

CXXXIV.—*Germanium. Part II. Germanium Tetrachloride and its Ammonia Compounds.*

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GERMANIUM tetrachloride was first described by Winkler (*J. pr. Chem.*, 1886, **142**, 177), who obtained it by the action of chlorine on heated germanium. Recently, Dennis and Hance (*J. Amer. Chem. Soc.*, 1922, **44**, 304) have prepared the compound in much larger quantities by a modification of Winkler's method. The disadvantage of this mode of preparation is that it involves the prior preparation of metallic germanium, and although this can be accomplished fairly readily by the reduction of the dioxide with potassium cyanide, as described by the present authors (*J.*, 1924, **125**, 816), it seemed desirable to investigate the possibility of preparing the substance from the dioxide by a simpler and more direct process.

An attempt to prepare germanium tetrachloride by the well-known method of passing chlorine over a strongly heated mixture of the dioxide and carbon did not yield very satisfactory results. However, by the action of a mixture of carbon monoxide and chlorine, or, better still, of carbonyl chloride on strongly heated germanium dioxide, germanium tetrachloride is very readily obtained.

Ten grams of germanium dioxide were placed in a porcelain boat in a silica tube which was heated to dull redness. Carefully dried carbonyl chloride, or a mixture of carbon monoxide and chlorine in approximately equal proportions, was then passed through the tube and a rapid reaction immediately took place. The products of the reaction were passed to the bottom of a long tube terminating in a bulb, of about 15 c.c. capacity, which was immersed in a freezing mixture. From this tube moisture was excluded by means of a phosphoric oxide guard tube attached to the exit. The reaction was complete in 2 hours, only a very small quantity of a yellowish-brown residue remaining in the boat. About 10 c.c. of a greenish-yellow liquid had condensed in the receiver. The colour, due mainly to dissolved chlorine, was less pronounced when carbonyl chloride was used. The dissolved gases were removed from the crude liquid by passing a stream of dry air through it as described by Dennis and Hance (*loc. cit.*), the containing vessel being surrounded by a freezing mixture. Twenty grams of a clear, colourless, and very mobile liquid were obtained. (Found: Ge, 33.6; Cl, 66.35. Calc. for  $\text{GeCl}_4$ : Ge, 33.7; Cl, 66.3%).

An experiment was next carried out in which germanium dioxide

was suspended in hot concentrated sulphuric acid through which a stream of hydrogen chloride was bubbled. It was hoped that the hydrogen chloride would react readily under these conditions with the dioxide and that the sulphuric acid would prevent hydrolysis of the resulting tetrachloride. The method did not give satisfactory results. No visible reaction occurred until the sulphuric acid had begun to fume ( $270^{\circ}$ ), but after the mixture had been kept at this temperature for several hours much of the germanium dioxide had disappeared and about 6 c.c. of distillate had collected in the well-cooled receiver. This distillate consisted of two layers, each of about equal volume. On re-distillation, the lower layer came over completely below  $75^{\circ}$ , whilst the upper layer boiled at  $107-108^{\circ}$ . The first fraction was germanium tetrachloride contaminated with hydrogen chloride. The exact nature of the heavier layer has not been determined, but the point is being investigated. It appears to be sulphuryl chloride.

In a subsequent experiment, 10 g. of pure germanium dioxide were placed in a small distilling flask with 100 c.c. of concentrated hydrochloric acid. The flask was connected with a small double-surface condenser, the delivery tube of which was drawn out to a long capillary tube which dipped to the bottom of a receiver similar to that described previously. This receiver was immersed in a freezing mixture. About 5 c.c. of concentrated sulphuric acid were placed in the receiver, and the flask was heated in a bath at  $90^{\circ}$ . During the distillation a tendency was observed for hydrolysis of the product to take place as the hydrochloric acid became less concentrated. To obviate this, a slow stream of hydrogen chloride was bubbled through the liquid while the distillation was in progress. The dioxide dissolved fairly rapidly. As soon as solution was complete, the process was stopped; a stream of dry air was passed through the well-cooled distillate for several hours in order to remove dissolved hydrogen chloride. The product was then distilled from the sulphuric acid and was collected with the usual precautions in a small distilling flask. After a further distillation, without the addition of sulphuric acid, 20.2 g. of very pure germanium tetrachloride were obtained, b. p.  $85.5^{\circ}$  (Found: Ge, 33.7; Cl, 66.3%). This proved to be the most convenient method of preparing germanium tetrachloride.\* Equally good results were obtained with germanium dioxide which had been ignited at a bright red heat as with the freshly precipitated substance.

During the distillation of germanium tetrachloride from sulphuric

\* Since this was written Tabern, Orndorff, and Dennis have described a somewhat similar method of preparing germanium tetrachloride (*J. Amer. Chem. Soc.*, 1925, **47**, 2039).

acid, an interesting phenomenon was observed. The two liquids do not mix and at the ordinary temperature the tetrachloride forms the lower layer. At  $0^{\circ}$ , the interface between the two liquids is perfectly flat. As the temperature rises, this interface becomes more and more convex until at  $50^{\circ}$  the lower layer resembles an egg with the pointed end upwards. Then, quite suddenly, the position of the two layers becomes reversed, the sulphuric acid being the denser, and the liquid interface is now concave. As the temperature is raised still higher, the curvature of this interface becomes less and less until, just below the boiling point of the tetrachloride, it again becomes quite flat and exhibits a very fine play of iridescent colour. On cooling, the liquids undergo the same changes in the reverse order.

*The Action of Dry Gaseous Ammonia on Germanium Tetrachloride.  
Hexamminogermanic Chloride.*

It is well known that ammonia reacts readily with stannic chloride (Rose, *Pogg. Ann.*, 1832, **24**, 109), with lead tetrachloride and with zirconium tetrachloride (Matthews, *J. Amer. Chem. Soc.*, 1899, **20**, 815, 839, 843). In each case solid compounds are produced which, however, do not appear to have been fully investigated. Further work in this direction is now being carried out in these laboratories.

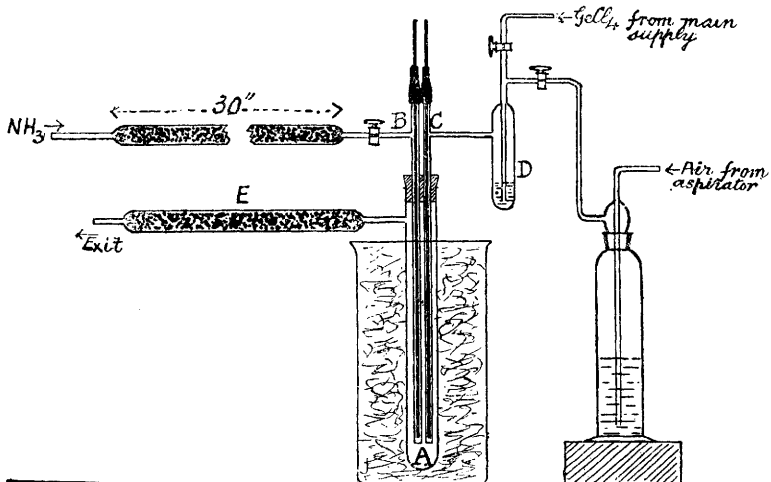
Germanium tetrachloride also combines readily with ammonia. In a preliminary experiment, dry ammonia was led on to the surface of germanium tetrachloride, cooled in a freezing mixture. A vigorous reaction took place, dense white fumes were formed, and much heat was evolved. Absorption of ammonia proceeded quietly after a time, and the passage of the gas was continued for several hours. The product was a white powder having a strong smell of ammonia which, however, disappeared after the substance had been exposed to the air for several hours (Found: Ge, 20.7; Cl, 40.75;  $\text{NH}_3$ , 24.3%. Ratio Ge:Cl = 1:3.99; Cl: $\text{NH}_3$  = 1:1.24). Analyses of other specimens prepared in the same way yielded similar results. In every case, the ratio Ge:Cl was the same within the limits of experimental error, but the ratio Cl: $\text{NH}_3$  varied considerably; further, from 14% to 20% of the material always remained unaccounted for.

These analytical results may, of course, be attributed to replacement of ammonia in the original ammine by water molecules derived from the moisture in the air. In order to test this possibility, a further preparation was undertaken in which every precaution was taken to exclude moisture. The apparatus employed is illustrated in Fig. 1.

The reaction vessel, A, was about 9 inches long and  $1\frac{1}{4}$  inches in

diameter. It was closed by means of a tight-fitting rubber stopper, through which passed two fairly wide tubes, *B* and *C*, which served to admit ammonia and germanium tetrachloride, respectively. In order to prevent the choking of these tubes by the product of the reaction, they were provided with thin glass rods, attached by means of rubber tubing, by the movement of which they could be cleared as necessity arose. After the apparatus had been thoroughly dried, about 1 c.c. of germanium tetrachloride was distilled into *D* from the main supply and through it a slow stream of dry air was bubbled; at the same time, *D* was heated to 50° by means of a bath of warm water. In this way, a steady stream of tetrachloride

FIG. 1.



vapour was introduced into *A*, which was kept cold by means of a freezing mixture. At the same time, dry ammonia was also admitted to the reaction vessel, the rate of flow of the gases being so regulated that a slight excess of ammonia was always present. This rate had to be slow, otherwise much of the finely divided product was carried away by the stream of air and lost. The waste gases escaped by the exit tube, *E*, which was fitted with a suitable guard tube to prevent ingress of moisture.

After all the germanium tetrachloride had been driven over, the flow of ammonia was continued for an hour to ensure complete combination and any excess, together with some adsorbed ammonia, was then removed by passing dry air through the apparatus until no smell of ammonia could be detected at the exit tube. The product was then transferred to a well-stoppered bottle and kept

over quicklime in a desiccator. It was a pure white, light, and extremely soft powder which proved to be  $\text{GeCl}_4 \cdot 6\text{NH}_3$  (Found : Ge, 22.95; Cl, 44.9;  $\text{NH}_3$ , 31.9. Ratio Ge : Cl = 1 : 3.97; Cl :  $\text{NH}_3$  = 1 : 1.49.  $\text{GeCl}_4 \cdot 6\text{NH}_3$  requires Ge, 22.8; Cl, 44.9;  $\text{NH}_3$ , 32.3%).

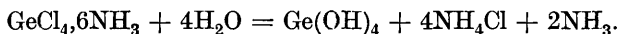
In order to obtain further information regarding the change which the hexammine undergoes when it is exposed to moist air, 2 grams of the freshly prepared substance were exposed to the action of moist carbon dioxide-free air and the change of weight was observed at frequent intervals. During the first 2 days, the weight increased rapidly; the increase then became more gradual, until after a month the weight was constant; the increase then amounted to 11.9% [Found : Ge, 20.4; Cl, 40.3;  $\text{NH}_3$ , 19.8;  $\text{H}_2\text{O}$  (diff.), 19.4%. Ratio Ge : Cl = 1 : 4.0; Cl :  $\text{NH}_3$  = 1 : 1.03]. This change in composition taken in conjunction with the observed increase of weight corresponds to the replacement of two molecules of ammonia by four molecules of water ( $\text{GeCl}_4 \cdot 4\text{NH}_3 \cdot 4\text{H}_2\text{O}$  requires Ge, 20.3; Cl, 40.1;  $\text{NH}_3$ , 19.8%, and an increase in weight of 12.03%).

According to Mendeléev (*Ber.*, 1870, 3, 422), water, in similar circumstances, replaces ammonia in pentamminocupric sulphate, molecule for molecule; from the analytical results, however, it is clear that such simple replacement does not occur in this case. Examples of the replacement of a molecule of ammonia by two molecules of water do not appear to have been observed and it may be pointed out that in this case such a replacement would involve a change in the co-ordination number of germanium, unless, indeed, double molecules of water are concerned, as Werner suggested is the case in the alums.

This replacement of ammonia by water molecules may, however, be explained in another way. Instead of replacement of ammonia according to the equation



the hexammine may undergo hydrolysis thus :



In either case, the solid product would have the same composition, and analytical methods cannot decide, therefore, which is the correct explanation. The behaviour of the substance on treatment with water points, however, to the second explanation. The hexammine itself dissolves completely in water to a clear and colourless solution which only becomes turbid after standing for several hours. A compound such as  $\text{GeCl}_4 \cdot 4\text{NH}_3 \cdot 4\text{H}_2\text{O}$  might be expected to behave in a similar way. The actual substance does

not dissolve completely in water, but leaves a residue which is readily soluble in sodium hydroxide and does not contain chlorine, a behaviour which might be expected from a mixture of ammonium chloride and hydrated germanium dioxide.

*The Action of Ammonia on Germanium Tetrachloride Dissolved in Ether.*

Germanium tetrachloride (1 c.c.) was dissolved in 100 c.c. of dry ether contained in a flask cooled in a freezing mixture, and dry ammonia was bubbled through the solution. A white precipitate at once formed and the heat of the reaction caused the ether rapidly to evaporate. The current of ammonia was continued until all the ether had thus been removed, and the white powder remaining was transferred to a bottle and stored in a desiccator over quicklime. It smelled strongly of ammonia. It was identical with the product obtained by the interaction of the gaseous substances (Found : Ge, 23.0; Cl, 44.8;  $\text{NH}_3$ , 31.85%). All the values are slightly low; this is probably accounted for by access of moisture during transference from one vessel to another.

The ammonia pressure of the hexamine is very small; a specimen was kept over concentrated sulphuric acid for a week without undergoing any appreciable change in weight. The compound is readily soluble in water, but is slowly hydrolysed in solution and the liquid becomes turbid. The solution smells strongly of ammonia. The hexamine is insoluble in ether, alcohol, chloroform and all the common organic solvents. When it is heated in dry air, the substance sublimes completely but with slight loss of ammonia. An analysis was made of a specimen which had been sublimed in a current of dry air in a specially constructed apparatus from which air was carefully excluded (Found : Ge, 23.2; Cl, 46.4;  $\text{NH}_3$ , 30.5%). Possibly a lower ammonia compound is formed at very high temperatures.

*The Interaction of Germanium Tetrachloride with some Amines.*

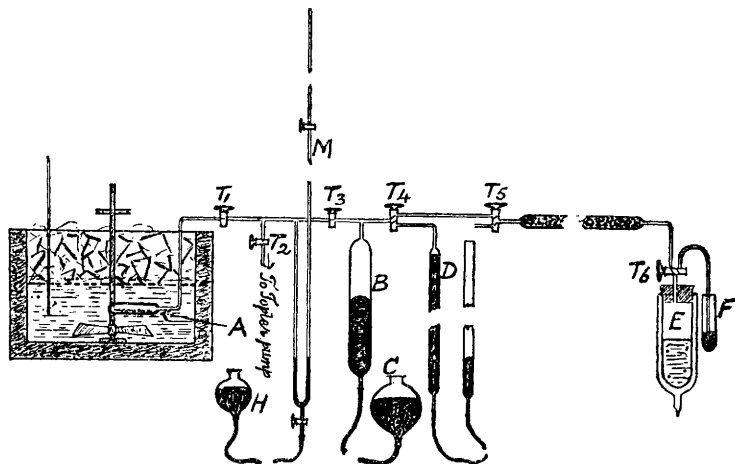
A number of amines being available in connexion with another investigation, the interaction of these substances with germanium tetrachloride was studied. Additive compounds with mono-, di-, and tri-ethylamine, with propylamine, and with butylamine were prepared by bringing the vapours of the two substances into contact in the same way as in the preparation of the ammonia compounds. These additive compounds were also obtained by passing amine vapour into solutions of germanium tetrachloride in ether. In every case, the product was a white powder closely resembling the hexamine both in appearance and in properties.

The amine derivatives are quite stable in dry air and have little or no smell. They are decomposed by moist air and under these conditions they smell strongly of the amine. They are readily soluble in water, but the solutions undergo hydrolysis and become turbid on standing. They are insoluble in the common organic solvents. They contain six molecules of amine to each molecule of the tetrachloride [Found for the diethylamine compound: Ge, 11.0; Cl, 21.7;  $(C_2H_5)_2NH$ , 67.2.  $GeCl_4 \cdot 6(C_2H_5)_2NH$  requires Ge, 11.1; Cl, 21.8;  $(C_2H_5)_2NH$ , 67.1%].

*The Existence of Higher Ammonia Derivatives of Germanium Tetrachloride.*

During the investigation of germanium tetrachloride hexamine, absorption of ammonia was observed to occur when this gas was

FIG. 2.



compressed in contact with the hexamine. In order to determine the nature of this change, a known weight of the solid was treated with ammonia under a pressure of about 3 atmospheres until no more of the gas was absorbed. Small, measured quantities of ammonia were then removed and after each such removal the equilibrium pressure was measured. Owing to the high pressures developed at higher temperatures, it was found most convenient to work at  $0^\circ$ . The apparatus employed is sketched in Fig. 2.

The hexamine (1.3756 g.), contained in a small stoppered bottle, was placed in the tube *A*, which was then sealed in such a way as to prevent ingress of moisture. The tap  $T_1$  being closed, the stopper of the bottle was removed by gentle shaking. After sealing *A* to

the remainder of the apparatus, the whole was thoroughly dried by alternately exhausting and then filling it with air which had passed over phosphoric oxide. The apparatus was then washed out several times with dry gaseous ammonia, obtained by the evaporation of liquid ammonia in the Dewar vessel, *E*, from which superfluous gas escaped by means of the mercury trap, *F*.

All the air being in this way removed, *A* was immersed in a thermostat kept at 0°, and the vessel *B*, having a capacity of 200 c.c., was filled with ammonia, which was then compressed into *A* by closing *T*<sub>2</sub> and *T*<sub>4</sub>, opening *T*<sub>1</sub> and *T*<sub>3</sub>, and raising the mercury reservoir, *C*. Under a pressure of 3 atmospheres absorption of ammonia took place very rapidly at first—600 c.c. were taken up in the first  $\frac{1}{2}$  hour. The process then became gradually slower, until eventually about 1100 c.c. of ammonia had been absorbed. By this time the substance in *A* had become liquid.

Ammonia was then removed from the reaction vessel in small quantities at a time, each amount being measured by means of the gas burette, *D*. All volumes were reduced to *N.T.P.* After each removal, the apparatus was allowed to stand until the pressure became constant. The pressure was measured by means of the manometer, *M*, which allowed of any pressure from 0 to 2400 mm. being determined. When not in use, *T*<sub>2</sub> and *T*<sub>3</sub> were sealed with mercury. All pressure measurements were made from the same point on the manometer, so that the volume of the apparatus was always the same. The amounts of ammonia and the corresponding equilibrium pressures are in Table I.

TABLE I.

Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.	Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.	Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.	Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.
0	1998	152.0	1041	553.4	1040	978.1	1040
12.9	1742	188.0	1040	586.4	1040	997.4	1040
26.3	1408	225.6	1042	634.4	1040	1018.4	814
51.0	1095	259.2	1041	682.4	1040	1026.0	720
53.6	1065	299.0	1042	716.8	1042	1040.1	522
56.0	1049	340.4	1041	767.4	1040	1049.0	425
60.3	1044	379.0	1040	812.6	1041	1063.0	295
77.1	1045	422.0	1041	854.4	1040	1087.2	95
95.3	1044	459.3	1041	896.1	1041	1105.3	0
114.8	1042	496.0	1040	936.9	1042		

From this table it is clear that only one higher ammonia compound can exist within the range of pressures examined and that the dissociation pressure of this compound at 0° is 1040 mm., that is to say, the compound cannot exist at the ordinary temperature and pressure. It is curious that this compound should be a liquid.

When all the ammonia had been removed, the volume of *A* was



determined by filling the vessel with dry air and then pumping off and measuring the volume of air used. The volume was 32 c.c. The vessel was then opened and a specimen of the solid, which had now acquired a porous structure, was analysed (Found: Ge, 22.9; Cl, 44.8;  $\text{NH}_3$ , 32.0. Calc. for  $\text{GeCl}_4 \cdot 6\text{NH}_3$ : Ge, 22.8; Cl, 44.9;  $\text{NH}_3$ , 32.3%). This proves the end-product to be the hexammine and confirms the statement made in an earlier paragraph that the ammonia pressure of this compound is extremely small.

From the quantities of ammonia removed, together with the weight of the hexammine originally taken, the formula of the higher ammine can be calculated. By a graphical method, it was estimated that the dissociation pressure of the compound was reached after the removal of 57.5 c.c. of ammonia and that the compound was completely dissociated after the removal of 1004 c.c. of the gas (both measured at *N.T.P.*). Thus, 1.3756 g. of the hexammine had combined with 946.5 c.c. of ammonia. Now the addition of each additional molecule of ammonia to the hexammine requires 96.92 c.c. of the gas, and hence, within the limits of experimental error, 10 additional molecules of ammonia have been taken up and the higher compound thus has the formula  $\text{GeCl}_4 \cdot 16\text{NH}_3$ .

The variation of the dissociation pressure of the higher compound was also investigated between the temperatures  $0^\circ$  and  $16^\circ$ . The pressures observed, which are in Table II, were found, when plotted against the temperature, to lie on a straight line. By extrapolating this curve, the dissociation pressure was found to be 760 mm. at  $-4^\circ$ .

TABLE II.

Temp. ....	$0^\circ$	$0.4^\circ$	$1.8^\circ$	$4.0^\circ$	$6.0^\circ$
Press. (mm.) ....	1040	1055	1164	1309	1462
Temp. ....	$7.9^\circ$	$9.9^\circ$	$11.9^\circ$	$13.4^\circ$	$16.1^\circ$
Press. (mm.) ....	1590	1733	1889	2001	2190

An examination of Table I shows that, in addition to the formation of the higher ammonia compound, adsorption of the gas also takes place, for neither the volume of ammonia removed in reducing the pressure from 1998 mm. to the equilibrium pressure nor the volume pumped off after the complete dissociation of the higher compound is in agreement with that calculated by means of the gas laws. The discrepancy was far greater at low pressures, for, whilst the removal of 57.5 c.c. of ammonia (measured at *N.T.P.*) reduced the pressure from 1998 mm. to 1040 mm., the ammonia remaining after the higher compound had completely dissociated occupied 101.3 c.c. under the same conditions. Thus it appears that adsorption of ammonia occurs to a greater extent at low pressures.

This abnormality is, however, easily explained by the fact that

$\text{GeCl}_4, 16\text{NH}_3$ , being liquid, exposes a comparatively small surface, whereas the hexammine produced by its dissociation is rendered extremely porous by the escape of ammonia during the process of dissociation.

The constitution of the hexammine is readily explained by means of Werner's co-ordination theory if the co-ordination number of germanium is taken to be 6 and the whole of the chlorine is ionisable. It is, however, somewhat difficult to reconcile this with the electron theory of valency. According to Langmuir's theory, the germanium atom (atomic number 32) has 2, 8, 8, 14 electrons in the various shells and requires 4 electrons to bring the number of electrons in the outer shell up to that of the inert gas immediately following. In the hexammine, the central atom  $[\text{Ge}(\text{NH}_3)_6]^{++++}$  must therefore have an outer shell of 22 electrons. But such a compound should be unstable and should readily lose ammonia, as do the solid hexammines of zinc, nickel, and copper. So far from this being the case, germanium tetrachloride hexammine is remarkably stable and shows no tendency to lose ammonia when kept free from moisture, although, on the addition of water, ammonia is immediately liberated. Possibly a tetrammine complex is formed in solution, but the rapidity with which hydrolysis takes place makes the investigation of this point difficult.

As yet no adequate explanation of the constitution of this substance, and still less of that of the higher compound, can be offered, but the nature of these compounds and also the ammonia derivatives of the tetrachlorides of tin and lead are being further investigated.

#### *Summary.*

1. Various methods for the preparation of germanium tetrachloride have been investigated. By the action of hydrogen chloride on germanium dioxide in concentrated hydrochloric acid, under suitable conditions, the compound may readily be obtained pure.

2. The action of gaseous ammonia on germanium tetrachloride vapour and also on a solution of the compound in ether has been investigated. In each case the compound  $\text{GeCl}_4, 6\text{NH}_3$  is produced. Amines react in a similar manner.

3. Hexamminogermanic chloride is a white, very light powder which is very stable in dry air but is hydrolysed by moist air, a residue of hydrated germanium dioxide and ammonium chloride remaining. The hexammine dissolves readily in water, but becomes turbid after a time owing to separation of hydrated germanium dioxide produced by hydrolysis of the compound.

4. The hexammine when treated with ammonia under pressure absorbs the gas readily at low temperatures. A higher compound,

$\text{GeCl}_4, 16\text{NH}_3$ , is produced which is a liquid at  $0^\circ$  and has a dissociation pressure of 1040 mm. at  $0^\circ$ , 2085 mm. at  $15^\circ$ , and 760 mm. at  $-4^\circ$ .

5. No evidence of any other ammonia compound was obtained.  $\text{GeCl}_4, 16\text{NH}_3$  dissociates directly to the hexamine, which is extremely stable, having no measurable ammonia pressure at  $0^\circ$ . At this temperature, it can be kept over concentrated sulphuric acid for days without losing weight.

6. The application to these compounds of the co-ordination theory and of the electron theory of valency is briefly discussed.

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