

that measurements with more dilute hydrochloric acid were not made, as in all probability the phenomenon would have been even more marked in such cases.

This is related here as a bit of evidence tending strongly to confirm the conclusion reached in the previous paper that potassium chloride exhibits a more marked tendency to the formation of complex compounds with stannous chloride in solution than does hydrochloric acid.

STANFORD UNIV., March 20, 1901.

THE REACTION BETWEEN CHLORINE AND AMMONIA.¹

BY WILLIAM A. NOYES AND ALBERT C. LYON.

Received May 17, 1901.

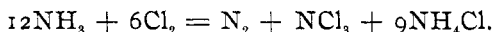
IN Hoffmann's well-known lecture experiment for the demonstration of the composition of ammonia, the introduction of the ammonia into the tube filled with chlorine, is followed by the addition of dilute sulphuric acid. Some years ago, when performing this experiment, it occurred to one of us that the use of the sulphuric acid was unnecessary, as any excess of ammonia would be absorbed by the large amount of water which is allowed to enter the tube later. The sulphuric acid was accordingly omitted, but with the surprising result that the tube was left only one-sixth full of nitrogen instead of one-third full, as it should have been. Recently an opportunity has been found to give the subject a more careful study.

A glass tube, having a capacity of about 95 cc. and closed at each end with a stop-cock, was prepared. This tube, after cleaning and drying, was filled with chlorine which was generated from manganese dioxide and hydrochloric acid and washed with water. The gas was passed through the tube from below till the portion escaping was completely absorbed by a solution of sodium hydroxide. After removing the chlorine from the tubes outside of the stop-cocks, aqua ammonia was allowed to enter the tube from above, and, after shaking gently, was followed by water till the residual gas was at atmospheric pressure. The amount of the nitrogen was then determined by filling the tube with water from a burette which was connected with its lower end.

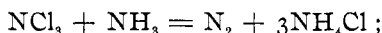
It was soon found that when strong ammonia is used in excess

¹ The work described in this paper forms the subject of a thesis by Mr. Lyon for the degree of Bachelor of Science at the Rose Polytechnic Institute.

the volume of the nitrogen is considerably greater than one-sixth of the volume of the chlorine, and may approach one-third of the volume of the chlorine but never reaches that limit. If, however, a solution containing 0.5 per cent of ammonia is used in such amount as to leave the solution faintly acid, the volume of the nitrogen approaches very closely to one-sixth the volume of the chlorine. If a 2 per cent. solution of ammonium chloride is used instead of the ammonia, the chlorine is almost completely absorbed and the volume of the nitrogen may be as low as only 1 or 2 per cent. of the volume of the chlorine. As will be shown below by quantitative results, the normal reaction between chlorine and ammonia is



This normal reaction is obtained, however, only when the ammonia is used very nearly in the proportion indicated. If an excess of ammonia is used, it reacts in part with the nitrogen trichloride, giving free nitrogen, in part, probably, giving ammonium hypochlorite.¹



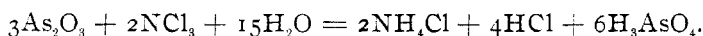
If, on the other hand, too little ammonia is used, the ammonium chloride formed by the reaction acts, in part, on the chlorine as stated above, with little or no evolution of nitrogen, and the volume of nitrogen liberated will be less than one-sixth the volume of the chlorine.

In studying the reaction quantitatively, the tube described above was covered with dark paper to prevent the action of light on the nitrogen trichloride formed. After filling the tube with chlorine an amount of 0.5 per cent. ammonia solution, equal to from 90 to 95 per cent. of that required by the reaction, was allowed to enter, the tube was shaken gently, and then water of the temperature of the original gas allowed to enter to atmospheric pressure. After gentle shaking a small additional amount of water would enter, indicating that an absorption of some kind had taken place, and the shaking was repeated till no more water would enter. Whether this small final absorption is due to residual chlorine, or to the fact that nitrogen trichloride has an appreciable vapor-pressure and is not quickly absorbed by the water,

¹ Schönbein: *J. prakt. Chem.*, **84**, 386; Fresenius: *Ztschr. anal. Chem.*, **2**, 59.

was not determined. The lower end of the tube was then connected with a burette and the amount of water required to fill the tube gave the volume of the residual nitrogen.

The contents of the tube were then transferred to a separatory funnel containing 10 cc. of benzene,¹ shaken, the benzene separated, and this repeated twice more. The benzene containing the nitrogen trichloride was shaken at once with an excess of a solution of arsenious oxide in sodium bicarbonate, and the excess of arsenious oxide determined with a standard iodine solution. The reaction is



Each atom of chlorine present is, therefore, equivalent to 2 atoms of "available chlorine."²

After titration the solution was distilled with an excess of caustic soda and the ammonia in the distillate was determined by means of a standard acid, thus proving that the substance extracted by the benzene was really nitrogen trichloride.

The solution which had been extracted with benzene, and which was, as has been explained, still slightly acid, was titrated with the same ammonia solution first used and the total ammonia required determined :

The results are as follows :

	Calculated.	I.	II.	Found. III.	IV.	V.
Volume of nitrogen as compared with chlorine	16.67	14.32	16.31	17.62	17.20	17.05
Available chlorine.....	50.0	49.3	43.4	35.7	45.5	41.7
Molecules of ammonia per atom of chlorine	1.0	0.97	1.03	1.04	1.01	0.98
Ammonia from NCl_3 . Mols. per mol of NCl_3	1.0	0.95	1.10	1.10	1.14	...

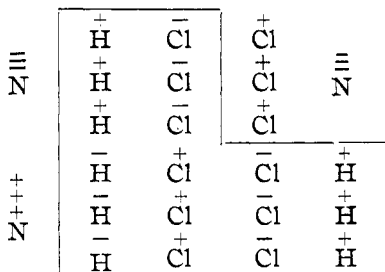
Owing to the instability of the nitrogen trichloride and to the secondary reactions which can never be entirely avoided, an exact agreement cannot be expected. The results satisfactorily demonstrate that the reaction already given is the primary one between ammonia and chlorine.

Probably the most interesting feature of the reaction here studied is the fact that 6 molecules of chlorine must react *simultaneously* with 3 molecules of ammonia, for, if the liberation of

¹ Hentschel: *Ber d. chem. Ges.*, **30**, 1434.

² Hentschel: *Loc. cit.*

nitrogen by the action of 1 part of the chlorine were independent of the formation of nitrogen trichloride by another part, the constant relation of 1 volume of nitrogen to 6 volumes of chlorine would be improbable. The following hypothesis as to the cause of this relationship is given with some hesitation and in the hope that it may lead to discussion and to a further consideration of similar cases. If we suppose, what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of those molecules, it would follow that elementary molecules, as well, may ionize into positive and negative parts. This explanation of the reaction may be represented graphically thus :



The explanation given involves the further idea that in the ionization of ammonia the hydrogen may become either positive or negative. When we remember the neutral character of ammonia and the fact that its hydrogen may be replaced by either chlorine or sodium, such a thought is not so improbable as it seems when first presented.

That the hypothesis here suggested is capable of a wide application need hardly be said.

TERRE HAUTE, IND., May 15, 1901.

THE BOILING-POINT CURVE FOR MIXTURES OF ETHYL ALCOHOL AND WATER.

BY WILLIAM A. NOYES AND R. R. WARFEL.¹

Received June 5, 1901.

It has long been known that it is impossible to obtain absolute alcohol from dilute alcohol by distillation. Some years ago Le Bel² showed, also, that a 98 per cent. alcohol could be separated

¹ An account of the work here described was presented to the Faculty of the Rose Polytechnic Institute as a thesis for the Degree of Bachelor of Science.

² *Compt. rend.*, 88, 912.