

latest spelling, *hydrosulfic* acid. Possibly the suggestion may start the uniform adoption of the simplest term.

ROGER C. WELLS.

REVIEW.

RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

Received November 4, 1909.

New Elements.—On the occasion of the completion of the twenty-fifth year of the professorship of Dr. Sakurai at the University of Tokio, a volume of chemical papers by his students was published. Among these were two preliminary communications by Ogawa (*J. Coll. of Sci., Imp. Univ., Tôkyô*, **25**, 15, 16) on two new elements discovered in residues from thorianite and molybdenite on which he had worked under Sir William Ramsay. One element, for which Ramsay suggested the name nipponium, has an equivalent weight of about 50 and from its properties seems to be the missing element, of atomic weight 100, standing between molybdenum and ruthenium ("eka-manganese"). The other element is somewhat similar in its properties and may have an atomic weight of 150, being a higher member of the manganese group. Skrabal and Artmann (*Chem.-Ztg.*, **33**, 143) consider that this second element may be identical with one met by them in the analysis of ferrovanadium, and possibly the same noticed by Boucher and by Ruddock (*Chem. News*, **76**, 99, 118) in pig iron and steel.

New Compounds, Group II.—Marsh and Struthers (*Proc. Chem. Soc.*, **24**, 266) find that in cold aqueous potassium hydroxide ketones are quantitatively precipitated by mercuric iodide, the hydrogen on the carbon atoms adjacent to the carbonyl group being completely replaced by Hg^2I or Hg. Thus with acetone the compound $CO : C_2(HgI)_2Hg$ is formed; with diethylketone, $(CH_3C(HgI)_2)_2CO$. By the action of mercuric sulphate on carbon disulphide, Estrup (*Z. anorg. Chem.*, **62**, 168) has prepared a mixed thiobasic sulphate of mercury, $4HgO \cdot 2HgS \cdot 3SO_3 \cdot 4H_2O$, in brilliant white crystals, which appears to be a definite chemical individual.

Group III.—When BCl_3 is led in a current of hydrogen over finely divided chromium (du Jassonneix, *Ann. chim. phys.* [8], **17**, 145) at 100° , CrB appears to be formed. If this is further heated in an electric furnace with iron and boron, complex alloys, but no definite compound, are formed. Aluminium decomposes the CrB with formation of AlB_2 . This last, described by Deville and Wöhler under the name of graphitic boron, becomes changed by heating with an excess of boron into octahedra, which the author calls diamond-like boron. If boron and aluminium are heated with carbon in the electric furnace, transparent hexagonal plates are formed which appear to be a solid solution of AlB_2 and Al_4C_3 . Below 1420° platinum does not take up over $4\frac{1}{2}$ per cent. of boron. Boron is insoluble in copper, silver and tin. Sir William Crookes has continued his work on scandium from wiikite (*Z. anorg. Chem.*, **61**, 349) preparing the fluoride, ScF_3 , and a number of salts of organic acids, most of which are basic. Crookes suggests that since $B \ 11 \times 16 = 176$, $Sc \ 44 \cdot 1 \times 4 = 176 \cdot 4$, $Y \ 89 \times 2 = 178$, and $Yb \ 173 \times 1 = 173$, and the variations from the number 176 may be due to uncertain atomic

weights, it is probable that the occurrence in nature together of these rare elements indicates the instability of ytterbium, which breaks up into two yttrium atoms, and these in turn into scandium and boron. The relatively rarer occurrence of ytterbium and scandium is owing to the relative instability of these elements. Gewecke (*Ann. chem. Pharm.*, **366**, 217) has prepared new halide salts of thallium of types $2\text{TlCl}_3 \cdot \text{M}^n\text{Cl}_n$, $8\text{H}_2\text{O}$, $2\text{TlCl}_3 \cdot \text{M}^n\text{Cl}_n \cdot 6\text{H}_2\text{O}$, and derivatives of double halides Tl^+Cl_2 and Tl^+Br_2 . Ephraim and Barteczko (*Z. anorg. Chem.*, **61**, 238) have also prepared a number of new double chlorides of univalent thallium with iron, chromium, antimony and bismuth. Tl_2SbCl_6 was not obtained.

Group IV.—When calcium and barium chlorides are treated with a solution of alkali bicarbonates at low temperatures Keiser (THIS JOURNAL, **30**, 1711) finds that the flocculent precipitate consists of a bicarbonate, approaching closely the formula $\text{H}_2\text{M}(\text{CO}_3)_2$. These bicarbonates are, as would be expected, very unstable. Rubidium carbonate, on treatment with H_2O_2 in concentrated solution, gives the percarbonate RbCO_4 , which does not completely lose its active oxygen on drying over P_2O_5 (Peltner, *Ber.*, **42**, 1777).

By the action of dry HCl on amorphous silicon Besson and Fournier (*Compt. rend.*, **148**, 555, 839) obtain SiH_3Cl and SiH_2Cl_2 . When SiCl_4 vapors are passed over calcium hydride below a red heat SiHCl_3 is formed, but no mono- or dichloride. On the other hand, by the action of electricity on a mixture of silico-chloroform and hydrogen, a yellow oil is obtained which consists of a mixture of chlorides of the type $\text{Si}_n\text{Cl}_{2n+2}$. By fractional distillation SiCl_4 , Si_2Cl_6 , Si_3Cl_8 , $\text{Si}_5\text{Cl}_{12}$, and $\text{Si}_6\text{Cl}_{14}$ were isolated. In 1863 Wöhler obtained, by the action of acids on calcium silicide, a compound containing Si, O, and H, to which he gave the name of "silikon," and which was converted by the action of light and oxygen into a similar compound which he called "leukon," and to which he assigned the formula $\text{Si}_2\text{H}_2\text{O}_3$, and which was possibly identical with silico-formic acid anhydride. In an investigation of the silicides prepared by Goldschmidt, Hönigschmid (*Monatsh. Chem.*, **30**, 497, 509) has prepared this "silikon" by the solution of CaSi_2 in fuming hydrochloric acid, and finds its formula to be $\text{Si}_3\text{H}_3\text{O}_2$. It consists of brilliant dark yellow flakes, pseudomorphs after the crystals of calcium silicide. In direct sunlight it quickly becomes white from absorption of oxygen; while heated in a vacuum it gives off hydrogen, leaving a grayish black residue, which is probably a silicon suboxide, Si_3O_2 . The compound formed by absorption of oxygen is probably Wöhler's leukon and has the formula $\text{Si}_3\text{H}_3\text{O}_4$. When leukon is heated in a vacuum it is decomposed leaving a new oxide of silicon, Si_3O_4 . Defacqz (*Compt. rend.*, **147**, 1050) has prepared a new uranium silicide of formula USi_2 by the action of aluminium on a mixture of SiO_2 and U_3O_8 . It shows the usual insolubility in all acids except HF.

By adding H_2O_2 to a solution of $\text{Ti}(\text{OH})_4$ in oxalic acid, Mazzucchelli and Pantanelli (*Atti accad. Lincei.*, [5], **18**, 1, 518, 608) obtain what they call an ozo salt of the formula $(\text{TiO})_2(\text{Ox})_2\text{O}$, which forms also double salts. Double ozo-sulphates and ozo-phosphates of titanium were also prepared.

Weinland has continued (*Z. anorg. Chem.*, **62**, 250) his work on the thiocyanates, by preparing a series of double stannic thiocyanates by the action of the thiocyanates on the chlorostannates. They have an analogous formula to the latter.

The double chlorides of thorium have been investigated anew by Chauvenet (*Compt. rend.*, **147**, 1046; **148**, 1267, 1519). The simplest method of preparing the anhydrous chloride ThCl_4 is by the action of COCl_2 on ThO_2 at a red heat. The often-noted white fumes proved to be a sublimed ThCl_4 , which, owing apparently to its physical condition, decomposes almost instantly in the air. Even the crystallized ThCl_4 is very hygroscopic. When the heptahydrate is heated in a current of dry HCl at 120 – 160° it gives the hygroscopic $\text{Th}(\text{OH})\text{Cl}_3 \cdot \text{H}_2\text{O}$; at a higher temperature a product, of composition between ThOCl_2 and $\text{Th}(\text{OH})\text{Cl}_3$, is obtained and only above 250° the anhydrous oxychloride ThOCl_2 . Caesium chloride gives with ThCl_4 a compound, $4\text{CsCl} \cdot \text{ThCl}_4$, and rubidium a similar double chloride, but the other alkali chlorides give double salts of the types $2\text{MCl} \cdot \text{ThCl}_4$, as do also caesium and rubidium, and of the type $\text{MCl} \cdot \text{ThCl}_4$, lithium, sodium and potassium giving only the latter type. These double chlorides are generally hydrated, and while the caesium and rubidium salts can be dehydrated in a dry current of hydrochloric acid, the others pass over into oxychlorides.

Group V.—An interesting compound, N_3Cl , has been obtained by Raschig (*Ber.*, **41**, 4194) by the action of sodium hypochlorite on NaN_3 . The compound, called by Raschig "chlorazide", is a colorless gas, with odor like hypochlorous acid, and explodes violently, often with no apparent cause. Its preparation is readily shown as a lecture experiment by mixing with 1 cc. normal solution of NaN_3 a few flakes of boric acid and then adding 1 cc. normal solution of NaClO . The mixture becomes yellow and foams with the evolution of a colorless gas. If carried out in a test tube wrapped in a towel and a spark be brought to the end of the tube, the gas explodes violently, shattering the tube. In this connection note may be made of the fact that Browne and Lundell (*THIS JOURNAL*, **31**, 435) have found that anhydrous hydrazoic acid, HN_3 , like anhydrous ammonia and hydrazine, has a very low electric conductivity. Its conductivity is greatly increased by the addition of KN_3 . On the electrolysis of such a solution hydrogen and nitrogen are evolved in quantities approximately 1 : 3, though traces of ammonia are formed, but no hydrazine. Certain phenomena during the electrolysis may be referred to the formation of traces of ozone, but it is also possible that small quantities of nitrine (N_3)₂, a polymer of nitrogen, are formed.

The work of Werner on the metal-ammines has been continued (*Ber.*, **41**, 3879, 3912; *Ann.*, **364**, 77), especially with reference to the octo- and deca-dicobaltammine bases and the iridium bases. Of the latter a number of new tetrammine and pentammine bases, as well as tetranitro iridates, are described.

From an investigation of the composition of the copper-ammonium base by the method of molecular extinction, Hantzsch and Robertson (*Ber.*, **41**, 4328) have determined that the copper-ammonium complex in solution is $\text{Cu}(\text{NH}_3)_4$, this being formed even when the solution is considerably diluted and the ammonia in only slight excess. With greater dilution and less ammonia, the NH_3 in the complex is replaced, molecule by molecule, by H_2O . Copper salts in other solutions than water, and with other acids, were also investigated by the same method. According to Ebler and Schott (*J. prakt. Chem.* [2], **79**, 72) hydrazine hydroxide has no action on metallic zinc in the absence of air, but when air is pres-

ent the zinc dissolves with evolution of hydrogen but not of nitrogen. It appears that not the oxygen but the carbon dioxide of the air enters into the reaction. The compound formed is a hydrazine-zinc carbonate with two molecules of hydrazine of crystallization. The salt is well crystallized and easily soluble in water. The hydrazine compounds of many inorganic salts have been formed by Franzen and von Mayer (*Z. anorg. Chem.*, **60**, 247). These compounds, called hydrazinates by the authors, correspond closely to the similar compounds with ammonia, one hydrazine molecule taking the place of two molecules of ammonia, e. g., $\text{NiCl}_2 \cdot (\text{N}_2\text{H}_4)_2$. In many cases the hydrazinate was formed by treating the ammonia compound with hydrazine; in others the metal salt was precipitated by hydrazine and the precipitate dissolved in hydrazine hydrate, out of which the hydrazinate crystallizes. A number of different methods were tried to prepare hydrazinates of trivalent cobalt, corresponding to the cobaltamines, but none were successful.

In their investigations on phosphine, Stock, Böttcher and Lenger (*Ber.*, **42**, 2839, 2847, 2853) prepare the solid phosphine, P_{12}H_6 , by leading the phosphine from the decomposition of calcium phosphide by water into concentrated HCl. The self-igniting phosphine is decomposed by contact with porous substances, granulated CaCl_2 being used, and P_{12}H_6 is formed. This is a bright yellow, amorphous powder, stable when preserved over sulphuric acid in the dark. In a vacuum or on heating, it loses PH_3 and a new, intensely orange-colored phosphine is formed, which has the formula P_9H_2 . This is fairly stable, but when heated in a vacuum to $340\text{--}360^\circ$ it loses PH_3 and red phosphorus is left. Both solid phosphines dissolve in liquid ammonia to a red liquid, which becomes paler and leaves, on evaporation, a black powder, which appears to be a salt of P_9H_2 in the form of a reversible colloid.

When tin is heated with phosphorus at atmospheric pressure, not more than 14 per cent. is dissolved, and up to this content of phosphorus the compound Sn_4P_3 is present in a solid solution of tin and phosphorus. The compound can be separated by electrolytic solution in sodium polysulphide. It is stable up to 480° and easily attacked by acids. Under pressure at 620° , 40 per cent. of phosphorus will dissolve in tin and the compound formed is SnP_3 , which is but slightly attacked by acids, and which begins to decompose at 415° into Sn_4P_3 and phosphorus. Other phosphides of tin which have been described are not chemical individuals (Jolibois, *Compt. rend.*, **148**, 636). By the action of hydrogen peroxide in concentrated solution upon the metavanadates, Melikoff (*Ber.*, **42**, 2291) has obtained orthopervanadates of ammonium and of potassium, of formula $(\text{NH}_4)_3\text{VO}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ and $\text{K}_3\text{VO}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. With an excess of hydrogen peroxide, acid salts with more oxygen are formed but could not be isolated. The work of Smith on the columbates and tantalates has been continued in conjunction with Balke (*THIS JOURNAL*, **30**, 1637) and a large number of new salts, including percolumbates and pertantalates, described. The latter are of the type $\text{M}'_3\text{CbO}_8$ and $\text{M}'_3\text{TaO}_8$. Various double fluorides and oxyfluorides of columbium were also prepared. The fluorides of columbium and tantalum, CbF_5 and TaF_5 , have been obtained by Ruff (*Ber.*, **42**, 492) by heating the metals in a current of fluorine. Both form white crystals, the former melting at $72\text{--}73^\circ$, and the latter at 94° , the boiling points being respectively 236° and 225° —

226.5°. Uranium hexafluoride, UF_6 , was also obtained by Ruff, but UCl_5 was used in its preparation instead of the metal, upon which the action of fluorine was too violent. UF_6 sublimes without melting, and is appreciably volatile at ordinary temperature under diminished pressure. All these fluorides are very hygroscopic.

Group VI.—The composition of Caro's acid has long been a subject of investigation and doubt. The acid has been further studied by Ahrle (*J. prakt. Chem.* [2], **79**, 129) and by Willstätter (*Ber.*, **42**, 1839) from different standpoints, and both come to the conclusion that the formula of v. Baeyer and Villiger, H_2SO_5 , is correct. Ahrle proceeds from the supposition that the equation $H_2O_2 + H_2SO_4 \rightleftharpoons H_2SO_5 + H_2O$ is reversible, and therefore to avoid the water prepares Caro's acid by the action of anhydrous hydrogen peroxide on SO_3 . By using equivalent quantities he obtains pure Caro's acid with the usual properties, and in one case in well-formed crystals, which had a melting point much below 0°. Analysis gave the formula H_2SO_5 . Willstätter replaces the hydrogen of the monopotassium salt of Caro's acid with the benzoyl group by the use of benzoyl chloride. The compound is now no longer an acid but a mixed peroxide, to which he assigns the formula $C_6H_5CO.O.O.SO_3K$. The analogous compound $C_6H_5.SO_2.O.O.SO_3K$ was also prepared similarly by the use of benzene sulphochloride. In alkaline solutions the former peroxide decomposes quantitatively into salts of benzoic acid and of Caro's acid, while in acid hydrolysis the separation is into sulphuric acid and the peroxide of benzoic acid. Since diethyl peroxide gives alcohol by the action of hydrogen in the presence of platinum, and since benzoyl peroxide gives quantitatively benzoic acid, Willstätter concludes that the formula of hydrogen peroxide is $H.O.O.H$ and not $\begin{matrix} H \\ \diagup \\ H \end{matrix} > O : O$. This, however, does not take into consideration the possibility of tautomerism. Pictet and Karl (*Bull. soc. chim.* [4], **3**, 1114) have prepared a number of mixed anhydrides of SO_3 with other anhydrides. By action of SO_3 on N_2O_5 there is formed a mixture of $(SO_3)_4.N_2O_5$, already described, and $(SO_3)_5.(N_2O_5)_2$, which can be separated by fractional distillation. The latter compound can also be prepared by the solution of its constituents in carbon tetrachloride. With B_2O_3 at lower temperatures, $SO_3.B_2O_3$ is formed and at a somewhat higher temperature (230°) $(SO_3)_2.B_2O_3$. $SO_3.CrO_3$ is formed by action of the anhydrides, but the product is contaminated by chromium sulphate formed at the same time with the evolution of oxygen. Attempts to prepare double anhydrides of SO_3 with SO_2 , CO_2 , and SiO_2 were unsuccessful. Muir's compounds with the oxides of nitrogen are mentioned later.

Bjerrum (*Z. anorg. Chem.*, **63**, 140, 151) has continued his investigations of chloro- and bromochromic sulphates. He finds that the hexaaquo-chromium group of these compounds can be replaced by similar hexaaquoaluminium, ferri, and vanadi groups, giving what would in the old nomenclature have been considered as double salts of chromous chloride and aluminum, ferric, and vanadic sulphates, though the chromium is really in trivalent condition.

By the action of SeO_2 on Pb_2O_3 a selenite is formed by direct union, having the formula $Pb_2Se_2O_7$. From this Marino concludes (*Z. anorg. Chem.*, **62**, 173) that Pb_2O_3 belongs to a new class of sesquioxides, and he

expresses the formula of the lead oxide $\begin{array}{c} \text{Pb} : \text{O} \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{Pb} : \text{O} \end{array}$, the lead being considered

quadrivalent, and the formula of the lead selenite $\begin{array}{c} \text{Pb.O.SeO}_2 \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{Pb.O.SeO}_2 \end{array}$, which at

200° goes over into the isomeric form $\begin{array}{c} \text{Pb.O.SeO} \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{Pb.O.SeO}_2 \end{array}$. He would also ex-

press the formula of lead dioxide, $\begin{array}{c} \text{Pb.O.SeO}_2 \\ | \quad | \\ \text{Pb} : \text{O} \\ / \quad \backslash \\ \text{O} \quad \text{O} \end{array}$, and in its isomeric

form, $\begin{array}{c} \text{O} \\ // \quad \backslash \\ \text{Pb} \\ \backslash \quad // \\ \text{O} \end{array}$, and that of red lead, $\begin{array}{c} \text{O.Pb} : \text{O} \\ | \quad | \\ \text{O.Pb} : \text{O} \end{array}$. Thallium selenite,

$\text{Th}_2(\text{SeO}_3)_3$, was also prepared by Marino, but no pure selenite of tin could be obtained.

A study of the tellurides has been carried on by Tibbals (THIS JOURNAL, 31, 902). The alkali tellurides can be formed by direct union, and the tellurides of the heavy metals by double decomposition in aqueous solution in a hydrogen atmosphere. Sodium telluride, Na_2Te , solution dissolves tellurium with the formation of polytellurides up to the proportion Na_4Te_3 , but no polytelluride could be crystallized out, decomposition into Na_2Te and Te taking place. Tellurides of normal composition were obtained with zinc, cadmium, and silver, while with nickel $\text{Ni}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$ was obtained, and with lead a telluride of similar formula.

In order to determine how far complex ions containing sulphur are modified by the substitution of selenium, Rosenheim and Pritze (*Z. anorg. Chem.*, 63, 275) have prepared a series of selenocyanides of mercury. $\text{Hg}(\text{SeCN})$, $\text{KHg}(\text{SeCN})_3$, and $\text{K}_2\text{Hg}(\text{SeCN})_4$ were prepared and several salts of the complex ion $\text{Hg}(\text{SeCN})_4^{--}$, which is fairly stable. $\text{Na}_2\text{Hg}(\text{SeO}_3)_2$ was also prepared and evidence found to show the existence of the ion $\text{Hg}(\text{SeO}_3)_2^{--}$, but this ion is stable only in the presence of an excess of selenious acid.

The hydrates of chromium hexafluoride have been studied by Werner (*Ber.*, 41, 4242), six being found. The heptahydrate is interesting as existing in two isomeric forms. Riesenfeld has further investigated (*Ibid.*, 41, 3941) the higher oxidation products of chromium, preparing salts of both the blue and the red perchromates. The blue salts are derived from the acid HCrO_5 and contain one O_2 group, while the red salts are from H_3CrO_8 and contain three O_2 groups. In both the acids the chromium is septivalent. A new chromyl subchloride, $(\text{CrO}_2)_5\text{Cl}_6$, has been prepared by Pascal (*Compt. rend.*, 148, 1463) by leading nitric oxide into cooled chromyl chloride, CrO_2Cl_2 . NOCl is formed at the same time.

Investigations on the complex inorganic acids have continued at the University of Pennsylvania and the results have been published in THIS JOURNAL (30, 1846, 1858). Blum has prepared seven series of phosphovanadomolybdates, and Daniels has studied the aluminotungstates

and their compounds with phosphoric, arsenic, and antimonie acids. Copaux (*Compt. rend.*, **148**, 633; *Ann. chim. phys.* [8], **17**, 217) has worked especially on the borotungstates and metatungstates. He considers that a portion of the water in the metatungstates, $M_2O \cdot 4WO_3 \cdot aq$, is not water of crystallization and writes the formula $6M_2O \cdot 3H_2O \cdot 24WO_3 + aq$, making them thus derivatives of the complex aquotungstic acid. He finds them isomorphous with the borotungstates of similar formula. He arranges the complex acids with $24WO_3$ in a series increasing in stability as they decrease in basicity: $6M_2O \cdot 3H_2O \cdot 24WO_3 + aq$, $5M_2O \cdot B_2O_3 \cdot 24WO_3 + aq$, $4M_2O \cdot 2SiO_2 \cdot 24WO_3 + aq$, $3M_2O \cdot P_2O_5 \cdot 24WO_3 + aq$. Ekeley (*THIS JOURNAL*, **31**, 664) finds that freshly prepared tungstic acid dissolves readily in aqueous solution of the aliphatic amines, giving well-crystallized salts, a number of which he has described.

Group VII.—Wöhler and Rodewald have investigated (*Z. anorg. Chem.*, **61**, 54) more completely a number of subhalides. The subfluoride of silver, formed by the action of finely divided metallic silver on a saturated solution of AgF , is very difficult to free from an excess of silver, but it proved to be a well-defined chemical individual, Ag_2F , which decomposes into silver and AgF at 90° , but is not decomposed by pressure. By action of metallic calcium on calcium chloride, iodide, and fluorspar, the corresponding subhalides were formed, but only at high temperatures under pressure. It is difficult to free them completely from the finely divided metal, and it appears, at least in the case of fluorspar, that the blue color often present is due, not to the presence of the subfluoride, but to traces of finely divided metallic calcium. Cambi (*Gazz. chim. ital.* [I], **39**, 361) has continued his study of double salts in non-aqueous solutions, crystallizing the chlorides and iodides of copper, cadmium, cobalt and nickel, out of formic acid, acetonitrile, pyridine, acetone, and other organic solvents. The double salts obtained are of simple type, and all contain one or more molecules of the solvent. As examples may be cited $CuCl_2 \cdot LiCl \cdot H_2CO_2$ and $NiI_2 \cdot 2NaI \cdot 9C_3H_6O$. Nitrosyl perchlorate, ClO_4NO , has been prepared by Hofman (*Ber.*, **42**, 2031) by leading a mixture of NO and NO_2 into very concentrated perchloric acid. The analogy of this compound with nitrosyl sulphuric acid is to be noted. Iodine oxyfluoride pentahydrate, $IOF_3 \cdot 5H_2O$, as well as numerous fluoiodates of organic bases, are described by Weinland and Reischle (*Z. anorg. Chem.*, **60**, 163). The former has also (*Ibid.*, p. 173) prepared $(NH_4)_2MnCl_6$ and Rb_2MnCl_6 , as well as the alkali salts of $MnCl_3$, by adding powdered permanganate to a 40 per cent. solution of hydrochloric acid. All are strongly hydrolyzed by water.

Group VIII.—Some work, but not conclusive, has been published by Pellini (*Z. anorg. Chem.*, **60**, 178; **62**, 203) and Tanatar (*Ber.*, **42**, 1516) on the peroxides of iron, cobalt and nickel. The compound formed by the action of hydrogen peroxide, when treated with HCN , yields a solution which contains H_2O_2 , but whether this compound is a true peroxide or merely a molecular compound of the hydroxide with H_2O_2 is uncertain. Pellini holds the latter view.

Wöhler has continued his work (*Ber.*, **42**, 3326) on the oxides of the metals of the platinum group and has at last succeeded in preparing the trioxide of platinum by electrolytic oxidation in alkaline solution. PtO_3 is formed on the anode in brilliant golden scales which still contain alkali and correspond by analysis to $K_2O \cdot 3PtO_3$, but the alkali can be wholly removed by dilute acetic acid. The trioxide is exceedingly unstable.

Later (*Ibid.*, 3958) Wöhler prepared the trichloride, PtCl_3 , by heating either PtCl_2 or PtCl_4 in a chlorine atmosphere at 390° , its range of stability in chlorine being from 275 to 400° . The hydrate of the sesquioxide, Pt_2O_3 , was also prepared, but no salts of trivalent platinum. Wöhler and Frey find (*Z. Elektrochem.*, 15, 129) that when PtO_2 dissociates with heat no intermediate oxide is formed, the dissociation being directly into platinum and oxygen. Solid solutions appear, however, to be formed and investigation of the products obtained in the direct oxidation of platinum is also complicated by the presence of similar solid solutions. The action of PCl_3 and PBr_3 on platinum has long been known from Geisenheimer's researches. Strecker and Schurigin (*Ber.*, 42, 1767) have now applied the reaction to the other metals of the platinum group. By heating iridium sponge with PCl_5 at 300 – 350° , chlorination first takes place and then the IrCl_3 unites with the halogen chloride to form two compounds. The more stable of these compounds is best prepared by heating the iridium with PCl_5 , then adding PCl_3 and reheating at 250° . It is not, however, formed by heating IrCl_3 with PCl_3 . The compound, which can be recrystallized from chloroform, is very stable and is only slowly decomposed by water. Its formula is $\text{Ir} \begin{matrix} (\text{PCl}_3)_3 \\ \text{Cl}_3 \end{matrix}$,

analogous to $\text{Ir} \begin{matrix} (\text{NH}_3)_3 \\ \text{Cl}_3 \end{matrix}$. The bromide has a similar formula. Under similar conditions ruthenium forms a more complex and more stable compound, which is not attacked by concentrated sulphuric acid nor by boiling aqua regia. Its formula, as determined by analysis and molecular weight determinations, is $\text{Ru}_2\text{P}_3\text{Cl}_{18}$, to which the constitution $\text{Cl} \cdot \text{PCl}_3 \cdot \text{Cl}$ is given. The bromine compound has an analogous formula.

The compound formed with palladium is $\text{PdCl}_2\text{PCl}_3$ (previously prepared by Fink), and is less stable, resembling the compounds of platinum. This is also formed by the direct action of PCl_3 on PdCl_2 , and is completely decomposed by water. Its constitution appears to be $\text{Cl} \cdot \text{Pd} \cdot \text{Cl} \cdot \text{Pd} \cdot \text{PCl}_3$. With rhodium only RhCl_3 is formed,

and on osmium OsCl_3 has no action. Hofmann and Buchner describe the action (*Ber.*, 42, 3392) of paratoluidine upon nitrito-platinous acid. The compound formed is $(\text{NO}_2)_3\text{PtC}_6\text{H}_9\text{N}$, and is analogous to the similar cobalt compound recently obtained by them. Bellucci (*Gaz. chim. ital.* [II], 38, 602) has studied the crystals which are obtained when a solution of palladous chloride in hydrochloric acid is evaporated in a vacuum over KOH , and which have the composition $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$. When dissolved in water, silver acetate precipitates a silver salt containing both hydrogen and oxygen, $\text{PdCl}_2(\text{OHAg})_2$. The hydrate is therefore to be looked upon as the dichloropalladous acid, $\text{H}_2\text{PdCl}_2(\text{OH})_2$. The thallos salt was also prepared, as well as a basic lead salt. According to Delépine (*Compt. rend.*, 148, 557), iridium disulphate is to be looked upon as a complex acid, $\text{H}_2\text{Ir}(\text{SO}_4)_2(\text{H}_2\text{O})\text{OH}$, in the ammonium salt of which one and one-half atoms of the ionizable hydrogen are replaced by NH_4 . The addition of more ammonia changes the acid into $\text{H}_3\text{Ir}(\text{SO}_4)_2(\text{OH})_2$, in which two and one-third atoms of the ionizable hydrogen are replaced by NH_4 . The former of these acids compares with sulphuric acid in strength.

Rare Earths.—Several papers on the rare earths have appeared during the year. Kolb (*Z. anorg. Chem.*, 60, 123) has prepared a large number of double nitrates and sulphates of the rare earths, especially thorium and cerium, with organic bases. The double nitrates are stable and very soluble in water, while the sulphates easily fall into their components by slight changes in their solutions. An examination by Morozewicz (*Anz. Akad. Wiss. Krakau*, 1909, 207) of mariupolite shows the presence of two rare earth minerals, beckelith, which contains chiefly the cerium group, and pyrochlor, which contains the tantalum group. The former mineral makes up about 0.3 and the latter about 0.2 per cent. of the mariupolite. The methods used in separating the earths are described. In connection with the double oxalate method of separation Hauser and Wirth give (*J. prakt. Chem.* [2], 79, 358) a full discussion of the conditions of formation of the oxalates of manganese. Urbain (*Compt. rend.*, 149, 37) describes the method of isolating terbium by the use of bismuth nitrate, and (*Chem.-Ztg.*, 33, 745; also *Chem. News*, 100, 73) gives a general review of the more recently isolated earths, discusses their phosphorescence spectra, and gives their identification with the rare earths described in the past by Crookes, Boisbaudran and Demarçay.

In his work on the rare earths James (THIS JOURNAL, 31, 913) describes the preparation and properties of the bromates of lanthanum, cerium, praseodymium, neodymium, samarium, and yttrium, all of which were obtained from the purest material. The best method of preparation was found to be the double decomposition of the sulphate by barium bromate.

Improved Methods of Preparation.—A new method of preparing liquid alloys of sodium and potassium is given by Jaubert (*Ber.*, 41, 4116), which depends upon the addition of metallic sodium to caustic potash, or metallic potassium to caustic soda. According to the temperature, the composition of the alloy tends toward NaK_2 or NaK . It is possible to obtain alloys containing upwards of 80 per cent. of potassium. The reaction, which is $2\text{Na} + \text{KOH} = \text{NaOH} + \text{NaK}$, depends upon the special equilibrium between the heat of combustion of the alloy and the heat of formation of the hydroxides (oxides). The best results are obtained by operating in a vacuum, but good results can be obtained in a test tube under a layer of paraffin. The alloy, NaK_2 , may be technically prepared by heating sodium with caustic potash in an iron autoclave with stirring apparatus at 350° . Smith and Bennett describe (THIS JOURNAL, 31, 799) a form of apparatus in which it is possible to prepare amalgams of the alkali and alkaline earth metals much more readily than has heretofore been possible.

Aluminium nitride, AlN , is readily prepared according to Sofianopoulos (*Bull. soc. chim.* [4], 5, 614) by heating aluminium powder in a porcelain tube to a low red heat, insufficient to fuse the aluminium, in a current of dry ammonia, for which hydrazine or hydrazoic acid may be substituted. Any unchanged aluminium is removed by rubbing with mercury and washing with water. The nitride is quite stable in dry air and not attacked by oxygen even when heated. Acids act on it in the cold with the formation of ammonia and the same is true of alkalies and hot water, while cold water decomposes it very slowly.

For the preparation of pure iodic acid, Guichard (*Compt. rend.*, 148, 923) distils over, from a mixture of fuming nitric acid and phosphorus pentox-

ide in a retort, N_2O_5 into iodine moistened with fuming nitric acid, and then crystallizes the iodic acid formed from nitric acid of sp. gr. 1.4, in which it is but slightly soluble. In this way a pure acid is obtained, which is impossible by the old methods. Muir (*J. Chem. Soc.*, **95**, 656) has prepared pure iodine dioxide by heating iodic acid with concentrated sulphuric acid and then allowing the oxide to crystallize, when it may be washed and dried on a tile in a vacuum. It is finally heated to 100° . It is reduced to iodine by oxalic acid and with water forms iodic acid and free iodine. The reaction $5I_2O_4 + 4H_2O = 8HIO_3 + I_2$ is quantitative. Iodine dioxide combines with SO_3 to form $I_2O_4 \cdot 3SO_3$, which is hygroscopic and fairly stable. With I_2O_5 sulphur trioxide forms $I_2O_5 \cdot 2SO_3$.

Investigations of Compounds.—That cuprous sulphate has not hitherto been isolated in a pure condition is due to its instant decomposition by water. Recoura has prepared it (*Compt. rend.*, **148**, 1105) by the action of cuprous oxide on dimethyl sulphate, $Cu_2O + (CH_3)_2SO_4 = Cu_2SO_4 + (CH_3)_2O$. The cuprous oxide is heated in methyl sulphate to 160° till it becomes light gray. The methyl sulphate is at once poured off or oxidation ensues. Cuprous sulphate is stable in dry air but is at once decomposed by water into cupric sulphate and metallic copper.

A number of potassium perborates of various compositions have been described by Christensen and others. Von Girsewald and Wolokitin (*Ber.*, **42**, 865), repeating the work, find that there are two potassium perborates, which have the formulas $2KBO_3 \cdot H_2O$ and $2KBO_3 \cdot H_2O_2$, and that all the others are mixtures of these. Incidentally they find that these perborates have an unexpectedly great antiseptic power, very much greater than that of boric acid.

Sodium alum has been definitely prepared by W. R. Smith (*THIS JOURNAL*, **31**, 245) by mixing solutions of the constituents to make a moderately supersaturated solution and cooling. Crystallization is induced by stirring or inoculation. That it is a definite compound is shown by its being formed from solutions containing different proportions of its constituents and by forming mixed crystals and layer crystals with other alums. Above 30° only aluminium sulphate crystallizes from the mixed solutions, and in contact with its saturated solution above 30° sodium alum is decomposed. Below 30° in the mixed solution the aluminium sulphate is gradually converted over into the alum. Efforts to prepare iron and chromium alums with sodium, or a lithium alum, were unsuccessful.

Habermann and Kurtenacker (*Z. anorg. Chem.*, **63**, 65) describe attempts to prepare the sodium sesquicarbonate, $Na_2CO_3 \cdot 2NaHCO_3$, and the one-fourth acid carbonate of text-books. A solution of sodium bicarbonate was evaporated to crystallization in a rapid current of air and then cooled. The crystals thus obtained were not pure but could be purified by solution in cold water and precipitation with alcohol. The first crop was generally the normal carbonate, but the second crop was invariably the one-fourth carbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. This could be similarly recrystallized and is undoubtedly a chemical individual. This is the composition of the mineral trona of the alkali deposits of this country. No other intermediate sodium carbonate could be made, nor could any intermediate potassium carbonate be prepared.

The preparation of metallic thorium is carried out by von Bolton (*Z.*

Elektrochem., **14**, 768) by first getting the chloride, ThCl_4 , by the action of CCl_4 on thorium dioxide, and then decomposing the chloride by metallic sodium. The metallic thorium is not attacked by caustic potash in solution nor by nitric acid, and but slightly by sulphuric acid. It dissolves readily in hydrochloric acid. If dilute acid is used and then concentrated acid added, a precipitate is formed which von Bolton calls "muriaticum-thorium." This is soluble in water, but the solution gives no precipitation with silver nitrate, nor does oxalic acid precipitate the thorium. The formula of this compound is given as $(\text{ThO}_2)_{10}(\text{HCl})_4$. R. J. Meyer (*Ibid.*, p. 809) claims that the metallic thorium obtained by this process is not pure but largely contaminated by the oxide. The "muriaticum-thorium" of von Bolton is "metathorium chloride," already described, which is formed in colloidal solution, and the chlorine is not precipitated by silver nitrate, owing to the protective action of the colloid.

An investigation of nitrogen chloride has been carried out by Chapman and Vodden, and its formula satisfactorily established as NCl_3 . The dried vapors carried by a current of nitrogen led through a solution of nitrogen chloride were decomposed by passing through a hot, quartz tube. Hardly a trace of hydrogen was found. By using a CCl_4 solution, the N : Cl ratio was found to be 1 : 3. NCl_3 hydrolyzes to NH_3 and HOCl .

The dynamic allotropy of sulphur has been studied by Kruyt (*Z. physik. Chem.*, **64**, 513; **65**, 486) and his results are a confirmation of the work of Alexander Smith. The work of Bruni and Borgo on the persulphides of hydrogen has been continued (*Atti accad. Lincei.*, [5], **18**, i, 138, 355), and they confirm the formulas H_2S_2 and H_2S_3 for the lower persulphides. While the higher sulphides gradually decompose with loss of sulphur into the lower sulphides, the reaction is not reversible, and all efforts to form the higher sulphides by addition of sulphur to the lower sulphides, either directly or in a solvent, were without success. A study of solutions in which sulphur was allowed to remain with H_2S_2 for some time showed that no H_2S_3 was formed and the sulphur was entirely uncombined. They do not consider the criticisms of Paterno (*Ibid.*, **17**, ii, 627) well founded. Olivari (*Ibid.*, **18**, ii, 94) finds that selenium, like sulphur, dissolves without reaction in fused HgCl_2 , and has for moderate concentrations the molecule Se_8 , but in dilute solutions the molecule dissociates into Se_4 and Se_2 . The sulphur molecule is S_8 and has much less tendency to dissociate.

Several studies on uranium by de Coninck have appeared in the Bulletin of the Belgian Academy (1908, 992; 1909, 173 * * 838). UO_2 is formed by the reduction of higher oxides in hydrogen, and this is first hydrated and then oxidized by H_2O_2 to $\text{UO}_3 \cdot \text{H}_2\text{O}$. A little of the dihydrate is formed, while if the reaction takes place at boiling temperature it is more rapid and the dihydrate is principally formed. In very dilute nitric acid UO_3 is dissolved without oxidation at moderate temperatures. Uranyl sulphate when heated first loses a part of its water and then sulphuric acid is given off. From the anhydrous sulphate SO_3 is given off, in both cases UO_3 being left. At higher temperatures UO_2 is formed and this gradually oxidizes to U_3O_8 . Uranic sulphate when heated with calcium phosphate is decomposed and the evolved sulphuric acid forms some calcium sulphate, but no uranium phosphate results. When uranyl chloride is heated with alkalis, the uranate is in general formed,

but in the presence of air peruranates result, M'_2UO_5 , which at higher temperatures lose oxygen and pass into the uranates. The author calls attention to the striking parallelism between the salts of uranium and those of chromium.

Gutbier (*Z. angew. Chem.*, **22**, 487) has studied ruthenium tetroxide and prefers the use of KOH and KNO_3 fusion, rather than Na_2O_2 , for the preparation of the ruthenate to be distilled by chlorine. Like Deville and Debray, as well as the reviewer, he finds RuO_4 a very treacherous substance to handle, violent explosions occurring unexpectedly. The vapors, while harmless, though unpleasant to some persons, are very poisonous to others, one very serious case occurring in Gutbier's laboratory. The hydrolysis of ruthenium trichloride (chloro-ruthenites) has been studied by Lind and Bliss (THIS JOURNAL, **31**, 868), and is expressed by the equation $K_2RuCl_5 + 2H_2O \rightleftharpoons 2KCl + 2HCl + Ru(OH)_2Cl$. The final result of the hydrolysis is not a true equilibrium, since it is not changed by dilution, temperature, or addition of acid. Gutbier (*Ber.*, **42**, 1437, 2205) finds that rhodium is quantitatively reduced from its compounds by hydrazine and if hydrazine hydrate is used instead of the sulphate, the rhodium is precipitated in brilliant flakes of the pure metal. Since halogens can be determined in the filtrate from the metal, an excellent method for the analysis of rhodium compounds is afforded. He has also (*Ibid.*, 3905; *Z. phys. Chem.*, Arrhenius-Jubelband) studied exhaustively the hexachlor- and hexabromiridates.

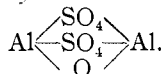
Studies of Reactions.—Briner and Wroczyński (*Compt. rend.*, **148**, 1518) have suggested the study of reactions under great pressure, by mixing the liquefied gases and sealing in a closed vessel which is then heated. Applying this method to mixtures of nitric oxide and hydrogen chloride, they find the reaction to be $2NO + 2HCl = NOCl + H_2O + 1/2Cl_2 + 1/2N_2$, the nitrosyl chloride and the water being in two distinct layers. Nitric oxide and sulphur dioxide give sulphur trioxide and nitrogen. Numerous other similar reactions were found. The influence of traces of impurities, such as arsenic, phosphorus and lead, on the action of copper on nitric acid, was studied by Stanable (*J. Soc. Chem. Ind.*, **28**, 268). With small quantities, the influence was found to increase up to a maximum, which was with arsenic 0.25 and with phosphorus 0.025 per cent. Lead-copper alloys containing up to 80 per cent. lead gave no trace of N_2O with nitric acid, although this oxide is always present when lead acts on nitric acid.

The use of gypsum as a flux in several metallurgical processes has led Hofman and Mostowitsch (*Bull. Am. Inst. Min. Eng.*, **1909**, 51) to investigate its behavior alone and with other substances at a high temperature. Chemically pure $CaSO_4$ was heated in a platinum boat in a quartz tube. A current of purified dry air was led over it and KI-starch, acid $BaCl_2$, and $BaCl_2 + Br$ absorption tubes were used. The gypsum lost most of its water at 500° , but was completely dehydrated only at 900° . No decomposition took place till 1200° was reached, when it began to decompose into CaO and SO_3 , and later into SO_2 and O . At 1360° the mass began to fuse and at 1400° the enamel-like fused mass consisted of a mixture of $CaSO_4$ and CaO , the composition depending upon the time of heating. When $CaSO_4$ was mixed with SiO_2 , decomposition began at 1000° and was complete at 1250° , the product containing only CaO and SiO_2 , and the proportion depending upon the amount of SiO_2 added. The formation of calcium silicates takes place below the melting points

of the constituents. Pure Fe_2O_3 remains unchanged in composition at 1500° and only sinters. When a mixture of CaSO_4 and Fe_2O_3 is heated, the reaction begins at 1100° and is complete at 1250° , $\text{CaO}\cdot\text{Fe}_2\text{O}_3$ being formed. This ferrite is liquid at 1250° and dissolves more CaSO_4 with decomposition, pointing to a more basic ferrite. Pure PbO does not attack CaSO_4 . As a corollary it appears that a basic furnace lining is corroded more rapidly the more basic the slag with iron, while slags with a moderate amount of silica are less severe on the lining. Since magnesium ferrite is less easily formed, at least below 1500° , magnesia linings are less readily attacked by iron slags than lime, as is the experience of the basic steel furnace.

Mostowitsch has also studied (*Metallurgie*, 6, 450) in a similar manner barium sulphate. The results are much the same as with calcium sulphate, except that BaSO_4 remains unchanged until 1400° is reached, and the first dissociation into BaO and SO_3 ($\text{SO}_2 + \text{O}$) takes place at 1500° . Carbon begins to reduce BaSO_4 at 600° and the reaction is completed at 800° . At the lower temperature CO_2 is formed, at the higher CO . The latter gas reduces BaSO_4 from 650 to 800° . The BaS formed in these reductions remains unchanged up to 1000° and, though at 1200° it loses a little sulphur, it does not change its appearance. In metallurgy, therefore, barite in the gangue is unchanged in roasting up to 1000° . In the blast furnace, above 1000° , it is acted on by silica and by ferric oxide, sulphur dioxide being evolved. Silicates and ferrites of barium are formed.

The insolubility of cryolite led Wilks (*Proc. Camb. Phil. Soc.*, 15, 76) to study the reaction between NaCl and AlF_3 , with the result of finding that fluor-aluminic acid is an excellent reagent for sodium. $\text{Al}(\text{OH})_3$ is digested with HF , an equal quantity of saturated copper acetate solution added, and an equal quantity of alcohol. Na is precipitated by the reagent practically quantitatively. Potassium and ammonium are not precipitated, but silver, magnesium, calcium, strontium, barium and lead are. A solution of ferric hydroxide in HF also precipitates sodium, but solutions of chromium or glucinum hydroxides in HF do not. The solubility of aluminium hydroxide in aluminium sulphate solutions is accounted for by Kremann and Hüttinger (*Jahrb. Geol. Reichsanstalt*, 58, 637) by the acidity of solutions of the sulphate, which react with the hydroxide as a base. The formula of the basic sulphate, alunian, which occurs in nature, is expressed by



Studies on the oxidation of hydrazine have been continued by Browne and Shetterly (*THIS JOURNAL*, 31, 221, 783). Examination of the action of over 30 oxidizing agents shows that they may be divided into at least three classes in respect to their action on hydrazine in acid solution: (1) Those which give much HN_3 and much NH_3 ; to this class belong H_2O_2 , KClO_3 and KSO_4 . (2) Those which give little or no HN_3 and much NH_3 , such as KMnO_4 , MnO_2 and Fe_2O_3 . (3) Those which give little or no HN_3 and little or no NH_3 , which is characteristic of KIO_3 , HgO and HgCl_2 . In the action of the first two classes the formation of intermediate N-H compounds of higher molecular weight is probable. For the preparation of hydrazoic acid from hydrazine, hydrogen peroxide is the best

oxidizing agent. In the action of nitrogen on barium carbide Kühling and Berkold (*Z. angew. Chem.*, **22**, 193) find that the supposed catalytic action of barium chloride is wholly imaginary. The action of barium oxide as a catalyzer is important. The cyanide is always formed with the cyanamide, and the most favorable temperature for the production of both is $920-930^{\circ}$, where the output of the former is about 3 per cent. and the latter 19.4 per cent. In studying the reaction between hydrogen sulphide and arsenates, L. L. de Koninck (*Bull. soc. belg. chim.*, **23**, 88) finds that if pure As_2S_3 is added to a solution of ammonium arsenate, acidified slightly with H_2SO_4 and boiled, the As_2S_3 dissolves and forms a fairly stable solution of monothioarsenic acid, H_3AsO_3S . This accounts for the difficulty of reducing and precipitating an arsenic solution with hydrogen sulphide. For complete precipitation he recommends reduction with SO_2 in the presence of HI. The reaction between stibine, SbH_3 , and silver nitrate has long been uncertain. Reckleben (*Ber.*, **42**, 1458) after a careful study has determined the reaction to be $H_3Sb + 3AgNO_3 = Ag_3Sb + 3HNO_3$, which is immediately followed by $Ag_3Sb + 3AgNO_3 + 3H_2O = 6Ag + H_3SbO_3 + 3HNO_3$. The precipitate thus consists of metallic silver and a trace of antimony, with much H_3SbO_3 , while a little of the latter is also in the solution. By the action of antimony chloride on finely pulverized metallic cobalt, Ducelliez (*Compt. rend.*, **147**, 1048) finds that at 800° $CoSb$ is formed, which breaks up at higher temperatures into $CoCl_2$ and antimony. Above 1200° $SbCl_3$ and cobalt give magnetic alloys containing less antimony than would correspond to $CoSb$. These alloys are decomposed by acids, leaving the non-metallic $CoSb$. Alloys prepared by direct union of the metals are magnetic when they contain less than 67 per cent. of antimony. By the action of metallic magnesium or aluminium on a solution of potassium antimonate (Schlippe's salt) Schulte (*Metallurgie*, **6**, 214) finds that the antimony is quantitatively precipitated, and that this method can be used for quantitative determination. When the reaction is carried out hot, a trace of stibine is evolved, this being the first-noticed case of its formation by the reduction of an alkaline solution.

Bourion has further (*Compt. rend.*, **148**, 170) investigated the action of the chloride of sulphur on metallic oxides, and finds good results in the formation of anhydrous chlorides, even in those cases where the action of chlorine with S_2Cl_2 has proved unsatisfactory. The reaction often begins at a low temperature. The method is especially good in the preparation of non-volatile chlorides, as those of the rare earths, and the difficultly volatile chlorides such as those of chromium and thorium. Nicolardot (*Ibid.*, **147**, 1304) has extended the study of the action of S_2Cl_2 to many elements, finding that sulphur and selenium, as well as white phosphorus, dissolve in S_2Cl_2 without any effervescence, while red phosphorus dissolves with copious foaming. Arsenic reacts only at 50° , but antimony reacts in the cold; carbon, silicon and boron are not attacked. On the other hand, the metals of the alkalies and the alkali earths, as well as magnesium, thallium, the noble metals, nickel, cobalt, chromium, tungsten, cadmium and bismuth, are wholly unattacked, even at the boiling point of S_2Cl_2 . Silver, copper and bismuth are only slowly attacked when hot, but tin, aluminium, mercury and iron are acted on. While piano wire, even at 136° , is without action, all other forms of iron are strongly attacked, with the formation of ferrous sulphide and ferrous

chloride, only a trace of ferric chloride being formed. In this respect S_2Cl_2 resembles HCl rather than chlorine. So also the lower chloride is formed with antimony, tin and mercury. That many metals, especially those of the alkalies, are not acted upon, seems to be due to the fact that their chlorides as well as sulphides are insoluble in S_2Cl_2 . The action of pyrosulphuryl chloride, $S_2O_5Cl_2$, on selenium and tellurium has been studied by Praudtl and Borinski (*Z. anorg. Chem.*, **62**, 24, 237). The chloride was prepared by the action of SO_3 on CCl_4 . In the cold selenium and tellurium seem not to be acted on, but on heating, SO_2 and SO_3 are evolved and the compounds $SO_3 \cdot SeCl_4$ and $SO_3 \cdot TeCl_4$ formed. These seem to be addition products of the same nature as $PCl_5 \cdot SeCl_4$, etc. When SO_3 and $SeCl_4$ are heated together a compound, $3SO_3 \cdot 2SeCl_4$, is formed, which, on further heating, goes over into $SO_3 \cdot SeCl_4$, and a similar reaction takes place between SO_3 and $TeCl_4$, except that first $2SO_3 \cdot TeCl_4$ is formed. When the bromides of selenium and tellurium are used, the ultimate products are $SO_3 \cdot SeOBr_2$ and $2SO_3 \cdot TeOBr_2$, indicating the more basic character of tellurium. The first action of the pyrosulphuryl chloride on selenium and tellurium seems to be chlorinating. Efforts to prepare $TeOCl_2$ by the usual methods of making oxyhalide compounds have been carried out by Lenier (*THIS JOURNAL*, **31**, 243), but in no case could any compound intermediate between TeO_2 and $TeCl_4$ be obtained.

Investigation of Systems.—A very full investigation of the binary systems of sodium and of lithium metasilicates with alkaline-earth metasilicates, and an investigation of a portion of the ternary system $Na_2O-Al_2O_3-SiO_2$ is given by Wallace (*Z. anorg. Chem.*, **63**, 1), but is not suited to a review. Baud and Gay (*Compt. rend.*, **148**, 1327) have studied the system NH_3-H_2O , using liquid ammonia. Determinations of heat evolved on mixing water and ammonia, and determination of contraction of volume were made, and both methods gave maxima which corresponded nearly to the ratio 1 : 1, indicating the existence of the compound NH_4OH , which in solutions of ammonia is in equilibrium with free water and free ammonia.

Beckmann has made a complete investigation of the system S-Cl (*Z. physik. Chem.*, **65**, 289) with the result that he finds three definite chemical individuals, S_2Cl_2 , SCl_2 , and SCl_4 . SCl_2 has a constant boiling point of normal molecular weight in several solvents. SCl_4 crystallizes out of sulphur-chloride-chlorine mixtures ranging from SCl_3 to SCl_6 , and begins to melt at -30° . Even at low temperatures it dissociates into SCl_2 and Cl. Finely divided sulphur dissolves in liquid chlorine with the molecule S_8 . To prepare SCl_2 , liquid chlorine is added to S_2Cl_2 at a low temperature, the vessel sealed and allowed to stand at room temperature until a garnet-red color is attained. The system S-I has been studied by Olivari (*Atti accad. Lincei.*, [5], **17**, ii, 512) by means of melting-point curves, cryoscopic determinations, and specific-volume curves. No evidence of any compound between the elements was found. Continuing his work on the P-S system, Stock (*Ber.*, **42**, 2062) finds that PS_2 (P_3S_6) does not exist. What has been supposed to be this compound, is a mixture of P_4S_7 with P_2S_5 . These two, with P_4S_8 , constitute the only compounds of phosphorus and sulphur. At the temperature of 300° mixtures readily react, giving an equilibrium. P_4S_7 is quantitatively formed at this temperature from a mixture of the two. Jonker (*Z. anorg. Chem.*,

62, 89) has a second contribution to his study of the As-S system, in which As_2S_2 and As_2S_3 are considered with their solubility relations to the elements. In a study of the system Te-S, Bellini (*Atti accad. Lincei.*, [5], 18, i, 701; 18, ii, 19) finds from the solidification curve of mixtures of the elements that there is no sign of any compound between tellurium and sulphur. On the other hand, both by dissolving tellurium in sulphur and by crystallizing a mixture of the elements out of several solvents, mixed crystals are obtained, as well of the rhombic as of the monoclinic system, showing the isomorphism between tellurium and sulphur. Since the isomorphism of these elements with selenium has previously been shown, there is a new justification of the place of tellurium in the sixth group of the periodic table.

Considerable work has been done by D'Ans (*Z. anorg. Chem.*, 62, 129) on the systems of calcium sulphate with the sulphates of the alkali metals, and by Barre (*Compt. rend.*, 148, 1604; 149, 292) on the same systems, as well as on those containing strontium sulphate and lead sulphate. The papers, however, do not lend themselves to an abstract. A study of the system $Na_2WO_4-WO_3$ by Parravano (*Gazz. chim. ital.* [II], 39, 55) shows the existence of only one higher tungstate, $Na_2W_2O_7$, though there were some indications of $Na_2W_5O_{18}$.

Miscellaneous.—The indexing of inorganic compounds receives an extended discussion at the hands of Rosenheim and Koppel in the preface to the general register of the first fifty volumes of the *Zeitschrift für anorganische Chemie*. There is not space enough in this review to analyze the principles set forth, but a perusal of the article is commended to all who are working in inorganic chemistry. The article has been, in general, well received, though some criticisms of special points have appeared. As this is the largest inorganic index which has been printed, unless possibly that in Gmelin's "Handbook," it is probable that the general principles laid down will stand.

By the use of metallic silver, which he had previously found an excellent substance to detect the presence of minute quantities of vapors of solids, Zenghelis (*Z. physik. Chem.*, 65, 341) finds that many gases as well as vapors pass through glass even at ordinary temperatures. No relation was found between volatility and permeability, as iodine passes through glass more readily than chlorine and bromine. Whether this passage of vapors is merely mechanical could not be determined, but it seems probable that this is the case. Zenghelis thinks that this phenomenon will account for at least some of the cases where Landolt found change of weight in chemical reactions. Glass covered with a layer of paraffin is not permeable to gases.

Several papers have appeared on the influence of radium in decomposing elements, first noticed by Ramsay. Perman (*J. Chem. Soc.*, 93, 1775) found, after several months of action of $Ra-BaBr_2$ on copper nitrate and on gold chloride, no trace of lithium. Ramsay, in a lecture before the general meeting of the Chemical Society (*Ibid.*, 95, 624), describes fully his later experiments. In the case of thorium under the influence of radium, the earlier experiments were negative as regards helium, but later helium was found. Here, however, the unexpected occurred, for carbon dioxide was invariably found and the same was the case when zirconium nitrate and fluosilicic acid were submitted to the action of radium. The results with lead were negative. A later communication

(*Ber.*, **42**, 2930) gives the results of these and later experiments systematically as follows, in terms of the milligrams of carbon which result from the action of one cubic millimeter of radium emanation: from H_2SiF_6 , 0.518; from $\text{Ti}(\text{SO}_4)_2$, 0.982; from $\text{Zr}(\text{NO}_3)_4$, 1.071, 0.873; from $\text{Th}(\text{NO}_3)_4$, 2.93, 0.968; from $\text{Pb}(\text{ClO}_3)_2$, 0.102. There seems to be a more ready decomposition of the atoms of high weight, but lead appears to have a greater stability. On the other hand, Angelucci, criticizing Ramsay's results (*Atti accad. Lincei.*, [5], **16**, ii, 526), claims that owing to the great stability of a double nitrate and oxalate of thorium, thorium nitrate invariably contains a trace of oxalic acid, and this is the origin of the carbon in Ramsay's experiments. By submitting pure amorphous gold to the action of the Ruhmkorff spark, Cobb (*Chem. News*, **99**, 209) finds that the gold acts on a photographic plate and that it contains copper. Soddy (*Physik. Z.*, **10**, 396) has detected radium in three specimens of uranium nitrate, which were free from radium three years ago. The radium production is in all three approximately proportional to the square of the time. This is in accordance with the theory of Rutherford based on the existence of only one intermediate product between uranium and radium. According to this, the mean life of ionium would be about ten thousand years. The action of radium on the color of precious stones is discussed by Doelter (*Monatsh. Chem.*, **29**, 1145; **30**, 179; *Oesterr. Chem.-Ztg.* [2], **12**, 32). Radium seems to have more effect on the color than the Röntgen rays, but this may be chiefly due to the different time of exposure. In some cases the color of stones changed by radium is restored by heating in oxygen, but in other cases this is not true. Ultra-violet light has little effect on color, but in some cases the color produced by radium is restored to the original by exposure to the arc light. The color of minerals has been very fully studied by Hermann (*Z. anorg. Chem.*, **60**, 369) by heating in oxidizing and reducing gases, using colored glasses for comparison. Iron, in its different stages of oxidation, is found to be the most frequent cause of color in minerals, and next to it chromium, manganese and also titanium. Organic substances, possibly hydrocarbons, often play a part. Spezia (*Zentr. Min. Geol.*, **1909**, 398) describes a series of experiments which go to prove that the blue color of some varieties of rock salt is not due, as has been held by many, to the presence of metallic or ionized sodium. While halite is colored blue by the vapors of sodium, artificially colored halite is of a different shade and has many differences from the naturally colored mineral. Paris (*Compt. rend.*, **147**, 933) finds that while chromium oxide colors crystallized alumina brilliantly, the color is superficial, but by adding a few per cent. of another oxide, such as lime, it is possible to color the mass, but the alumina is amorphous. Artificial sapphires can be produced in this way. Verneuil (*Ibid.*, p. 1059) comments on this paper, claiming it as a confirmation of his own results, and adds that the color of artificial (amorphous) sapphires is easily distinguished from that of the genuine stone, in which the color is due to other causes.

In a paper before the Gesellschaft der Wissenschaften at Göttingen, Biltz discusses the relation of valence, especially of the metals toward oxygen, to temperature and pressure. Thus the limit between PtO_2 and PtO at an oxygen pressure of one atmosphere is 430° , between PtO and Pt is 555° . Similarly, between MnO_2 and Mn_2O_3 it is 570° , between Mn_2O_3 and Mn_3O_4 it is 1090° , between Mn_3O_4 and MnO it is 2500° , and

between MnO and Mn it is 4050° . These temperatures, determined for a number of metals, show that the corresponding temperature decreases with the noble character of the metal. Biltz introduces the term of valence-isobar to indicate the correspondence of pressure and temperature for the same condition of valence. Rügheimer (*Ann.*, **364**, 51) discusses the nature of positive valence, and points out the almost complete absence of tendency on the part of metals to unite with each other after the analogy of the carbon chains. The only exception among the metal-organic compounds is tin triethide, where $\text{Sn}(\text{C}_2\text{H}_5)_3$ tends to polymerize into $\text{Sn}_2(\text{C}_2\text{H}_5)_6$. In a $1^{3/4}$ per cent. solution in ether the molecules are only one-half polymerized, showing the slight tendency of the metals to unite with each other.

Wedekind (*Z. physik. Chem.*, **66**, 614) has continued his researches on the magnetic qualities of alloys of non-magnetic elements. In the case of manganese he finds that the magnetic quality is in many cases dependent on a definite compound, as for example MnB, MnSb_2 , MnSb, and MnP. In some of these compounds, which were fully studied, the magnetic character was very marked.

The most important paper of the year on the theory of solutions is that by Jones (*Am. Chem. J.*, **41**, 19), who sums up his work for the past ten years on the solvate theory, the existence and nature of hydrated ions in solution. Many lines of work from different standpoints all point to the truth of this theory, which may now be considered as well established.

Cornu (*Z. prakt. Geol.*, **17**, 143) has published a paper on the distribution of hydrogels in the mineral kingdom, in which he attempts a systematic classification. These gels have originated largely by weathering and are widely distributed. Among them are the aluminium silicate gels, the iron hydrate gels, which include all the technically important hydrated iron ores, aluminium hydrate gels, including bauxite, and phosphate gels, which include the iron and aluminium phosphates and possibly the calcium phosphate deposits. The nature of these gels has been largely overlooked in the past, partly from insufficient investigation of these minerals, partly because most of these gels have corresponding to them crystalloid minerals of similar composition, and partly because many of them exhibit a double refraction due to strain, which has been mistaken for true double refraction. He classifies these gels into (a) simple gels, as opal; (b) mixed gels, as bauxite, where iron hydrogel is mixed with the aluminium hydrogel; and (c) adsorption gels, as psilomelane, where manganese hydrogel has adsorbed alkalies or BaO. To this latter class belong many substances in which the adsorbed material has heretofore been considered as an impurity, as the P_2O_5 content of limonites. This is further developed by Doelter and Cornu in Vol. 4 of *Z. Chem. Ind. Kolloide*, which is largely taken up with a discussion of colloids in the mineral kingdom.

If the distribution of radium in the interior of the earth were the same as near the surface, the temperature of the earth would be higher than it is, unless the formation velocity of uranium X and hence that of radium is less at high temperatures. To test the latter point Forsyth (*Phil. Mag.* [6], **18**, 207) kept a portion of a sample of uranium nitrate at 1000° for some time and then compared it with the remainder. The increase

in activity of both specimens was the same, indicating no change in formation velocity of uranium X at 1000°.

The doubt raised by Tanatar and others as to the bivalence of glucinum has led Galecki (*Z. Elektrochem.*, 14, 767) to re-examine the subject from the standpoint of ionic precipitation of colloids. For the latter As_2S_3 was used, and glucinum was found to act the same as barium, calcium and magnesium salts, confirming the bivalence of glucinum. By the electrolysis of concentrated $MgCl_2$ solution Hof obtains (*Chem.-Ztg.*, 33, 693) a basic chloride of the composition $MgCl_2 \cdot 5MgO \cdot 14H_2O$. By mixture of MgO with concentrated solution of $MgCl_2$, a similar oxychloride containing 13 H_2O is formed, after all excess of $MgCl_2$ is removed by absolute alcohol. Other hydrates can be formed by heating, but the oxide-chloride ratio remains unchanged. When this oxychloride is powdered and exposed for some time to carbon dioxide, a small portion of the oxide is converted into the carbonate and the oxide-chloride ratio becomes 4.4 : 1. To this action Hof attributes the limited durability of magnesia Sorel cements. These results are disputed by Kallauner (*Chem.-Ztg.*, 33, 871), who finds that all the $MgCl_2$ of a Sorel cement can be extracted by water, and he considers that the cement is not a definite oxychloride, but a solid solution of magnesium hydroxide and magnesium chloride.

The constitution of the charcoal molecule is considered by Aschan (*Chem.-Ztg.*, 33, 561). The suggestion of Dewar that the molecule consists of a benzene nucleus surrounded by a second similar nucleus is improbable because the resultant strain would give an unstable molecule. In any plausible scheme account must be taken of the following facts: the charcoal molecule is stable and must have little stress within the molecule; since mellitic acid is formed by oxidation, it must contain benzene nuclei, with a carbon atom attached to each carbon atom of the nucleus; since pure diamond is colorless and coal is black, powerful chromophoric groups must be present; the hydrogen and oxygen (and sometimes nitrogen) present are not to be looked on as impurities. In the decomposition of organic matter, first CH_4 is given off, then compounds with the benzene ring, then higher condensation products like pyrene and chrysene, then compounds still poorer in hydrogen are formed, such as are found in the last residues of coal-tar, and finally coal itself, which is thus a high-molecular condensation product. An arrangement of six benzene groups (Kekulé's formula) around a center (three naphthalene groups or two phenanthrene groups give the same result), each adjacent pair being common to another group of six, conforms to all the requirements of the case. The center of each group forms itself a six-carbon ring corresponding to trichinoyl, upon which the black color could depend. Such large groups could unite together indefinitely, or extend around a sphere, giving a porous character to charcoal. Animal charcoal contains nitrogen as a probable constituent, which could be accounted for by the presence of pyridine groups in the place of some of the benzene groups, and the basic character thus imparted would account in part for the decolorizing power. Charpy (*Compt. rend.*, 148, 920) discusses the distinction between graphite and amorphous carbon and finds that the oxidation to graphitic oxide is not a safe criterion. He considers density a surer test. He also suggests in the place of Brodie's reagent (fuming HNO_3 and $KClO_3$), the use of H_2SO_4 -

KMnO_4 or H_2SO_4 - CrO_3 mixture, the latter being most energetic. In the change of the diamond to coal by the cathode rays any neon, krypton, or other rare gas present would probably be set free. Swinton (*Proc. Roy. Soc., London (A)*, **82**, 176) has carried out the experiment, but with negative results. An investigation of the viscosity of silicate fusions has been carried on by Greiner (*Neues. Jahrb. Min. Geol.*, 1908, ii, 152) with the following results: Infusions of sodium metasilicate the viscosity of the melt is increased for the same temperature by addition of equivalent quantities of other metasilicates in the following order: FeSiO_3 , MnSiO_3 , $\text{Fe}_2(\text{SiO}_3)_3$, MgSiO_3 , CaSiO_3 , $\text{Al}_2(\text{SiO}_3)_3$. Potassium metasilicate with free silica is decidedly more viscous than the corresponding sodium metasilicate. The viscosity of the acid fusion, $\text{Na}_2\text{SiO}_3 \cdot \text{SiO}_2$, is lowered by FeO , MnO , Fe_2O_3 , MgO in this order, but raised by CaO and Al_2O_3 . In general, addition of a basic constituent lowers the viscosity, but Al_2O_3 or $1/3$ equivalent of Fe_2O_3 increases it. Addition of silica always increases viscosity, while B_2O_3 and especially WO_3 decreases it. Fluidity increases with the temperature but at decreasing rate, and probably soon reaches a maximum.

The fact that the atmosphere contains thorium emanation has led Joly (*Phil. Mag.* [6], **17**, 760) to investigate as to whether thorium is a constant constituent of the earth's crust. After removal of radium emanation, the material is examined for thorium emanation by the electroscope. Practically every mineral tested was found to contain thorium, the quantity varying from $0.2-3 \cdot 10^{-5}$ g. per gram substance. Lava from Vesuvius was particularly rich in thorium. Sea water contains only $1 \cdot 10^{-8}$ g. thorium per cubic centimeter. In a later paper, Joly (*Ibid.*, **18**, 140) changes slightly these figures. He finds also that in most rocks the proportion between thorium and uranium is constant, but there are notable exceptions. Calling attention to the very discrepant figures that have been given for the amount of radium in sea water, Eve (*Ibid.*, p. 102) gives the results obtained by him with six samples collected in crossing the Atlantic Ocean. The values varied from $0.47-1.50 \times 10^{-12}$, the mean being 0.94×10^{-12} gram per cubic centimeter. A study of monazite by Kress and Metzger (*THIS JOURNAL*, **31**, 640) shows that the thorium present is in the form of phosphate and not silicate, as has been held by some.

The occurrence of sulphur in Japan is described by Fukuchi (Abstr. in *Neues. Jahrb. Min. Geol.*, 1909, i, 163) as follows: 1, (Technically most important) massive, and as crystals as a sublimation product in volcanoes; 2, impregnating rocks about solfataras, replacing certain minerals or even most of the rock; 3, deposits on the bed of crater-lakes, derived from sulphurous vapors; 4, fused in many very active solfataras and occasionally flowing like a lava stream, from several volcanoes; 5, in some hot lakes the fused sulphur forms hollow balls and small flat plates. A new chapter to the question of the complexity of tellurium is added by Browning and Flint (*Z. anorg. Chem.*, **64**, 112; also *Am. J. Sci.*), who got around from the fact that when TeCl_4 is hydrolyzed by pouring into water, while most is precipitated, some always remains in solution, no matter how much water is used. Proceeding from this observation they have carried out an extended fractionation of tellurium and determined the atomic weights of the end fraction by different methods. The atomic weight for the portion precipitated by water was found to be 126.49

and for the water-soluble portion 128.85. The work is published as merely preliminary.

The preparation of tungsten, molybdenum and other refractory metals from their chlorides at high temperatures has been studied by Pring and Fielding (*J. Chem. Soc.*, **95**, 1497) together with photometric observation of the efficiency of the elements as light producers at high temperatures. The chlorides were volatilized, with or without hydrogen, into a flask containing a carbon rod, electrically heated. With boron trichloride and silicon tetrachloride little reaction took place unless hydrogen was present. At 1500° a little boron was deposited on the rod, and at higher temperatures boron carbide, B_3C , was readily formed. Silicon was deposited at 1700° and above this the carbide. With tungsten hexachloride the reactions took place equally well in the absence of hydrogen. Deposition of metallic tungsten began at 1000° and the deposit was silvery-white, adherent and smooth. Above 1500° the carbide, W_3C , was formed. With $MoCl_4$ and $MoCl_5$ a smooth bright deposit of metallic molybdenum was formed at 1280°, and above this Mo_3C . Chromium could not be deposited as metal or as carbide. The photometric efficiency of the tungsten deposit was three times that of carbon at 1600° and nearly double at 1775°. Molybdenum was slightly below tungsten at 1600° and slightly higher at 1775°. The boron deposit was low in efficiency and the same was true of the rod coated with silicon carbide.

From a not too concentrated solution of bleaching-powder Orton and Jones (*Ibid.*, p. 751) obtain crystals in which the ratio of chloride to hypochlorite is 1 : 1. This ratio is uninfluenced by excess of calcium chloride or by temperature, and seems to indicate a compound of both salts. On the other hand, from a more concentrated solution calcium hypochlorite tetrahydrate crystals are obtained.

The volatility of metals in a vacuum has been studied by Knocke (*Ber.*, **42**, 206), who finds that platinum volatilizes easily at 700° and a trace of deposit is found at 540°, but none at 538°. The lowest limit of volatility of iridium was 660°, and of palladium 735°. For osmium this point was not determined, but it volatilizes at 800°. Iron gives a fine metallic mirror at 755°. Cobalt volatilizes sensibly at 640°, while the volatility of nickel seems to lie between that of iron and cobalt, but was not accurately determined. The lower limit of volatility for magnesium lies at 415°, for calcium 398°, for strontium 375°, and for barium 355°.

Claude (*Compt. rend.*, **148**, 1454) has utilized his method of extracting the rare gases from the atmosphere to determine the amount present in the air, and finds that in a million volumes of air there are present 15 volumes of neon, 5 volumes of helium, and less than one volume of hydrogen. Strutt has investigated experimentally (*Proc. Roy. Soc., London (A)*, **82**, 166) the escape of helium from uranium and thorium minerals and finds that it is much greater than would be expected from radioactive transformation, from which it must be inferred that the conditions for retaining helium are more favorable in the interior of the earth. The fact that fossil bones and other minerals do not contain the amount of helium to be expected from their geological age and their radioactivity, becomes more explicable. It is possible that the weathering of crystal faces may play a part in the escape of helium. Collie (*Ibid. (A)*, **82**, 378) notes the fact that when shaken with mercury, either at ordinary pressure or

at less, neon is remarkably luminescent. The phenomenon is inhibited by the presence of moisture or of CO_2 , but not by hydrogen. After several hours the luminescence diminishes, but is restored by the induction spark.

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA.

ON THE CRYSTALLINE ALKALOID OF CALYCANTHUS GLAUCUS.

THIRD PAPER.—ON ISOCALYCANTHINE, ISOMERIC WITH CALYCANTHINE.¹

BY H. M. GORDIN.

Received September 28, 1909.

In previous papers² I have shown how to extract calycanthine from the seeds of *Calycanthus glaucus* and prepare the usual salts of the alkaloid. It was shown that calycanthine contained half a molecule of water of crystallization which was removable by heating the crystals to 120° for a few hours, that the anhydrous alkaloid was a monacid base having the formula $\text{C}_{11}\text{H}_{14}\text{N}_2$ and that the formulas of all the salts, of which a considerable number were prepared and analyzed, corroborated this formula.

Having exhausted all the material on hand,³ I ordered a new batch of the same seeds from the same dealer and worked them up by exactly the same method as before. But while the seeds of the second batch looked exactly like those of the first batch and the alkaloid itself prepared from the second batch looked exactly like the calycanthine isolated from the first batch, it very soon became evident that the alkaloid from the second batch was not in every respect identical with the one from the first batch. Calycanthine melted, crystalline at $216-18^\circ$ and anhydrous at $243-4^\circ$ and lost its water of crystallization at 120° without otherwise being changed by the heat. The alkaloid of the second batch of seeds melts crystalline at $212-4^\circ$ and its water of crystallization cannot be removed by heat without partial decomposition of the base, as is indicated by its becoming yellowish and then having no definite melting point. That the alkaloid from the second batch also contains water of crystallization is shown by its losing weight when kept *in vacuo* over sulphuric acid or phosphoric anhydride. But the loss of water of crystallization under these conditions, while fast in the beginning, soon becomes so exceptionally slow that, unless a considerable amount of the alkaloid be taken, the loss during 24 hours ceases to be indicated by the balance. I have been drying about 2 grams of the alkaloid *in vacuo* over sulphuric acid for

¹ I wish to express my thanks to Ely Lilly and Company for the special care with which they extracted for me, free of charge, a large quantity of the seeds.

² THIS JOURNAL, 27, 144 and 1418.

³ Having been assured by the dealer of his ability to supply me with all the seeds I might need, I neglected to keep a sample of calycanthine or of its salts for later comparisons.