

Citation:

Postma, S. & A. Smits, On the compounds of ammonia and water. (first comm.), in:
KNAW, Proceedings, 12, 1909-1910, Amsterdam, 1910, pp. 186-188

above, and that in a following paper a communication will be made as to the experimental confirmation.

At the same time the v,x - and p,x -figures will be considered, which allow a closer investigation of the said remarkable phenomena.

Amsterdam, June 1909.

Inorg. Chem. Lab. University.

Chemistry. — “*On the compounds of ammonia and water.*” By Prof. A. SMITS and S. POSTMA. (Communicated by Prof. A. F. HOLLEMAN).

(First Communication).

(Communicated in the meeting of June 26, 1909.)

Often it has been asked what happens when ammonia and water come together, but nobody has succeeded as yet in giving an entirely satisfactory answer.

That we are dealing here with a chemical transformation besides the physical process, is shown by the deviations from HENRY'S law as well as by the great heat of mixing; but the nature of this chemical transformation is as yet unknown.

If we consider what are the most important facts which we have learned in respect to the solutions of NH_3 in water, these are the following ones:

On dissolution of NH_3 in water the OH' -ion concentration is increased, so that NH_3 dissolved in water behaves as a comparatively weak base.

It further appeared that the solution contains the same NH_4 -ions as are split off from ammonium salts, as the electrolytic dissociation in the aqueous NH_3 -solution can be reduced not only by increase of the OH' -ion concentration, but also by increase of the NH_4 -ion concentration.

The fact that free ammonia is present in an aqueous solution of ammonia was shown by HANTZSCH and SEBALDT¹⁾; they shook such a solution with solvents for NH_3 , such as chloroform from which it appeared that the distribution of NH_3 between water and chloroform depends on the temperature; at higher temperature more NH_3 passes into the chloroform layer.

From this has been drawn the conclusion that on dissolving NH_3 in water we are dealing with a compound whose concentration increases with a decrease in temperature.

The behaviour of the substituted organic ammonia derivatives has

¹⁾ Zeitschr. f. phys. Chem. 30, 258 (1899).

led to HANTZSCH and SEBALDT's attempt to render it plausible that this compound is not NH_4OH , but a hydrate $(\text{NH}_3)_m (\text{H}_2\text{O})_n$ of unknown composition.

ABEGG and RIESENFELD¹⁾ have felt able to support this idea by demonstrating that the NH_3 -pressure of an aqueous ammonia solution increases most on addition of salts which do not yield complex compounds with NH_3 , if these salts have themselves a great tendency to form hydrates.

If we consider this and other arguments which have led to the conclusion that in aqueous solution of ammonia hydrates of the same should be present, and not NH_4OH , it appears that the argument is far from convincing and that the conclusion is, therefore, subject to great objections.

When instead of NH_4OH we write $\text{NH}_3 \cdot \text{H}_2\text{O}$, we only mean to say in fact that we are dealing with a compound which does not behave as a base. Now, the solution of NH_3 in water does behave as a base, but this it is endeavoured to explain in the light of the theory of WERNER, by assuming that a part of the free NH_3 -molecules will, in consequence of their secondary valencies, unite with the H^+ -ions of the water to cations, the water equilibrium being shifted in such a manner that the OH^- -ions may appear in large excess.

It is true that the phenomena observed may be explained, even when we deny the existence of NH_4OH , but for this denial there is no sufficient evidence, while there is not a single phenomenon opposed to the assumption that NH_4OH occurs in the aqueous ammonia solution, which is, on one side, in equilibrium with NH_3 and H_2O and on the other side with the ions NH_4^+ and OH^- .

The research, the first results of which will be communicated here, did not relate to the investigations of previous workers but was simply undertaken to answer the question "what are, apart from the structure, the compounds which may be deposited on cooling from mixtures of NH_3 and H_2O ". This question seemed to us an important one, also because from the separation of a compound in solid condition, it may be concluded with a high degree of probability that such compound was previously present in the solution.

The investigation of the melting point line now gave the following result.

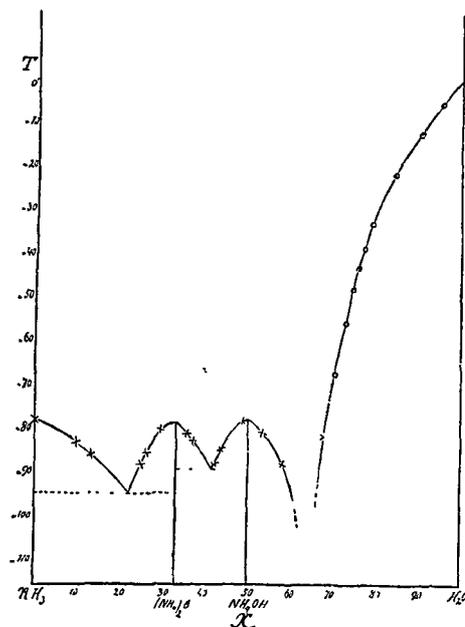
In this graphical representation the results of PICKERING's investigations²⁾ are indicated by circlets, and thus we notice that, whereas

¹⁾ Zeitschr. f. phys. Chem. 40, 84, (1902) and 45, 462 (1903).

²⁾ Journ. Chem. Soc. 63, 141 (1891).

owing to an incomplete investigation, he has found nothing special, two compounds have now been discovered in which NH_3 and H_2O have united in the proportions of 1:1 and 2:1.

This result is not without significance; for looking at the analogy



between the ammonium salts and those of the alkalis could we expect that NH_4 might combine with the OH-group, and with oxygen in the same proportions as in the case of potassium, and if now, for the reasons stated above, we do not write the compounds found in the form of hydrates but in the form of ammonium salts, we obtain indeed NH_4OH and $(\text{NH}_4)_2\text{O}$, the first of which melts at -77° and the second at -78° .

The communication of further details will be postponed till later on, but here it may yet be mentioned that, as was to be expected, at the water-side and at a low temperature, the investigation was much impeded by the great viscosity of the liquid, so that the eutecticum of H_2O and NH_4OH could not be determined for the present.

This investigation, continued in various directions is also being extended to amines.

Amsterdam June 1909.

Inorg. Chem. Lab. University.