

considerable amount of time, since in exact work these concentrations must be determined with an accuracy of at least 0.01%. The new apparatus should prove of considerable value in all cases where a very exact analytical control of pure solutions of electrolytes is desired.

URBANA, ILL.

RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

Received December 30, 1912.

Elements.—A very complete investigation of the precipitation of silver on glass in mirror form has been made by Kohlschütter (*Ann.*, **387**, 86). The solution used was ammoniacal silver nitrate with some reducing agent such as formaldehyde, grape sugar, milk sugar, tartaric acid, hydrazine, and others. In the solution very little silver is present as Ag^+ , but there is a relatively large number of OH^- ions. The precipitation of silver in mirror form depends upon the very slow oxidation of the reducing agent, silver oxide being the oxidizing agent, and the concomitant formation of substances of high molecular weight or of colloidal form, everything which antagonizes sol-formation being unfavorable to mirror formation. The character of the mirror is greatly influenced by the composition of the silvering solution and also by the character of the glass upon which the mirror is precipitated. The reason for the precipitation of the silver on the glass is that the silver hydroxide is adsorbed by the glass (hence the influence of the kind of glass), and the reducing agent must also be adsorbed by the glass. Thus everything that affects the surface tension of the solution affects the mirror. Microscopic and ultramicroscopic examination shows that the silver is amorphous and homogeneous, and it may be considered to be in a state of colloidal division. Thus while the mirror is unchanged by alkalies, it is easily removed by very dilute acids, though not dissolved. The sudden appearance of electrical conductivity in the mirror and its rapid increase are explained by the precipitate being laid down in discrete particles which in time bridge over the intervening spaces. The increase in conductivity of the finished mirror corresponds to the spontaneous coagulation of a metal-sol, while the increase under the influence of acids corresponds to the electrolytic precipitation of the sol. The mirror formed by the cathodic dusting of silver in dilute gases varies in character with the gas used, as does the precipitated mirror with the solution.

The rapidly increasing use of many of the rarer metals has led to fuller investigation of their properties. Efforts to get a pure vanadium have been made by Ruff and Martin (*Z. angew. Chem.*, **25**, 49), but without complete success. Previous attempts to reduce the easily fusible V_2O_5 to metal having been unsuccessful. V_2O_3 , which fuses at 2000° , was reduced by aluminum, as well as by carbon and vanadium carbide. The best product obtained was nearly 99% pure. The difficulty of getting a pure metal lies in the fact that the vanadium dissolves the oxide VO , as well as aluminum and carbon, hence no latitude in proportion of reducing material is permissible, and the whole mass must react uniformly, conditions practically impossible of attainment. The melting point of the pure metal was calculated as 1715° and the density as 5.688. Brunck

(*Chem. Ztg.*, **36**, 1233) suggests the use of tantalum as material for electrodes, especially for analytical purposes. For cathodes tantalum can wholly replace platinum, being lighter, firmer, insoluble in aqua regia, without tendency to alloy with zinc and cadmium, cheaper, and is not attacked in the electrolysis of alkalis. Alone, it cannot be used for anodes, as it quickly becomes coated with a very thin, but non-conducting layer of oxide (probably Ta_2O_4), but tantalum anodes which are very thinly plated with platinum serve every purpose. Tantalum has also been suggested as a superior material to platinum for accurate weights. Ruder (*THIS JOURNAL*, **34**, 387) has described the solubilities of malleable tungsten and molybdenum, and finds the former very slightly attacked by any acids or alkalis in solutions, though dissolved by fused alkalis. A saturated solution of sodium hypochlorite attacks it slowly and it is dissolved by a mixture of nitric and hydrofluoric acids, but not by chromic acid mixture. Molybdenum, on the other hand, presents little resistance except to hydrofluoric acid and alkali solutions. It is more readily dissolved by dilute than by strong acids. In a paper before the Section of Electrochemistry at the Congress of Applied Chemistry the properties and applications of ductile tungsten are very fully described. Among possible laboratory applications in replacing platinum are resistance furnaces, filtering gauze, acid-proof dishes and tubes, and analytical weights. The volatility of the metals of the platinum group, under conditions which appertain in the analytical laboratory, has been studied by Sir William Crookes (*Proc. Roy. Soc. London*, (A) **86**, 461) using an electric resistance furnace as a source of heat. At 900° platinum is not volatil, but at 1300° it loses in 2 hours 0.019% and in 30 hours 0.245%. This would mean a loss of weight of 24.5 mg. from a 10 gram crucible. The loss is due to sublimation, the sublimed metal being deposited in hexagonal flakes with metallic luster. Iridium proves to be decidedly more volatil, losing 0.030% in 2 hours and 0.092% in 22 hours at 900° , while at 1300° the loss in 2 hours is 0.828% and in 22 hours 7.297%. Between 100° and 1400° the loss is proportional to the temperature. The loss is due to the formation of a volatil oxide. Rhodium suffers no change in weight at 900° , even after 8 hours heating, and at 1300° loses but 0.021% in 4 hours and 0.131% in 30 hours. It is thus the least volatil of the metals of the group. Ruthenium at 1300° loses 25% of its weight in 8 hours, and this is attributable to the formation of an oxide. The reviewer may add that on heating ruthenium in a current of air in an ordinary combustion furnace the odor of RuO_4 is very distinct and a lower oxide sublimes on the inside of the tube and on the porcelain boat containing the metal. The boiling point of a number of metals at atmospheric pressure has been obtained by Greenwood (*Z. Elektrochem.*, **18**, 319), using a carbon crucible hung in a carbon tube which served for electrical heating, and determining the temperature of distinct boiling by a Wanner pyrometer. For those metals which are attacked by carbon a graphite crucible with fused magnesia lining was used. The following boiling points were found:

Mg 1120°	Sb 1440°	Al 1800°	Ag 1955°	Sn 2275°	Fe 2450°
Bi 1420°	Pb 1525°	Mn 1900°	Cr 2200°	Cu 2310°	

The boiling-point curves for other pressures are shown in curves but the figures are not given.

The action of metals on fused alkalis has been continued by LeBlanc

and Weyl (*Ber.*, **45**, 2300) and the results obtained with potassium hydroxide are found to be in many respects very different from those with sodium hydroxide. While sodium decomposes NaOH quantitatively at 450° with evolution of H and formation of Na₂O, K is without action on KOH even at 550°. When Na acts on KOH there is weak evolution of H, and K volatilizes. With K on NaOH some H is given off but no metal. Evidently an equilibrium, $K + NaOH \rightleftharpoons Na + KOH$ is soon attained and then the Na acts on the NaOH. Al has no action on KOH, but it acts on NaOH moderately with evolution of H and H₂O. Cr, Mo and W act on KOH slowly with evolution of H and formation of chromates, molybdates and tungstates and some evolution of K. The reactions appear to be, $6KOH + M = M(OH)_6 + 6K$; $M(OH)_6 + 2KOH = K_2MO_4 + 4H_2O$; $4H_2O + 4K = 4KOH + 2H_2$. With C there is evolution of H, formation of K₂CO₃ and some K. The K appears to have no action on the K₂CO₃. With Mg there is evolution of H with KOH and precipitation of MgO, while with NaOH, Mg gives off both H and H₂O. With Si the reaction is violent and the formation of SiO₂ quantitative, but the H given off is somewhat less than the expected 4H for each atom of Si. With Ni, Co, and Fe there is no evolution of H or H₂O from KOH (as there is from NaOH) but the metals are attacked with the formation of a small amount of oxide. In general KOH is much more stable than NaOH.

In 1910 it was found by von Bolton that hydrocarbons were reduced by alkali-amalgams to carbon, a part of which appeared to be in the form of diamond. Utilizing the fact that crystallizing substances have a strong tendency to be deposited on crystals of the same substance if present, von Bolton (*Z. Elektrochem.*, **17**, 971) led moist illuminating gas for four weeks through 14% sodium amalgam in a tube coated with a very fine suspension of diamond powder in waterglass. The whole was kept at 100°. Under the microscope the powder was apparently amorphous but after the experiment minute crystals were clearly visible. These showed the properties of diamonds, and while the quantity did not suffice for quantitative analysis it seems extremely probable that diamonds are thus formed by the reduction of hydrocarbons. Two important papers on ozone have appeared during the year, one by Harries (*Ber.*, **45**, 936) and one by Traube (*Ibid.*, 2201). The former finds that by the action of ozone on symmetrical butylene four products may be formed. When the ozone has been previously led through NaOH and H₂SO₄, there are formed a monomeric ozonide, C₄H₈O₃, which can be distilled in a vacuum, and a dimeric form (C₄H₈O₃)₂, which is not volatil. If the ozone is not previously purified, two similar products are obtained but with the formulas C₄H₈O₄ and (C₄H₈O₄)₂, which Harries calls oxozonides. Similar products are formed with other hydrocarbons containing a double bond. From these experiments Harries concludes that ordinary 11-14% ozone is made up of about two-thirds ozone, O₃, and one-third oxozone, O₄, and that the latter is largely destroyed by leading it through alkali and acid, though the purified ozone still contains a little oxozone. Traube's experiments deal with the action of ozone on solid KOH. A red compound is formed which resembles in appearance K₂Cr₂O₇, and which decomposes in water or acids, giving off oxygen, chiefly as O₂, but with some O₃, while the solution contains some H₂O₂. On standing or heating, this red compound loses its color and the white product decomposes with

formation of H_2O_2 and evolution of oxygen. It is evident that the red product is a higher oxide, probably K_2O_7 , which Traube calls potassium ozonate, but it contains some proportion of a lower oxide and also unchanged KOH. The oxide which is present with it and into which it decomposes on standing is doubtless the tetroxide, K_2O_4 , since like this it gives H_2O_2 and oxygen in approximately molecular proportions. As Traube's ozone was passed over concentrated H_2SO_4 before absorption, no evidence appeared of the presence of oxozone.

The possible action of pressure in causing chemical reactions in the metamorphosis of minerals was several years ago suggested by Van Hise, and this has led to an experimental examination of the subject by Spezia (*Atti accad. sci. Torino*, **46**, 19). By using pressures of 6000 to 9500 atmospheres, corresponding to depths of 20 to 30 kilometers, and in some cases continuing the pressure for several months, no instance of chemical action could be found. No action took place between silica and calcite, indicating no silicification. Alabaster, alum, and limonite, embedded in pulverized quartz for 8 months at a uniform pressure of 8000 atmospheres, showed no loss of water. The great difference between the action of heat and of pressure was shown by the fact that goethite, heated in water to 330° for 7 days, became anhydrous, while it remained unchanged under 9500 atmospheres pressure continued for 26 days. To test reduction, CuO was kept in contact with magnesium and then with potassium for months at 9500 atmospheres pressure without change, although the sum of molecular volumes would have been decreased by a reaction; nor was calcite changed to arragonite. Bismuth was not liquefied by a pressure of 9000 atmospheres. *A propos* of plasticity under pressure, Spezia calls attention to the great difference between one-sided pressure and a pressure uniform on all sides; the latter alone cannot liquefy metals nor plastic substances.

Bergius (*Z. Elektrochem.*, **18**, 660), working on reactions under pressure, finds that when peat is heated in water to $250\text{--}350^\circ$ it is charred, and from the velocity of the reaction he considers it possible to calculate the time necessary for bituminous coal formation in nature. His calculations place the time at seven to eight million years, which he considers agrees with geological estimates.

Group II.—According to Bleyer and Müller (*Z. anorg. Chem.*, **75**, 285) from the chemical nature of glucinum it would be expected that compounds of glucinum and arsenic acid would be strongly hydrolyzed, yet that in them the glucinum and the acid would be in a definite molecular ratio. This was confirmed experimentally, and tri-glucinum salts obtained when the di-glucinum would be normal, and basic salts where tri-glucinum would be called for. Thus disodium arsenate precipitated tri-glucinum arsenate from glucinum sulfate, and trisodium arsenate a monobasic salt, $Gl_3(AsO_4)_2 \cdot GlO \cdot 8H_2O$. Monoglucinum arsenate, $Gl(H_2AsO_4)_2$ and the di-glucinum salt, $GlHAsO_4$, were prepared by dissolving the calculated quantity of glucinum hydroxide in arsenic acid. The ammonium salt, $NH_4GlAsO_4 \cdot 4.5H_2O$ was fairly stable but the other alkali salts were basic and the hydrolysis became greater on allowing the salt to stand in its mother liquor. Except the monoglucinum arsenate, which consisted of hygroscopic crystal-flakes, all the compounds were amorphous. The behavior of glucinum with arsenic acid seems thus to be

somewhat similar to that with phosphoric acid, though the glucinum phosphates have not been worked out with sufficient definiteness to show a clear analogy.

Group III.—There have been many attempts to isolate hydrogen boride, which is formed when magnesium boride is acted on by acids and which colors the flame of the simultaneously evolved hydrogen green, and which is also recognizable by its bad odor. The amount of hydrogen boride present is exceedingly small and it is so unstable that until very recently all efforts to isolate it for analysis have been futile, although Ramsay and Hatfield considered it probable that for formula of the gas they obtained was H_3B_3 . Stock and Massenez (*Ber.*, 45, 3539) have now in part solved the problem and their results are a surprise, for the simplest gas evolved in the above reaction is $H_{10}B_4$, and this is accompanied by another whose formula is probably $H_{12}B_6$, as well as others, apparently formed by the decomposition of the latter, which were present in too small quantity to be studied. The difficulties of previous experimenters has arisen from the small quantities of the borides formed, their great instability, especially in the presence of water, the difficulty of separating the different borides formed in the reaction, and the unavoidable presence of at least the hydrogen silicides, from the silicides in the magnesium boride used. The hydrogen borides were prepared by letting the finely powdered magnesium boride fall slowly into acid, and condensing by liquid air, the total yield being under most favorable circumstances 1.2 cc. per liter of evolved hydrogen. The liquid obtained was fractioned, and after great difficulties sufficient of the above compounds obtained for study. $H_{10}B_4$ boils at 16° and $H_{12}B_6$ at a higher temperature, probably near 100° . Both ignite in contact with the air, and decompose in water, giving compounds similar or identical with those described by Travers and Ray. These chemists (*Proc. Roy. Soc. London*, (A) 87, 163), by fusing a mixture of magnesium powder with B_2O_3 in hydrogen, obtained a gray powder which, when treated with water, slowly evolved a gas. The solution became yellow and was slightly alkaline. On boiling this solution hydrogen is given off and when treated with acid still more copiously. The gas has a peculiar odor and burns with a green flame, but analysis shows it to be nearly pure hydrogen. It apparently contained traces of a boron hydride (as Stock has found). On distilling the solution a compound passes over which has the formula B_2O_3 , but which is not boric anhydride, though evidently an isomer of it. The authors consider that the original powder contains not only Mg_3B_2 , but also Mg_2B_1 ; that from these are formed by the action of water B_4O_2 and B_6O_3 , which are further acted on by the water with the formation of the oxide B_2O_3 above mentioned and "boron hydrates" (a name not well chosen) of the respective formulas, $B_2O_2H_6$ and $B_2O_3H_6$.

In the continuation of his work on scandium, Meyer (*Nernst-Festschrift*, 302; *Chem. News*, 106, 13) calls attention to the fact that unless a very large excess of KIO_3 is used in separating thorium from scandium, a small amount of thoria remains dissolved in the solution of scandium iodate. This scandium, and also scandium separated by the sodium carbonate method, showed no radioactivity and was spectroscopically pure, yet had an atomic weight of 45. Further purification with KIO_3 , with great sacrifice of scandium, brought the atomic weight down to 44,

and thorium could be identified in the portion precipitated. It is thus possible for scandia to contain upwards of 0.5% thoria which cannot be detected directly by chemical or physical means. However, Meyer shows that the magnetic method of detection is available, since the product with atomic weight of 45 is paramagnetic, while the pure product (44) is diamagnetic. He calls attention to the fact that scandium, lanthanum and yttrium, which unquestionably belong in the third group of the periodic system, are distinguished by their magnetic character from all the other rare earths. Among the other works which have appeared on the rare earths are those of James (*THIS JOURNAL*, **34**, 757) on their separation; of Jantsch (*Z. anorg. Chem.*, **76**, 303) on the double nitrates; of Wirth (*Ibid.*, 174) on the solubility of the oxalates and sulfates in sulfuric acid; and of Barnebey (*THIS JOURNAL*, **34**, 1174) on the reactions of the rare earths in non-aqueous solutions. Urbain and Bourion (*Compt. rend.*, **153**, 1155) have also prepared and studied the chlorides of europium, EuCl_3 , EuCl_2 and EuOCl . These papers are all valuable contributions to this interesting subject, but do not lend themselves to brief abstraction.

Group IV.—The question as to what is the first reaction that takes place when carbon burns in oxygen has long been a subject of controversy. The commonly accepted view that the initial combustion is to CO_2 , which in the presence of incandescent carbon is reduced to CO, rests experimentally chiefly on the work of Lang, who found that in a slow oxygen stream carbon was oxidized at 500° almost exclusively to CO_2 , while no CO_2 was reduced to CO at this temperature. The formation of *some* CO in a more rapid gas current Lang attributed to local heating, which did not occur in the slow current. The conclusions drawn from these and other experiments by Lang were called in question by Dixon, and his experiments and those of Baker on explosion rates seemed to show that at least in the case of gaseous carbon the formation of CO precedes that of CO_2 . C. J. Baker also showed that while moist oxygen absorbed by carbon at -12° was given up as CO_2 when the carbon was heated to 100° , dry oxygen (by P_2O_5) absorbed by dry carbon at $+12^\circ$ was not given up till 450° and then mainly as CO, it appearing thus that CO is the first product of oxidation. Rhead and Wheeler (*J. Chem. Soc.*, **101**, 831, 846) have approached the subject from the standpoint of determining the velocity of the reaction (a) $\text{C} + \text{O}_2 = \text{CO}_2$; (b) $\text{CO}_2 + \text{C} = 2\text{CO}$; (c) $2\text{C} + \text{O}_2 = 2\text{CO}$; and (d) $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, at different temperatures. If it could be shown that either reaction (a) or reaction (c) proceeded at a temperature at which, under the same experimental conditions, the rates of reactions (b) and (d) were inappreciable, the problem would be solved. It was, however, not found possible to obtain a temperature at which the velocity of carbon oxidation was appreciable, where there was conclusive evidence of the primary formation of either oxide to the exclusion of the other. Some CO is produced by the oxidation of carbon at low temperatures under conditions which do not admit of its being formed by the reduction of CO_2 , but on the other hand CO_2 is undoubtedly produced at low temperatures in quantity which cannot be altogether accounted for by the supposition that CO is first formed and then oxidized to CO_2 . The conclusion is therefore drawn that when carbon is burned at low temperatures CO_2 and CO are produced simultaneously, a conclusion quite in accord

with practically all previous experimental evidence. A further paper is promised on what reaction between carbon and oxygen can account for this simultaneous production of two oxides. The question as to whether carbon monoxide burns directly to the dioxide, $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, has in the past stimulated much investigation, especially since it seems certain that the reaction does not go on, even at high temperatures, unless at least a trace of water is present. Now Wieland (*Ber.*, 45, 679) has shown that carbon monoxide is oxidized by moist palladium black, even in the absence of oxygen. It appears that the first step of the reaction is the union of CO and H_2O to formic acid, and that this is in turn decomposed to CO_2 and hydrogen, the latter being absorbed by the palladium black. If the same reaction goes on in the ordinary combustion of carbon monoxide, then the hydrogen evolved is at once oxidized to water and the cycle repeated. Wieland was able to show the formation of formic acid in the combustion of carbon monoxide by directing the flame against ice, when formic acid was detected in the water.

An examination of the air collected on the Charcot Antarctic expedition has been made by Müntz and Lainé (*Compt. rend.*, 153, 1116) and the amount of CO_2 found to vary from 1.447 to 2.553 parts per 10,000, the mean being 2.0524. The small amount compared with the normal content is to be accounted for by the temperature of the ocean water, generally below 0° , thus reducing the dissociation pressure of the dissolved bicarbonates. This is in confirmation of the theories of Schloesing, and shows that, contrary to the idea of Gay-Lussac, the movement of the atmosphere is not sufficient to cause a uniform distribution of CO_2 . It is to be hoped that there will soon be opportunity for a study of the atmosphere over the Antarctic plateau, where the influence of the ocean would be eliminated. The composition of the higher layers of the atmosphere is considered by Wegener (*Z. anorg. Chem.*, 75, 107) to be very different from that of the lower strata. His views are based on the changes of density as shown by the suspension of the Krakatoa dust-clouds, diffuse reflection of light, and also of sound, the glow of meteors and spectra of the aurora and of meteor trails, and also the analogy of the sun's atmosphere. At 40 kilometers oxygen is reduced one-half and nitrogen correspondingly increased. Above this these gases rapidly decrease while hydrogen increases and helium is at a maximum of 4%. At 200 kilometers and above, the chief constituent is a gas lighter than hydrogen, called by Wegener geo-coronium, resembling the coronium of the sun, and possibly identical with Mendeléef's element with atomic weight of 0.4.

A further substantiation of the theories of Franklin on ammono-compounds, fully recapitulated by him and also applied to the mercury-ammonia compounds (*Am. Chem. J.*, 47, 285, 361), is furnished by the work of Ruff (*Ber.*, 45, 1364) on the nitrogen compounds of quadrivalent titanium. The starting point was TiBr_4 , formed by the action of bromine in a stream of carbon dioxide on metallic titanium or its carbide. On treatment with ammonia this gives an ammonate of approximately the composition, $\text{TiBr}_4 \cdot 8\text{NH}_3$. By washing with liquid ammonia this is more or less ammonolyzed, giving a product (ammono-basic bromide) containing both titanium amide, $\text{Ti}(\text{NH}_2)_4$, and bromide, of somewhat variable composition. From this, by action of potassamide, KNH_2 , there was formed a new titanium nitride, Ti_3N_4 , and a potassium ammono-titanate

of the formula KHTiN_2 (structurally, $\begin{array}{c} \text{KN} \\ \diagdown \\ \text{Ti} \\ \diagup \\ \text{HN} \end{array}$). The nitride, Ti_2N_4 ,

is hydrolyzed by water with the formation of titanitic acid and ammonia, and on heating is converted into the nitride of trivalent titanium, TiN , and nitrogen. The possibility of utilizing this reaction for the synthesis of ammonia from its elements is suggested by the author, and an experiment of heating a mixture of hydrogen and nitrogen to 360° in the presence of the above mentioned potassium salt showed a contraction of volume, which indicated ammonia formation. The potassium ammono-titanate ignites spontaneously in the air and is violently decomposed by water. A portion of the potassium (3/10) can be removed by washing sufficiently with liquid ammonia. With potassium iodide or sulfide the potassium seems to be replaced by iodine or sulfur, indicating, as would be expected, the amphoteric nature of the TiN_2 group.

Group V.—A rather extensive piece of work has been carried out by Ferratini (*Gazz. chim. ital.*, **42**, I, 138) on the double salts of hydrazine. These were generally prepared by mixing solutions of the components, if soluble, but occasionally by solution of the oxide or halide in an acid solution of the hydrazine salt. In many cases, especially with bivalent metals, the salts were hydrated, and in a few cases contained "hydrazine of crystallization" (hydrazinates). No systematization of the types appears possible. For example, Cu^1 gives $3\text{CuCl}\cdot\text{N}_2\text{H}_5\text{Cl}$, $\text{CuCl}\cdot\text{N}_2\text{H}_5\text{Cl}$, $\text{CuCl}\cdot\text{N}_2\text{H}_5\text{Cl}\cdot 0.5\text{H}_2\text{O}$, $3\text{CuBr}\cdot 2\text{N}_2\text{H}_5\text{Br}$, $2\text{CuCN}\cdot\text{N}_2\text{H}_5\text{CN}$; Sb and Bi give the $\text{SbCl}_3\cdot 3\text{N}_2\text{H}_5\text{Cl}$ type, but Fe^{II} and Mn^{II} give the same, as $\text{FeCl}_2\cdot 3\text{N}_2\text{H}_5\text{Cl}$; while Co and Ni give $\text{CoCl}_2\cdot 2\text{N}_2\text{H}_5\text{Cl}\cdot 2.5\text{H}_2\text{O}$ and $\text{CoCl}_2\cdot 2\text{N}_2\text{H}_5\text{Cl}\cdot 0.5\text{N}_2\text{H}_4$. Zn gives $\text{ZnI}_2\cdot 2\text{N}_2\text{H}_4\cdot 1.0.5\text{H}_2\text{O}$, while the similar salt of Cd is anhydrous. In many respects these salts naturally show much analogy with the corresponding NH_4 salts. An interesting derivative of hydrazoic acid with cyanogen has been prepared by Darzens (*Compt. rend.*, **154**, 1232). By the action of NaN_3 upon cyanogen bromide, $\text{N}\equiv\text{C}\cdot\text{N}_3$ is formed, called by Darzens carbon pernitride, but better cyanogen trinitride (or hydrazoate). CN_4 is a colorless oil which crystallizes in needles melting at 36° , and is soluble in most organic solvents. Slightly volatile in a vacuum, it begins to decompose at 70° and explodes at 170° with great violence. It is exceedingly sensitive to shock, but in a perfectly pure condition can be preserved a long time. It readily undergoes polymerization, forming a solid which is insoluble in ether, and not exploded by a blow. The aqueous solution of CN_4 readily hydrolyzes to the acid, N_3COOH , which in turn decomposes into HN_3 and CO_2 .

Three papers have appeared from Ephraim (*Ber.*, **44**, 3405, 3414, 3416) on substituted phosphoric acids. Owing to hydrolysis the only tetrathiosphosphate hitherto prepared is that of sodium. It is possible that the anion of this salt, PS_4^{--} , hydrolyzes, but more probable that it must be considered as decomposing, $2\text{Na}_3\text{PS}_4 \rightleftharpoons 2\text{Na}_2\text{S} + \text{P}_2\text{S}_5$, the P_2S_5 then hydrolyzing. Antagonizing this reaction by the use of a large excess of alkaline sulfide with a minimum of water, Ephraim was able to prepare from P_2S_5 the tetrathiosphosphates of potassium, ammonium, and barium, but with strontium only a hydrogen trithio-salt, $\text{Sr}_3\text{H}_6(\text{PS}_3\text{O})_4\cdot\text{aq}$. Ephraim protests against these compounds being called *sulfo* phosphates, since a *sulfo*-compound should be derived from

SO_3H . They should be called thiophosphates, *thio* being used for those compounds in which bivalent sulfur replaces oxygen. For the different acids of this series he proposes the names: for $(\text{HO})_3\text{P} : \text{S}$, *thion-phosphoric acid*; for $(\text{HO})_2\text{P}(\text{HS}) : \text{O}$, *thiol-phosphoric acid*; for $(\text{HO})(\text{HS})\text{P} : \text{O}$, *dithiol-phosphoric acid*; and for $(\text{HO})_2\text{P}(\text{HS}) : \text{S}$, *thion-thiol-phosphoric acid*.

When the lower oxides, P_4S_8 and P_4S_7 , react with sodium sulfide, the same product seems to be formed, though with differing amounts of water of crystallization. The formula corresponds to $\text{Na}_3\text{PS}_8\text{.aq}$. but the compounds are not thiophosphates, since after removal of the sulfur by water a compound is left which reduced permanganate. In spite of the fact that the acid is tribasic (trithiophosphorous acid should be dibasic), Ephraim is inclined to think the compound is sodium trithiophosphite. When P_4S_8 is used in its preparation there is an evolution of spontaneously combustible phosphine, but with P_4S_8 only ordinary phosphine and hydrogen.

By the treatment of the compound $\text{P} \begin{matrix} \diagup \text{OC}_6\text{H}_5 \\ \diagdown \text{Cl}_2 \end{matrix}$ with sulfur there

is formed $\text{S} : \text{P} \begin{matrix} \diagup \text{OC}_6\text{H}_5 \\ \diagdown \text{Cl}_2 \end{matrix}$, and this with ammonia gives a beautifully crystallized and stable phenyl ester of diamino-thion-phosphoric acid,

$\text{S} : \text{P} \begin{matrix} \diagup \text{OC}_6\text{H}_5 \\ \diagdown (\text{NH}_2)_2 \end{matrix}$. The free acid can be obtained from this by saponification with solid KOH and acidification, but not in a pure condition. The

chloride of the diphenylester of phosphoric acid, $\text{O} : \text{P} \begin{matrix} \diagup (\text{OC}_6\text{H}_5)_2 \\ \diagdown \text{Cl} \end{matrix}$ gives with hydrazine the ester of hydrazino-phosphoric acid, from which salts of this

acid, $\text{O} : \text{P} \begin{matrix} \diagup (\text{OH})_2 \\ \diagdown \text{NH.NH}_2 \end{matrix}$, can be prepared, as well as those from the mono-phenyl ester. The free acid is unstable but can be kept in alkaline solution. More than ten different salts of these two acids are described.

Group VI.—A number of studies of peroxy-salts have appeared during the year, among them two by Riesenfeld and Rau on the percarbonates (*Ber.*, **44**, 3589, 3595), who recognize three types of these compounds, the carbonate with H_2O_2 of crystallization, the true percarbonates Na_2CO_4 , and those of the $\text{Na}_2\text{C}_2\text{O}_6$ type. The compounds, $\text{Na}_2\text{CO}_3\text{.H}_2\text{O}_2\text{.}0.5\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_4\text{.}1.5\text{H}_2\text{O}$ (types 1 and 2) are isomeric, but show even in solution different chemical characteristics. D'Ans and Friederich (*Z. anorg. Chem.*, **73**, 325) have used as a method of preparing peroxides of alkalis and alkaline earths the solution of the metal in an ethereal solution of H_2O_2 .

Quite an extensive study of aminosulfonic acid and its derivatives has been made by Hofmann (*Ber.*, **45**, 1394, 1731). The use of the acid, which crystallizes pure and anhydrous, out of a not too concentrated solution of hydroxylamine hydrochloride which has been saturated with sulfur dioxide, is suggested as a standard for acidimetry. The acid is

not hygroscopic and can be accurately weighed. It can be titrated in 0.1 *N* strength against 0.1 *N* KOH with phenolphthalein or methyl orange, against 0.1 NH_3 with rosolic acid, and against 0.01 BaOH with phenolphthalein. In all these cases it gives accurate acid values. The 0.1 *N* solution is hydrolyzed by 90 minutes boiling to the extent of 38.5%, and 88% in 11 hours. At 40° the hydrolysis is very slow and at 15° not recognizable at the end of a week. Since the hydrolysis gives rise to ammonium hydrogen sulfate it does not affect the acid value, but owing to the presence of ammonium cannot be used with phenolphthalein as an indicator. Aminosulfonic acid is an excellent reagent for the preparation of aryl-sulfuric acids and phenol-sulfonic acids. An interesting series of salts is described in which the hydrogen of the NH_2 group is more or less replaced by Hg, Ag, or Au, as for example, $\text{Hg:N.SO}_2\text{OK}$, $\text{AgHN.SO}_2\text{OK}$, and $\text{Au}_2(\text{N.SO}_2\text{OK})_3$.

The work of Gutbier on chloro- and bromo-tellurates has been continued (*J. prakt. Chem.*, [2] **86**, 150) by the preparation of a large number of these salts of organic bases, chiefly belong to the aromatic series. The chlorotellurates are all yellow and the bromotellurates red. All are anhydrous and not one crystallizes in the regular system. To these must be added (*Ibid.*, **85**, 321) a large number of bromo-selenates, both of the alkali metals, which are all octahedral, and of alkylammoniums. Hexabromoselenic acid, H_2SeBr_6 , was prepared by acting on finely divided selenium in concentrated hydrobromic acid with bromine. On adding the bromide of the base, the anhydrous bromoselenates crystallize out. They are all easily hydrolyzed, and the organic salts do not crystallize in octahedral form.

Group VII.—Salvadori (*Gazz. chim. ital.*, **42**, I, 458) has investigated the hydrates and ammoniates of the perchlorates of the bivalent metals. The typical hydrate, as would be expected, is $\text{M}''(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, where M'' is Co, Ni, Mn, Cd, Zn, or Cu. A tetrahydrate is also formed in each case except that of Co, and with Cu the tetrahydrate is the stable form. Hexa-ammoniates, $\text{M}''(\text{ClO}_4)_2 \cdot 6\text{NH}_3$, are formed with Co, Ni, and Cd, and tetra-ammoniates with Co, Cd, Zn, and Cu. Mn and Cu, while not giving hexa-ammoniates, form mixed compounds of the hexa-type, $\text{Mn}(\text{ClO}_4)_2 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$. Cu has also a strong tendency to form basic perchlorates. An interesting case is that of five cobalt perchlorates, with respectively 6NH_3 , 4NH_3 , 3NH_3 , $4\text{NH}_3 \cdot 2\text{H}_2\text{O}$, and $3\text{NH}_3 \cdot 3\text{H}_2\text{O}$, which readily pass from one into the other on increasing or decreasing the vapor pressure of water and ammonia surrounding them. These are all strongly colored, red, blue or green, but another cobalt perchlorate exists, $\text{Co}(\text{ClO}_4)_2 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$, which is yellow, more stable than the others and seemingly of an entirely different character. Another attempt has been made to prepare perbromic acid and the perbromates (Robertson, *Chem. News*, **106**, 50) and again unsuccessfully. Even up to 250°, bromine in the presence of KBr had no effect upon KClO_4 , nor was the slightest trace of iodine given off from KIO_4 by the action of bromine. On heating KBrO_3 with PbO_2 the only product of the reaction was KBr. Robertson considers that in the formation of perbromic acid the vibration of the atoms within the molecule may be too great for such a system to exist. On the other hand, since both perchlorates and periodates are stable, it seems more probable that chemists have

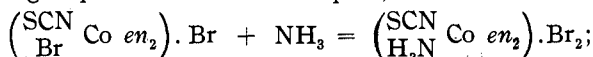
merely failed thus far to catch just the conditions demanded for the formation of the perbromates, as they have failed also to get the oxides of bromine.

Group VIII.—The colors formed by heating cobalt nitrate with various oxides, as in qualitative analysis, furnishes a perennial subject of research. Hedvall (*Ber.*, 45, 2095) has prepared Rinmann's green in hexagonal crystals of some size (2-3 mm.²), by heating zinc oxide with cobalt carbonate to 1100° with KCl as flux. The cobalt is in bivalent form and the CoO : ZnO ration is 1 : 4.8, or perhaps 1 : 5. All this, however, does not have any bearing on the vital question as to whether, in these crystals, one has to do with a chemical individual or only a solid solution. A little more progress seems to be made by Burgstaller (*Chem. Zentr.*, 1912, II, 1523), who, noting the fact that the colors in question are blue, red or green, considers that we are dealing in the blue and red with solid solutions which show the usual colors of cobalt in solution. In the green with ZnO we have blue on a substratum of yellow. While ZnO is white at ordinary temperatures, when heated it passes into a yellow modification, and it seems that in the presence of CoO the reversal into white on cooling is prevented. If this theory is true it would seem possible by carefully choosing conditions to obtain a blue color with zinc. Burgstaller's ratio of CoO to ZnO in his Rinmann's green was 7.05 : 100, very different from that of Hedvall.

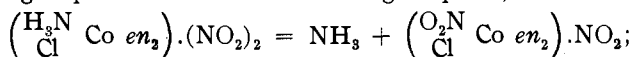
The work of Levy (*Proc. Chem. Soc. London*, 28, 91) on the cyanoplatinites has confirmed Hadow's explanation of the action of bromine on these salts, except that the formula of the brown salt should be 6 $K_2Pt(CN)_4 \cdot K_2Pt(CN)_4 \cdot Br_2$, instead of 5 molecules of the unoxidized salt, as Hadow thought. Levy also oxidized the cyano-platinite by MnO_2 or PbO_2 in sulfuric acid solution, obtaining a similar compound to that obtained by the action of bromine. It thus seems that ($7K_2Pt(CN)_4$) is capable of acting as a feebly positive bivalent base. More interesting were the results obtained by oxidizing the cyano-platinite with hydrogen peroxide, especially in the form of "perhydrol," when salts of the type, $M'Pt(CN)_4$ (simple and double) are formed. These seem evidently to be salts of trivalent platinum, and to have the composition which may be expressed by $MCN.Pt(CN)_3$. In the discussion which followed the reading of this paper, Professor Reynolds called attention to a lithium salt in his laboratory which seemed to have the composition, $Li_2Pt(CN)_5 \cdot 2H_2O$, which might be $2LiCN.Pt(CN)_3 \cdot 2H_2O$. Further work on these salts will be awaited with interest.

Complex Compounds.—Perhaps the most important work in inorganic chemistry during the past year has been that of Werner in his development of inorganic stereoisomerism and optical isomerism, especially in the complex compounds of cobalt. In the *Annalen* (386, 1) he gives a complete review of his work on the stereoisomerism of cobalt compounds, much of which has been published from time to time in the *Berichte*. A few points in this work may be noted. Diethylenediamine compounds having different radicals in the other two places within the coordinated group as $\left(\begin{matrix} A \\ B \end{matrix} Co en_2 \right) \cdot C$, give rise to what Werner calls ionization-metamerism, and furnish three isomers, according as the negative ion is A, B, or C. In addition each of these isomers may exist in both *cis* and *trans*

form, according as A and B (or B and C, or A and C) are on contiguous or opposit corners of the fundamental octahedron of the coördinated group. Thus there are six possible isomers, and in the case where A, B, and C represent NO_2 , Cl and SCN, all six have actually been prepared. Some considerable progress has been made toward the systematization of the properties of these compounds. For example, *cis* compounds generally are more soluble than the *trans* isomers, as is true of organic compounds; the color of a compound is far more influenced by an element or group within the coördinated radical than by one outside; the order in which different groups within the radical affect the color is the following, the first named having least effect: CN, CO; NO_2 , *en*, NH_3 , NCS; SO_3 ; OH_2 , O.NO, O-Acyl, OH; Cl, Br, I. In various intramolecular reactions transformation of isomers often occurs, but the direct transformation of stereoisomers into each other is rare, and probably results only from the formation of intermediate products. Three types of these reactions in which rearrangement may take place are noticed: one (Einlagerungsreaktion) in which NH_3 or H_2O enters the complex radical, forcing the ionization of group or atom of the complex, as

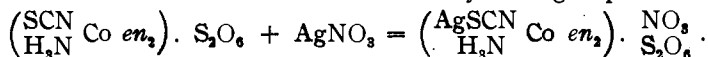


one (Verdrängungsreaktion) where NH_3 or H_2O passes out of the complex, an atom or group outside the radical taking its place, as



and a third, (Substitutionsreaktion) where one negative atom or group is replaced by another. Inasmuch as the ordinary conception of replacement of atoms or groups, according to which an atom passes out of the group and the substituting atom takes its place, is inadequate to account for the stereometric changes which occur, Werner suggests a new theory. Every atom or group in the second sphere of a complex salt, that is outside the coördinated group, is attracted by the central cobalt atom, which seeks to draw the outside atom into the coördinated group. The *direction* of this attraction will depend upon the constitution of the complex; at all events this attraction will be stronger in some directions than in others. This will determine in what position the atom (or group) will enter the complex. On its entrance, the cobalt atom having but six coördination valences, some other atom (or group) must leave the complex, and it will be the one for which the cobalt atom has (under the circumstances) the least attraction, and it may or may not be the atom which previously occupied the place where the newly entering atom has entered. Re-arrangements are thus not anomalous, but are founded on the ordinary course of the reaction. Werner suggests that the same idea is applicable to organic chemistry, where such transformations are by no means infrequent, and in particular calls attention to its applicability to the Walden rearrangement.

One other class of products must be noted, which are formed by direct addition to groups within the coördinated complex. Such, for example, is the addition of a silver atom to the isothiocyanate group:



In such cases frequently the silver atom is not removed on treatment with HCl. This type of reaction is also exemplified by Kirmreuther's sulfaminic acid derivatives of the chloroplatinites described last year.

Werner has also developed the work begun the previous year on the optical isomerism of the cobalt complex (*Ber.*, **44**, 3272, 3279; **45**, 121, 3281, 3287, 3294). Numerous compounds of the types $\left(\begin{smallmatrix} A \\ B \end{smallmatrix} \text{Co } en_2\right)$ and $\left(\begin{smallmatrix} A \\ A \end{smallmatrix} \text{Co } en_2\right)$ have been prepared, and the racemic form split into the optical isomers, most frequently by the use of the bromocamphorsulfonates. In many cases it is possible to go from one compound to another without changing the character of the activity. The phenomenon of mutarotation sometimes appears; the chloronitro-compound increases from a rotation of $[a]_D = 20^\circ$ to a final constant of 52° . In other cases, as with the chlorobromo-compounds, the rotation decreases rapidly and within an hour all activity has disappeared. Complexes were also prepared in which A and B in the above formulas are represented by a single bivalent group, as carbonate and oxalate. The two compounds showed an opposit activity from that of the dichloro-compounds from which they were derived, the levo-dichloro-compound giving a dextro-carbonato- and dextro-oxalato-salt. The carbonato-salts have a high rotation, that of the chloride, $(\text{CO}_3\text{Co } en_2)\cdot\text{Cl}$ being $[a]_D = \pm 350^\circ$, while the carbonato-dithionate is $[a]_D = \pm 216^\circ$, a much greater difference than is usual for different salts of the same complex. While the carbonato-salts go slowly over into the racemic form, the oxalato-salts retain their activity even on boiling. Perhaps the most remarkable case of isomerism is that of the triethylenediamine compounds $(\text{Co } en_3)$, where there are three identical bivalent groups in the complex, but which should exist in two non-superposable forms. Here the bromocamphorsulfonates gave no assistance in resolving the isomers, but by adding sufficient silver tartrate to precipitate two of the three atoms of chlorine in $(\text{Co } en_3)\cdot\text{Cl}_3$, the dextro-chlorotartrate crystallized out and the levo-salt form was recoverable from the mother liquor. From these salts both forms of optically active chlorides, bromides and nitrates were formed. The corresponding triethylenediamine chromium racemates could not be resolved by tartrates nor by bromocamphorsulfonates, but by using nitrocamphor this was accomplished (*Ber.*, **45**, 865). The rotation of the optical isomers of these chromium salts was less than that of the cobalt salts, confirming what had already been found regarding the dichloro-diethylenediamine salts of these two metals. A further development of this work on inorganic optical isomerism is the preparation by Werner (*Ibid.*, 1228) of the optical isomers of triethylenediamine rhodium salts. Here the racemates could be split both by the tartrate and the nitrocamphor method, and the isomers showed decided stability, it being possible to evaporate the solutions without decreasing their optical activity. How much the nature of this activity depends upon the special nature of the central atom is shown by the fact that while the rotation of the rhodium compounds is quite similar in amount to that of the corresponding chromium compounds, it is opposit in sign, those rhodium salts having the same composition and configuration as the dextro-chromium salts, being levorotary. Werner was also able to prepare (*Ibid.*, 433) by the tartrate method the levorotary form of tri- α α -dipyridyl iron chloride, bromide and iodide.

The rotation is very high (in the neighborhood of 500°), but falls rapidly owing to formation of the racemate. It thus appears that inorganic optical isomerism is not confined to ethylenediamine compounds, nor to the compounds of trivalent metals, since the iron in the pyridyl compound is bivalent. It should, however, be noted that in spite of the most brilliant confirmation of Werner's theories by his work of the last two years, the whole coördination theory is quite severely handled by Stewart in his "Recent Advances in Physical and Inorganic Chemistry" (Longmans, Green & Co., 1912, pp. 160ff).

In this connection attention may be called to the work of Costachescu (*Ann. scient. Univ. Jassy*, 7, 87, 132), who by action of pyridine on ferrous chloride obtains $(\text{FePy}_4)\text{Cl}_2$. Evaporated with HCl there is formed $(\text{Fe}_2.3\text{PyHCl})\text{Cl}_6$, or with HBr, $(\text{Fe}_2.3\text{PyHBr})\text{Cl}_2\text{Br}_4$. With $(\text{Cr}(\text{H}_2\text{O})_6)\text{F}_3$ pyridine gives $(\text{Cr} \begin{smallmatrix} \text{Py}_3 \\ \text{F}_3 \end{smallmatrix})$, and by elimination of one pyridine, the aquo-

fluoride, $(\text{Cr} \begin{smallmatrix} \text{Py}_2 \\ \text{F}_3 \\ \text{H}_2\text{O} \end{smallmatrix})$. The conductivity of both these compounds is zero,

as would theoretically be expected, and neither chromium nor fluorine is precipitable. By the further action of pyridine there were formed salts of the univalent radical, $(\text{Cr} \begin{smallmatrix} \text{Py}_4 \\ \text{F}_2 \end{smallmatrix})$, which acted like a univalent metal.

A study of the equilibrium between purpureo- and roseo-cobalt chlorides, $(\text{Co} \begin{smallmatrix} \text{Cl} \\ (\text{NH}_3)_5 \end{smallmatrix})\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{Co} \begin{smallmatrix} \text{H}_2\text{O} \\ (\text{NH}_3)_5 \end{smallmatrix})\text{Cl}_3$, by Lamb and Marden (*THIS JOURNAL*, 33, 1873) shows that this is a monomolecular reaction, and apparently consists in the slow ionization of the chlorine atom of the purpureo-complex, a water molecule taking its place. By analogy the same thing would be expected in the dissociation of an ordinary electrolyte. In the dry state the roseo-salts have a critical vapor pressure above which only a very slow loss of water occurs, but the change does not appear to be reversible.

A method of investigating residual valence for ammonia in ammoniates is given by Peters (*Z. anorg. Chem.*, 77, 137), which consists in subjecting the dry salt to the action of a measured amount of ammonia in a eudiometer, driving off the ammonia by a vacuum and then resaturating it. The results with nearly a hundred salts are tabulated, and the compounds are, in general, what would be expected from Werner's theory, the number of ammonia molecules taken up being most frequently six or a multiple of six. In some cases the ammonia was evidently taken up by both cation and anion, but the distribution could not generally be determined. By this work an interesting line of study has been opened up. Inghilleri (*Atti Accad. Fisiocrit. Siena*, 1909, 6) has prepared by the action of quinoline on uranyl salts, a series of complex salts of the general type, $((\text{C}_8\text{H}_7\text{N})_2\text{UrO}_2)\text{X}_2$, including the nitrate, sulfate, acetate, oxalate and tartrate, as well as double salts. By using aniline in the place of quinoline (*Ibid.*, 1911, 3, 4), the sulfate, acetate and oxalate of the base, $((\text{C}_6\text{H}_5\text{NH})_2\text{UrO}_2)$, were obtained, as well as the compound, $\text{C}_6\text{H}_5\text{N}.\text{UrO}_2.6\text{H}_2\text{O}$. In connection with complex salts mention should also be made of the continuation of Weinland's work on the chromi-acetates (*Z. anorg. Chem.*, 75, 293), where the complex cation contains three chromium atoms

with six or less acetate groups, and OH, H₂O, or NH₃. More than a score of different types are described, though they seem as yet not capable of systematization. In studying the ammoniates of cuprous-mercuric iodides, Anderlini (*Gazz. chim. ital.*, **42**, I, 321) has prepared CuHgI₃.2NH₃, CuHg₂I₅.3NH₃, and CuHg₂I₅.4NH₃, all of which are rather unstable and become red on standing in the air.

Ephraim (*Ber.*, **45**, 1322) has made use of the ammoniates in his studies of "Nebenvalenzen." While it would be difficult to measure directly the force which holds molecular complexes together, it is possible to measure the energy which must be added to decompose them. The decomposition is dependent on pressure, temperature and the affinity which holds them together. If the pressure is kept constant the temperature of decomposition is a direct function of the energy of formation. Thus, Ephraim has determined for a large series of ammoniates of the salts of bivalent metals, and finds that the decomposition temperature increases with the decrease in atomic volume of the central (metallic) atom; indeed the product of the cube root of the decomposition temperature (absolute) by the atomic volume of the central atom is approximately constant. The vapor pressure of the ammoniates can thus be approximately calculated from the atomic volume. The atomic volume is naturally not the only factor which controls the stability of the ammoniates. Thus no metal whose atomic volume is greater than 14 can form a hexa-ammoniate at ordinary temperature, and no atom except those of the alkaline earths can hold more than six ammonia groups; the octa-ammoniates of these earths must have a special interpretation. The negative atom or group has also something of a determining influence, and the relation between the difference in influence of different negative groups (as Cl-Br) is constant for different metals. Another class of complex salts which is being studied by Copaux (*Z. anorg. Chem.*, **74**, 351) and Rosenheim (*Ibid.*, **75**, 141; **77**, 239) as well as by Miolati, is the hetero-poly-acids, containing WO₃ and MoO₃. Copaux draws a distinction between what he considers the normal and the secondary basicity of these acids, a distinction which Rosenheim deems unnecessary, and which would, if logically carried out, demand that we should consider phosphoric acid normally dibasic and secondarily tribasic. The free dodeka-acids are represented by H₄(P(W₂O₇)₆).28H₂O, H₈(Si(W₂O₇)₆).28H₂O, and H₈(B(W₂O₇)₆).28H₂O, which are isomorphous; the two former of these are metastable at ordinary temperature and lose water passing into the 22-hydrate. Isomorphous molybdo-phosphoric and molybdo-silicic acids exist, the former also as a 22-hydrate. The 22-hydrates are also isomorphous with each other. The only hydrate of metatungstic acid which Rosenheim could prepare was the 12-tungsto-aquo acid, H₁₀(H₂(W₂O₇)₆).22H₂O, though he considers the 28-hydrate probably capable of existence. This metatungstic acid is also isomorphous with the other 22-hydrates. Prandtl has begun (*Ibid.*, **73**, 223) the systematization of the poly-acids containing vanadic acid, which seem to be derived from a hexa-vanadic acid, H₄V₆O₁₇, whose salts can be made. The seleno-vanadates are derived from this acid with the addition of 4SeO₂, or in some cases 4H₂SeO₃, and also with a larger number of SeO₂ molecules, probably with 5, 6, 8, 10, and 12 SeO₂. The NH₃ and K salts of the last, dodeka-selenite, were obtained, and this seems to be the limiting compound. The tungsto- and molybdo-vanadates seem also to be derivatives of the same hexa-vanadic acid.

Finally, under the head of complex compounds mention must be made of further development of the work of Tschugajew (*Compt. rend.*, **154**, 33) on the platinum bases containing organic sulfides and of Fritzmann (*Z. anorg. Chem.*, **73**, 239) on analogous selenium compounds. The addition of dithioglycoldiethylether to potassium bromo-platinite gives a gray salt, $[\text{Pt} \cdot 2(\text{C}_2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{C}_2\text{H}_5)] \cdot \text{PtBr}_4$, a salt of the type of Magnus' salt. On warming this goes over into the monomeric form, $\text{Pt}(\text{C}_2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{C}_2\text{H}_5) \cdot \text{Br}_2$. Since the sulfide is bivalent, only the *cis* form is possible, and no isomer of the monomeric form was found. With methyl (and other) selenides, three isomers (with chloro-platinite)

were found, the *cis* and the *trans* forms, $(\text{CH}_3)_2\text{Se} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{Pt} \begin{array}{l} \diagdown \\ \diagup \end{array} \text{Cl}$ and $(\text{CH}_3)_2\text{Se} \begin{array}{l} \diagdown \\ \diagup \end{array} \text{Pt} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{Cl}$ and $(\text{CH}_3)_2\text{Se} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{Pt} \begin{array}{l} \diagdown \\ \diagup \end{array} \text{Cl}$, and also the dimeric form corresponding to

Magnus' salt, $[\text{Pt}((\text{CH}_3)_2\text{Se})_4] \cdot \text{PtCl}_4$. With diethyltrimethylene diselenide only two isomers were formed, since here, where there are two selenium atoms in the same group, no *trans* form is possible. This corresponds to the case with ethylenediamine. Many other papers on complex compounds must be passed over, but it is evident that this is to-day the most active field of investigation in inorganic chemistry. In the past, while many of these compounds were known, chemists had to pass them over with possibly an empiric formula. To-day, armed with all the modern refinements of research the chemist is beginning to bring order out of chaos.

In conclusion it may be noted that nothing further has been heard regarding canadium, the new metal of the platinum group, supposed to have been found in British Columbia. Nor have the efforts to confirm the results of Flint in splitting tellurium by hydrolysis had any positive outcome.

NOTES.

Substitution of Ground Glass Stopper in Combination Barometer and Manometer.—In the *Bull. soc. stiinte. Buc.*, **20**, 288, a manometer is described, of which the special feature is the substitution of a ground glass stopper for the usual sealed end. According to Radulescu the limit of accuracy of this instrument is 1–2 mm. for differences in level of 10–20 mm.

A similar device has been in use in this laboratory for over a year on a combination barometer and manometer. The presence of a simple mercury seal around the ground glass stopper increases the efficiency to such an extent that practically no leakage occurs.

The larger tube which constitutes the mercury cup—capacity 10–15 cc.—may be fused to the main tube if desired, and is easily stoppered to prevent volatilization of the mercury. No lubricant is needed for the ground glass joint.

ROSS ALLEN BAKER.