Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Ammonia Vapor Pressure of Ammoniacal Solutions of Ammonium and Copper(II) Sulfates

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THE PRESENCE of ammonium and copper(II) salts in aqueous ammonia solutions has a strong influence on the vapor-liquid equilibrium of the ammonia-water system, the ammonia vapor pressure being increased or decreased according to the nature and concentration of the salts. Early investigators (*6*, *9*) have reported isolated values of the variations of the ammonia vapor pressure caused by the addition of numerous salts to ammonia solutions. More recently, Scheffer and de Wijs (*17*) and Bjerrum (*1*) have determined the ammonia vapor pressures over ammoniacal solutions of ammonium and copper(II) chlorides and nitrates at low copper(II) concentration and room temperature. In view of the absence of quantitative data on ammoniacal solutions of ammonium and copper(II) sulfates and of the current interest in the treatment of metal-ammine sulfates solutions (*11*), it was thought worthwhile to determine the ammonia vapor pressure of such a system over a range of temperatures and to correlate the results with solution composition. As an application of this study, some aspects of the distillation of metal-amine solutions are discussed.

EXPERIMENTAL

Ammonia vapor pressures were determined at 25° and 40° C. indirectly by means of pH measurements. In the 25° to 89° C. temperature range, the gas saturation method was also used and at 100° C. a dynamic method was preferred.

Indirect Method with pH Measurements. The linear relationship between the logarithm of the ammonia vapor pressure and solution pH was used for indirect determinations of the vapor pressure.

In a solution containing ammonia and ammonium salts the equilibrium $NH_3 + H^+ \rightleftarrows NH_4^+$ leads to the following relation between the activities of the species:

$$\frac{a_{NH_3} \times a_{H^+}}{a_{NH_4^+}} = K \qquad (1)$$

The fugacity of ammonia in the vapor in equilibrium with such an ammoniacal solution is proportional to ammonia activity. At the low pressures used, the error made in replacing fugacity by partial pressure is less than 1% (*13*) so that:

$$p_{NH_3} = p^{\circ}_{NH_3} \times a_{NH_3} \qquad (2)$$

K and $p^{\circ}_{NH_3}$ are constants at a given temperature. If the ammonium ion activity is fixed—i.e., at constant concentrations of ammonium and copper(II) salts—it follows that:

$$\log p_{NH_3} = \mathrm{pH} + A \qquad (3)$$

The pH of solutions of known composition was measured at 25° and 40° C. with a radiometer pH meter. The value of constant A was later deduced from determinations with the gas-saturation method.

Gas-Saturation Method. Nitrogen was saturated by passage through the ammoniacal solution. A train of three saturators of the gas-washing bottle type, maintained in a constant temperature bath, were used for saturation. The gas flow rate was usually 12 liters per hour (6 liters per hour for the 89° C. determinations). The total pressure in the third saturator was measured by means of a mercury manometer. The ammonia content of the saturated gas was determined by passage through two washing bottles maintained at 25° C. and containing a known volume of titrated hydrochloric acid solution and a few drops of methyl red as indicator. The excess acid or ammonia was back-titrated. A blank correction for the indicator was applied when necessary. Ammonia absorption was complete in the first bottle within the accuracy of the titration. A wet-gas meter was used to record gas volume after absorption. The glass tubing between saturators and absorbers was electrically heated to prevent any condensation. The solution in the third saturator was analyzed before and after the experiment and the average concentration was taken (the difference between both values amounting to less than 3%). The ammonia concentration was determined by potentiometric titration, and that of copper, by electrolysis. The ammonium sulfate concentration was known from the weight of salt used in making up the solution.

The method was tested to establish how closely the vapor-liquid equilibrium was approached. The ammonia vapor pressure of a 0.05N ammonia solution was determined at three nitrogen flow rates: 6, 12, and 18 liters per hour. The values found agreed within 1%. The ammonia vapor pressures of 0.06 and 0.4N ammonia solutions were also determined at 25° C. in order to compare them with literature data. Using the author's data and those of Scheffer and de Wijs (*17*), the ammonia vapor pressure of a 0.1N ammonia solution was calculated by assuming proportionality between pressure and concentration. These calculated values are given below:

Approximate ammonia concentration	0.06N	0.4N
Calculated p_{NH_3}, mm. Hg for 0.1N solution		
Scheffer and de Wijs	1.280	1.306
This work	1.252	1.285

The agreement between both sets of values is satisfactory, considering that the accuracy of the measurements in both series is about 1%. Furthermore, taking into account the differences in the concentrations of ammonia, other results at 40° and 60° C. are in substantial agreement with Perman's (*15*) and Konowalow's (*9*) values.

Determinations were made at 25°, 40°, 60°, and 89.1° C., the temperatures being known within 0.2° C.

Dynamic Method with Condensate Recirculation. The ammoniacal solution was distilled, the vapor condensed, and the condensate returned back to the still. A slightly modified version of the simple Othmer recirculation still (*14*) was used. The sample stopcock on the still was replaced by a three-way stopcock on the condensate return line. External electric heating was first used and the boiling rate was adjusted at about 3 ml. of condensate per minute. Samples of condensate and solution were taken after 90 minutes of boiling (condensate volume changed 15 times) to ensure attainment of steady-state conditions. For convenience, experiments were carried out under atmospheric pressure rather than at constant temperature.

The ethyl alcohol-water system was used to test the Othmer recirculation still with external electrical heating. Vapor composition results determined by density measurements were consistently higher than existing vapor-liquid equilibrium data (*7*). Electrical heating was replaced by gas heating by means of three microburners applied off-center, far from the condensate return line, in an effort to improve mixing of the condensate with the bulk of the boiling solution. After this modification, the experimental results agreed within 4% with existing vapor-liquid equilibrium data.

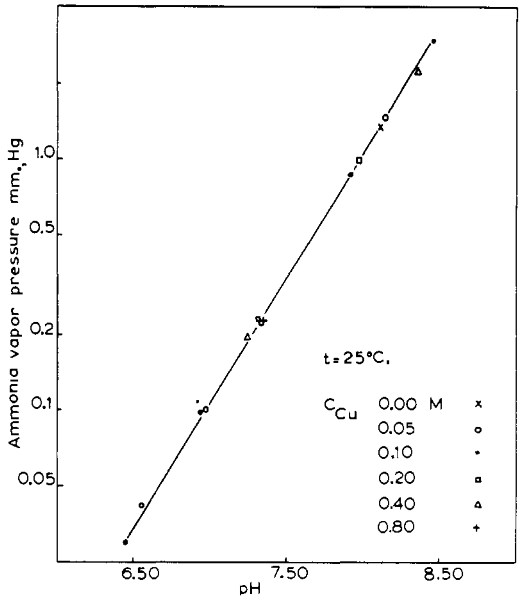

Figure 1. Relationship between ammonia vapor pressure and solution pH

Furthermore, the ammonia vapor pressure of a 0.1N ammonia solution was calculated as 16.8 mm. at 97.9° C. from an experimental value obtained for a 0.3N solution. This is in agreement with an interpolated value of 17.0 mm. obtained from Clifford's results (*4*).

Attainment of vapor-liquid equilibrium was therefore considered satisfactory.

RESULTS

Relationship between Ammonia Vapor Pressure and Solution pH. The previously established linear relationship (*3*) between the logarithm of the ammonia vapor pressure and solution pH was checked at 25° C. (two determinations were also made at 40° C.) by a series of vapor pressure determinations by the gas saturation method and by pH measurements.

The solutions used were 2M in ammonium sulfate, from 0 to 0.8M in copper(II) sulfate, and from 0.05 up to 2.6M in ammonia. The values of log p_{NH_3} at 25° C. were plotted *vs.* solution pH in Figure 1. Representative points fell on a straight line,

$$\log p_{NH_3} = \text{pH} - 7.97 \qquad (4)$$

regardless of copper(II) sulfate concentration. This latter result implies that the ammonium ion activity coefficient is not noticeably affected by copper(II) sulfate concentration. At 40° C. the relation was

$$\log p_{NH_3} = \text{pH} - 7.22 \qquad (5)$$

Both relations made possible the rapid, indirect determination of ammonia vapor pressure by the simple measurement of solution pH.

Effect of Ammonium Sulfate Concentration on Ammonia Vapor Pressure. Ammonia vapor pressures of a 0.4N ammonia solution and 0.05N ammonia solutions with ammonium sulfate concentrations up to 3M were determined at 25°, 40°, 60°, and 97.9° C. When no ammonium sulfate was present, a 0.4N ammonia solution was used instead of the more dilute one to avoid correction due to the dissociation of ammonia. At the highest temperature, the ammonia partial pressure was determined by using the

Othmer still at atmospheric pressure. The solution boiling point was therefore a function of ammonium sulfate concentration. Experimental pressures were reduced to 97.9° C. by using the known temperature coefficient of the pressure, in the absence of ammonium sulfate and also by assuming the ammonia activity coefficient to be constant in the small temperature interval considered.

The experimental values of the pressure were reduced to a 0.1*N* ammonia concentration assuming proportionality between pressure and concentration. Plots of the logarithm of the ammonia vapor pressure against the molar concentration of ammonium sulfate were straight lines as shown in Figure 2.

Effect of Copper(II) Concentration on Ammonia Vapor Pressure. pH was measured at 25° and 40° C. on solutions 2*M* in ammonium sulfate, from 0.02 to 0.3*M* in copper(II) sulfate, and with ammonia concentrations corresponding to ratios of ammonia to copper(II) molar concentrations from $r = 2.0$ to $r = 5.5$. In spite of the presence of ammonium sulfate, hydrolysis of copper(II) set in at low *r* values and thus limited the composition range of solutions that could be studied. In Figure 3, pH values were plotted *vs.* *r* for various copper(II) concentrations. The log p_{NH_3} scale deduced from Equation 4 is also given on the graph. The pH (or log p_{NH_3}) values depend little on the copper(II) concentration when the latter is below 0.1*M*, and when *r* is lower than about 2.8. The pH values increase with *r*, at first almost linearly and then they tend to level off.

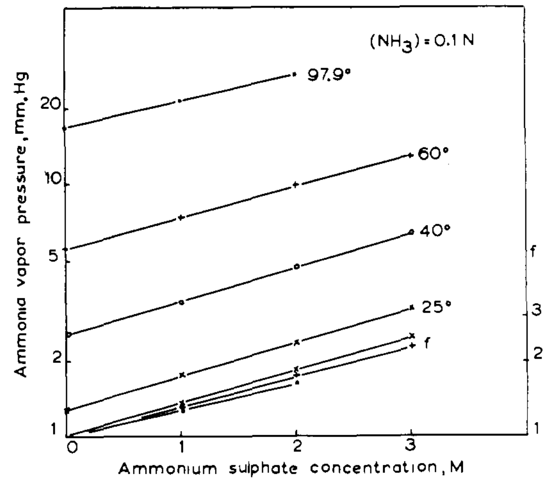

Figure 2. Effect of ammonium sulfate concentration on ammonia vapor pressure of 0.1*N* ammonia solution at various temperatures

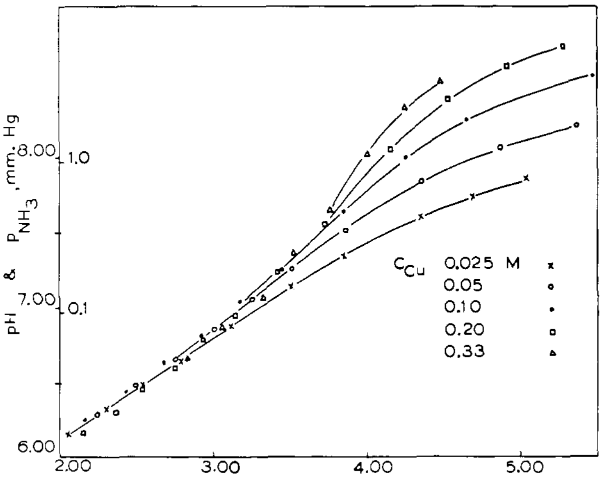

Figure 3. Ammonia vapor pressure and solution pH for various copper(II) concentrations vs. ammonia to copper(II) molar ratio at 25° C.

A few pH measurements were also made on solutions 0.5, 1.0, and 3.0*M* in ammonium sulfate and with low copper(II) and ammonia concentrations, in order to establish ammonium sulfate influence in the presence of copper(II).

Further determinations of ammonia vapor pressures were carried out at 60°, 89.1°, and 101.7° C. on 2*M* ammonium sulfate solutions with 0.1 to 0.4*M* copper(II) concentrations and various ammonia concentrations (Figure 4). The gas saturation method was used at 60° and 89.1° C. and the dynamic method at 101.7° C. As the total pressure had been kept constant, the latter temperature varied, but by less than 0.5° C., according to the solution composition.

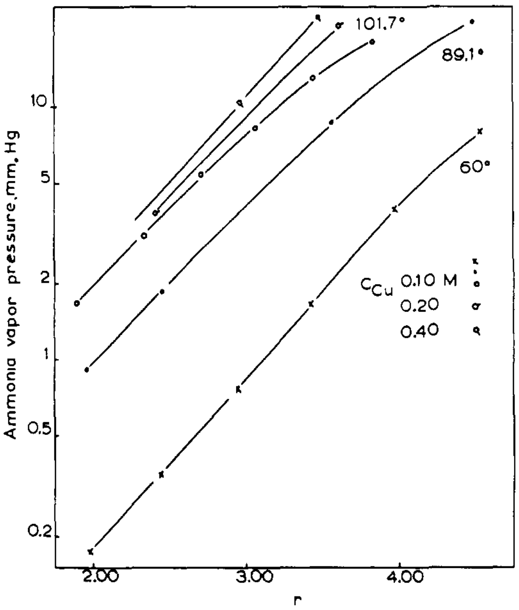

Figure 4. Ammonia vapor pressure for various copper(II) concentrations vs. ammonia to copper(II) molar ratio at various temperatures

CORRELATION

The ammonia-water system is nonideal, showing negative deviations although no minimum in the pressure-composition relationship. For the study of dilute aqueous ammonia solutions it is convenient to choose the standard state so that the ammonia activity coefficient f_{NH_3} approaches unity when ammonia concentration (NH$_3$) approaches zero, then

$$p_{NH_3} = p^\circ_{NH_3} (NH_3) f_{NH_3} \qquad (6)$$

at a given temperature. The ammonia activity coefficient was taken here as 1.00 for a 0.4*N* ammonia solution.

Experimental data can be efficiently presented and extended by examining successively the influence of solution composition and temperature on liquid-vapor and solution equilibria.

Influence of Ammonium Sulfate Concentration and Temperature on Liquid Vapor Equilibrium. Generally, addition of an electrolyte to an aqueous solution of a nonelectrolyte increases the vapor pressure of the nonelectrolyte. Various theories have been advanced to explain this salting-out effect—hydration and electrostatic theories, internal pressure concept (*10*). When the nonelectrolyte concentration is low, the logarithm of the nonelectrolyte activity coefficient varies linearly with electrolyte concentration. The addition of ammonium sulfate to a dilute ammonia solution was therefore expected to result in an increase of the ammonia activity coefficient according to

$$\log f_{NH_3} = kC_{(NH_4)_2SO_4} \tag{7}$$

From the experimental results on the effect of ammonium sulfate concentration, the values of f_{NH_3} were calculated and plotted in Figure 2, *vs.* ammonium sulfate concentration. The variation is linear. From the few isolated measurements made by Gaus (*6*) and Konowalow (*9*) on ammonia vapor pressures and by Dawson and McCrae (*5*) on partition of ammonia between aqueous solutions and chloroform, values of the coefficient k of Equation 7 were calculated and found to agree with the author's values.

Table I. Comparison of Data

Source	Temp., ° C.	$C_{(NH_4)_2SO_4}$ M	k
Gaus	25	0.2	0.150
Dawson	20	0.5	0.142
This work	25	0 to 3	0.134
Konowalow	60	0.4	0.125
This work	60	0 to 3	0.124

The temperature dependence of the activity coefficient is small, the corresponding ΔH being about 0.15 kcal. The negative temperature coefficient is in agreement with the usual increase in solution ideality at higher temperatures.

Influence of Copper(II) Concentration. The addition of copper(II) sulfate to an ammoniacal solution of ammonium sulfate greatly lowers the ammonia vapor pressure. Although there is a minor salting-out effect, it is overshadowed by a major salting-in effect resulting from a series of equilibrium reactions between the cupric ions and the ammonia molecules:

$$Cu(H_2O)_n^{+2} + NH_3 \rightleftarrows CuNH_3(H_2O)_{n-1}^{+2} + H_2O$$

$$CuNH_3(H_2O)_{n-1}^{+2} + NH_3 \rightleftarrows Cu(NH_3)_2(H_2O)_{n-2}^{+2} + H_2O \ldots$$

The corresponding equilibrium concentration constants at ionic strength I are after simplification of notations

$$k_n = \frac{[Cu(NH_3)_n^{+2}]}{[Cu(NH_3)_{n-1}^{+2}][NH_3]} \tag{8}$$

Bjerrum's method (*2*) is widely used for dealing with such step equilibria. Calling C_{NH_3} and C_{Cu} respectively the total ammonia and copper(II) concentrations:

$$C_{NH_3} = [NH_3] + \sum n[Cu(NH_3)_n^{+2}] \tag{9}$$

$$C_{Cu} = [Cu^{+2}] + \sum [Cu(NH_3)_n^{+2}] \tag{10}$$

The absence of polynuclear complexes is assumed. Since the stability of the copper(II) sulfate complex (*12*) is such that its concentration is approximately equal to that of Cu^{+2} for $2M$ sulfate solution, it is therefore negligible in the solution where $r = C_{NH_3}/C_{Cu}$ is above 2.0.

Concentration of these complex ions can be expressed in terms of free ammonia and cupric ions concentrations and the equilibrium constants:

$$\frac{C_{NH_3} - [NH_3]}{C_{Cu}} = \bar{n} = F\{[NH_3], k_n\} \tag{11}$$

This expression indicates that $[NH_3]$, the free ammonia concentration, is at ionic strength I, a function of $\bar{n}$, the average number of ammonia molecules bound per cupric ion. The ammonia vapor pressure which is under these conditions proportional to $[NH_3]$, is also only $\bar{n}$ dependent.

Experimental values of ammonia vapor pressure can therefore be best correlated and subsequently extrapolated through use of the $\bar{n}$ concept. At the same time the consistency of the data can be tested. However, it was preferred to establish from the values of p_{NH_3} corresponding to each ammonia and copper(II) concentration, the more fundamental curve giving $[NH_3]$ *vs.* $\bar{n}$, rather than the curve p_{NH_3} *vs.* $\bar{n}$. In this manner, the influence of temperature and ionic strength on solution equilibria could be dealt with independently without taking into account the already established influence of temperature and ammonium sulfate concentration on liquid-vapor equilibrium.

Experimental values of the ammonia vapor pressure were therefore used to calculate the free ammonia concentration and the corresponding $\bar{n}$ values. By assuming the same ammonia activity coefficient in absence and in presence of copper(II) in $2M$ ammonium sulfate solution, $[NH_3]$ was obtained using relations such as:

$$\log [NH_3] = \log p_{NH_3} \text{ (mm. Hg)} - 1.38 \tag{12}$$

at 25° C.; $\bar{n}$ was calculated from $[NH_3]$ and the corresponding values of C_{NH_3} and C_{Cu}.

The curve giving $\log [NH_3]$ against $\bar{n}$ at 25° C. (Figure 5) is the so-called "formation curve" characteristic of the system $Cu(II)-NH_3$ in a $2M$ ammonium sulfate medium.

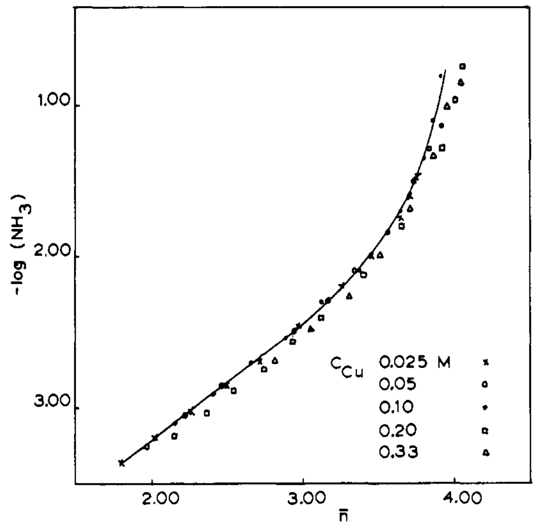

Figure 5. The formation curve—i.e. the relationship between log $[NH_3]$ and $\bar{n}$ for various copper(II) concentrations, at 25° C.

The points corresponding to copper(II) concentrations up to $0.1M$ fall on the same curve emphasizing the consistency of the data. However, for 0.20 and $0.33M$ copper(II) concentrations, representative points fall somewhat aside on a line approximately parallel to the formation curve. This could be due to an appreciable increase of ionic strength on the values of the equilibrium constants k_n (an increase in the concentration of salts such as ammonium sulfate and ammonium nitrate leads to the same effect). There could also be an opposite and therefore smaller effect of higher ionic strength on the ammonia activity coefficient.

Influence of Ammonium Sulfate Concentration on Solution Equilibria. Ammonium sulfate concentration affects solution equilibria because values of the concentration constants k_n in Equation 8 depend on solution ionic strength.

Although, experimental values corresponding to 0.5, 1.0, and $3.0M$ $(NH_4)_2SO_4$ concentrations were not numerous enough to draw the complete corresponding formation curves, the influence of ammonium sulfate concentration on log $[NH_3]_{\bar{n}}$ was calculated as:

$$\log [NH_3]^C_{\bar{n}} = \log [NH_3]^\circ_{\bar{n}} + 0.08C \qquad (13)$$

log $[NH_3]^C_{\bar{n}}$ and log $[NH_3]^\circ_{\bar{n}}$ being, respectively, the log $[NH_3]$ values at $\bar{n}$ and at the ammonium sulfate molar concentration C and 0. Bjerrum (*2*) also gave a coefficient of 0.08 to account for the influence of ammonium nitrate concentration. The salt influence of ammonium nitrate and ammonium sulfate on the equilibrium constants k_n is therefore approximately the same, despite the different effects of both salts on f_{NH_3} (*1*).

The formation curve corresponding to an ammonium sulfate concentration, C, would be parallel to that for $2M$ $(NH_4)_2SO_4$, the translation along the log $[NH_3]$ axis being calculated as $0.08\ (C - 2)$.

The formation curve obtained by Bjerrum (*2*) at 30° C. for a $2M$ ammonium nitrate medium nearly coincides with the present curve at 25° C. for $2M$ ammonium sulfate as shown in Figure 6. This indicates that the values of the equilibrium constants, k_n, for a zero salt concentration would be in satisfactory agreement with Bjerrum's values—actually the difference would be $\Delta \log k_n \sim 0.06$.

Influence of Temperature on Solution Equilibria. The solution equilibria are temperature dependent and the formation curves corresponding to the various temperatures (Figure 6) are merely displaced in parallel. This indicates that the heats of formation of the various cupriamine complexes are approximately the same, which is in agreement with the findings of other authors (*16, 19*). The corresponding ΔH_n can be estimated because (*2*)

$$K_n = \frac{1}{[NH_3]_{\bar{n} = n - 1/2}} \frac{1 + A}{1 + B} \qquad (14)$$

where A and B are corrective terms. In other words, ΔH_3 and ΔH_4 can be deduced from the slopes of the curves giving, respectively, log $[NH_3]_{\bar{n} = 2.5}$ and log $[NH_3]_{\bar{n} = 3.5}$ against $1/T$ as plotted in Figure 7. The values found are:

$$\Delta H_3 = \Delta H_4 = 6.2 \pm 0.3 \text{ kcal. between } 25° \text{ and } 40° \text{ C.}$$

and

$$\Delta H_3 = \Delta H_4 = 7.3 \pm 0.3 \text{ kcal. between } 60° \text{ and } 89.1° \text{ C.}$$

Assuming also $\Delta H_1 = \Delta H_2 = \Delta H_3$, this would give $\Delta H_{1-4} = 24.8 \pm 1.2$ kcal. between 25° and 40° C. Values reported in the literature (*2, 3, 18, 19*) mostly for ammonium nitrate media vary between 20 and 24 kcal. near 25° C. The somewhat higher value found in the present work may be due to a medium influence on the temperature coefficient of the activity coefficients.

The above change of ΔH_3 with temperature is best accounted for by using another method of calculation. ΔH_3 was calculated from the variation of log $[NH_3]_{\bar{n} = 2.5}$ with temperature. However, as

$$[NH_3]_{\bar{n} = 2.5} = \frac{p_{\bar{n} = 2.5}}{p^\circ \cdot f},$$

ΔH_3 can also be obtained as the difference between two ΔH: one corresponding to temperature influence on ammonia vapor pressure of a solution with $\bar{n} = 2.5$, the other corresponding to temperature influence on ammonia pressure of an ammonia $2M$ ammonium sulfate solution. It was found that $\frac{d \log p_{\bar{n} = 2.5}}{d(1/T)}$ is nearly independent of temperature, and the corresponding ΔH is 14.6 kcal. However, $\frac{d \log p^\circ f}{d(1/T)}$ varied from 8.3 kcal. between 25° and 40° C. to 7.3 kcal. between 60° and 89.1° C. The values are in good agreement with the heat of solution of ammonia (for dilute solutions) calculated as 8.3 kcal. at 20° C. and estimated as 7.3 kcal. at 100° C. (*8*). The increase of ΔH_3 and consequently ΔH_{1-4} with temperature would therefore be due to a decrease in the heat of solution of ammonia with temperature.

APPLICATIONS

Calculation of Ammonia Vapor Pressures. The previous correlation makes possible computation of the ammonia vapor pressure of ammoniacal solutions of ammonium and copper(II) sulfates in the temperature range 25° to 100° C. for any solution composition. The steps to be followed in such a calculation are: Knowing the ammonium sulfate concentration, C, and the temperature, $T°$, the formation curve log $[NH_3] = F(\bar{n})$ is drawn parallel to the one for $2M$ $(NH_4)_2SO_4$ (Figure 6). The translation along the log $[NH_3]$ axis is calculated as the sum of a temperature effect obtained from the curve in Figure 7 giving log $[NH_3]$ against $1/T$, and an ammonium sulfate effect $0.08\ (C - 2)$. An $[NH_3]$ value is assumed, and the corresponding $\bar{n}$ is deduced from the previous formation curve. Knowing the copper(II) concentration in solution, C_{NH_3} is obtained as $C_{NH_3} = [NH_3] + \bar{n}\, C_{Cu}$. The corresponding ammonia vapor pressure p_{NH_3} is calculated from $[NH_3]$, f_{NH_3} (according to Figure 2) and $p^\circ_{NH_3}$ ammonia vapor pressure of a $0.1N$ ammonia solution at temperature T: Equation 6. This process is repeated for several values of $[NH_3]$. p_{NH_3} is plotted against C_{NH_3} and the value corresponding to the ammonia concentration C_{NH_3} of the solution considered is obtained by interpolation.

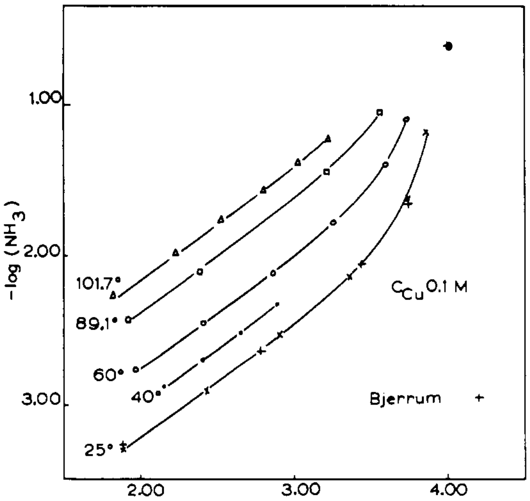

Figure 6. Effect of temperature on formation curve

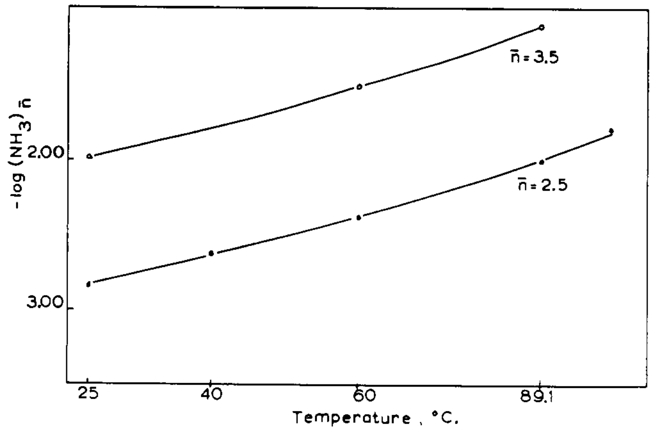

Figure 7. Relationship between log $[NH_3]_{\bar{n} = 2.5}$ and log $[NH_3]_{\bar{n} = 3.5}$ and the reciprocal of absolute temperature

However, the values of the ammonia vapor pressures of solutions with high copper(II) concentrations—above 0.1M for 2M $(NH_4)_2SO_4$—would only be approximate because of opposing effects on the formation curve and on the ammonia activity coefficient.

Study of Distillation. Some aspects of the distillation of ammoniacal solutions of ammonium and copper(II) (or other metal-amine-forming elements) salts may now be considered.

The study of the distillation of binary mixtures is usually made with the help of graphical liquid-vapor equilibrium relationships such as those giving vapor composition against solution composition at constant pressure. The variations of vapor and solution composition during distillation of metal-amine solutions can be predicted from some simple heat and material balance calculations and from the curves giving the ammonia vapor pressure (or preferably the ammonia mole fraction) plotted against either ammonia concentration (or mole fraction) in solution for various metal concentrations, or the ratio of ammonia to metal molar concentrations.

Let us suppose that a 0.1M Cu(II), 2$M(NH_4)_2SO_4$, and 0.5N NH_3 solution is to be distilled under pressure p and let us consider the curves at the corresponding temperature giving p_{NH_3} or $y = p_{NH_3}/p$ plotted against C_{NH_3} or r (Figure 8). Let us call W the total number of moles of ammonia and water, x the corresponding ammonia mole fraction, and y the ammonia mole fraction of the equilibrium vapor. The simplest case, that of batch steam distillation without rectification, is considered first.

BATCH STEAM DISTILLATION. The introduction of dW moles of saturated steam to a boiling solution will cause vaporization of dW' moles of ammonia and water. An ammonia material balance gives:

$$ydW' = d(xW) \tag{15}$$

If the ratio of ammonia to metal molar concentrations is relatively low, the latent heat of vaporization of the solution is approximately equal to the latent heat of condensation of the steam (the heat of dissociation of the cupri-amine complexes makes this approximation more exact) and $dW = dW'$; W remains constant. Supposing further that under these conditions the partial molar volumes of ammonia and water are approximately the same, then the solution volume as well as the concentrations of copper(II) and ammonium sulfates will remain constant during distillation. The point representing the composition of vapor and solution during distillation follows the curves corresponding to $C_{Cu} = 0.10\ M$ on the graphs giving p_{NH_3} against C_{NH_3} or r (full lines marked with arrows). The effect of the small variation of temperature during distillation is neglected.

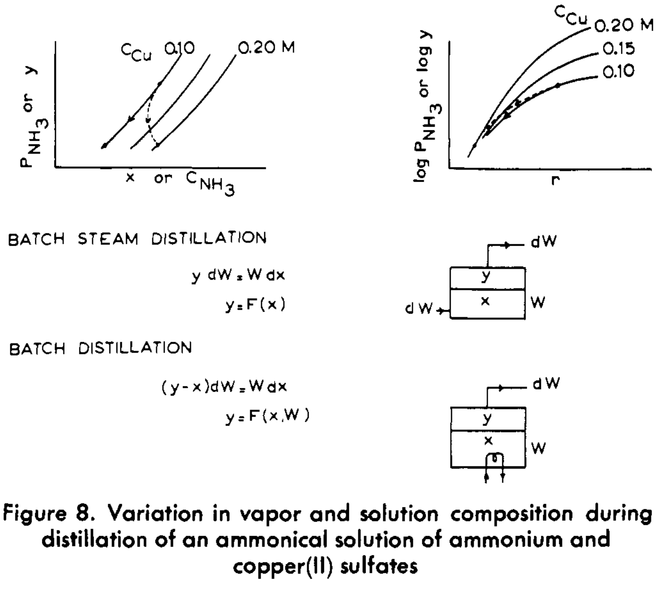

Figure 8. Variation in vapor and solution composition during distillation of an ammonical solution of ammonium and copper(II) sulfates

To calculate a given distillation completely the relation:

$$ydW = Wdx \tag{16}$$

is used with the curve, $y = F(x)$ [deduced from $p_{NH_3} = F'(C_{NH_3})$ at the given copper(II) concentration].

SIMPLE BATCH DISTILLATION. The heat required to carry out the distillation is supplied externally. The number of moles of ammonia and water, W, and the salts concentration in solution will continuously decrease and increase respectively during distillation.

The relation used to calculate a given distillation is $ydW = d(xW)$ or

$$(y - x)dW = Wdx \tag{17}$$

with the curves, $y = F(xW)$ [deduced from $p_{NH_3} = F(C_{NH_3}, C_{Cu})$] and another relation which would be obtained from a heat balance. Equation 17 makes possible some predictions as to the variations of y and x during distillation:

When the ammonia concentration in solution is high, y is greater than x and as dW is always negative, dx is negative: The ammonia mole fraction in solution (or C_{NH_3}) will decrease on distillation as well as y.

Then, when $y = x$, $dx = 0$. With binary mixtures such a condition would indicate that the solution is an azeotropic mixture and that on further distillation the compositions of vapor and solution remain identical. However, this is not the case here: dy does not cancel out, as it depends also on W; as $dy = (\partial y/\partial W)dW$ when $dx = 0$, y keeps on decreasing.

When y becomes smaller than x—i.e., at low ammonia concentration—dx becomes positive: The ammonia mole fraction in solution (or C_{NH_3}) increases on further distillation. This otherwise surprising fact has been confirmed experimentally.

The point representing the composition of the vapor and the solution during distillation follows a curve such as the dotted line in Figure 8.

ACKNOWLEDGMENT

The author is grateful to the National Research Council of Canada for financial support and expresses appreciation to J. Lessard and P. Roberge for their part in the experimental work.

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RECEIVED for review March 14, 1960. Accepted September 21, 1960. Division of Inorganic Chemistry, 136th Meeting, ACS, Atlantic City, N. J., September 1959.