors consider to be the lead ammonium salt of imino-chromic acid, the formula being written $Pb(OCrO(NH)ONH_4)_2$. A potassium ammonium salt of this acid, KNH_4CrO_3NH, is prepared by the action of ammonia on potassium chlorochromate. A more complex imino-salt was obtained by the action of ammonia on chromyl chloride. Similar salts were obtained with molybdenum and tungsten trioxides and with arsenic pentoxide.

In the oxidation of ammonium chromate with hydrogen peroxide, Riesenfeld finds that in the presence of insufficient hydrogen peroxide or when the temperature of the solution is allowed to rise above zero, there is formed perchromic acid triamine, $CrO_4.3NH_3$. While this salt crystallizes in two different habits, there are not two isomeric compounds as supposed by Hofmann and Hiendlmaier, but the two forms are probably identical compounds. By a similar oxidation of chromic acid in the presence of ethylene diamine, a perchromic acid compound of this base is formed, $CrO_4.C_2H_8N_2.2H_2O$, and in an analogous manner the hexamethylene tetramine derivative, $CrO_4.C_6H_{12}N_4$, was obtained. More than a dozen papers have appeared during the year from Werner and from Pfeiffer on the chromium and cobalt ammonia bases, but the limits of this review preclude even a brief summary of the results on this interesting class of compounds. Similarly several papers of Gutbier's on the palladosamines must be passed with mere mention. Jörgensen continues his work on the platinum bases, retaining the old constitutional formulas. He describes a new isomer of the salt of Magnus, (*Ibid.*, **48**, 441) formed by the action of platodiaminechloride on potassium chloroplatinate. Unlike the other isomers, the salt is red, and it goes over into the green salt on boiling with water, but the action does not appear to be reversible. Tarugi gives (*Gazz. chim. ital.*, **36** i, 364) an easy method of preparing quantitatively the hydroxyplatidiaminesulphate of Cleve. The ordinary solution of chloroplatinic acid is treated with a strongly ammoniacal concentrated solution of ammonium perchlorate and warmed. The ammonium chloroplatinate at first formed goes into solution and just as the boiling point is reached there is suddenly a copious precipitate of $(HO)_2Pt(NH_3)_4SO_4$.

The problem of the fixation of atmospheric nitrogen is recognized as one of the most important in the whole realm of chemical technology. An exhaustive paper on the subject was read by Guye at a meeting of the London Section of the Society of Chemical Industry last May (*J. Soc. Chem. Ind.*, **25**, 567). Two methods of accomplishing the desired result have already been put into practice. The first of these, which is said to be

a commercial success at Notoden, Norway, and possibly elsewhere, consists in burning nitrogen in the electric arc. Equilibrium is reached when a very low percentage of NO is present, but the higher the temperature, the more NO is formed. The calculated theoretical yield is 1800 kilos of pure nitric acid per kilowatt year, and while the most favorable results published indicate a production of 900 kilos, 500 kilos seems to be a fair average. This would seem to indicate that the process could be used successfully when the cost of the current is very low. The other method thus far found for the commercial fixation of nitrogen is the heating of calcium carbide in nitrogen, when calcium cyanamide is formed. This by the action of water is converted into calcium carbonate and ammonia. As this reaction goes on in the soil, it is proposed to use the cyanamide directly as a fertilizer. The observations as to its value in comparison with the same amount of nitrogen as ammonia are by no means concordant, and it is obvious that the experiments in this direction need to be further continued. At any rate, it can be said that the great problem of the utilization of the nitrogen of the air for fertilizing purposes is nearing an economical solution.

That yellow phosphorus is readily acted on by hydrogen peroxide is shown by Weyl (*Ber.,* **39**, 1307), hydrogen phosphide being evolved, while phosphorous and phosphoric acids are found in the solution. If amorphous phosphorus is used, or that described by Schenck, the action is more energetic, and with higher than 8 per cent. peroxide dangerous. Rosenheim, Stadler and Jacobsohn have studied (*Ber.,* **39**, 2837) hypophosphoric acid, and find that it is not a mixture of phosphorous and phosphoric acids. The mixture of these two acids acts in every way like a mixture, which is not the case with hypophosphoric acid, H_2PO_3. This they consider to be a derivative of quadrivalent phosphorus. By the action of methyl iodide on the silver salt, the methyl ester of hypophosphoric acid was easily formed, and boiling-point determinations showed the simple formula, $(CH_3)_2PO_3$. Quite a series of pyrophosphates have been prepared by Pahl (*Arkiv Kemi, 2 i,* No. 6) which show the fact that like the metaphosphates, the pyrophosphates form very complex salts, in which a number of P_2O_7 groups are present. An example is the salt, $K_2Pb_{13}(P_2O_7)_7.2H_2O$.

Besson and Rosset (*Compt. rend.,* **143**, 37) have continued the work of the former on the reaction between phosphorus trichloride and ammonium chloride, and find that the chloronitride formed has the formula, $(PCl_2N)_3$. It is soluble in organic solvents but not in water, though gradually decomposed by it. It forms an addition product with NO_2 and with SO_3, but these are unstable. Heated in a closed tube, the chloronitride reacts with NO_2, reducing it to N_2O, and the latter reacts with the phosphorus pentoxide, giving the addition product, $2P_2O_5.N_2O$. This latter can also be prepared by heating P_2O_5 with NO_2 in a closed tube. By the action of ammonia on phosphorus tribromide below —70°, Hugot (*Ibid.,* **141**, 1235) obtains phosphorus amide, $P(NH_2)_3$, which at zero decomposes into phosphorus imide, $P_2(NH)_3$. Phosphorus triiodide acts similarly at a somewhat higher temperature, but owing to its solubility in the ammoniacal ammonium iodide solution, the amide cannot be separated, though the imide can. The question of the existence of several sulphides of phosphorus is not yet settled. Giran (*Ibid.,* **142**, 398), recognizing that no compound of sulphur and phosphorus is formed below 100°, heated several mixtures of the two elements in a closed tube to 200° and then de-

termined the fusion points. He finds that the curve has four maxima and four minima. The former correspond to the compounds, P_4S_3, P_2S_3, P_2S_5, and PS_6. The minima indicate eutectic mixtures which would correspond to P_2S, PS, PS_2, and PS_3. Boulouch disputes (*Ibid.,* **142**, 1045; **143**, 41), these results, having studied in a similar way a mixture of phosphorus and P_4S_3. He finds that there is no compound between P_4S_3 and P_3S_5, and it is doubtful if P_3S_5 is a chemical individual. Only mention can be made of the extensive work of Stock and his pupils (*Ber.,* **39**, 1967) on the products formed by the action of ammonia on phosphorus pentasulphide. A number of series of imido- and nitrilo-thiophosphates have been prepared in which the imido group or the nitrogen atom replace the oxygen of phosphates and thiophosphates. The paper occupies forty pages of the Berichte.

Stock and Siebert (*Ibid.,* **38**, 3837) have prepared the yellow modification of antimony in quantities up to 0.1 gram by the action of chlorine on a solution of stibine in liquid ethane. It is much more unstable than the corresponding yellow modification of arsenic, and changes into the black modification at $-90°$. One form of explosive antimony described by Cohen, the authors think may be identical with the black modification. The black form of antimony is best prepared by decomposing stibine in a vessel surrounded by liquid air, the heat being furnished by an electrically heated platinum spiral surrounded with glass and immersed in the vacuum vessel into which the stibine is led. The most interesting work done in connection with bismuth is on some of its organic compounds. Rosenheim and Vogelsang (*Z. anorg. Chem.,* **48**, 205) have investigated the tartrates, preparing double bismuth tartrates with other acids and with the alkalies. They have also prepared thiocyanates, of the $(NH_4)_3Bi(SCN)_6$ type, one of which had previously been prepared by Vanino. Vanino and Hartl (*Arch. der Pharm.,* **244**, 216) have used an acetone solution of bismuth chloride as a precipitant for a large number of organic bases. The precipitates are well characterized compounds and are formed by the direct union of the base with one or several molecules of bismuth chloride, *e. g.,* $(C_6H_5)_2NH.BiCl_3$. They have also (*J. prak. Chem.,* [2] **74**, 142) prepared compounds of bismuth nitrate with mannitol, sorbitol and dulcitol. They find first that a solution of mannitol-bismuth nitrate in acetone is the best reagent for the preparation of organic salts of bismuth by double decomposition. The paper describes many salts of bismuth with organic acids.

Group VI. When sulphur dioxide and hydrogen sulphide act upon each other in the presence of water there is a precipitate of sulphur and polythionic acids are formed. Debus has described the precipitated sulphur as a new allotropic form, called by him $S\delta$ and capable of forming a colloidal solution. This has been investigated by Spring (*Rec. trav. chim. Pays-Bas.,* **25**, 253) and found not to be an allotropic form, but a hydrate of sulphur, $S_8.H_2O$. In its colloidal condition it can be freed from the polythionic acids by several month's dialysis, and then evaporated to dryness in a vacuum. It loses water very slowly over sulphuric acid, and hence has a perceptible vapor pressure, and while a part of the hydrate is thus destroyed, some of it will take up water again. Gautier (*Compt. rend.,* **142**, 1465) has studied the action of the vapor of water upon sulphides of the heavy metals at a red heat, and finds that in general hydrogen sulphide, sulphur dioxide and hydrogen are formed, the sul-

phide being in many cases more or less completely reduced to the free metal. Thus in the case of copper sulphides, Cu_2S, the reaction is $Cu_2S + 2H_2O = Cu_2 + SO_2 + 2H_2$. The sulphur in hydrogen sulphide is also oxidized by the oxygen of water at a red heat, SO_2 and hydrogen being the chief products, while sulphur, sulphuric acid and thionic acids are formed in small quantity. These experiments show that atmospheric oxygen is not necessary to account for the sulphur dioxide present in volcanic gases.

Further work upon the question of isomorphism between selenium and tellurium has been done by Pellini (*Atti. accad. Lincei, Roma*, [5] **15**, i, 629, 711; **15**, ii, 46). $(C_6H_5)_2TeBr_2$ is dimorphous, crystallizing from carbon disulphide in tetragonal crystals and from benzene in triclinic. From both media the corresponding selenium salt crystallizes in the triclinic system. Pellini finds that mixed crystals are easily obtained. Up to a little over 50 per cent. of the selenium salt the crystals belong to the triclinic system. Above 95 per cent. they have the habit of the tellurium crystals. Between these two points mixed crystals could not be obtained. The selenium and tellurium compounds are thus isodimorphous. In the case of the rubidium acid tellurates and selenates, for a very limited space (42 percent. to 53 percent. selenate) mixed crystals of the selenate type were formed, but those of the tellurate type could not be prepared. In general these results confirm those of Norris and Kingman (*Am. Ch. J.*, **26**, (1901), 318). Pellini also examined the solidification temperatures of mixtures of selenium and tellurium, finding that they all lie between the solidification temperatures of the components, and that the curve is regular. The elements thus form a continuous series of mixed crystals, and from this standpoint the two elements are to be looked upon as isomorphous. Three papers have appeared by Marc (*Ber.*, **39**, 697; *Z. anorg. Chem.*, **48**, 393; **50**, 446) on the conductivity of selenium. He finds that there are two allotropic forms of selenium, which he calls A and B, and whose transition point is 210°. A, when pure, hardly conducts electricity, but a trace of selenium dioxide makes it a conductor. The B form conducts electricity. The transition point can be displaced by traces of metals, silver particularly having great influence. It also appears that the transition equilibrium is affected by light and that this may be the cause of the influence of light on the conductivity of selenium. Attempts to prepare the iron alums of selenic acid have hitherto been unsuccessful. Roncagliolo (*Gazz. chim. ital.*, **35**, ii, 553) has prepared the rubidium and cesium alums by dissolving pure ferric hydroxide in excess of selenic acid and adding the alkaline carbonates. The crystals are violet and resemble the sulphate alums. Previous attempts appear to have been confined to the potassium and ammonium alums, and the author suggests that it might be possible to prepare these if temperatures below zero were to be used.

Biltz and Gärtner find (*Ber.*, **39**, 3370) that the preparation of metallic molybdenum by the aluminum process is very much simplified by using, instead of the volatile molybdenum trioxide, the dioxide, which they prepare by gently heating ammonium molybdate until the ammonia is given off and then reducing to the dioxide in a stream of hydrogen. They obtained an output 93 per cent. of the theoretical, and the metallic molybdenum was 98.5 per cent. pure. Rosenheim (*Z. anorg. Chem.*, **50**, 320) gives a useful method of preparing molybdic acid, which is applicable to the ammonium molybdate obtained from molybdenum residues in the

laboratory. An aqueous solution of commercial ammonium molybdate is prepared with 150 grams to the liter. This is poured at ordinary room temperature into an equal quantity of 29-30 per cent. nitric acid with constant stirring. To this solution is added solid ammonium nitrate in the proportion of 100 grams to the liter and dissolved by stirring; a few crystals of molybdic acid (molybdenum trioxide dihydrate) are then added. In from eight to ten days the precipitation of molybdic acid is complete.

Marckwald calls attention (*Ber.*, **39**, 200) to the fact that while most of the double salts of uranium do not act upon the photographic plate, this is not true of the uranyl nitrates of potassium, ammonium and rubidium. There is no difference in action of uranium salts on the electroscope, and the α- and β-radiation of all uranium salts appears to be the same. The action upon the plate is probably due to the strong fluorescence of these double salts, which does not disappear even after they have been preserved several weeks in the dark. It therefore appears that a portion of the Becquerel rays can be converted into light rays, and that this action is somewhat proportional to the strength of the fluorescence of the salt. All the salts which show this action upon the photographic plate are strongly fluorescent.

Group VII. Our knowledge of fluorine has been considerably extended by the work of Prideaux (*J. Chem. Soc.*, **89**, 316). Liquid fluorine does not dissolve iodine nor does it have any action upon it. The gas reacts with the formation of iodine pentafluoride, but no higher fluoride could be prepared. Similarly liquid fluorine has no action on bromine, but with the gas, bromine trifluoride is formed, and no pentafluoride. The trifluoride has according to Lebeau, who discovered it independently (*Compt. rend.*, **141**, 1018), very similar properties to those of fluorine itself. Prideaux further investigated the solid fluorides of selenium and tellurium prepared by Moissan, but failed to find evidence of any definite chemical compound. The hexafluorides are, however, formed at low temperatures. The tellurium hexafluoride is slowly but completely decomposed by water, but the selenium hexafluoride is much more stable. Neither has any action upon glass. The vapor pressure curves for these two compounds and for sulphur hexafluoride were obtained and found to be similar. SF_6, SeF_6 and TeF_6 have a vapor-pressure of 760 mm. at $-62°$, $-39°$, and $-35.5°$, respectively. The melting points of the first two lie below their temperature of vaporization at 760 mm., while that of TeF_6 lies just above. The critical temperatures are respectively: $54°$, $72.35°$, and $83.25°$. Their molecular volumes at temperatures equally distant from their melting points are practically the same. In these investigations tellurium was found to behave wholly as would be expected of an element of the sixth group. Lebeau (*Ibid.*, **143**, 425) in his further study of fluorine finds that down to $-182.5°$ fluorine has no action on chlorine. Liquid chlorine will dissolve fluorine, but there is no evidence of chemical combination. If water is present with fluorine and chlorine, a reaction takes place with the formation of hydrofluoric acid and hypochlorous acid, while a part of the water is decomposed by the excess of fluorine and oxygen evolved. Ruff and Graf have also continued their work on fluorine (*Ber.*, **39**, 67) proving the existence of arsenic pentafluoride, which had been foreshadowed by Moissan, from the action of fluorine on the trichloride. When antimony pentafluoride acts upon arsenic trifluoride, no pentafluoride of arsenic is formed, unless a molecule of bromine is added. AsF_3

is a colorless gas, boiling at —53°, not very active in the cold when dry, but attacking almost everything, even copper, when heated. Thomas and Depuis have published (*Compt. rend.*, **143**, 282) a number of reactions of liquid chlorine. Iodine dissolves with the formation of ICl_3 and the same compound is precipitated from several iodides, such as PbI_2. Bromine first forms BrCl and then apparently $BrCl_3$, though owing to analytical difficulties this was not satisfactorily established. Sulphur reacts with liquid chlorine only in the neighborhood of its boiling point, but selenium and tellurium react more readily, giving first the dichlorides and then the tetrachlorides. SO_2 unites directly to form SO_2Cl_2. Arsenic reacts near the boiling point and gold is attacked only with exceeding slowness, the trichloride being formed in both cases. Antimony and bismuth have no action and the same was found to be the case with lead chloride, manganese chloride and potassium permanganate. Carbon disulphide mixes in all proportions with liquid chlorine, but without any chemical action.

In the light of what has been done in this country on the chlorine content of waters, it seems a little surprising to find Knipscheer advocating (*Pharm. Weekbl.*, **42**, 1042) the chlorine content of rain water as a test for contamination. He would condemn a water with more than 25 mg. per liter and regard with suspicion one with 10 to 25 mg. (And this at Edam!). Jorissen (*Chem. Weekbl.*, **3**, 42) writing from Helder, shows that in the neighborhood of the North Sea, as also shown by Nonhebel, these figures do not hold. He gives the average of 92 rain waters as 29.6 mg., while two contained respectively 880 and 1090 mg. Later (*Ibid.*, 647) he gives 154 additional analyses, with an average of 32.5 mg. chlorine. In the paper of Knipscheer there is a useful method given of testing whether a cistern is free from outside seepage. Close beside the cistern, holes are made half a meter deep and into them is poured a solution of fluoresceine. After some ten days a portion of the water is shaken with animal charcoal and the coal then extracted with weakly alkaline alcohol. This reaction shows a trace of fluoresceine in the water.

Attention should be called to a series of papers by Bray on the oxyhalogen compounds and especially on chlorine dioxide, (*Z. physik. Chem.*, **54**, 463, 569; *Z. anorg. Chem.*, **48**, 217). The subject, too long for abstraction, is treated very fully and includes the interaction of the chlorine acids. Bernard (*Z. chem. Apparatenkunde*, **1**, 81) gives a simple method of preparing pure chloric acid by dissolving barium chlorate in water and adding with cooling the theoretical quantity of sulphuric acid. The use of this solution for oxidization in the place of potassium chlorate is suggested, especially to dissolve the sulphide of tin in the electrolytic determination of this metal in bronzes and brass. In a paper on the polyiodides of the alkalies, Abegg and Hamburger (*Z. anorg. Chem.*, **50**, 403) find the following to be stable at 25°: KI_7; NH_4I_3; RbI_3, RbI_7; RbI_9, CsI_3, CsI_9. Lithium and sodium form no solid polyiodide. The method of investigation consisted in shaking the crystals for some time in benzene or in a benzene solution saturated with iodine. In this solution the salts themselves are insoluble but the loosely bound iodine dissolves. The stability of the polyiodides, or what amounts to the same thing, the tendency to polyiodide formation, decreases from cesium to potassium, ammonium standing between rubidium and potassium.

Group VIII. The presence of Widmannstätten figures in an iron has been considered strongly confirmatory of its siderial origin, but it is

shown by Arnold and McWilliam (*Nature,* **71**, 32) that it is possible to reproduce these figures in small castings of steel which contain slightly less than a half per cent. of carbon. Such a steel when polished and etched shows a network of ferrite containing darker pearlite particles which strongly resemble the kamasite and taenite of meteorites. On heating and cooling again the figures disappear, and it is probably owing to slow cooling that they do not appear in large castings. The perennial question as to the cause of the rusting of iron seems not yet to be settled. Dunstan having shown that in the complete absence of carbon dioxide iron does not rust, he now with Jowett and Goulding (*J. Chem. Soc.,* **87**, 1584) takes the view that the water is directly decomposed by the iron with the formation of hydrogen, which is at once oxidized to hydrogen peroxide. This in turn unites with the ferrous oxide, oxidizing it to a hydrate. He proposes three equations: $Fe + H_2O = FeO + H_2$; $H_2 + O_2 = H_2O_2$; $2FeO + H_2O_2 = Fe_2O_2(OH)_2$. The oxidation of iron is hindered by the presence of substances which destroy hydrogen peroxide. By the action of air and water on copper, mercury, silver, lead, bismuth, tin and zinc, hydrogen peroxide is produced and can be recognized analytically, but this is not the case with iron. Those metals which are oxidized by hydrogen peroxide also oxidize in moist air, while those which hydrogen peroxide does not attack are not oxidized by air. The composition of iron rust is always that given above. These ideas are disputed by Divers (*Pr. Chem. Soc.,* **21**, 251), who considers that the reaction is merely the oxidation of iron by oxygen and water, the latter being considered as hydrogen hydroxide. He finds no evidence of hydrogen peroxide playing any part. Moody on the other hand (*Ibid.,* **22**, 101) insists that the cause is to be found in the presence of carbon dioxide, and that iron is not affected in the presence of moist air if precaution is taken to have every trace of carbon dioxide excluded. Further he holds that the composition of iron rust is not constant, but that ferrous oxide and carbonate are always present at first, though subsequently oxidized.

The occurrence of platinum and palladium in Brazil is the subject of a paper by Hussak (*Z. pr. Geol.,* **14**, 284) in which three types of occurrence are described. One from Rio Abaete in Minas Geraes, closely resembles the Uralian platinum, both in composition and in associated minerals. The second form is from Condado in the same state and is rich in palladium, running as high as 21 per cent., but contains no gold or silver. This is not accompanied by magnetite and chromite, but by rutile and xenotime and by diamonds. The platinum from Carrego das Lages is free from iron and poor in palladium, and occurs in quartz which carries tourmaline. Palladium-gold from Itabira do Matto Dentro contains from 7 to 11 per cent. palladium and is found in a schisty quartzite, in little cavities and veins, accompanied by limonite, pyrolusite, tourmaline and other minerals. Nernst and Wartenberg have determined (*Ber. phys. Ges.,* **4**, 48) the melting points of platinum and palladium by means of a Wanner pyrometer, using apparatus of iridium. The melting point of palladium is found to be 1541° with an uncertainty of about three degrees. This is in good agreement with previous determinations. Platinum melted at 1745° with an uncertainty of five degrees. This is from 16° to 35° higher than that found by other recent observers. Moissan (*Compt. rend.,* **142**, 189) has volatilized all the metals of the platinum group in the electric furnace, osmium being the most refractory. Using a current of 500

to 700 amperes at 110 volts, and 150 grams of the metal, all fuse in one or two minutes and boil quietly within four minutes. In five minutes there distilled of ruthenium 10 gm., rhodium 10.2 gm., palladium 9.6 gm., osmium 29 gm., iridium 9 gm., and platinum 12 gm. Only in the case of osmium was the current strength above 500 amperes. Although melting lower than platinum, palladium does not appear to be more volatile. The metals were condensed on the surface of a water-cooled copper tube, and appeared in balls and flakes, but most frequently in minute crystals. All of the metals dissolve carbon when fused, but give it up in the form of graphite on cooling. According to Guntz and Bassett (*Bull. soc. chim.*, [3] **33**, 1306) platinum is decidedly volatile at temperatures far below its melting point, as at from 1000° to 1300°. When used for electric heating a platinum wire of 0.3 mm. diameter lost in 600 hours five per cent. of its weight. The platinum condensed on the neighboring lime or other re-fractory backing in crystals, generally in octahedra, though other forms were found. Delépine (*Compt. rend.*, **141**, 886, 1013) has investigated the action of concentrated sulphuric acid on platinum, finding no action in an open vessel but considerable in a flask. The difference he attributes to the higher temperature reached in the latter case. In the presence of ammonium sulphate some of the ammonia is oxidized to nitrogen, and he draws the conclusion that no platinum should be present in the Kjeldahl analysis. Quennessen (*Ibid.*, **142**, 1341) has gone more thoroughly into the question of the solubility of platinum in sulphuric acid, using different varieties of platinum, and higher temperatures in closed tubes. Ordinary commercial platinum loses little when heated with 94 per cent. acid in a vacuum, but in an oxygen atmosphere the loss at 400° is large, (0.124 gm. per square decimeter surface per hour). Pure platinum loses almost nothing in a vacuum and only 0.0227 gm. in oxygen. Acid containing two per cent. anhydride dissolves about the same amount of pure platinum in a vacuum, but the amount decreases rapidly as the strength of the acid decreases. Quennessen attributes the action of ordinary sulphuric acid on platinum to the presence of the oxygen of the air, but when sulphuric anhydride is present, this is capable of furnishing the oxygen in a vacuum. The dark color which appears when carbon monoxide is led into a solution of palladium chloride is attributed by Donau (*Monatschefte Chem.*, **27**, 71) to the formation of colloidal palladium, and is identical with the coloration of the borax bead by palladium. The colloidal solution is fairly stable and can be heated and concentrated to 0.01 per cent before the palladium is precipitated. Little work has been done on the compounds of the metals of the platinum group. Delépine (*Compt. rend.*, **142**, 1525) has studied the double sulphate of iridium and potassium described by deBois-baundran, and finds that it is the potassium salt of iridiosulphuric acid, and that the formula should be written, $Ir(SO_4K)_3.H_2O$. Salts with various metals are formed by double decomposition and in none of these can the sulphate ion be detected by ordinary reagents. Werner and Dinklage (*Ber.*, **39**, 499) have prepared a series of salts by the action of alkaline bromides on the solution formed by treating potassium osmiamate with hydrobromic acid. They are nitrilo-compounds and have the formula $OsNBr_5R_2$, except in the case of the potassium salt, which has the formula, $OsNBr_4K$.

Noble Gases. Moureu (*Compt. rend.*, **142**, 1155) has examined the water of 43 springs and finds argon present in all and helium in 39. The argon

generally bears the same proportion to the nitrogen present as in the atmosphere, but in a few springs it is several times this quantity. By using Dewar's method of absorption with animal charcoal neon was also found (*Ibid.*, 180) in the waters of 22 springs. Using fractional distillation, combined with Dewar's method, on the residues from 7000 cubic meters of air, and then studying the spectrum, Schmidt (*Ber. phys. Ges.,* 4, 277) obtains lines which cannot be identified and concludes that xenon is not a simple gas, but a mixture of the true xenon with another gas, (or gases) now unknown, of higher atomic weight. Dorn (*Physik. Z.,* 7, 312) has heated helium in a platinum-iridium bulb up to 1420° with no change of pressure in the bulb in an hour. This alloy thus seems to be impermeable for helium and it is probable that helium can be thus used in high temperature thermometry. Since compounds of argon and helium, if they can exist, must be strongly endothermic, Cooke (*Pr. Roy. Soc.,* 77A, 148), has endeavored to determine whether they may not be formed at high temperatures, by determining the vapor density of several elements in these gases at temperatures between 1200° and 1300°. Aberrant results would indicate the possibility that under such circumstances compounds are formed. With arsenic and sulphur the results obtained are the same as usual; mercury and selenium give doubtful results, but the density of cadmium is higher in helium than in hydrogen, while that of zinc is 12 per cent. higher in argon than in nitrogen. This seems to point to some combination of the two elements.

A few papers which cannot be classified above may be noticed in conclusion. Landolt (*Sitzber. Akad. Wiss. Berl.,* 1906, 266) has continued his studies regarding a possible change of weight in chemical reactions. A change might be due to (1) participation of the ether in the reaction, (2) appearance or disappearance of electrons, or (3) disintegration of the atoms, due to the violence of the reaction. Out of 75 reactions tested, 61 showed a loss of weight, in numerous cases outside of the limits of experimental error. The most marked change was found in the reaction between silver sulphate and ferrous sulphate. If the vessel in which the reaction took place was coated on the interior with paraffin, there was no loss of weight. In the electrolysis of cadmium there was no change of weight. Landolt concludes that any change must be due to the third of the above causes, the projected particles of the disintegrated atom passing out through glass but not through paraffin.

In the *Philosophical Magazine* ([6] 11, 226) Stevenson continues his work on the chemical and geological history of the atmosphere. This paper is chiefly concerned with the possible changes in the amount of carbon dioxide. Analyses cannot settle the problem, as no old analyses are accurate enough for use. Comparative analyses of the air over land and over the sea might afford indications, but the solubility of carbon dioxide in the ocean water may well account for the slight deficiency which has been found in ocean air. Owing to this constant loss it can be inferred that there must be a constant excess in supply. Perhaps this is due to the increasing combustion of coal. Note must also be taken of the fact that different classes of plants consume different quantities of carbon dioxide, the algæ especially taking up a large quantity. Hence the amount of the gas in the atmosphere in past time could have been influenced by the predominance of different forms of vegetation.

The formation of sparks and even minute explosions when metallic cal-

cium is struck on steel or quartz is connected by Ohmann (*Ber.,* **39**, 866) with "striking fire" in general. There is here a change of kinetic energy into heat, and accompanied often by change in state of aggregation. The phenomenon is particularly marked with those elements which soften easily by heat and have great affinity for oxygen. With calcium the action is more noticeable in an oxygen atmosphere. The phenomenon is particularly marked with lithium, and can be produced even with red phosphorus.

Lexington, Va., Jan. 1, 1907.

NEW BOOKS.

ELEMENTS OF GENERAL CHEMISTRY WITH EXPERIMENTS BY JOHN H. LONG, M. S., Sc. D, Fourth Edition. Philadelphia; P. Blackiston's Son & Co., 1906. Pages x + 443. Price $1.50.

This is an admirable text-book for beginners in chemistry. It is clearly and concisely written and the student is not overburdened with a multiplicity of detail. The important principles and theories are introduced gradually and only after the student has had some experience with chemical work. Thus it is only after oxygen, hydrogen, water, hydrogen dioxide, chlorine and hydrochloric acid have been studied that definitions of elements and compounds are given. Then follow some brief statements in regard to atoms and molecules and it is not until page 82 that we find the first symbols and equations.

The directions for laboratory work are very clear and the experiments are well selected and illustrate the essential facts of descriptive chemistry. In the reviewer's opinion it would have been better not to tell the student in every case what he is expected to notice but rather make him observe for himself and then by a number of questions make him think and reason in regard to what he is doing. Students have a way of following directions mechanically in the laboratory without putting much thought upon their work and then in a short time forgetting all about it. It might have been well at page 80 to have stated the laws of definite, multiple and reciprocal proportions and to have added a few quantitative experiments that would have illustrated them.

In this new edition the facts have been brought well up-to-date, a chapter on theories of solution and mass action has been added, radium and its behavior, its change into helium, find mention.

There are almost no errors in the book and few criticisms to be made. On page 126 in experiment 94 the gas obtained is not nitrogen trioxide; as this compound does not exist at ordinary temperatures but is dissociated into nitric oxide and nitrogen tetroxide. On page 399, it might·be nferred that radium had been obtained in free condition whereas only its compounds have been obtained. On page 409 the illustration of the iron blast furnace is of a rather old form and out of date.