AMMONIA DISTILLATION IN THE PRESENCE OF MAGNESIUM OR CALCIUM SALTS.

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Received June 15, 1908.

It is a well-known fact that the time required to distill off ammonia in Folin's[1] urea determination is three to four times longer than the time required for ordinary distillations. Moreover, in the literature on the subject there seem to be considerable discrepancies[2] in the results of ammonia distillations, especially when they are made in the presence of magnesium salts. To throw some light on these variations[3] and discrepancies, and to show that a general principle underlies them all, is the object of this paper.

As an explanation of the delayed distillation in his urea method, Folin states that the hypothesis of the formation of magnesium ammonium phosphate was untenable, considering the following:

(*a*) That calcium chloride works as well as magnesium chloride and requires as much time.

(*b*) The precipitation and removal of phosphates by calcium chloride and sodium hydroxide, before digesting, do not lessen the time required for distillation.

(*c*) The distillation of pure urea lasts as long as that of urine-containing phosphates.

Folin explains the delay on the basis of the above facts, namely that it is due to lack of free water during digestion, which causes the urea to partly split up into cyanuric acid. On distillation with alkali, cyanuric acid decomposes slowly but quantitatively into ammonia and carbon dioxide. From this he draws the conclusion that water of crystallization cannot produce hydrolysis.

Surely, Dr. Folin has not produced any evidence that there is present in the solution cyanuric acid, nor has he exhausted the possibilities in this case.

The modification of Saint Martin[4] seems to show that no cyanuric acid is *formed* when urea is heated to 160°–70° in a saturated solution of some chlorides. This modification consists in digesting the urea solution with lithium chloride. The subsequent distillation of ammonia can then be completed in thirty minutes.

In applying the air current apparatus[5] to the distillation of ammonia from urea determinations (Folin's) no ammonia was obtained, even

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[1] Folin, *Z. physiol. Chem.*, **36**, 333.

[2] *Ibid.*, **39**, 477.

[3] Arnold and Mentzel, *Ibid.*, **36**, 49.

[4] M. L. G. de Saint Martin, *Compt. rend., de la Société de Biologie*, **1905**, p. 89.

[5] THIS JOURNAL, **30**, 1131, July, 1908.

though 0.7 gram of sodium hydroxide had been added to the solution. Was this due to a complete transformation of urea into cyanuric acid, which, without heat did not break up into ammonia and carbon dioxide, or was this due to some other cause?

Further experimentation showed that ammonia chloride gave no ammonia under the same conditions. Since the solution contained only magnesium and ammonium chlorides it was easily seen that the retention of ammonia was due to the presence of magnesium chloride.

Formerly the solvent action of ammonia and its salts on magnesium hydroxide was explained by assuming the formation of a complex salt. That the action is to be explained by the aid of the laws of mass action and the ionization hypothesis, independent workers who have studied the equilibrium and concentration relations, all agree.

The reaction according to Lovén,[1] Treadwell,[2] Herz and Muhs[3] is a reversible one.

$$MgCl_2 + 2NH_4OH \rightleftarrows Mg(OH)_2 + 2NH_4Cl.$$

The mass law states that the speed of a reaction is proportional to the concentration of the reacting substances. In a reversible reaction the speed of the reverse action increases as the speed of the direct action decreases, until they are equal. The reacting substances are then said to be in equilibrium. If one of the products of a reversible reaction be removed, the reaction will go on in the direction to form more of that product.

A change of temperature will also change an equilibrium. An increase of temperature will cause an equilibrium to change so that the heat-absorbing reaction takes place.

In the distillation of Folin's urea determinations, there is present a large excess of magnesium chloride, some ammonium chloride, magnesium hydroxide and ammonium hydroxide. As the concentration of magnesium hydroxide is extremely small, and the concentration of magnesium chloride relatively great, equilibrium will only be found when most of the ammonium is in the form of the chloride. Of the small amount of ammonium hydroxide a portion will be removed by distillation. This disturbs the equilibrium, which shifts so that more ammonium hydroxide will be formed. This shifting of equilibrium will follow the removal of ammoina by the distillation and gives the explanation of the delay in urea distillations made with magnesium chloride or calcium chloride. This also explains how Arnold and Mentzel,[4] on additional distillation, obtained more ammonia and how Folin[5] continued to obtain ammonia

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[1] Lovén, *Z. anorg. Chem.*, 11, 409.

[2] Treadwell, *Ibid.*, 37, 386.

[3] Herz and Muhs, *Ibid.*, 37, 38.

[4] *Z. phys. Chem.*, 36, 49.

[5] *Ibid.*, 39, 477.

with the Hausmann method after the first distillation. As magnesium hydroxide is formed with the evolution of heat, the increase of temperature obtained by distillation shifts the equilibrium so that less magnesium hydroxide is formed and therefore the more ammonium hydroxide and ammonia.

In the reaction,

$$MgCl_2 + 2NH_4OH \rightleftarrows Mg(OH)_2 + 2NH_4Cl.$$

If a = the conc. of $MgCl_2$; b = the conc. of NH_4OH; c = the conc. of $Mg(OH)_2$; d = the conc. of NH_4Cl,

then
$$\frac{a.b^2}{c.d^2} = K.$$

"K" is a constant, dependent on the temperature and independent of the concentration. As "c" and "d" are formed with the evolution of heat, the value of "K" will decrease as the solution is heated to boiling; in other words, the equilibrium shifts, as it were, from right to left, but the equilibrium law still holds, and therefore the last traces of ammonia would be very difficult to remove. Since the value of "c" can never be large, a large concentration of "a" means a very small amount of "b" and a relatively large amount of "d". This balanced reaction holds equally as well with calcium salts.

There seems to be the impression[1] that an alkaline solution must, when heated to boiling, liberate ammonia. The following simple experiment will show that no ammonia is given off on boiling a magnesium chloride solution.

One cc. of $N/10$ ammonium chloride was added to 25 cc. of saturated magnesium chloride and after the addition of 3 drops of saturated caustic soda the solution was brought to boiling. A sensitive Nessler solution showed no traces of ammonia in the vapors at any time.

It is very difficult, if not impossible, to distil off any ammonia from an alkaline saturated solution of calcium chloride or magnesium chloride.

Therefore the Folin condenser[2] is useless for the purpose of preventing the loss of ammonia, during the digesting of urea with an acid magnesium chloride solution, because the solution cannot become alkaline before it has become saturated.

It is also quite obvious that quantitative ammonia distillations should not be made in the presence of much magnesium or calcium salts.

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[1] *Z. phys. Chem.*, **36**, 335 and 339.

[2] The Folin condenser is, however, quite convenient for keeping the solution acid.