

962. *Studies on the Behaviour of Halides of the Transition Metals with Ammonia. Part I. The Reaction of Niobium Pentachloride with Ammonia.*

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Ammonium chloride has been shown to form only a triammoniate with ammonia, and the dissociation pressure of this compound has been measured over the temperature range -23° to -63° . The reaction between niobium pentachloride and ammonia has been investigated tensimetrically at -36° , -44° , and -63° , and explained by the formation of the amido-chloride $\text{NbCl}_3(\text{NH}_2)_2$ and ammonium chloride. This amido-chloride is obtained in a pure state by heating the reaction product *in vacuo* to 200° , ammonium chloride subliming away; further heating decomposes the amido-chloride with the eventual formation of the nitride NbN at 800° .

THE complexes formed by ammonia and the halides of the characteristic elements of Groups IVB and VB have been studied fairly completely (cf. Fernelius *et al.*, *Chem. Reviews*, 1940, **26**, 4); in general, ammonolysis decreases with increasing atomic weight of the metal. For example, silicon tetrachloride is completely ammonolysed with the formation of the amide $\text{Si}(\text{NH}_2)_4$, but only three of the four chlorine atoms in stannic chloride are replaced.

With the exception of tantalum pentachloride, the reaction of the A sub-group halides with ammonia has not been investigated in any detail, and our researches have been directed towards elucidating their behaviour, and the thermal decomposition of the complexes.

The reaction between niobium pentachloride in ethereal solution and ammonia was reported by Smith and Hall (*Chem. News*, 1905, **92**, 276) to give a heavy precipitate, which they suggested was a mixture of ammonium chloride and a nitride of niobium. Removal of ammonium chloride with water left a white residue which was thought to be Nb_3N_5 . These ideas are incorrect, since any nitrogen complex produced in the initial reaction would be hydrolysed.

The analogous reaction of ammonia with tantalum pentachloride was first investigated by Linder and Feit (*Z. anorg. Chem.*, 1924, **132**, 13), who obtained an unstable yellow complex. Later, Moureu and Hamblet (*J. Amer. Chem. Soc.*, 1937, **59**, 33) carried out the reaction with boiling liquid ammonia (-33.5°), and obtained a pale yellow, heterogeneous product on evaporation of the excess of ammonia. These workers concluded from tensimetric observations at 0° that two of the original five chlorine atoms had been replaced by amino-groups, giving the composition $\text{TaCl}_3(\text{NH}_2)_2 \cdot 7\text{NH}_3 + 2\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$, corresponding to the addition of 17 moles of ammonia to each mole of tantalum pentachloride. By heating this mixture to 250° and then treating it with more liquid ammonia, an increased ammonolysis was obtained. Spacu (*Z. anorg. Chem.*, 1937, **232**, 225) also indicated the initial addition of ammonia at low temperatures, ammonolysis only taking place at 0° .

Brubaker and Young (personal communication) have found that, although niobium trichloride reacts only incompletely with gaseous ammonia (the reaction product coating the trichloride and preventing any further reaction), nevertheless, ammonium chloride is formed and can be sublimed away or extracted by liquid ammonia.

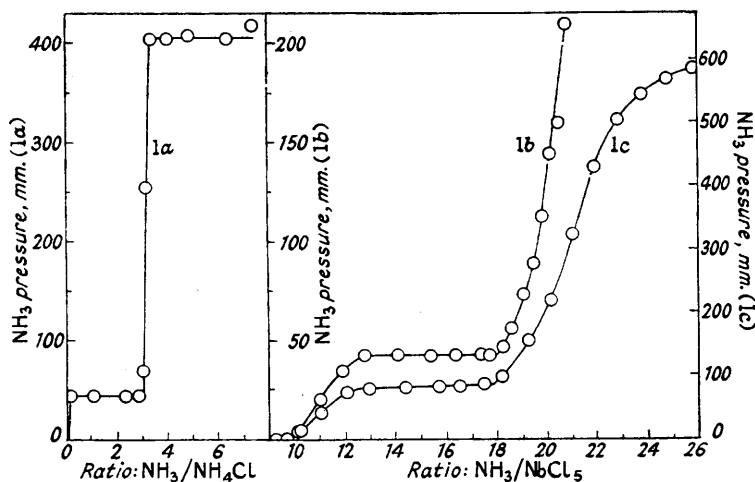
Ammonium chloride is a probable product of the reaction of niobium pentachloride with liquid ammonia, and Troost (*Compt. rend.*, 1879, **88**, 578), Abe *et al.* (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 18), and Spacu and Voichescu (*Z. anorg. Chem.*, 1937, **233**, 197) have shown that ammonium chloride combines with ammonia at low temperatures and forms a triammoniate, $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$, but their values for its dissociation pressures are not consistent, and in no case have they been measured below -50° . Troost also reports the existence of a hexammoniate, although Spacu and Voichescu's work did not confirm this. Spacu (*Z. anorg. Chem.*, 1937, **232**, 225) has suggested, however, that the triammoniate is non-existent at 0° , and in fact decomposes at -27° .

We have made a careful study of the reaction at -44° and -63° , and have shown that only the triammoniate exists, which is stable to at least -23° .

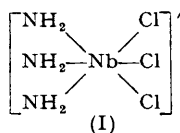
Experimental work now described shows that niobium pentachloride takes up 18 moles of ammonia at temperatures between -36° and -63° (Figs. 1b and 1c). At this point, the pressure-composition curve becomes horizontal with a pressure value corresponding to the dissociation pressure of ammonium chloride triammoniate, and remains so until six moles of ammonia have been removed. This suggests that 6 moles of ammonia in the complex are bound as the ammoniate of ammonium chloride, and that two of the five chlorine atoms in niobium pentachloride have been replaced by amino-groups according to the equation $\text{NbCl}_5 + 18\text{NH}_3 = \text{NbCl}_3(\text{NH}_2)_2, 8\text{NH}_3 + 2\text{NH}_4\text{Cl}, 3\text{NH}_3$. A further 3 moles of ammonia are lost at the reaction temperature, leaving a complex with the overall composition $\text{NbCl}_5, 9\text{NH}_3$, and probable composition $\text{NbCl}_3(\text{NH}_2)_2, 5\text{NH}_3 + 2\text{NH}_4\text{Cl}$.

The five loosely-bound ammonia molecules are lost in two stages when the complex

FIG. 1.



is heated to 160° , and a mixture of ammonium chloride and the amido-chloride $\text{NbCl}_3(\text{NH}_2)_2$ is left. Since all five ammonia molecules are given up quite readily, this simple mechanism seems more likely than one involving the breakdown of complex niobium anions of the type (I). The ammonium chloride present sublimes as the temperature is raised (cf. Moureu on tantalum pentachloride).



The subsequent decomposition of this amido-chloride is complicated by the simultaneous production of ammonia, hydrogen chloride, and a mixture of nitrogen and hydrogen. Probably hydrogen chloride and ammonia are produced by competing reactions, and being dry, only slowly combine to form ammonium chloride on the vessel walls. The permanent gases present are most likely due to the catalytic breakdown of ammonia by the mixture of niobium-nitrogen-chlorine compounds formed at 350° (similar to the catalytic effect of iron nitride). The compound produced by 8 hours' heating at 800° is almost chlorine-free, but contains less nitrogen than would be expected for NbN . Many of these nitrides, however, are unstable *in vacuo*, Pollard and Woodward (*Trans. Faraday Soc.*, 1950, 46, 190) having shown, for example, that titanium nitride decomposes at 900° , so niobium nitride may be formed in the first instance, and subsequently decomposed slowly on prolonged heating. This seems particularly likely since the sample which was heated for 8 hours contained less nitrogen than that heated for only 2 hours, and in both cases a niobium metal mirror was formed.

EXPERIMENTAL

Niobium pentachloride was prepared by the action of chlorine on niobium metal at 400° , and purified by sublimation as suggested by Alexander and Fairbrother (*J.*, 1949, S 223). Analysis confirmed the purity of the product (Found: Nb, 34.1; Cl, 66.0. Calc. for NbCl_5 :

Nb, 34.4; Cl, 65.6%). Liquid ammonia was obtained in cylinders from Imperial Chemical Industries Limited, dried with sodium, and distilled into a storage vessel under vacuum.

Low-temperature baths. Solid-liquid equilibrium baths were found convenient, since they maintained a constant temperature for at least 15 hours before they had to be renewed. The materials used for this purpose were: Carbon tetrachloride, -23.0° ; bromobenzene, -30.6° ; ethylene dichloride, -36.0° ; tetrachloroethane, -44.0° ; chloroform, -63.0° . These baths were made by passing liquid air through a glass spiral immersed in a Dewar vessel of one of the above liquids until a thick slush had formed. Ordinary technical chemicals were used, resulting in general in an initial freezing point rather lower than that of the pure substance, the temperature reaching the true value after several hours. The temperature of these baths was measured with an ammonia vapour-pressure thermometer, except for carbon tetrachloride, for which a calibrated pentane thermometer was used.

Tensimetric Investigation of the Ammonium Chloride-Ammonia Reaction.—The experimental procedure will be described in some detail, since it is the same as that used for the study of the niobium pentachloride-ammonia reaction.

A weighed quantity of "AnalaR" ammonium chloride was pumped under high vacuum for 2 days to remove any water vapour. Ammonia (8 moles per mole of ammonium chloride) was

FIG. 2.

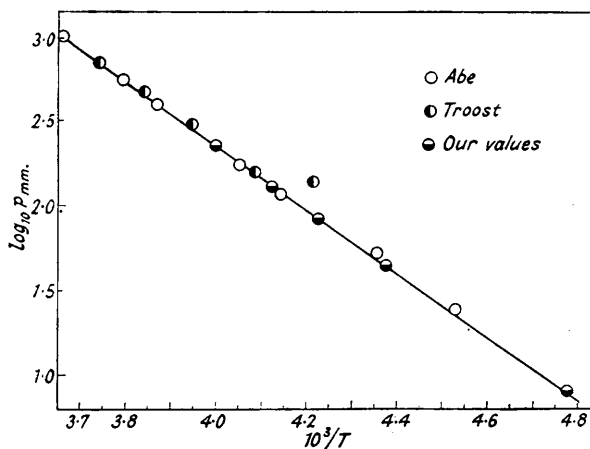
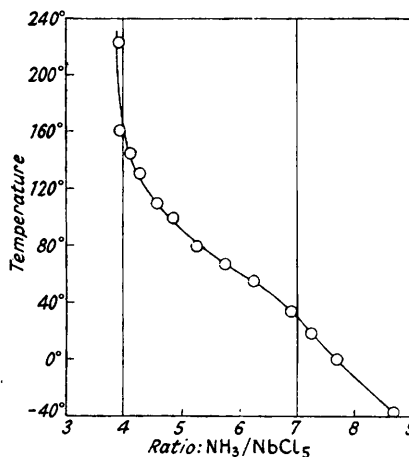


FIG. 3.



condensed on to the ammonium chloride, which was then surrounded by a suitable low-temperature bath for 18 hours. The pressure of ammonia in the apparatus was measured with a mercury manometer, and then 0.5—1.0 mole of ammonia was removed by exposure to a calibrated bulb, cooled in liquid oxygen. When the system had again reached equilibrium (assumed if no further pressure change occurred after 6 hours), the pressure was observed, and a further measured quantity of ammonia removed. In this way, successive amounts of ammonia were taken off until all the ammonia originally added had been removed.

The equilibrium pressure-composition values obtained for the reaction at -44° , plotted in Fig. 1a, give a curve having three distinct sections: (1) A horizontal portion which evidently corresponds to free ammonia in the system; (2) an almost vertical section; (3) a second horizontal part at 43.8 mm., corresponding to the univariant system $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3 \rightleftharpoons \text{NH}_4\text{Cl} + 3\text{NH}_3$.

The equilibrium pressure of ammonia in this system was measured over the temperature range -63.7° to -23° ; the values obtained are shown in the Table. The temperatures quoted, which are accurate to $\pm 0.1^{\circ}$, are somewhat lower than the true values eventually attained by the low-temperature baths. The pressure was first measured at the highest temperature, and then another freshly prepared bath was placed around the reaction bulb and the new equilibrium pressure measured after 3—4 hours.

Equilibrium pressures of ammonium chloride triammoniate.

Temp.	-23.2°	-30.7°	-36.7°	-44.7°	-63.9°
Press., mm.	229.0	129.7	84.8	43.8	7.9

The equilibrium pressure and absolute temperature are related by the equation

$$\log_{10} p_{\text{mm.}} = -1909.5/T + 10.0012$$

over the temperature range 0° to -63.9° ; and this equation takes into consideration the values of Abe and Troost above -23° . From our equation, the dissociation energy of the triammoniate is calculated to be 8.74 kcal. The reaction at -63° gives an analogous pressure-composition curve, and in neither case is there any evidence for the formation of a hexammoniate.

Tensimetric Study of the Niobium Pentachloride-Ammonia Reaction.—By using a similar technique, equilibrium pressure-composition curves have been obtained at -63° , -44° , and -36° , the last two being produced in Figs. 1*b* and 1*c*. The curve obtained at -63° was of the same shape.

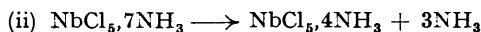
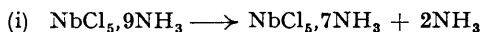
These curves are completely reproducible, but it is necessary to allow at least 12 hours between each pressure reading for equilibrium to be fully attained. This long equilibrium time is probably a result of the slow diffusion of ammonia through the surface layers of decomposed material (cf. Moureu). Bowden ("The Phase Rule and Phase Reactions," Macmillan, 1950, p. 70) discusses this topic in some detail in connection with the dehydration of hydrates.

More nearly ideal curves may be obtained by using larger amounts of niobium pentachloride, but this of course lengthens the equilibrium time. The most convenient amount was found to be about 1 g.

At each reaction temperature, the compound left after the removal of excess of ammonia had the composition $\text{NbCl}_5 \cdot 9\text{NH}_3$, and was an almost colourless substance which lost ammonia readily when warmed to room temperature, and was rapidly hydrolysed.

Thermal Decomposition of $\text{NbCl}_5 \cdot 9\text{NH}_3$.—Preliminary experiments indicated that the complex $\text{NbCl}_5 \cdot 9\text{NH}_3$ decomposed when heated *in vacuo* with the liberation of ammonia, the composition changing from $\text{NbCl}_5 \cdot 9\text{NH}_3$ at -36° to $\text{NbCl}_5 \cdot 4\text{NH}_3$ at 160° . No other gases were evolved while the complex was being heated to this temperature. At higher temperatures, ammonium chloride, hydrogen chloride, nitrogen, and hydrogen were evolved, leaving a substance with a composition approximating to NbN at 800° .

The complex $\text{NbCl}_5 \cdot 9\text{NH}_3$ was heated *in vacuo* for 2 hours at successive intervals of 20° , the ammonia liberated at any temperature being condensed into the calibrated bulb and measured. For each temperature, the ammonia was mostly given off during the first hour, although it was still being evolved slightly at the end of the second hour, indicating the continued slow decomposition of the complex. The composition change was investigated in this way over the temperature range -36° to 224° (Fig. 3). Even when conditions are varied, the curve formed shows a discontinuity, indicating that ammonia is probably given off in two stages:



Although the niobium complex formed initially at -36° is almost colourless, it becomes yellow and gradually darkens as the temperature is raised and ammonia is removed. The pale yellow substance present at 40° assumes an orange-rust hue at 80° and finally deep rust at 160° . All these complexes are easily hydrolysed.

Ammonium chloride sublimed on to the cooler parts of the vessel walls between 160° and 210° , and at 250° the complex turned dark red and hydrogen chloride started to be liberated. A mixture of condensable and non-condensable gases was given off at 350° and the compound turned black. The amount of permanent gas present was quite small, and was a mixture of nitrogen and hydrogen. The condensable gases were evidently a mixture of hydrogen chloride and ammonia, since their pressure gradually decreased with the simultaneous deposition of ammonium chloride on the walls of the apparatus, leaving finally some condensable gas, which was shown by density measurements to be hydrogen chloride.

The blackish material left had a variable composition, the Nb : N : Cl ratio varying from 1 : 1.59 : 2.16 to 1 : 1.17 : 1.49. This black complex was less easily hydrolysed, although it was immediately decomposed by concentrated nitric acid with the formation of hydrated niobium pentoxide.

After being transferred quickly to a quartz tube, the black complex was heated *in vacuo* to 800° ; more hydrogen chloride was liberated, together with a mixture of nitrogen and hydrogen, the hydrogen content varying from 25 to 50%.

Two samples were heated *in vacuo*, the first to 800° for 8 hours, and the second was heated strongly with a Bunsen burner for 2 hours. In each case, a black shiny mirror, which consisted of niobium metal containing only a trace of nitrogen, was deposited on the walls of the quartz tube immediately outside the hot zone. The main products had a black lustrous appearance, and were not easily hydrolysed by water or concentrated acids. With the second

sample, addition of concentrated nitric acid produced a vigorous reaction accompanied by spontaneous ignition, but after this the product remained fairly inert, and dissolved only slowly in boiling nitric acid. This ignition may possibly be due to the formation of hydrogen by the action of nitric acid on very finely divided niobium metal present. The products of both of these decompositions were dissolved in fused potassium hydrogen sulphate containing a little free sulphuric acid, and analysed for niobium, nitrogen, and chlorine in the usual way. These analyses suggest the formation of niobium nitride (NbN) which decomposes on prolonged heating *in vacuo*.

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