the various requirements admirably; in a series of over 200 experiments no sign of leak has been observed.

Four new crystalline alkali silicates—namely, $K_2Si_2O_5$, $KHSi_2O_5$, $Na_2Si_2O_5$ and Na_2SiO_3—have been prepared. Of these the first three are derivatives of disilicic acid; they all form orthorhombic crystals, but differ markedly in their behavior toward water. $K_2Si_2O_5$ is quickly attacked by water, $Na_2Si_2O_5$ less readily, while $KHSi_2O_5$ may be left in contact with water, even for some hours at 100°, without appreciable decomposition. The fourth compound is anhydrous sodium metasilicate, which is readily attacked by water; this compound has been known heretofore only as a somewhat indefinite hydrate.

In addition to the crystalline products, a series of hydrous glasses was obtained. These glasses are merely supercooled liquids, each of which represents the composition of a solution unsaturated under the conditions of experiment. They are perfectly hard, even though they contain up to 25% water; when heated in the air they lose their water, swelling up in the process in a sponge-like structure often with extremely thin vesicular walls.

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RECENT WORK IN INORGANIC CHEMISTRY.

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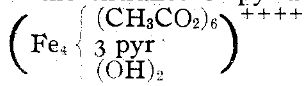
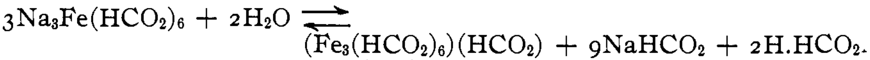
While the past twelve months have witnessed no startling developments in the field of inorganic chemistry, there has been no diminution in volume of work. Perhaps the two strongest tendencies are (1) to go over old work with modern methods and in the light of modern theories, with resulting confirmation or otherwise, and (2) to project new theories into wider fields to test their applicability and breadth. This has been notably the case with Werner's ideas in their application to complex compounds. Here there has been no such remarkable discovery as that of two years ago regarding the optical isomerism of inorganic compounds, nevertheless there has been an increasing use of these ideas in the explanation of the constitution of compounds which are inexplicable by any of the older theories; as for example Weinland's work on basic salts and that of Rosenheim on the poly-acids of molybdenum, tungsten, etc. Continuing his work on the ferric acetates, where the dominating kation contains three ferric atoms and six acetate groups (hexacetato-triferri base), Weinland has studied (*Z. anorg. Chem.*, 80, 402) the compounds formed by the action of pyridine on a solution of a ferric salt in anhydrous acetic acid. Different compounds are formed according to the proportions used, but the characteristic point is that the ratio of iron to acetate in the kation changes with the entrance of pyridine from 3 : 6 to 2 : 3. A typical formula is



$\left(Fe_4\left\{\begin{matrix}(CH_3CO_2)_6\\ 3\ pyr\\ (OH)_2\end{matrix}\right.\right)^{++++}$

, though other kations are formed containing

4, 5, and 6 molecules of pyridine. In a later paper (*Ber.*, **46**, 3144) Weinland gives the action of sodium formate on ferric salts. When the formate is in large excess the salt of the hexaformato-ferric acid is obtained, $Na_3Fe(HCO_2)_6$, corresponding to ferricyanides, etc. This anion is pale green, resembling in this respect the ferrioxalate ion, $Fe(C_2O_4)_3$. If, however, in mixing the ferric salt and sodium formate, the latter is not in large excess, the kation of a hexaformato-triferri base is formed, $(Fe_3(HCO_2)_6)(OH)_3$. This is deep red and is the cause of the color when a formate is added in small quantities to a ferric solution. In intermediate solutions there is present the equilibrium,



$$3Na_3Fe(HCO_2)_6 + 2H_2O \rightleftharpoons \underset{(OH)_2}{(Fe_3(HCO_2)_6)(HCO_2)} + 9NaHCO_2 + 2H.HCO_2.$$

Since both acid and base are trivalent, a number of different salts containing both can be obtained, as for example: $(Fe_3(HCO_2)_6)(Fe(HCO_2)_6)$ and $\underset{(OH)_2}{(Fe(HCO_2)_6)_3}(Fe(HCO_2)_6)$. By using a large excess of sodium formate with chromium salts a hexaformato-chromate, $Na_3Cr(HCO_2)_6$, was obtained. This salt is green-violet and corresponds to the chromoxalates, perhaps more properly named, oxalato-chromates. In this connection mention may also be made of the ferric urea compounds described by Barbieri (*Atti accad. Lincei, Rome,* [5] **22** i, 867) which have the formula $Fe(CO(NH_2)_2)_6.X_3$, and are isomorphous with the corresponding chromium urea compounds, but less stable; and of the compounds of platinous chloride with aminoacetal described by Tschugajew (*Compt. rend.*, **155**, 1021). These have the formulas, $Pt(2A)Cl_2$, $Pt(4A)Cl_2$, and $Pt(2A.2NH_3)Cl_2$ ($A = NH_2.CH_2.CH(OC_2H_5)_2$). Isomers to the last salt could not be obtained. The compounds of platinum with thio-bases will be considered farther on. The work of Rosenheim has been extended to include the dekamolybdates (*Z. anorg. Chem.*, **79**, 292), which seem to exist in two isomeric forms, differing greatly in solubility, and the organic arseni-molybdates (*Ber.*, **46**, 539), or again better called from their constitution, molybdato-alkyl (or phenyl) arsinates. Guanidinium salts proved themselves here, as frequently in the study of other polyacids, best suited to the study of the basicity of the compounds, and were formed by adding guanidinium chloride to the solution of cacodylic or other arsinic acid saturated with molybdic oxide. It is interesting to note that in these polymolybdic acids a portion of the molybdic trioxide or heptoxide can be replaced by alkyl, phenyl, or even substituted phenyl groups. Another line of investigation which has at least an indirect bearing on Werner's ideas is that of Ephraim (partially reported last year) on "Nebenvalenz," perhaps most correctly translated *secondary valence* (*Z. physik. Chem.*, **81**, 513, 539; **83**, 196; *Ber.*, **46**, 3103) Ephraim has studied particularly the ammonia compounds (ammoniates) of the halides of bivalent metals, and has endeavored to measure the strength of the secondary valence which holds the ammonia by measuring the vapor-pressure of these ammoniates. He finds that the affinity of ammonia for the salt is the greater, the less the atomic volume of the central metal; the expression $\sqrt[3]{v}.\sqrt[3]{T}$, in which v is the atomic volume of the metal and T the dissociation temperature, being nearly a constant. There is also a constant relation between the dissociation-temperatures of most of the ammoniates of chlorides and those of the corresponding bromides, iodides, and sulfates. The ammoniates appear to differ from hydrates in that the ammonia is given off molecule by molecule, while intermediate hydrates of salts are frequently lacking; but this Ephraim thinks is merely apparent, and that it is only owing to their solubility relations that all possible hydrates are not realized in solid form. Biltz, however (*Z. physik. Chem.*, **82,** 688) denies the conclusion which Ephraim has drawn from his experiments, that ammonia is given off molecule by molecule, and presents experimental evidence that $Ni(NH_3)_6Cl_2$ passes directly into $Ni(NH_3)_2Cl_2$ without the formation of any intermediate ammoniate. In his last paper, Ephraim compares the dissociation-temperature of ammoniates with that of ammonium salts, finding a marked similarity, and draws the conclusion that ammonium salts may be looked upon as ammoniates of hydrogen salts, *i. e.*, acids. This is, of course, what Franklin has already found to be true in respect to ammonium salts dissolved in liquid ammonia. Ephraim also finds a parallelism in the dissociation-temperature of phosphonium compounds, which may from this standpoint be written, $H(PH_3)Cl$, etc.

In determining whether a given salt is to be considered as "double" or "complex," Dhar (*Z. anorg. Chem.*, **80,** 43) would use molecular conductivity as a criterion, relying upon the fact that this is dependent on the velocity of the ions and the latter in turn is strongly influenced by the size of the ion. He presents the measurements of a long list of salts, which show that many of the complex ions are very stable even at great dilution. Ephraim, however, points out (*Fortschritte Chem.*, **8,** 198) that these results indicate merely whether the complex is stable in dilute solution, and not whether the complex really exists or not under other conditions, *e. g.*, at greater dilution or in other than aqueous solutions.

In the first of a series of studies on chemical crystallography (*J. Chem. Soc.*, **101,** 2484), Barker calls attention to the value of Werner's coördination theory in explaining many otherwise inexplicable anomalies of isomorphism. Among a number of examples cited we may note as examples: $CuTiF_6.4H_2O$, $CuCoOF_5.4H_2O$, $CuWO_2F_4.4H_2O$, which according to the coördination theory, would be written, $(TiF_6)Cu + 4H_2O$, $(\mathrm{Co}\genfrac{}{}{0pt}{}{O}{F_5})\mathrm{Cu} + 4H_2O$, $(\mathrm{W}\genfrac{}{}{0pt}{}{O_2}{F_4})\mathrm{Cu} + 4H_2O$; and $MnCl_2.4H_2O$, Na_2GlF_4, which would be written $(Mn4H_2O)Cl_2$, $(GlF_4)Na_2$. It seems rather remarkable that such a working out of the application of the coördination theory to crystallography has not been undertaken long ago. In this connection it is worth while to call attention to the plea of von Fedorov (*Z. Kryst. Min.*, **52,** 22) for a more complete study of the chemical molecule in its spatial relations, with reference to the crystal molecule and its symmetry.

In a Russian text-book (abstract in *Zentrbl. Min. Geol.*, **1912,** 758), Wernadski has given a table of 106 minerals which consist of native elements. The fact that 5% of all minerals are not stoichiometric compounds, but either free elements or homogeneous mixtures of elements, points to a peculiar chemical condition of the earth's crust. Many things favor a destruction of chemical compounds; as for example the fact that in volcanic extrusions many elements are in gaseous condition, a state peculiarly susceptible to the action of electric phenomena, of ultraviolet light and radioactive emanations; and the fact that in cosmic solutions, in which many elements are present in exceedingly minute amounts, there is no possibility of all being united in stoichiometric compounds. In every smallest portion of the earth's crust many, if not all, the elements may be found, when sufficiently exact analytical methods shall be devised. The concentration of these elements is infinitesimally low, and the author speaks of them as being in a *microcosmic mixture.* Most minerals composed of native elements are "rare," and altogether they make up hardly 0.1% of the earth's crust; still not less than 47 of the known elements occur in native condition. Possibly Wernadski's microcosmic mixture may prove to be identical with colloidal solid solution, or merely colloidal solution in the case of sea-water. This idea of a solid colloidal solution is brought out by von Veimarn in a paper on the condition of gold in gold quartz (*Z. Chem. Ind. Kolloide*, **2**, 287). Such quartz is milk-white and translucent and the gold must be in super-ultramicroscopic condition; this colloidal condition may be ascribed to the action of silicic acid as a protective colloid. We may also note that Merrill (*Am. J. Sci.*, [4] **35**, 509) has gone over much of his former work on the chemical constituents of meteorites, using most modern methods in searching for the elements present in minute quantity, and in each case using not less than 50 grams of substance. The following elements, heretofore supposed to be present, were not found: antimony, arsenic, gold, lead, tin, tungsten, uranium and zinc. The occurrence of platinum was placed beyond dispute, especially in the Perryville iron, where 4 mg. were found in 25 grams substance, as well as a minute trace of palladium. In this same iron 14 mg. of ruthenium and 28 mg. of iridium were found in 100 grams of substance. Traces of vanadium were found in two falls. In no case were barium, strontium or zirconium present. A paper by Chamberlain (*J. Geol.*, **17**, 534) on the gaseous content of rocks is an interesting contribution to cosmic chemistry. Space does not permit of complete abstraction, but a few points may be noticed. All rocks contain gases, the basic eruptives most in quantity. While some of this gas results from decomposition, some is present in an occluded condition (solution). This is very different in composition from the atmosphere. Of the gases, certainly H_2O and CO_2 were constituents of the original magma, and as these were liberated CO and CH_4 were also formed by interaction. Oxygen is found only in combined condition in rock masses of the earth. The earth interior is very poor in oxygen and the earth crust not extremely rich, for, as a whole, the crust is suboxidized. Atmospheric oxygen was of late appearance, formed from the decomposition of oxides, especially water, and was later increased by the decomposition of CO_2, after plant life had appeared. The hypothesis of a primary gas content of the earth interior is in accord with the planetesimal hypothesis.

An investigation of the most refractory oxides in the carbon resistance vacuum furnace has been carried on by Ruff (*Z. anorg. Chem.*, **82**, 373) both for the purpose of getting fixed normal temperature points, and also to determine the most refractory materials for high temperature work. Alumina was found to give a definite melting point of 2010° ± 10°, too low however for a very refractory material. The only other possibly definite points were the melting points of glucina at about 2525° and zirconia at about 2585°; but it is not yet certain that these remain entirely unreduced under the influence of the high temperature, low pressure, and reducing gases in the carbon tube. They are, however, entirely satisfactory as refractory materials. Magnesia is also refractory, fusing about 2550°, but volatilizes rapidly, and while lime has probably nearly as high a melting point it is even more volatile. Other oxides, such as ceria, yttria, thoria, and Cr_2O_3, were more or less converted into carbides before fusing. Work by Kaye and Ewen (*Proc. Roy. Soc. Lond.*, (*A*) **89,** 58) on the sublimation of metals at low pressure, carried out with iridium, copper, iron and tungsten, leads to the conclusion that vapors of two sorts are given off under the conditions of the experiments, (1) ordinary vapors of the gaseous element, and (2) a vapor of metallic particles passing off in right lines normal to the metallic surface, with a path one centimeter long in a vacuum. These particles appear to be electrically charged metallic particles, whereas the ordinary vapors are electrically neutral.

Passing from these more general investigations to those confined to single elements and their compounds, we follow the periodic table.

Group I.—In connection with measurement of the vapor pressure of metals by the dynamic method, von Wartenberg (*Z. Elektrochem.*, **19,** 482) noted that silver is appreciably more volatile in oxygen than in nitrogen, and attributes this to the formation of silver oxide at a high temperature. Although this oxide is unstable at low temperatures, owing to its high heat of vaporization it should be possible for it to exist at high temperature as a gas. From the equilibrium $4Ag + O_2 \rightleftharpoons 2Ag_2O$ it should be possible, according to the law of mass action, for some Ag_2O to exist at high temperatures when the oxygen concentration is great. The reviewer has found it possible to obtain PH_3 by leading hydrogen over (red) phosphorus at its volatilization point, and has also found, quite in analogy with the work of von Wartenberg, that RuO_4 can be detected in oxygen which has been led over metallic ruthenium at a high red heat, although RuO_4 decomposes with violence when heated to about 100°.

Group II.—Metallic glucinum has been prepared by Fichter and Jablczynski (*Ber.*, **46,** 1604) by the electrolysis of a fusion containing GlF_2 and NaF. The metal was obtained in crystalline form, but was covered with a thin film of oxide. This rendered the determination of its fusing point difficult, but it appears to be 1280° ± 20°. It volatilizes at above 1900°. The freshly filed metal is steel-gray and has a hardness of 6–7. Though brittle at ordinary temperatures, when heated it becomes ductile. Owing to its coating of oxide the metal appears to be resistant to reagents, but it is actually slowly acted on by boiling water. It is less attacked by 0.01 *N* HCl than magnesium but more than aluminum. Nitric acid (1.4) acts on it only when heated; and the same is true of 10% potassium hydroxide, while a 50% solution dissolves it in the cold. Its properties thus accord with its position as the first element of Group II.

In determining the vapor pressure of the hydrogen in CaH_2, Moldenhauer and Roll-Hansen (*Z. anorg. Chem.*, **48,** 137) found that, when the porcelain tube was lined with iron, the pressure differed according to whether pure CaH_2 or a mixture of CaH_2 with Ca was used. This could be accounted for by assuming the existence of a lower hydride, CaH. When an unprotected porcelain tube was used a different but constant pressure was obtained, and it was found that there was an evident slight volatility of the lower hydride and reaction with the porcelain. In reviewing this paper in the Fortschritte, Ephraim mentions that a hydride of calcium appears to exist which is volatile at ordinary temperatures, which Hoffmeister has also found in commercial acetylene. Edler finds (*Ber.*, **46**, 2264) that calcium hydride reduces barium sulfate according to the reaction $BaSO_4 + 4CaH_2 = BaS + 4CaO + 4H_2$, which is strongly exothermic. This reaction appears to be excellently applicable (*Z. anorg. Chem.*, **83**, 149) for the concentration of radium, for the mass after reaction is porous and dissolves readily in HCl. By using 1/1 *N* HCl any PbS and SiO_2 is left undissolved and the barium and radium can be fractionally precipitated by HCl gas, while calcium and any iron remain in solution.

Group III.—In 1912, Stock, for the first time, isolated two borides of hydrogen, $H_{12}B_6$ and $H_{10}B_4$, both exceedingly unstable compounds. The past year (*Ber.*, **46**, 1959) he has added another boride to these two, H_6B_2, which proves to be decidedly more stable, but so extremely sensitive to the presence of water that it has hitherto escaped discovery. Its recognition now is due to the fact that $H_{10}B_4$ decomposes spontaneously at ordinary temperature, and more rapidly when heated, into H_6B_2 and hydrogen, together with a small quantity of less volatile borides. The H_6B_2 is separated from any unchanged $H_{10}B_4$ by fractional distillation. The boiling point of H_6B_2 at atmospheric pressure is —87 to —88°, and its melting point is below —140°. Its density is 13.8, which is close to theory for the formula H_6B_2. It is fairly stable at ordinary temperatures, but decomposes slowly with the formation of solid borides. This decomposition is more rapid when the gas is heated. In this boride, the boron seems to be quadrivalent and the compound analogous to ethane. Its boiling point also corresponds to that of ethane (—90°); that of silico-ethane is —7°. Similarly, $H_{10}B_4$ may correspond to butane; its boiling point is 16° and that of normal butane 1°. In a later communication (*Ibid.*, 3353), Stock describes the volatile solid hydrogen boride which is formed when H_6B_2 is decomposed. Its formula, as determined by analysis and molecular-weight determination by freezing-point depression in benzene, is $H_{14}B_{10}$. It fuses sharply at 99.5° to a water-clear liquid which readily crystallizes again. It is fairly stable, being largely unchanged on passing through a tube heated to 400° (*in vacuo*), but on heating slowly above 200° it is, partially at least, converted into another boride which is insoluble in carbon bisulfide. $H_{14}B_{10}$ is soluble in alcohol, ether, benzene and especially in carbon bisulfide, and can be recovered from its solutions, but with great loss owing to its volatility. It is not acted on by water, in which it is insoluble, and scarcely attacked by concentrated nitric acid. The difficulty attending its production is partly realized when one considers that the yield from decomposing 1 cc. of H_6B_2 is 0.5 mg. In this decomposition two other solid borides were obtained, one soluble and the other insoluble in carbon bisulfide, but the quantity was too small for complete investigation. The former contains hydrogen and boron in a ratio of 4H : 5B, and is thus decidedly poorer in hydrogen than any of the other borides found. The other boride has a molecular weight (in benzene) of about 142, and thus probably contains 12 atoms of boron in the molecule. Stock has thus isolated altogether seven borides of hydrogen, five of which have been accurately studied and their formulas determined. The existence of three others has been noticed but they have been in too small quantities for any investigation. Since some of the borides prepared by Moissan and by Moody and Tucker contained carbon as carbide, or aluminum, Wedekind (*Ber.*, **46**, 1198, 1885) has used other methods for the preparation of borides, old and new.

In several cases success was attained by the use of the vacuum arc furnace, the electrodes being made of a mixture of boron with the desired metal, sufficiently fritted to conduct the current. In this way Zr_3B_4, VB, and UB_2 were prepared. WB_2 was also obtained, corresponding to that prepared by Moody and Tucker, but borides of molybdenum and titanium could not be made in pure condition. CaB_6 was prepared by the reduction of calcium borate by metallic calcium in an iron tube. It resembles that obtained by Moissan in the electric furnace, except that its color is light brown, while that of Moissan was black, doubtless owing to impurities. In the borides of this type there seems to be present a very stable group, B_3, and it is possible that a hydrogen boride with formula HB_3 is present in the solid borides obtained by Stock.

A new contagious disease of metals is described in the *Chemical News* (**108**, 4) which affects the alloy of 97% aluminum and 3% copper used by the French government for the manufacture of helmets and other military objects. The disease is epidemic and spreads by contact from one object to another, corroding the metal and making holes in it. The metal looks as if attacked by eczema, and thus far no remedy has been found.

Group IV.—In discussing, a year ago, the combustion of coal, Rhead and Wheeler drew the conclusion that both CO and CO_2 are formed, and promised an explanation of this phenomenon. This has now appeared (*J. Chem. Soc.*, **103**, 461), and consists in the hypothesis that carbon absorbs oxygen with the formation of a carbon-oxygen complex, which is stable up to high temperatures, and which on decomposition under the influence of heat gives off both CO and CO_2. That this absorption of oxygen is not a mere physical absorption seems apparent from the fact that no gas is given off by merely diminished pressure, and that coal which has been highly heated does not absorb CO or CO_2. The composition of this carbon-oxygen complex, C_xO_y, depends upon the temperature at which it is formed; when this takes place at 300° the formula is $C_{100}O$, but it is not to be looked upon as a uniform chemical compound. While it is true that this hypothesis would satisfactorily account for the facts of the combustion of coal, the evidence presented in its support seems pretty meager. Methane has a strong tendency to decompose above 600°, but at this temperature, under ordinary circumstances, carbon is not deposited; but if a metal is present with which carbon has a tendency to unite which is stronger than its tendency to be deposited as elementary carbon, then a carbide will be formed. The lower the temperature the less tendency to deposit free carbon, but as lowering of the temperature decreases the velocity of the reaction, hydrogen may be mixed with the methane, diminishing the dissociation and allowing a higher temperature to be used. Hilpert and Ornstein (*Ber.*, **46**, 1669) have used this method of heating the metal in a current of methane and hydrogen, for the preparation and study of carbides. An analogous method, in which there is less trouble from concomitant deposition of carbon, consists in heating the metal in CO, the equilibrium being $2CO \rightleftharpoons C + CO_2$. In this case the tendency to deposit carbon decreases with the increase of temperature. At 1000°, with molybdenum, Mo_2C was the limiting carbide, while at 800° MoC was rapidly reached, but still more carbon was slowly taken up, with a probable limiting value of Mo_3C_4. At 600°, however, the limiting compound was, as at 1000°, Mo_2C. With tungsten below 900°, with methane, WC was quickly reached; at 1000°, with CO, W_3C_4 was the limiting compound. In the CO atmosphere tungsten was appreciably volatile (formation of a tungsten carbonyl?). This reaction for the formation of carbides would undoubtedly be strongly influenced by the heat of formation of the carbide, and in this connection it may be noted that this heat of formation has been determined by Ruff (*Ibid.*, 400) for Mn_3C, Fe_3C, and Ni_3C to be respectively, $+12.9 \pm 2.14$, -15.3 ± 0.2, and -394 ± 10 Cal. This substantiates the fact that Mn_3C undergoes no apparent change on cooling. Fe_3C can be obtained in 90% yield by rapid chilling, while it is difficult to preserve any Ni_3C even in great dilution and with most rapid chilling. Curiously, however, no carbide of definite composition could be obtained by Hilpert (*Ibid.*, 3479) on heating metallic manganese in methane. In pure methane the carbide mass contains upwards of 20% carbon, and in a mixture of equal parts methane and hydrogen 15% carbon. The saturation limits varied with the temperature to which the manganese was heated, but in no case did the mass present any simple atomic ratio. The reaction with acids also indicated that no derivatives of simple hydrocarbons were present. All of these manganese carbide masses are ferromagnetic. To the three compounds of carbon and nitrogen, cyanogen, paracyanogen of Gay-Lussac and Johnston, and the recently discovered carbon pernitride, NCN_3, of Darzens, is now to be added a fourth, C_3N_2, prepared by Pauly and Waltzinger (*Ber.*, **46**, 3129) by heating imidazole tetraiodide. This iodide, when heated in a vacuum, loses three atoms of iodine below 200° and the fourth at about 400°, leaving a mass which resembles soot, and bears a strong resemblance to animal charcoal. On heating to 800–900° it decomposes into cyanogen and carbon, and on heating with soda-lime gives off all its nitrogen as ammonia. While not identical with paracyanogen, it is evidently of similar nature. While it is insoluble in all indifferent solvents and infusible, the fact that it is formed quantitatively from $C_3N_2I_4$, as well as its chemical properties, indicates that it is a definite chemical individual.

By the action of metallic calcium on a mixture of silicon and aluminum, Reynolds (*Proc. Roy. Soc.*, (*A*) **88**, 37) has prepared a compound, $Ca(SiAl)_2$, which he calls calcium silical-cyanid, that is a cyanid in which the carbon is replaced by silicon and the nitrogen by aluminum. The compound is exceedingly stable and indifferent to oxygen even at high temperature but great interest must attach to it from the fact that when heated to a low redness in a current of *moist* oxygen it gives a compound, $CaAl_2Si_2O_8$, which in composition, appearance and other properties bears the closest resemblance to anorthite. Much interest must also attach to a compound which bears a relationship on one side to a complex silicate and on the other to a cyanide.

By the solution of potassium stannate in hydrofluoric acid Marignac obtained two distinct salts to which he gave the formula $K_2SnF_6.H_2O$. This has now been cleared up by Briggs (*Z. anorg. Chem.*, **82**, 441). When the fluo-stannate, best prepared by the method of Emich from $SnCl_4$ and KF, is dissolved in water the reaction is acid. On the addition of exactly one molecule of KOH the solution becomes neutral, and from it is crystallized the second salt of Marignac, in thin brilliant flakes, which have the formula $K_2SnF_5OH.H_2O$, a hydroxy-pentafluo-stannate. At 170°, water is given off and an anhydride, probably $K_4(SnF_5.O.SnF_5)$, formed, which, on solution in warm water, regenerates the original hydroxy-salt.

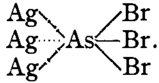
Group V.—The orange-yellow cloud-like luminescence observed when the electric discharge is passed through nitrogen at pressures from 1 to 10 mm. is ascribed by Strutt to an active modification of nitrogen. This is disputed by Comte (*Physik. Z.*, **14,** 74) who finds that when pure nitrogen is used the luminescence is reduced to a minimum, and ascribes the phenomenon to the reaction between nitrogen and a little oxygen present as impurity. The same view is held by Tiede (*Ber.*, **46,** 340). On the other hand, Strutt (*Physik. Z.*, **14,** 215) shows that in his experiments oxygen was practically absent, and that intentional additions of oxygen inhibit the phenomenon proportionally. Comte's results may have been due to impurities introduced in removing the oxygen. In a later article (*Proc. Roy. Soc.*, (*A*) **88,** 539), Strutt gives further details regarding active nitrogen and its reactions. With vapors of mercury, cadmium, zinc, arsenic, sodium and sulfur, nitrides are at once formed which are at once decomposed by water with evolution of ammonia. Carbon bisulfide gives a blue polymeric nitrogen sulfide, $(NS)_x$, and a polymeride of carbon monosulfide. Active nitrogen reacts with many organic substances, giving in almost every case hydrogen cyanide, but no cyanogen. None of these reactions would be characteristic of an oxide of nitrogen. The action of ozone on liquid ammonia at low temperatures would seem, according to Manchot (*Ber.*, **46,** 1089), to be analogous to that on the caustic alkalies, for here also an intense orange-red color is formed, which becomes pale when the temperature is allowed to rise to —65°. If a few drops of water are present the color is stable to a somewhat higher temperature. In perfectly dry non-aqueous solvents, when saturated with ammonia, no color appears on addition of ozone, even at very low temperatures, nor do liquid organic amines give a color with ozone, although there is an evident reaction. It seems probable that the reaction of ozone with ammonia is really with the hydroxide, NH_4OH, which is stable at low temperatures and is more closely akin to KOH and NaOH than are dimethyl- and trimethylamine. Some fifteen years ago Melikoff and Pissarjewski prepared, by the action of ammonia on hydrogen peroxide, an ammonium hydroperoxide, NH_4O_2H. In repeating their work, D'Ans and Wedig (*Ber.*, **46,** 3075) led dry NH_3 into a 98% solution of hydrogen peroxide in absolute ether at —10°. At first beautiful clear crystals appear, which are the hydroperoxide, m. p. 14°, but on further addition of NH_3 these fuse and there is formed at the bottom of the flask a heavy oily layer. On cooling to —40° this oil freezes to a crystalline mass. This mass was washed with ether in a specially constructed apparatus, cooled by a carbon dioxide-ether mixture. The pure crystals thus obtained are ammonium peroxide, $(NH_4)_2O_2$. On warming they begin to lose ammonia, forming NH_4O_2H, and melt at about —2°. They are somewhat soluble without decomposition in cold ether.

A study of the fixation of nitrogen by a mixture of barium oxide and carbon has been carried out by Ewan and Napier (*J. Soc. Chem. Ind.*, **32,** 467). Fixation appears to take place according to one or both of the two reactions, $BaO + 2C + N_2 \rightleftharpoons BaCN_2 + CO$, and $BaO + 3C + N_2 \rightleftharpoons$

$Ba(CN)_2 + CO$. Both of these reactions are reversible but were not found to be appreciably affected by any catalytic agents, although the presence of a little (up to 11%) K_2CO_3 lowered the reaction temperature 10 to 20°. The second reaction is connected with the reaction $Ba(CN)_2 = BaCN_2 + C$, which does not appear to be reversible. When nitrogen is led over the baryta-carbon mixture at 1100°, it is rapidly absorbed until nearly half the baryta has been converted into a nitrogen compound. The further absorption of nitrogen goes on with extreme slowness, although it would seem that no true equilibrium would be reached (the nitrogen supply being continuous and the CO removed) until all the barium is combined with nitrogen. The best that could be attained was 57% yield, and this only after 80 hours' heating. The rather sudden impeding of the reaction seems to be due to the formation of a compound, $BaO.Ba(CN)_2$, in which the BaO is far less active than when free; this would also seem to account for the fact that there is even at 1150° no volatilization of the $Ba(CN)_2$, which by itself is somewhat volatile at a decidedly lower temperature. Another reaction which must possibly be taken into account is $BaO + 3C \rightleftharpoons BaC_2 + CO$. The equilibrium pressure of this reaction at 1200° is 1 mm., hence it is probable that barium carbide is hardly to be considered an intermediate product in the absorption of nitrogen. On the other hand, in the reaction between lime, carbon and nitrogen, the carbide is probably an intermediate product of importance. The fixation of nitrogen by aluminum has been studied by Fichter (*Arch. Sci. phys. et nat., Genève*, [4] **35**, 369; *Z. anorg. Chem.*, **82**, 192), Fraenkel (*Z. Elektrochem.*, **19**, 362), and Wolf (*Z. anorg. Chem.*, **82**, 159). Fichter finds that the affinity of aluminum for nitrogen is very considerable. When a nickel tube filled with aluminum powder is heated to 700° and nitrogen led over it, the temperature rises suddenly to 820° and nitrogen is rapidly absorbed. The temperature in the interior of the mass rises to above 1300°. The product contains some particles of aluminum which have been unacted on, but by powdering and again heating in nitrogen a pure product can be obtained which has the formula AlN. The affinity of aluminum is so great that when air is led over the heated metal, some nitride is found in the oxide formed. Water easily decomposes the nitride with the formation of ammonia, and in moist air the nitride always has an odor of ammonia. While hydrochloric acid acts readily on the nitride, if metallic iron and aluminum are present as impurities they can be sublimed away by heating in a stream of perfectly dry HCl gas, leaving the AlN pure. By long action of HCl gas, or at a higher temperature, the nitride is itself attacked. By heating with alkalies and carbon the nitrogen of the nitride is converted, but not completely, into cyanide nitrogen. In order to obtain the nitride by the action of nitrogen on a mixture of alumina and carbon, the temperature must not rise above 1800–1850°, or the oxide will melt and carbide be formed, which inhibits the reaction. The reaction, $Al_2O_3 + N_2 + 3C \rightleftharpoons 2AlN + 3CO$, first carried out by Serpek, has been studied by Fraenkel, who finds that when soot is used the reaction begins at 1400° and increases rapidly in velocity with rising temperature, while the nitrogen pressure has little influence. The reaction is inhibited by mixing CO with the nitrogen, and is reversible. At 1500° and 760 mm. equilibrium is reached with 25–40 volume per cent. CO; at 1600° with 50–65%. Above 1500° carbide begins to be formed. The velocity of the reaction is strongly influenced by the nature of the carbon used. Wolf finds that the purity of the aluminum plays an important part in its reaction with nitrogen, and that by using aluminum bronze it was possible to convert only 2.47% of the aluminum into the nitride. The presence of oxygen in the nitrogen is also objectionable. The fixation of nitrogen by boron is the subject of a detailed investigation by Stähler and Elbert (*Ber.*, **46**, 2060). Owing to its strong affinity for nitrogen and the fact that of all solid nitrides that of boron contains the highest per cent. of nitrogen, boron seems specially suited for the fixation of nitrogen. Boron nitride is further valuable as a refractory material, and from it may be obtained not only ammonia but also cyanides. B_2O_3 can be reduced to boron by carbon at 1200°; borax can be reduced to boron by the electric current with iron electrodes with a current yield of 12.1% theoretical. Reduction of boric acid by calcium carbide takes place at 1625°, the resultant product being from qualitative examination calcium boride, and this the most convenient method of preparing it. Borocalcite, $CaB_4O_7.4H_2O$, and carbon were heated together but even at 1700° no formation of calcium boride took place, but when nitrogen was led over the heated mass it was readily absorbed. Not only nitride but also cyanamide seems to be formed, and the reaction appears to be $CaB_4O_7 + 8C + 3N_2 = 4BN + CaCN_2 + 7CO$. No study appears to have been made as to the reversibility of this reaction. For the reaction $B_2O_3 + 3C + N_2 \rightleftarrows 2BN + 3CO$, 1500° to 1700° is the most favorable temperature. At 1800° the heating should not be continued more than 30 minutes. Even at pressures of 40 to 70 atmospheres the amount of absorbed nitrogen was not increased (a result to be theoretically expected). The absorption of nitrogen at atmospheric pressure per gram boron is much larger when borocalcite is used than with boric acid. BN loses no weight when heated to 2200° in a graphite boat, but at 2450° it was completely destroyed, the carbide of boron being formed. These studies on nitrides are all of great value as throwing light on an extremely important industrial problem.

An investigation of the sensitiveness of the azides to the light, by Wöhler and Krupko (*Ber.*, **46**, 2045) throws some light on the photographic latent image. The action of the light on mercurous, silver, cuprous, and lead azides was studied. Especially in the first two cases no evidence of a subazide was found, though the effect of the light was in every way analogous to its action on the silver halides. The azide darkened gradually according to the amount of light, and in every case the free metal was formed with the liberation of nitrogen. Evidence is thus afforded from analogy that the latent image in photographic processes is not due to the formation of a subhalide, but to reduction to metallic silver, which forms an adsorption compound in the excess of silver halide. A basic lead azide, $PbO.PbN_6$, and a basic cupric azide of similar formula were also obtained.

A painstaking investigation of the vapor density of phosphorus has been made by Stock (*Ber.*, **45**, 3527) in a special apparatus of transparent quartz, the result showing that the molecule of phosphorus is P_4 up to 700°. The dissociation above this temperature is $P_4 \rightleftarrows 2P_2$, and the amount of P_2 is at 800° about 1/100, at 1000° 1/10, at 1200° 1/3, all at atmospheric pressure. At one-fourth atmospheric pressure the amount of P_2 is 2/3.

A new and peculiar type of compound has been discovered by Hilpert and Herrmann (*Ber.*, 46, 2218). When molecular silver is shaken with fused $AsBr_3$ so much of the metal is taken up as corresponds to the compound Ag_3AsBr_3. That this is a chemical individual appears evident from the decomposition reactions. With aqueous ammonia or alkali, metallic silver is formed and $AsBr_3$ goes into solution; that there is a direct union between the arsenic and the bromine is evident from the action of phenylmagnesium bromide, which gives triphenyl arsine in a yield of 70%; when treated with KCN solution free arsenic is precipitated, the tendency of the silver to enter into a cyanide complex being so great that it carries the bromine with it. The compound is very stable and only at a low red heat is the arsenic sublimed in a carbon dioxide atmosphere. The constitution of the compound would seem to be  $\begin{matrix}Ag\\Ag\\Ag\end{matrix}\rangle As \langle\begin{matrix}Br\\Br\\Br\end{matrix}$. The secondary valence of $AsCl_3$ and $AsBr_3$ is so strong that we have the addition products $AsCl_3.3NH_3$ and $2AsCl_3.7NH_3$. Corresponding to these the authors have prepared not only $AsBr_3.3Ag$, but also $2AsCl_3.7Ag$, $2AsCl_3.7Cu$ and $2AsBr_3.7Cu$. This investigation opens a wide field. Perhaps to the same type may belong the silver subfluoride described by Wöhler (*Z. anorg. Chem.*, 78, 239), Ag_2F, which from this standpoint could be written $Ag\cdots Ag\text{-}F$, or $AgF.Ag$; and the same may be true of the subhalides $Ca\cdots CaCl_2$, $Ca\cdots CaI_2$, and $Ca\cdots CaF_2$.

It is interesting to note that Harned (THIS JOURNAL, 35, 1078) has succeeded in preparing a columbium chloride analogous to the tantalum chloride of Chapin, and possessing similar properties. While the empiric formula is $Cb_6Cl_{14}.7H_2O$, the compound is in reality the chloride of the base $Cb_6Cl_{12}(OH)_2.8H_2O$, which is amphoteric, dissolving in HCl with the formation of the chloride $(Cb_6Cl_{12})Cl_2.7H_2O$, and in concentrated alkali with the production of (probably) $(Cb_6Cl_{12})(ONa)_2.aq$. The base also dissolves in HBr giving $(Cb_6Cl_{12})Br_2.7H_2O$.

Group VI.—A quantitative study of the oxidation of inorganic salts by ozone by Yamauchi (*Am. Chem. J.*, 49, 55) deserves notice as throwing light on the mechanism of the reaction, and possibly also on the constitution of ozone. By means of a specially constructed apparatus the author was enabled to measure the ratio between the substance oxidized and the ozone used. In the case of arsenious oxide the equation representing the reaction is $As_2O_3 + 2O_3 = As_2O_5 + 2O_2$, and also in the case of thallous nitrate, mercurous nitrate, and ammonium ferrous sulfate, each ozone molecule furnished one atom of oxygen for oxidation. In the case of stannous chloride, however, the reaction was $3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$, all three atoms of the ozone being used for oxidation. As a matter of fact, in this case rather more stannous chloride was oxidized than indicated by the equation, which would throw some doubt upon the correctness of the equation. The first reaction between sodium thiosulfate and ozone is simply the splitting off of sulfur, $3Na_2S_2O_3 = 3Na_2SO_3 + 3S$, and in the second stage two of the three molecules of sulfite are oxidized to sulfate, $2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2$. In general it would seem that the normal reaction with ozone is the splitting off of a single atom of oxygen, which would be quite in accordance with the formula $O = O^{IV} = O$ for ozone.

In the course of investigations of the action of sulfur trioxide on salts (*Ber.*, **46**, 2513, 2525) Traube has obtained fluosulfonic acid and its salts. SO_3 is absorbed by both NaF and NH_4F, in both cases with the formation of fluosulfonates, $NaSO_3F$ and NH_4SO_3F. The fluosulfonates are stable salts, dissolving in water without decomposition to a neutral solution. So great is the tendency of these salts to form, that if potassium pyrosulfate and ammonium fluoride are dissolved in a little aqueous ammonia, alcohol will precipitate ammonium fluosulfonate from the solution. By dissolving the ammonium salt in fuming sulfuric acid and warming, the free fluosulfuric acid distils over, and by adding ammonia to the distillate the ammonium fluosulfonate is obtained. When dry sodium fluosulfonate is heated in a carbon dioxide atmosphere a gas is given off which is probably sulfuryl fluoride, SO_2F_2.

The work of Flint in splitting tellurium continues to be attacked and no one has succeeded in repeating his results. Morgan (THIS JOURNAL, **34**, 1669) has purified tellurium by repeated hydrolysis, but all his samples continued to give atomic-weight figures which lie around 127.2. Similar results have been obtained by Dudley. Uhler and Patterson (*Am. J. Sci.*, [4] **36**, 135) have made a close study of the arc spectrum of tellurium as compared with the spectrum of possible impurities, and find that that portion of Flint's tellurium which gave lower atomic weight was by no means pure, as Flint supposed, but contained traces of iron and copper. Kusnezow (*Iswestja Donschen Polyt. Inst.*, 1, ii, 380) in discussing the possibility of the atomic weight of tellurium being actually greater than that of iodine, calls attention to the fact that the increments in the atomic-weight series rise and fall alternately, 7–9–11–12–14–16–19–20–23–24, etc., and consequently the elements can be divided into two series, in each of which the atomic weight increases by the comparatively regular increment of 4, and while the atomic weight of each element in the second series is generally slightly greater than that of the corresponding element in the first series, it is not necessarily greater, and this may account for the apparently anomalous atomic weight of tellurium (and argon and cobalt?). The elements may thus be looked upon as being derived from a primitive material of two types. (A somewhat similar possibility was suggested several years ago by the reviewer.)

A rather complete study of the tellurites has been made by Lehner (THIS JOURNAL, **35**, 718) who finds that the tellurites of the alkalies exist in three types, mono, di, and tetra-tellurites, as $K_2O.TeO_2$, $K_2O.2TeO_2$, and $K_2O.4TeO_2$, all hydrated and soluble in water. The tellurites of the alkaline earths are normal and slightly soluble. Barium tellurite forms very stable double salts (solid solutions?) with barium chloride. The tellurites of the heavy metals are all insoluble in water. Tellurites oxidize by heating in the air to 440–470°, although potassium ditellurite oxidizes only to $K_2O.TeO_2.TeO_3$, and the tetratellurite does not oxidize at all.

Of the series of hydrazine salts of the types $M''Cl_2.2N_2H_4$ and $MSO_4.(N_2H_4)_2SO_4$ prepared by Curtius and Schrader in 1894, the compounds with bivalent chromium were missing. These have now been made by Traube and Passarge (*Ber.*, **46**, 1505) and prove to be unique among chromous salts in being stable in the air, indeed the dihydrazin chloride is not oxidized when suspended in water and left in contact with the air for a considerable time. This stability appears to be due in part to the slight solubility of the compounds and in part to the counteracting influence of the hydrazine. When these compounds are dissolved in acids or in ammonia they are rapidly oxidized, like other chromous salts.

Another gap has been filled the past year in the preparation of the first crystalline salts of trivalent tungsten by Olsson (*Ber.*, **46**, 566). While the white tungstic acid precipitated from tungstates by HCl goes readily over into the yellow insoluble form, it is possible by rapid working with cold HCl to carry the white acid over into a clear solution. If metallic tin is added to this clear solution it is reduced, passing through several color changes. If potassium tungstate has been used and the solution warmed with tin to 40–60°, it finally reaches a stable dark yellow-green, and on saturating this solution in the cold with HCl gas a yellow-green crystalline precipitate is obtained which is a double chloride of trivalent tungsten, of formula $K_3W_2Cl_9$, or $3KCl.2WCl_3$. From this salt by double decomposition the rubidium, cesium and thallous salts were made, and from ammonium tungstate, by a similar reduction, the ammonium chlorotungstate. All have analogous formulas and properties, insolubility in water increasing with molecular weight. The slightly soluble rubidium and cesium salts are soluble in very dilute NaOH, and a small amount of the same reagent does not precipitate solutions of chlorotungstates, but concentrated NaOH gives with these solutions a reddish brown precipitate which is insoluble in excess. In these compounds trivalent tungsten shows the same tendency to the formation of complex salts as is shown so characteristically by tungstic trioxide. By the electrolytic reduction of tungsten hexachloride in alcohol solution Fischer (*Z. anorg. Chem.*, **81**, 102, 170) has obtained a green compound which can be purified by recrystallization out of a mixture of alcohol and chloroform, and which has the formula $Cl_2W(OC_2H_5)_3$, a compound of quinquivalent tungsten. All the properties of the compound agree with this formula, but a molecular-weight determination seems to indicate a double formula, two tungsten atoms perhaps being weakly combined.

Mazzucchelli and d'Alceo (*Atti accad. Lincei, Rome*, [5] **21**, ii, 620) suggest three criteria for the recognition of complex salts; the simplest is when the complex salt is less soluble than its constituents and hence separates out of solution; if the salt is more soluble than its components, especially if one of these components is but slightly soluble, one may conclude that a complex salt is present; or if in the third place there is an abnormal distribution of the components between an aqueous and a nonmiscible solvent, a similar conclusion may be drawn. If all of these criteria are wanting it is still possible that a complex salt may be present, but the stability of the complex must be very small. The authors have used these methods in testing the tendency of hexa- and quadrivalent uranium to form complex salts and addition products. Thus uranyl nitrate has no tendency to unite with mercuric cyanide, urea or thiourea; uranyl oxalate is indifferent to urea and to hexamethylenetetramine. In general, uranyl salts have no tendency to complex building with nitrogen compounds. Uranous salts with weak acids are generally basic, but a complex malonate, $Na_2U(C_3H_2O_4)_3$ was formed by the electrolytic reduction of sodium uranyl malonate. Urano-oxalic acid, $H_2U(C_2O_4)_3.8H_2O$ (oxalato-uranous acid) was readily formed and some of its salts with organic bases. Uranous sulfate, $U(SO_4)_2$ proved to be quite stable in solution.

Group VII.—An important investigation of the fluorides of the noble metals (and platinum metals) has been carried out by Ruff (*Ber.*, **46,** 920, 929). In various attempts to prepare the fluoride of platinum it was found that neither HF nor KHF_2 had any action on platinum chloride (nor on Au_2Cl_4), nor could the fluosilicate of Berzelius be obtained by evaporating the solution of PtO_2 in fluosilicic acid, hydrolysis taking place. On adding KF to a concentrated solution of $PtCl_4$, a precipitate of K_2PtCl_5OH was obtained. The action of elementary fluorine upon the other platinum metals was tested, using boats and tubes of a mixture of 7 parts cryolite with 3 parts lithium fluoride. Rhodium was hardly attacked, even at a red heat. Palladium reacted only slowly at a red heat, becoming covered with a red-brown crystalline coating of what was probably PdF_4. Iridium also was only acted on at a low red heat. At higher temperatures heavy white fumes were formed. Ruthenium showed an action similar to that of osmium (below), but the amount of volatile compound formed was small and it was less stable than that of osmium. With osmium, fluorine reacts very readily, three different fluorides being isolated. Below 250° OsF_4 is chiefly formed, at 250° OsF_6 when the stream of fluorine is slow, and OsF_8 when the fluorine is in large excess. The study of these fluorides was carried on with great difficulty owing to several facts. Fluorine is hard to prepare, osmium is expensive, glass is more or less attacked by the fluorides, strongly if a trace of water is present, platinum tubes are opaque and the reactions cannot be seen, it is impossible to wholly exclude oxygen which contaminates everything with OsO_4, the fluorides themselves are far from stable compounds, and it is far from easy to analyze an osmium-fluorine compound or to determine the state of oxidation of the osmium. Taking these facts into consideration, the investigation was very satisfactory and deserves to be placed alongside of the work of Stock on the borides of hydrogen. OsF_4 is the result of incomplete treatment of osmium with fluorine, is soluble in water with an acid reaction, and appears to be non-volatile. OsF_6 is volatile, with a boiling point of 202–205°. It attacks glass so that its melting point could not be determined, but lies above 50°, where the action on glass begins, and below 120°. It is characterized by reacting with water, with which it gives a precipitate of OsO_2, resembling the action of SiF_4 on water. It coats anything damp, or organic, with which it may come in contact, black, in this respect resembling OsO_4. It is, however, the compound OsF_8 which presents the greatest interest, for this is the first compound containing an element which is octavalent beyond dispute (one may argue for the quadrivalence of Os and Ru in OsO_4 and RuO_4), and the only binary compound containing eight atoms of a single kind united with only one other atom, or eight atoms around a single central atom. OsF_8 is a lemon yellow, crystalline compound, with a melting point of 34.4° and boils at 47.5°. Its molecular weight corresponds to OsF_8 and the valence of the osmium is eight. It does not attack gold or platinum, but is decomposed by silver and most other metals with the formation of fluorides. Organic substances are violently attacked. It dissolves to a colorless solution in water, but obviously with decomposition, since the solution smells strongly of OsO_4. It unites with alkali fluorides extremely easily to form salt-like compounds, which decompose on treatment with NaOH with evolution of oxygen and ozone. In a platinum tube it begins to decompose at 225°.

As a source of salts of trivalent manganese, Meyer (*Z. anorg. Chem.*, **81**, 385) recommends potassium manganicyanide, which is readily prepared by drawing air through a concentrated solution of manganese carbonate in KCN. The manganicyanide can be recrystallized from a 10% KCN solution and is fairly stable in cold water. On dilution or on heating it hydrolyzes with the formation of manganic hydroxide, which is perfectly stable and which dissolves readily in acids with the formation of manganic salts. These salts with oxy-acids are intensely red or violet-red and in concentrated acid solution can be boiled without change, but are instantly hydrolyzed on dilution. Except in cold solutions HCl evolves chlorine, but HF dissolves this hydroxide to form a stable fluoride, which gives double salts, among which the red K_2MnF_5 was isolated.

Group VIII.—A paper of some importance in its bearing on the origin of pyrite deposits has appeared by Dosz (*Z. prakt. Geol.*, **20**, 453), in which a new iron disulfide, melnikowite, is described from the miocene clay in the Russian province of Samara. This mineral occurs in small, dense, dull, opaque masses, strongly magnetic, with composition FeS_2. It has an acid reaction and dissolves easily in dilute or concentrated HCl. From all its properties it is an iron disulfide gel which has become crystalloid and passes over very gradually into pyrite as a stable phase. This, Dosz considers, offers an explanation of many pyrite deposits, which are to be looked upon as syngenetic rather than epigenetic. The process of formation he describes somewhat as follows: In shallow lakes the iron is furnished as bicarbonate. This, either by hydrolytic conversion into the hydroxide with subsequent change into sulfide, or by direct precipitation as hydrosulfide, has taken up more sulfur with loss of water, forming melnikowite. The sulfur has been furnished by decomposing organic matter, and the whole course of reaction quite possibly went on under bacterial influence. Bacteria have been traced back at least to Devonian strata, and Dosz could detect fossil iron-bacteria (gallionella ferrunginea) in melnikowite. In earlier periods of geological history sulfur played a more important part in the upper portion of the earth's crust than today, and sulfurizing and desulfurizing bacteria must have had larger influence. The abundance of pyrite in round masses is much better explicable under this theory that pyrite is the stable form derived from a hydrogel.

Bellucci and Corelli (*Atti accad. Lincei, Rome* [5], **22 i**, 603) have made a careful study of the well-known reduction of potassium nickel cyanide solutions by reducing agents, and come to the conclusion that univalent nickel is actually present. As a reducing agent they found sodium amalgam most satisfactory, and while, in accordance with Moore's results some years ago, the nickel-cyanide ratio seems to be 6 : 5, an examination of the valence of the nickel in the red reduced solution, by measuring the hydrogen evolved in its oxidation, and by oxidizing with iodine and with hydrogen peroxide, shows that univalent nickel is present, though no compound of univalent nickel has yet been isolated.

In the analysis of platinum ores from the urals, Holtz (*Ann. chim. Phys.*, [8] **27**, 559) has found certain anomalies which seem to point to the presence of a new metal. After precipitating the platinum from the *aqua regia* solution with sal ammoniac, the other platinum metals (and any copper) are precipitated by metallic zinc. After drying and weighing, this "black" is treated with dilute nitric acid to dissolve the palladium and copper. The other platinum metals should be insoluble, and it is just here that the anomaly occurs, for the palladium and copper come far from accounting for the loss of weight of the "black." After the removal of the palladium and copper there is left a yellow solution which gives a black foam on reduction with zinc. This black material after drying glows when heated in hydrogen and loses slightly in weight. The oxide of the metal is insoluble in all acids but dissolves in NaOH with yellow color, which does not change on acidifying with HCl. The oxide is not attacked by soda-saltpeter fusion. The metal itself is soluble in HNO_3 and HCl and its solution in the latter is not precipitated by NH_4Cl. The metal also dissolves in $KHSO_4$ fusion with red-brown color, but unlike rhodium leaves no white residue of basic sulfate on solution in water. Holtz suggests that this apparently new metal may be identical with French's canadium and Courtis' amarillium. To the reviewer, however, it seems possible that Holtz may be dealing with an impure rhodium, which sometimes itself acts in a rather anomalous manner. An interesting piece of work has been carried out by Wöhler on the stability and conditions of existence of the chlorides of platinum and iridium (*Ber.*, **46**, 1577, 1591, 1720). The method used was to heat the metal, or better in the case of platinum the tetrachloride, in a current of chlorine at different temperatures, the limiting temperatures of formation and decomposition being determined by trial. $PtCl_4$ loses chlorine at 374° but takes it up again at 364°. The greenish black $PtCl_3$ is stable at 435°, losing chlorine at 440° and taking it up at 430°. The brown-green $PtCl_2$ remains unchanged in composition at 560°, though quite volatile at this temperature. If kept at 581–583° a light yellow vapor is given off and occasionally a light green residue is left with the metallic platinum in the boat, which contains both platinum and chlorine and is without much doubt the monochloride, PtCl. This has very narrow limits of stability, certainly of not more than a degree or two, at about 582°. $IrCl_4$ in a stream of chlorine loses chlorine above 200°, indeed at 100° the chlorine pressure is already greater than 1 atmosphere. $IrCl_3$ is best formed by heating iridium in chlorine at about 600°, but it is stable over the extraordinarily large range of 100–763°. At the latter temperature it loses chlorine forming $IrCl_2$, which is stable at 770° but at 780° goes over into IrCl. This also has narrow limits of existence for at 798° the metal is formed. IrCl is also more volatile than the other chlorides. The tetrachloride differs markedly in its properties from the other chlorides. It is soluble in water but the solution on evaporation in chlorine at 40° does not leave an anhydrous chloride, as chlorine is given off and the salt is more or less hydrolyzed. Gutbier (*Ber.*, **46**, 2098) has continued his work on the halogen salts of the platinum metals by preparing the hexabromo-osmates (osmeates). These cannot be satisfactorily made by the action of concentrated hydrobromic acid on the chloro-osmates, owing to the fact that the hydrobromic acid exercises a reducing action on the salts. On the other hand, by using the sodium sulfito-osmate, $2Na_2SO_3.OsO_2(SO_3)_2.5H_2O$, first prepared by Rosenheim, it was possible, by the addition of concentrated HBr, to obtain a solution of sodium hexabromo-osmate, Na_2OsBr_6. By the addition of alkali bromides to this solution the hexabromo-osmates of ammonium, potassium, rubidium and cesium were prepared, all giving fine dark red-brown octahedra. Mention should be made of the continuation of the work of Tschugajew (*Z. anorg. Chem.*, **82**, 401, 420; **83**, 8) on the complexes of platinum with dithioethers, and the extension of this work to the compounds of quadrivalent platinum with organic sulfides, and of the work of Ramberg (*Ber.*, **46**, 1696, 2353) on platinum complexes with xanthogenates and ethylthioglycolates, which is of a similar character. The work is interesting and of great theoretical importance, but is not yet sufficiently generalized for a brief abstraction. Tschugajew also shows (*Z. anorg. Chem.*, **83**, 1) that dimethylglyoxime forms complex compounds with rhodium which much resemble those with cobalt but are more stable. The complex of rhodium with two molecules of the dioxime and two atoms of chlorine is a univalent negative ion, sufficiently stable for the isolation of the free acid, while the similar complex with the chlorine replaced by ammonia is a univalent kation.

The oxidizing properties of osmium tetroxide have been studied by Hofmann (*Ber.*, **45**, 3329; **46**, 1657) and it proves to have very marked catalytic properties. Its action as a carrier of atmospheric oxygen is rather slow, but more rapid under 10 atmospheres pressure and at 50–100°. 200 cc. of 40% alcohol were oxidized, chiefly to acetic acid, within three to four hours by the use of 0.01 gram OsO_4 as oxygen carrier. The catalytic action of OsO_4 is much more marked when the oxygen is furnished by chlorates. A mixture of arsenic and potassium chlorate undergoes no reaction even in the presence of dilute H_2SO_4, but if a little osmium tetroxide solution is added the temperature immediately rises and within a minute the arsenic is completely oxidized to arsenic acid with a very violent reaction. (This is valuable as a lecture experiment.) Organic substances are readily oxidized, as anthracene to anthraquinone. A paper covered with osmium dioxide hydrate is bleached in a few seconds when immersed in a neutral chlorate solution, the dioxide being oxidized to the tetroxide. It seems, from various experiments of Hofmann, that an addition compound is formed between the osmium tetroxide and the chlorate, and that this compound may act as an oxidizing agent; it must itself first unite with the substance to be oxidized, either through secondary valence or adsorption power. Hofmann finds that ruthenium tetroxide possesses a similar catalytic oxidizing power but far less strong than that of the osmium tetroxide. It seems also, from an article by Lehmann (*Arch. Pharm.*, **251**, 152), that osmium dioxide can act as a catalytic reducing agent, especially as a carrier of hydrogen to unsaturated fats. A lecture experiment is described in which 0.1 gram OsO_4 is dissolved in 10 grams olive oil and the whole heated. Then hydrogen is led into the hot oil for half an hour, and on cooling the oil solidifies. It is unfortunate that osmium is such an expensive element, as great possibilities for its industrial as well as laboratory use are indicated in these articles.

Much has been done during the past year on the radioactive elements and it looks as if their decomposition products would soon yield themselves to system and possibly even find places in the periodic system. In the near future they may come to demand a place in a review of inorganic chemistry. At present they should still be treated by themselves.