VIII.—*Germanium. Part VIII. The Action of Ammonia on Germanium Tetrachloride: Germanium Imide.**

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IN a previous communication (J., 1926, 1051) the formation of a substance having the formula $GeCl_4,6NH_3$, by the direct combination of ammonia with germanium tetrachloride, was described; it was also pointed out that this substance when treated with ammonia under pressure forms a higher compound $GeCl_4,16NH_3$, the dissociation pressure of which is 1040 mm. at 0°.

The exact nature of the substance $GeCl_4,6NH_3$ was not determined. Two alternatives are possible. (1) It may be considered to be a simple addition compound such as metallic salts commonly form with ammonia, and this view is supported by the description by Rosenheim and Schütte (*Z. anorg. Chem.*, 1901, **26**, 239) of a hexammine of titanium tetrachloride. (An investigation of the titanium compound, however, does not support the view of those authors as to its nature. These results will shortly be published.)

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* The subject matter of this paper was contributed to Section B of the British Association at its Cape Town meeting in 1929.

(2) On the other hand, the substance may be a mixture of ammonium chloride and germanium imide, $Ge(NH)_2$ or $NGeNH_2$, produced, as Franklin suggests (*J. Amer. Chem. Soc.*, 1905, **27**, 820; 1924, **46**, 2137; *Amer. Chem. J.*, 1912, **47**, 285), by the ammonolysis of germanium tetrachloride :

$$\begin{array}{rcll} \mathrm{GeCl_4} + 8\mathrm{NH_3} & = & \underset{\text{(unstable)}}{[\mathrm{Ge(NH_2)_4}]} & + 4\mathrm{NH_4Cl} \\ & & \downarrow & \\ & & \mathrm{Ge(NH)_2} & + 2\mathrm{NH_3} \end{array}$$

The halogen derivatives of the non-metals and of the metalloids are known to behave in this way; for instance, Stock and Blix (*Ber.*, 1901, **34**, 3039) obtained a mixture of borimide and ammonium bromide by the action of ammonia on boron tribromide, and Joannis (*Compt. rend.*, 1902, **135**, 1106) showed that the first product of this reaction at − 50° is the amide $B(NH_2)_3$, which loses ammonia as the temperature rises, forming the imide. Similarly, Lengfeld (*Amer. Chem. J.*, 1899, **21**, 531) and Blix and Wirbelauer (*Ber.*, 1903, **36**, 4220) have obtained silicon tetramide and also silicon imide admixed with ammonium chloride.

The present investigation was undertaken with the object of deciding whether germanium tetrachloride hexammine is a pure compound or whether it is a mixture of germanium imide and ammonium chloride. Since the completion of this work, Schwarz and Schenk have investigated the compounds of germanium with nitrogen (*Ber.*, 1930, **63**, 296), and their conclusions regarding the substance $GeCl_4,6NH_3$ confirm the views of the present authors. A careful microscopic examination of the substance revealed no evidence of heterogeneity. Nevertheless, certain observations already noted by the present authors (*loc. cit.*) point to the second alternative. The vapour pressure of the substance at the laboratory temperature is extremely small: it may be kept for days over concentrated sulphuric acid without suffering any appreciable loss in weight, whereas additive ammonia compounds invariably exhibit an appreciable ammonia pressure.

The absorption of ammonia by the hexammine, with the formation of the higher derivative previously mentioned, also supports the second alternative. Troost (*Compt. rend.*, 1879, **88**, 578) has shown that ammonia and ammonium chloride combine to form a compound $NH_4Cl,3NH_3$, the dissociation pressure of which at 0° is variously given as 1035 mm. and 1041 mm. By accepting the second alternative, however, another difficulty is introduced. If the substance is a mixture of germanium imide with ammonium chloride, each molecule of the latter being assumed to combine with

3 mols. of ammonia, it should give a higher compound yielding 18 mols. of ammonia for each mol. of germanium tetrachloride. From generally accepted valency considerations a higher compound of the composition $GeCl_4,18NH_3$ should also be formed if the hexammine is a molecular compound.

In order that there should be no doubt about this point, as a first step in the present investigation, the amount of ammonia taken up by the substance $GeCl_4,6NH_3$ and the dissociation pressure of the product were re-determined. The results previously obtained were confirmed, and no evidence of the existence of a compound $GeCl_4,18NH_3$ could be found. Ample time was allowed for the system to reach equilibrium and, in the authors' opinion, the shortage of ammonia is not due to a failure to establish equilibrium owing to the slowness of the reaction as the equilibrium point is approached.

On the other hand, assuming the original substance to be a mixture, the imide groups may themselves take the place of 2 molecules of ammonia in satisfying the residual valencies of the ammonium chloride molecules. This possibility is tentatively suggested as an explanation of the observed shortage of ammonia.

EXPERIMENTAL.

The Attempted Separation of the Substance $GeCl_4,6NH_3$ *into Germanium Imide and Ammonium Chloride.*—Ammonium chloride is known to dissolve in alcohols. It is more soluble in methyl than in ethyl alcohol; according to Lobry de Bruyn (*Z. physikal. Chem.*, 1892, **10**, 787), its solubility in these solvents at 19·5° is 3·35% and 0·62% respectively.

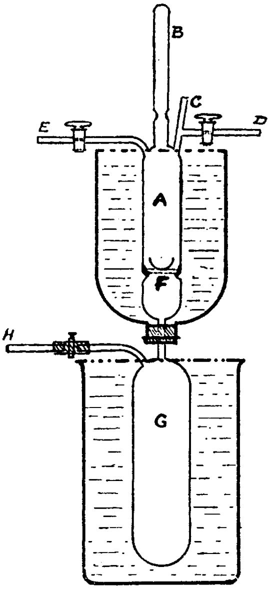
In a preliminary experiment, freshly prepared hexammine was shaken with absolute methyl alcohol. The substance did not dissolve completely, but the filtered liquid, on evaporation, yielded crystals of ammonium chloride. Later, 1·035 g. of germanium tetrachloride were dissolved in 100 c.c. of absolute methyl alcohol and an excess of dry ammonia was at once passed into the solution. The liquid became very hot but no precipitate formed, even on cooling. When the liquid was quite cold, 300 c.c. of dry ether were added and a bulky white precipitate was at once formed. This was separated, washed with a mixture of alcohol and ether, and dried; it weighed 0·9986 g. and contained Cl, 63·2; NH_4, 32·3%; Ge, a trace (not estimated). The ratio $NH_4 : Cl$ in this precipitate is 1 : 1·01, and 92% of the chlorine originally present in the germanium tetrachloride is accounted for. The filtrate, on evaporation to dryness, yielded a white solid which, after drying at 90°, weighed 0·4782 g. (Found: Ge, 59·5; Cl, 3·3; NH_4, 1·49%; $NH_4 : Cl = 1 : 1$). The substance dissolved in water with difficulty and without noticeable evolution of heat. It appeared to be hydrated germanium dioxide containing a little ammonium chloride.

A number of other experiments carried out on these lines all yielded similar results. In every case 2 mols. of ammonia were lost, possibly owing to alcoholysis of the imide, but, since the presence of secondary amine could not be detected in the solution, more probably by hydrolysis of the imide during drying or at some other stage of the experiment. Although a practically complete separation of ammonium chloride from the hexammine can be effected in this way, because of the reactive nature of the solvent, it is unsafe to conclude from the results of these experiments that the substance is a mixture of imide and ammonium chloride. This objection has less force when liquid ammonia, one of the constituents of the substance, is employed as solvent; Franklin and Kraus have shown (*Amer. Chem. J.*, 1892, **20**, 820) that ammonium chloride dissolves readily in this solvent.

A series of experiments was therefore carried out with the object of separating the constituents by means of liquid ammonia. In the earlier experiments the hexammine was prepared by the action of dry ammonia on a solution of germanium tetrachloride in dry ether. The liquid, with the precipitate, was blown into a stoppered and weighed filter of sintered glass, and the precipitate was there washed with dry ether and dried in a current of dry air. In some experiments the substance was prepared in the filter by the action of dry ammonia on germanium tetrachloride. The solid was then washed with carefully dried liquid ammonia, the filtrate being collected in a Dewar vessel. On evaporation of this liquid, crystals of ammonium chloride containing only a trace of germanium were obtained. Dry air was passed over the solid remaining in the filter in order to remove the free ammonia, and the filter was then detached, rapidly corked, and weighed. The solid was dissolved in a measured volume of dilute sulphuric acid and this solution was analysed. In every case the residue was found to be free from chlorine. A typical analysis gave the following figures : Ge, 67; NH_3, 26·2% [Calc. for $Ge(NH)_2$: Ge, 70·73; NH_3, 33·17%]. In no case did the analytical results account for more than 92% of the material. This observation agrees with that of Schwarz and Schenk (*loc. cit.*), who, using a similar method of separation, obtained a product the analysis of which accounted for only 92% of the material. These authors regard the substance as germanium imide, but they do not appear to have obtained it in any higher degree of purity.

These low analytical results are to be attributed to the readiness with which the imide is hydrolysed when exposed to traces of water vapour. Although, in the experiments quoted above, great precautions were taken to prevent the ingress of moisture, the filter had to be opened when it was being detached from the rest of the apparatus. During the experiment the filter became coated with a thick layer of ice which, when melting, left a thin film of water round the junction of the rubber stopper used and the funnel, and this film was very difficult to remove. For this reason an all-glass apparatus was constructed in which the substance $GeCl_4,6NH_3$ could be prepared, washed with liquid ammonia, dried, and weighed for analysis without its being opened at any stage.

Fig. 1.



This apparatus (see Fig. 1) consisted of a tube *A* about 1½″ in diameter, to which, at its upper end, a tube *B* 8″ long and ½″ in diameter was sealed. The tube *B* was somewhat constricted at a point 2″ from its lower end to facilitate sealing when required. To the upper end of the wide tube *A* two other tubes were sealed : *C*, with its side tube *D* carrying a stopcock, served for the introduction of germanium tetrachloride and ammonia, whereas *E*, which was also provided with a stopcock, was an exit tube by means of which the pressure in the apparatus could be regulated. At a point some 2″ above its lower end, the tube *A* was constricted in order to provide support for a filter *F* of sintered glass. This was cut from a sintered-glass Gooch crucible of porosity 3, and was maintained in position and made liquid-tight by means of a ring of rubber cut from thick-walled rubber tubing. On the filter rested a small platinum capsule. This upper portion of the apparatus was cooled by means of a mixture of alcohol and solid carbon dioxide placed in the vessel with which it was surrounded. The upper part of the apparatus was connected to a large vessel *G*, which was also surrounded by the cooling mixture. *G* was provided with an exit tube *H*, connected by means of thick-walled rubber tubing, which could be closed by means of a screw-clip, to a long train of drying tubes; this was also the case with exit *E*.

The apparatus having been thoroughly dried, both the upper and the lower vessel were cooled, and germanium tetrachloride was introduced into the platinum capsule in the following way. The liquid, contained in a small bulb at the end of a tube which had been drawn out to a long fine capillary, was frozen. The end of the capillary was then broken, and the tube rapidly inserted through a rubber tube attached to the end of *C*. In this way a flexible but air-tight joint was made. When the bulb was gently warmed, the germanium tetrachloride was transferred to the platinum capsule and, without withdrawal of the capillary, the tube *C* was sealed. (In the earlier experiments the capsule was omitted, but the germanium tetrachloride was then found to soak into the filter, which became clogged as soon as the reaction with ammonia occurred.) Carefully dried ammonia was then slowly admitted into the apparatus, the screw-clip at *H* being left open, and a steady reaction occurred. When the reaction appeared to be over, the screw-clip was shut and liquid ammonia began to condense in the upper vessel. As soon as it was about half full, the screw-clip was opened and filtration then occurred, the filtrate being collected in *G*. This was repeated two or three times, the stream of ammonia was then stopped, and the excess of ammonia was removed from the upper vessel by a current of dry air. The tube connecting *A* and *G* was then sealed, and after removal of the cooling mixture from the outer vessel, the apparatus was inverted so that insoluble residue with some pieces of capillary tube fell into *B*, which was now drawn off at the constriction provided for the purpose. *B* was then weighed, and opened under sulphuric acid, in which the product dissolved. After the tube had been thoroughly washed, the liquid was filtered, the small pieces of capillary being collected and weighed with the tube itself. Thus the weight of the product was obtained. The solution was made up to known volume and analysed. The following figures were obtained for the residue insoluble in liquid ammonia : Ge, 69·63; NH_3, 31·28% [$Ge(NH)_2$ requires Ge, 70·73; NH_3, 33·17%]. This substance, which was free from chlorine, was the purest specimen of *germanium imide* obtained in the course of this work.

It thus appears that the substance $GeCl_4,6NH_3$, hitherto called the hexammine, can be separated into 1 mol. of germanium imide and 4 mols. of ammonium chloride. It is recognised that the separation by means of liquid ammonia may also involve chemical action between the substance and the solvent but, taking into account all the evidence, we are of opinion that the substance is really a mixture rather than a molecular compound of germanium chloride and ammonia.

Germanium imide is a light white powder which is immediately decomposed by water, forming a turbid liquid which smells strongly of ammonia. On treatment with dilute acids a clear solution is obtained. When heated gently, the imide loses ammonia with the formation, according to Schwarz and Schenk (*loc. cit.*), of germanam, Ge_2N_3H.

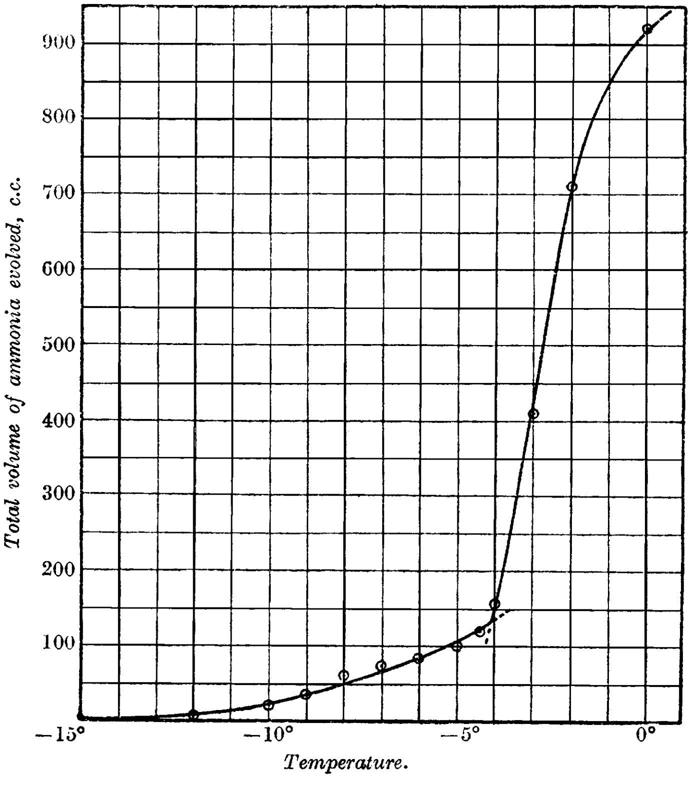
The Possible Intermediate Formation of Germanium Amide, $Ge(NH_2)_4$.—It has already been pointed out that, in the formation of imides of boron and silicon, amides are obtained as intermediate products. Germanium might be expected to behave similarly, and a series of experiments was therefore carried out in order to ascertain whether or not germanium amide is formed as an intermediate product. Attempts to isolate the amide at low temperatures (— 20°) failed, and it is clear, therefore, that if this compound does exist it must be extremely unstable. An examination of the pressure–temperature curves obtained in the course of experiments on the absorption of ammonia by the mixture of germanium imide and ammonium chloride gave no indication of the existence of any such compound, but these observations did not extend far below 0°. By use of a somewhat modified method, the region from 0° to — 20° was now investigated. The apparatus used was similar to that previously described by the authors (J., 1926, 1051), but the ammonia and the germanium tetrachloride were allowed to react at — 20° and the product was then allowed to absorb ammonia. On very slowly raising the temperature, ammonia was given off, and this was steadily removed so that the pressure was kept practically constant at 760 mm. The volume of gas liberated during each degree rise of temperature was measured, and the results thus obtained are shown in Fig. 2, in which the total amount of ammonia evolved is plotted against the temperature.

As will be seen from this diagram, a gradual evolution of gas was observed between —15° and — 4°, probably ammonia that had been adsorbed on the fine powder. Between these points the curve shows no break such as one would expect if the dissociation temperature of an amide lay in this region. Indeed, the total volume of ammonia given off between — 15° and — 5° corresponds to little more than one molecular proportion. In the neighbourhood of — 4°, however, the curve exhibits a sudden change of direction owing to the rapid evolution of a large volume of gas. This is the only pronounced break shown by this curve and it indicates the dissociation of the compound $NH_4Cl,3NH_3$, the dissociation temperature of which, as the authors have shown (*loc. cit.*), is in the neighbourhood of — 4°. It would appear then, that if germanium amide exists, its dissociation temperature is either below — 20° or in the neighbourhood of — 4°. The latter alternative, in the light of all the available evidence, seems very improbable, and we conclude that if germanium amide exists it can only do so at very low temperatures.

The Action of Hydrogen Chloride on Germanium Imide.—When dry hydrogen chloride is passed over germanium imide or its mixtures with ammonium chloride, the gas is rapidly absorbed and the substance becomes very hot. Owing to the difficulty of preparing the pure imide, the mixture of imide with ammonium chloride, prepared by the action of ammonia on germanium tetrachloride, was used in the following experiments.

Mixtures which had been kept for some time in a desiccator over concentrated sulphuric acid and also specimens which had been freshly prepared behaved in the same way. In both cases the gas was rapidly absorbed. As soon as the solid became cool, it was removed from the reaction vessel, kept in a desiccator over sodium hydroxide and concentrated sulphuric acid for several hours, and then analysed. The following analyses are typical of products obtained in this way: Ge, 14·9; Cl, 56·4; NH_3, 28% [$Ge(NH)_2,2HCl,4NH_4Cl$ requires Ge, 18·48; Cl, 54·69; NH_3, 26·14%].

FIG. 2.



These results indicate the absorption of 2 mols. of hydrogen chloride by each mol. of imide. The high value obtained for ammonia can be accounted for by incomplete removal of the gas in the preparation of the mixture. The high chlorine and low germanium values cannot be so explained, and further experiments were therefore made with the object of accounting for them.

The mixture of imide and ammonium chloride was prepared in a small bulb, and after the excess of ammonia had been pumped off, dry hydrogen chloride was admitted into the reaction vessel. After the first rapid absorption, the gas was allowed to remain in contact with the solid for several days, during which a further slow absorption of hydrogen chloride occurred. When no further gas was taken up, the excess of hydrogen chloride was pumped out, and the remaining solid analysed (Found: Ge, 11·91; NH_3, 28·21; Cl, 58·2%). The ratio Ge : NH_3 : Cl is thus 1 : 10 : 10·1, instead of the expected 1 : 6 : 6. The ratio NH_3 : Cl is, however, 1 : 1 and the above result could therefore be due to the absorption of more than 2 mols. of hydrogen chloride and subsequent loss of germanium chloride, thus :

$$Ge(NH)_2 + 2HCl = Ge(NH)_2,2HCl;$$
$$Ge(NH)_2,2HCl + 4HCl = GeCl_4 + 2NH_4Cl.$$

To test this assumption, the experiment was repeated, but the gas pumped off at the close was absorbed in sodium hydroxide. Dry air was then admitted and the evacuation was repeated in this way several times. On analysing the residue, the ratio Ge : NH_3 : Cl was again found to be 1 : 10 : 10, but 40% of the germanium originally present was now found in the sodium hydroxide solution.

A final experiment was then performed in which the volume of hydrogen chloride absorbed by a known weight of the imide–ammonium chloride mixture was measured. In this case the apparatus was not exhausted at the conclusion of the experiment, and a correction had, therefore, to be made for the hydrogen chloride remaining unabsorbed in the reaction vessel. The volume of gas actually taken up by the mixture was found to correspond to 5·85 mols. of hydrogen chloride per mol. of germanium chloride taken at the outset, thus giving a final composition for the product expressed by the ratio Ge : NH_3 : Cl = 1 : 6 : 9·85.

On analysing the product, however, a ratio 1 : 6·26 : 9·36 was obtained. The discrepancy between this result and the ratio obtained from the volume of hydrogen chloride absorbed is probably due to some of the very volatile germanium chloride having diffused back into the hydrogen chloride reservoir during the several days over which the experiment extended.

The authors feel justified in concluding that, when treated with hydrogen chloride, germanium imide first rapidly combines with 2 mols. of the gas, forming the hydrochloride of the base. This substance then reacts slowly with a further quantity of hydrogen chloride, forming germanium tetrachloride and ammonium chloride.

The Action of Heat on the Mixture of Germanium Imide and Ammonium Chloride.—Since ammonium chloride volatilises at comparatively low temperatures, it was thought that its separation from its mixture with germanium imide might be effected by heating this mixture.

In a preliminary experiment, the mixture was heated to 210° in a stream of dry hydrogen. A large portion of the material sublimed, but, although the ratio Cl/NH_3 was slightly higher in the sublimate than in the residue, no marked difference in composition could be detected between the two products. Similar results were obtained when the mixture was heated in a vacuum, the ammonia evolved being pumped off as the reaction proceeded. The following is a typical analysis of products obtained in this way :

Residue = 0·1276 g. (Found : Ge, 25·4; Cl, 47·8; NH_3, 26·65%; Ge : Cl : NH_3 = 1·6 : 6 : 7).

Sublimate = 1·494 g. (Found : Ge, 24·52; Cl, 47·6; NH_3, 25·6%; Ge : Cl : NH_3 = 1·5 : 6 : 6·8).

The quantity of germanium actually determined in the residue was very small, so the precise value for germanium in the corresponding ratio is uncertain; the ratio Cl : N = 6 : 7, however, has considerable significance.

It is clear from these analyses that loss of ammonia has occurred. Calculating the Ge : Cl : NH_3 ratio on the residue and sublimate combined, the value 1 : 4 : 4·44 was obtained, and, since this ratio in the original substance = 1 : 4 : 6, approximately 1·5 mols. of ammonia have been lost for each mol. of germanium tetrachloride taken at the outset of the experiment.

The most obvious explanation of this loss of ammonia would be furnished by imagining germanium imide to react with ammonium chloride, thus : $Ge(NH)_2 + 2NH_4Cl = Ge(NH)_2,2HCl + 2NH_3$. This reaction would, however, require a loss of 2 mols. of ammonia for each mol. of germanium chloride taken. A series of experiments was therefore performed in which the mixture of imide and ammonium chloride was heated for several days to various temperatures, and the ammonia produced was steadily pumped off and measured. The temperatures at which experiments were made were 130° (boiling amyl acetate), 184·4° (boiling aniline), 224° (boiling methyl salicylate), 300° (fused mixture of sodium and potassium nitrates). The amount of ammonia collected was in each case approximately the same, namely 1·5 mols. per mol. of germanium tetrachloride taken initially. This result agrees well with the volume of ammonia calculated from the analyses of the residue and the sublimed material in the experiment previously described. The volume of ammonia appeared also to be independent of the amount of sublimate formed.

On passing the evolved ammonia back into the apparatus, it was reabsorbed rapidly until about seven-eighths of it had been taken up; the remainder was absorbed very much more slowly. During this reabsorption of ammonia, the solid in the reaction vessel became very hot. When the sublimate was small in amount this heat was developed mainly in the residue, but in those cases in which a large quantity of sublimate was produced this also became hot during the reabsorption of ammonia. A small quantity of ammonia, usually 1—1·5% of the volume driven off, could not be reabsorbed.

These observations, taken together, appear to indicate that the evolution of ammonia which occurs when the mixture is heated cannot be satisfactorily explained on the basis of the simple reaction mentioned previously. This view was confirmed by the results of attempts to measure the equilibrium pressure for the reaction at 130°. It was found that the pressure rose at this temperature to a steady value, 343 mm. (the volume of the apparatus was 25·6 c.c.). On removal of 4 c.c. of the gas (measured at *N.T.P.*), the pressure fell and finally assumed a steady value at 301 mm. Removal of successive small quantities of ammonia, until a total of 86·5 c.c. had been collected, was accompanied by stepwise decreases of pressure until, when no more ammonia could be pumped off, the manometer recorded zero pressure. No steady equilibrium pressure, such as the simple reaction referred to above would require, could be obtained.

Any explanation of the loss of ammonia must account for (1) the evolution of only 1·5 mols. of this gas for each mol. of germanium chloride present; (2) the fact that the greater portion of this residue can be rapidly reabsorbed, the remainder only slowly; (3) the absence of a definite equilibrium pressure; and (4) the presence of germanium in the sublimate which has also very nearly the same composition as the residue. These conditions can all be satisfied by assuming the following changes to occur:

$$\begin{cases} 2Ge(NH)_2 \rightleftharpoons Ge_2N_3H + NH_3, \\ Ge_2N_3H + 2NH_4Cl \rightleftharpoons Ge_2N_3H,2HCl + 2NH_3, \end{cases}$$

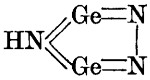
also $$Ge(NH)_2 + 4NH_4Cl \rightleftharpoons GeCl_4 + 6NH_3,$$

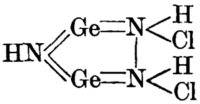
or $$Ge_2N_3H + 8NH_4Cl \rightleftharpoons 2GeCl_4 + 11NH_3.$$

Either of the last pair of reactions would account for the presence of germanium in the sublimate, for the germanium tetrachloride and ammonia formed would recombine in the cool part of the tube, although the temperature there would still be sufficiently high for the first pair of reactions indicated in the above scheme to take place.

As regards these reactions, it may be pointed out that Schwarz and Schenk have shown (*loc. cit.*) that germanium imide does lose ammonia when heated to a comparatively low temperature (150°), with the formation of germanam; on the other hand, the imide prepared by these investigators was by no means pure. If, however, the decomposition of germanium imide were the only reaction to occur, only 0·5 mol. of ammonia would be produced for each mol. of germanium chloride present. By assuming germanam to have the structure (I), which might be expected to undergo addition of hydrogen chloride as in the second equation above, forming (II), the liberation of 1·5 mols. of ammonia would be accounted for.

(I.)





(II.)

Finally, the existence of these two reactions, especially if the first took place much more rapidly and gave rise to a higher equilibrium pressure than the second, would account for the absence of an equilibrium pressure for the conditions under which the experiment was carried out.

Summary.

(1) To account for the fact that the substance $GeCl_4,6NH_3$ can take up only 10 additional molecules of ammonia, it is suggested that a molecule of germanium imide takes the place of 2 molecules of ammonia in satisfying the residual valencies of ammonium chloride.

(2) By using liquid ammonia as solvent for ammonium chloride and a specially designed apparatus, the substance $GeCl_4,6NH_3$ has been separated into germanium imide and ammonium chloride. A specimen of germanium imide of 97·2% purity was obtained.

(3) Some properties of germanium imide are described.

(4) No evidence of the formation, above — 20°, of germanium amide as an intermediate product of the action of ammonia on germanium tetrachloride could be obtained.

(5) Germanium imide rapidly reacts with 2 molecules of hydrogen chloride, forming a salt of the base which then slowly reacts with more hydrogen chloride, giving germanium tetrachloride.

(6) The action of heat on mixtures of germanium imide and ammonium chloride has been investigated, and an explanation of the results obtained, based on the assumed formation of a hydrochloride of germanam, is advanced.

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[*Received, September 23rd,* 1930.]