Vaporization Equilibria Generated by NH4AlCl4

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Pyrex diaphram and transpiration studies indicate that the complex compound NH4AlCl4 vaporizes by dissociation into the ammine, NH3AlCl3, and HCl. The ammine and the complex are miscible in the liquid phase over a substantial concentration and temperature range. An ideal solution model is proposed which correlates the vapor pressure behavior of the liquid mixtures satisfactorily. NH4Cl is also found to dissolve in the liquid complex. Thermodynamic constants for the various vaporization processes from the liquid and solid phases are derived.

Introduction

The addition compound $NH_4^+(AlCl_4^-)$, formed when ammonium chloride interacts with aluminum chloride, was first reported by Baud.[1] X-Ray diffraction and infrared spectral data[2] as well as density and electrical conductivity[3] are said to be consistent with the ionic model. The alkali metal analog, NaAlCl4, is well known.[4] Ammonium tetrachloroaluminate has been reported to melt congruently at 303°[2] and Morozov and Toptygin[5] concluded that it vaporizes without decomposition with a boiling point of 402°. Sob[6] studied various mixtures of NH4Cl and AlCl3 and reported a boiling point maximum at 50 mol %. Vaporization of the complex without decomposition would be of unusual interest in view of the well-known behavior of the simple ammonium salts. Indeed Suvarov and Shybaev[7] subsequently concluded from vapor density measurements that molecular NH4AlCl4 is at most a minor component of the vapor. However, they were unable to explain their observations satisfactorily; when ammonia, hydrogen chloride, and aluminum chloride were assumed to be the principal vapor components, the heat of formation derived was in poor agreement with a value based on Baud's heat of solution measurements[1] and the entropy derived also seemed unreasonable.

In an effort to establish the principal molecular components of the vapor and to characterize the system thermodynamically we have undertaken a further study using Pyrex diaphragm gauge, transpiration, and quadrupole mass spectrometric techniques. Preliminary experiments indicated that NH4AlCl4 may behave similarly to the corresponding gallium complex, studied by Friedman and Taube,[8] in which the ammine NH3GaCl3 plays a dominant role. Indeed, the results to be presented can be explained satisfactorily if the principal mode of vaporization is assumed to be

$$NH_4AlCl_4(s) = NH_3AlCl_3(g) + HCl(g) \qquad (1)$$

At a higher temperature the complex and the liquid ammine are miscible, and the composition of the solution has a significant effect on the total pressure. The meaning of terms such as "boiling point" for the complex must be carefully described.

Vaporization Characteristics of Solid Ammonium Tetrachloroaluminate

Transpiration experiments with argon and hydrogen chloride, respectively, as carrier gases were carried out as described by Richards.[9,10] NH4AlCl4 was prepared in an all-Pyrex vacuum system, using vacuum "break-seal" techniques.[11,12] A large sample (ca. 4 g) of aluminum trichloride was isolated (after several resublimations under vacuum) in a small preweighed capsule and the quantity determined by weight difference; an equimolar amount of ammonium chloride was prepared similarly. The two capsules were opened by rupturing break-seals inside the vacuum system and the contents sublimed into a Pyrex tube. This sealed reactor was held at 150° for 16 hr to ensure conversion to the tetrachloroaluminate. The product was transferred to the transpiration apparatus in a nitrogen-filled drybox; a sample was analyzed for Al and Cl and the expected composition confirmed.

In one series of experiments argon (Air Reduction Co., 99.9%) at ca. 1000 Torr (the vapor pressure of Ar at the boiling point of liquid oxygen) was caused to flow over the sample at rates between 5.7 and 51.5 cm³ min⁻¹; in this range partial pressures calculated showed no systematic dependence on flow rate and were assumed to characterize the equilibrium state. In a second series of experiments hydrogen chloride (Matheson Gas Products, Commercial grade samples which had been vacuum distilled from Dry Ice to liquid oxygen temperatures several times) was used as the carrier gas at flow rates between 2.3 and 46.3 cm³ min⁻¹; again in this range results gave no indication of a flow rate dependence. HCl pressures were held at constant values between 650 and 950 Torr by immersing the source (an excess of liquid HCl) in Dry Ice baths.

The apparent partial pressure of aluminum-containing species was found markedly dependent on the HCl partial pressure. The condensate containing aluminum collected in the effluent tube just outside the reactor furnace. After a run the collection tube was removed and quickly replaced with a duplicate while protecting the main sample with an inert atmosphere. The condensed material was then washed out with water and the aluminum content determined by analysis with a Perkin-Elmer atomic absorption spectrophotometer. Free hydrogen chloride, collected in a following trap cooled with liquid oxygen, was determined by titration. Apparent partial pressures were calculated from Dalton's law. The number of moles of aluminum was assumed equal to the number of moles of ammine in the vapor. Three times this number was subtracted from the total number of moles of chloride ion (in the condensate at well as the trap) to obtain the number of moles of HCl transported when argon was the carrier gas. The partial pressure of HCl was taken as the measured total pressure when HCl was the carrier gas; the contribution of the vaporized species to the total pressure was negligible.

A plot of the logarithm of the apparent pressures of the aluminum-containing species against $1/T$ showed substantial scatter and, in particular, a wide variation between the results for the different carrier gases. See Figure 1. If NH4AlCl4 were the dominant vapor species, such effects would not be expected. On the other hand, when the vaporization is assumed to proceed by reaction 1, all the data correlate well; corresponding values of log K_1 are also shown in Figure 1. The partial pressures of HCl ranged from 0.2 to 990 Torr in these experiments.

In about two-thirds of the runs the Cl:Al ratio in the solid condensate was found to be appreciably greater than 4.0, varying unpredictably between 4 and 5. In several of these cases two reasonably well-separated bands of condensate were noted; the one nearest the furnace had a Cl:Al ratio near 4.0 and that farther away a ratio near 20. The latter appeared to be largely NH4Cl. It is suggested that NH4Cl may have been generated by reaction of the main sample with traces of moisture inadvertently admitted when the sample was transferred or when collection tubes were exchanged, although
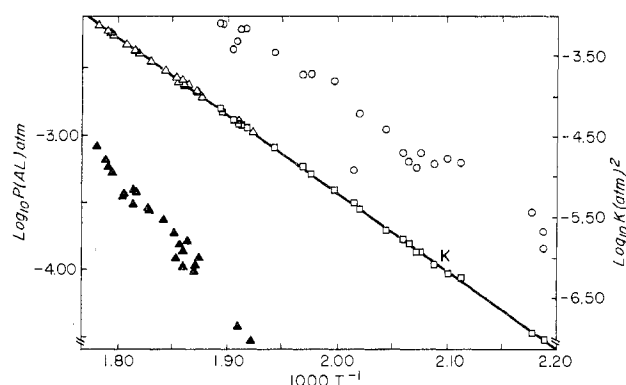
Figure 1. Transpiration data: ▲, HCl carrier gas; ○, argon carrier gas. The results are plotted as $P(Al)$, i.e., the apparent pressure of aluminum-containing species as indicated by the number of gram-atoms of aluminum transported, using the ordinate scale on the left. Points △ (HCl carrier gas) and □ (argon carrier gas), which generate the line labeled K, represent the same data interpreted as the equilibrium constant for the reaction $NH_4AlCl_4(s) = NH_3AlCl_3(g) + HCl(g)$, using the ordinate scale on the right.
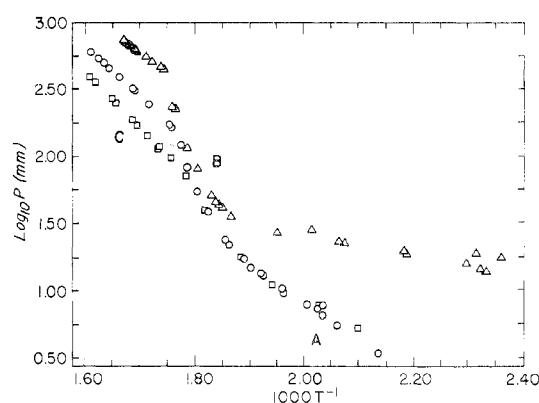

Figure 2. Total pressure-temperature relationships for mixtures of NH_3AlCl_3 and NH_4AlCl_4, sample 1. See text for discussion of regions A, B, and C: △, series 1 ($X_3 \approx 0.03$ in region C); ○, series 2 ($X_3 \approx 0.08$ in region C); ◫, series 3 ($X_3 \approx 0.14$ in region C).

every effort was made to minimize such contamination. It is also possible that some NH_4Cl and $AlCl_3$ may not have been completely converted to NH_4AlCl_4 in the initial reactor; in this event the more volatile $AlCl_3$ would be expected to sublime away during the bakeout treatment. Any NH_4Cl present in or generated by the sample would also be expected to sublime to the entrance of the transpiration vessel during the period of reverse gas flow as the reactor was brought to temperature. During forward flow some of this material, if condensed in a region at sufficiently high temperature and variably dependent on placement of the furnace, might be revaporized into the carrier gas. The apparent partial pressure of the ammonia in these runs was only of the order of a few percent of that expected if $NH_4Cl(s)$ were actually present at unit activity at the temperature of the main sample. The fraction of the HCl contributed from this source in any given run appeared to remain constant, since equilibrium constants for reaction 1, evaluated using the total chloride transported to derive the HCl partial pressure in the argon runs, were found to be independent of the variable Cl:Al ratio in the condensate, i.e., independent of the amount of NH_4Cl concomitantly transported. This would be expected as long as the HCl partial pressure remained constant during a given run. Calculated HCl pressures in these cases were, of course, substantially higher than calculated ammine pressures. An alternative possibility that NH_4Cl may have been generated solely from a dilute solid solution formed with NH_4AlCl_4 seems unlikely.

Equilibrium constants evaluated from all of the argon and HCl transpiration runs, including those in which the condensate had a Cl:Al ratio >4, were subjected to a least-squares treatment in the form

$$\log K_1 \ (atm^2) = A - BT^{-1}$$

The resulting line is shown in Figure 1; from the van't Hoff slope and intercept the values $\Delta H° = 43.9 \pm 2$ kcal mol⁻¹ and $\Delta S° = 64.0 \pm 0.3$ cal deg⁻¹ mol⁻¹ were derived for reaction 1 at the mean temperature of 510°K. Using results for the ammine[11] and JANAF values for $HCl(g)$,[4] a $\Delta H°$ value for formation of $NH_4AlCl_4(s)$ of -257.9 kcal mol⁻¹ and an $S°$ value of 83.2 cal mol⁻¹ deg⁻¹ were derived at 500°K.

To compare the enthalpy of formation with that based on the heat of solution studies by Baud[1] it is necessary to estimate the heat capacity of the complex. If $\bar{H}°_{500} - \bar{H}°_{298}$ for $NH_4AlCl_4(s)$ is assumed the same as the sum of corresponding values for NH_4Cl and $AlCl_3(s)$,[4] $\Delta H°$ of formation corrected to 298°K is -261.4 kcal mol⁻¹. The value based on Baud's

measurements is -257.1. The difference appears slightly more than experimental error; however, the relative enthalpy estimate is complicated by the occurrence of a transition in ammonium chloride.

The standard entropy derived at 500°K is ca. 8 cal mol⁻¹ deg⁻¹ larger than the sum of the entropies of $NH_4Cl(s)$ and $AlCl_3(s)$. This difference seems somewhat larger than expected. Again, the relative effect of possible transitions in the complex as compared to ammonium chloride as well as bonding differences cannot be assessed. Semenenko, Surov, and Kedrova[2] reported that a differential thermal analysis study of the complex (temperature range not specified) gave no evidence of a solid-state transition. Measurement of the heat capacity of the complex at low temperatures extending to the melting point would be of considerable interest.

A quadrupole mass spectral analysis of the vapor effusing from an effusion cell containing a sample of NH_4AlCl_4 at 153° was made. The sample had been previously sublimed under vacuum and from the observed melting point (272°) and experiments to be described in the following sections, appeared to contain about 20 mol % ammine. Mass peaks, generated with an ionizing potential of 70 V, were identified with the ions NH_3^+, Al^+, Cl^+, HCl^+, $NH_3AlCl_2^+$, $AlCl_2^+$, $NH_3AlCl_2^+$ (most intense), and $NH_3AlCl_3^+$. These results appear consistent with the proposed vaporization mechanism; masses corresponding to a parent ion peak of NH_4AlCl_4 were not detected.

## Equilibrium Pressures above Liquid Phases Formed by Ammonium Tetrachloroaluminate

Experimental evidence to be presented shows that the complex is not appreciably soluble in the ammine at temperatures below 200° but that the solubility increases rapidly as the melting point of NH_4AlCl_4 is approached. Variation of the mole fraction of the ammine in the liquid phase has a significant impact on the total vapor pressure. Three independent samples, studied in Pyrex diaphragm gauges, gave results which correlate well on the basis of the vaporization mechanism proposed if one assumes an "ideal solution model" for the liquid phase. Figure 2 shows a series of total equilibrium vapor pressures generated by sample 1. This sample was formed by first reacting a relatively large amount of purified aluminum chloride (ca. 5 g) with an equimolar amount of NH_3. The vapor pressures and melting point of the product were found to correspond well with results reported previously for the ammine.[11] Pressures were higher than expected at low temperatures believed due to the presence of a small excess of $AlCl_3$ (ca. 0.1 mol %). A measured quantity of HCl was then introduced to convert the ammine to the tetrachloroaluminate. Reaction did not occur at an appreciable rate until

the ammine was liquefied. After reaction appeared complete, the reactor was cooled to room temperature and the system pumped out before the diaphragm gauge was sealed. Total pressures measured as a function of temperature are shown in Figure 2. Regions A, B, and C are labeled for convenience of discussion.

In the first series of measurements relatively high pressures were observed in region A, where vapor pressures generated by the ammine or the complex are very low. This was attributed to the continued presence of the small excess of aluminum chloride, an assumption supported by the observation that measurable pressures were not detected below 100°. After the first series of measurements the system was reconnected to the vacuum line and pumped on while heating, primarily to remove a measured amount of HCl, and the gauge was subsequently resealed. This treatment also appeared to remove the excess aluminum chloride since the initially high pressures in region A were not observed in the second series of measurements (circles, Figure 2). A second aliquot of HCl was similarly removed before the third series of measurements (squares, Figure 2). Final analysis of the contents for aluminum (using a Perkin-Elmer atomic absorption spectrophotometer) gave 3.297×10^{-2} mol which agreed within experimental error with the value based on capsule weight difference. The HCl admitted was measured in several aliquots; on final review of the results of all three sets of data it was found that changes in pressure in region C could best be correlated with composition changes by assuming that a total of 0.1213 g-atom of chlorine (as chloride) was present in the first series of measurements. This quantity corresponds to addition of 5% less than the number of moles of HCl based on the measured pressures of the aliquots. The difference suggests loss of some HCl during the pump-out period prior to the initial seal-off of the gauge; the slow reaction during the final stages of the conversion of the ammine made it difficult to achieve complete conversion to the chloroaluminate. The following interpretation accounts satisfactorily for the behavior observed in the three stages of these experiments.

In region A, Figure 2, the system is believed to form a small amount of a liquid phase, which, based on the relative magnitudes of the ammine vapor pressure, K_1, and the measured pressure, appears to be virtually pure ammine; most of the sample in this region is in the form of the solid tetrachloroaluminate. The second and third series of measurements, i.e., after removal of the excess aluminum chloride and conversion of some complex to ammine by removal of HCl, gave nearly identical pressures in region A, indicating that the composition of the condensed phases was not dependent on their relative amounts.

As the temperature increases into region B, the total pressure increases rapidly, due to the normal increase of the ammine vapor pressure with temperature and simultaneously an increase in the solubility of the tetrachloroaluminate, or alternatively HCl, in the ammine; as a result the proportion of HCl in the vapor phase increases rapidly through region B. A and B are then viewed as regions in which the total pressures are determined by equilibrium 1 and simultaneously a solubility equilibrium of solid complex in ammine; the liquid phase changes from virtually pure ammine at the lower temperatures to a phase rich in tetrachloroaluminate as region C is approached. In region C the solid tetrachloroaluminate appears to have completely melted and the pertinent vapor–liquid equilibria are

$$NH_4^+(l) + AlCl_4^-(l) = NH_3AlCl_3(g) + HCl(g) \qquad (2)$$

and

$$NH_3AlCl_3(l) = NH_3AlCl_3(g) \qquad (3)$$
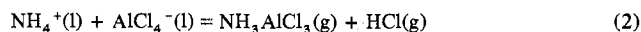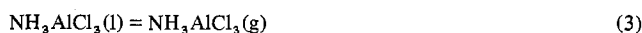
with a single liquid phase. The substantial displacement of

the three curves from each other in region C corresponds to the change in composition of the liquid. The partial pressures and composition of the liquid can be calculated using the following set of equations

$$P_g = P_{HCl} + P_{NH_3AlCl_3}$$

(P_g is the measured pressure)

$$n_{Al}RT/V = "P_4" + P_{NH_3AlCl_3} + "P_3"$$

(n_{Al} is the total number of moles of aluminum, "P_4" and "P_3" are the pressure equivalents of the number of moles of tetrachloroaluminate and ammine, respectively, in the liquid phase, and V is the volume of the gauge)

$$n_{Cl}RT/V = "P_4" + P_{HCl}$$

(n_{Cl} is the number of moles of HCl introduced or remaining after aliquots were removed)

$$P_{NH_3AlCl_3} = X_3 P^0_{NH_3AlCl_3}$$

($P^0_{NH_3AlCl_3}$ is the vapor pressure of pure liquid ammine and X_3 is the mole fraction of the ammine in the liquid). The last equation assumes an "ideal solution" in which the ammine molecule occupies the equivalent of an NH_4^+ site and an $AlCl_4^-$ site in the complex-rich mixture; i.e., $X^+ + X_3 = 1$ and $X^+ = X^-$, where X^+ and X^- represent the mole fractions of NH_4^+ and $AlCl_4^-$, respectively. K_2 may then be evaluated: $K_2 = P_{NH_3AlCl_3}P_{HCl}/X^+X^-$. In region C, X_3 values for the three mixtures studied were in the ranges 0.03, 0.08, and 0.14, respectively.

To prepare the second sample a small amount of $AlCl_3$ was isolated in the diaphragm gauge; its pressure was measured when the sample was completely vaporized to determine the quantity present; an approximately equimolar amount of NH_4Cl was then introduced. The amount was determined later by final analysis for chloride. The third sample was prepared by collecting a large quantity of $AlCl_3$, determining the quantity by capsule weight differences, and again adding an approximately equimolar amount of NH_4Cl. After reaction the material was sublimed in the vacuum system (some HCl was lost during this process). A small part of the sublimate was isolated in the diaphragm gauge. After measurement of liquid–vapor equilibrium pressures and total pressure when the sample was completely vaporized, approximately half of the sample was removed in an attached finger, and measurements were repeated on the remainder. The quantities of material and composition during these measurements were based on a final analysis of the aliquot removed and the sample remaining. The composition of the final sample corresponded to NH_4AlCl_4; the initial sample appeared to be ca. 5 mol % ammine and 95 mol % complex. The overall treatment of data for these samples followed the same general procedure described for sample 1. Vapor density values for samples 2 and 3 were consistent with the assumption that the ammine and HCl were the principal components. No evidence was found to suggest the presence of NH_4AlCl_4 molecules.

Equilibrium constants for (2) were calculated from each of the six sets of data and were correlated by least squares in the form $\log K_2 (atm^2) = A - BT^{-1}$. The calculated mole fractions of the ammine in the various liquid phases fell in the range 0.03–0.35; results are shown graphically in Figure 3. At the midtemperature (590°K) values of ΔH° and ΔS° for reaction 2 were found to be 37.7 ± 0.2 kcal mol^{-1} and 53.3 ± 0.3 cal deg^{-1} mol^{-1}. The uncertainties are the mean deviations given by the least-squares fit.

Results for (1) and (2) may be combined to predict ΔH° and ΔS° for the fusion of NH_4AlCl_4 and give 6.1 ± 0.5 kcal mol^{-1} and 10.7 ± 0.6 cal deg^{-1} mol^{-1}. These quantities may also be predicted from the variation of the solubility with
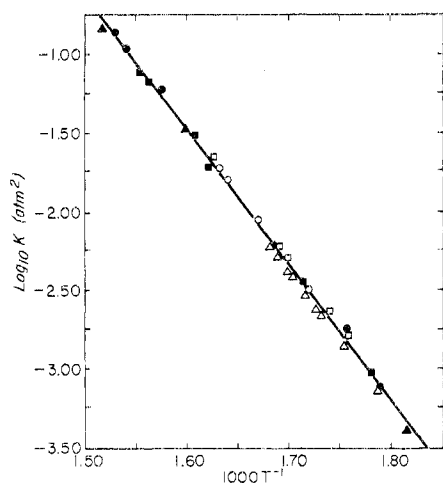
Figure 3. Equilibrium constants for the reaction $NH_4^+(l)$ + $AlCl_4^-(l) = NH_3AlCl_3(g) + HCl(g)$; $K = P_{NH_3AlCl_3}P_{HCl}/X^+X^-$ atm^2. Every third point from a complete table of data[12] was selected as a representative display. (X_3 values below rounded at ca. 570°K): $\triangle$, sample 1, series 1, $X_3 \approx 0.03$; $\circ$, sample 1, series 2, $X_3 \approx 0.08$; $\square$, sample 1, series 3, $X_3 \approx 0.14$; $\bullet$, sample 2, $X_3 \approx 0.24$; $\blacktriangle$, sample 3, series 1, $X_3 \approx 0.20$; $\blacksquare$, sample 3, series 2, $X_3 \approx 0.23$.

temperature indicated in region B, where the equations

$$K_1 = P_{NH_3AlCl_3}P_{HCl}$$

$$P_g = P_{NH_3AlCl_3} + P_{HCl}$$

$$P_{NH_3AlCl_3} = X_3 P^0_{NH_3AlCl_3}$$

are assumed valid. The partial pressures may be evaluated from the first two relationships and the mole fraction of the ammine in the liquid phase from the third. K_s may then be taken as X^+X^-, a solubility constant for the tetrachloroaluminate. The temperature dependence of this quantity is shown in Figure 4 and gives values of 5.91 ± 0.2 kcal mol^{-1} and 10.10 ± 0.4 cal mol^{-1} deg^{-1} for the $\Delta H°$ and $\Delta S°$ of fusion. The difference in the two sets of values is within experimental error. The first set predicts a melting point of 297° and the second 313°; the observed melting point (under HCl) is 303°.

Morozov and Toptygin,[5] in a transpiration study of the vapor above liquid NH$_4$AlCl$_4$, used nitrogen and hydrogen as carrier gases and assumed the NH$_4$AlCl$_4$ to be the only molecular species in the vapor phase. In view of our results it appears fortuitous that their calculated enthalpy of vaporization (37 kcal) corresponds closely to the value we derive for reaction 2. It would appear from our results that the composition of the liquid phase generated in their experiments must have changed substantially during their series of measurements. Alternatively, if reaction 2 were studied by transpiration with a constant HCl pressure, then the temperature dependence of the ammine pressure alone would reflect the variation of K_2 with temperature.

Behavior of Mixtures of NH4Cl and NH4AlCl4

A small sample of NH$_4$Cl was weighed out and sublimed into the diaphragm gauge. The number of moles (5.5×10^{-5}) was determined by assuming perfect gas behavior and recording the pressure developed at several temperatures after all of the solid had vaporized. The gauge was cooled to room temperature and reconnected to the vacuum system by rupturing a vacuum break-seal. A small quantity of AlCl$_3$ (2.26×10^{-5} mol, determined by subsequent analysis) was then introduced. Total pressures generated by this mixture were measured as a function of temperature and results are shown in Figure 5. Three distinct regions labeled A, B, and C are apparent.

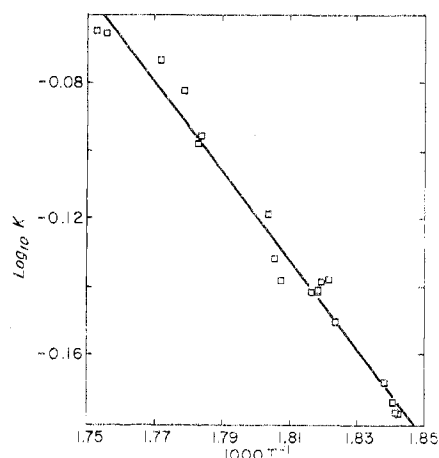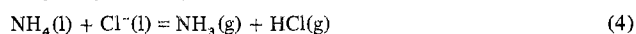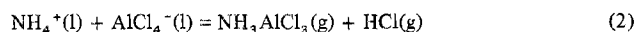Based on conclusions reached in the previous discussion, the

Figure 4. Solubility constants for NH$_4$AlCl$_4$(s) in NH$_3$AlCl$_3$(l), derived from data in region B, Figure 2, sample 1, series 2 and 3: NH$_4$AlCl$_4$(s) $\rightleftharpoons$ NH$_4^+$(l) + AlCl$_4^-$(l); $K = X^+X^-$.

total pressure generated at the highest temperatures, region C where all the material is vaporized, should be essentially the same as when only the NH$_4$Cl was in the gauge; i.e., the AlCl$_3$ may be expected to combine with NH$_3$ to form the ammine in equimolar quantities. With the excess of NH$_4$Cl present (hence NH$_3$) dissociation of the ammine at the pressures and temperatures involved may be neglected. The pressures in the high-temperature range correspond to this expectation.

In the low-temperature region A measured pressures were not significantly different from the equilibrium vapor pressure (NH$_3$ + HCl) of solid ammonium chloride,[4] indicating little or no solubility of NH$_4$AlCl$_4$ in solid NH$_4$Cl. The HCl pressure generated by vaporization of the excess ammonium chloride represses the ammine pressure expected from reaction 1 to a negligible value.

In the intermediate region B, it is believed that the tetrachloroaluminate has melted and that the excess ammonium chloride has dissolved in the liquid phase. As the temperature increases, the composition of the liquid may be expected to change until the liquid has completely vaporized in region C. Reactions of interest in region B are

$$NH_4^+(l) + AlCl_4^-(l) = NH_3AlCl_3(g) + HCl(g) \tag{2}$$

$$NH_3AlCl_3(l) = NH_3AlCl_3(g) \tag{3}$$

$$NH_4^+(l) + Cl^-(l) = NH_3(g) + HCl(g) \tag{4}$$

Using equilibrium constants derived for (2) and (3), equilibrium constants for (4) may be found if the ideal solution model is also assumed valid here. The basic data available are (in mole form)

$$n_{NH_4Cl} = n_{NH_3(g)} + n_{NH_3AlCl_3(g)} + n_{NH_4AlCl_4(l)} +$$
$$n_{NH_4Cl(l)} + n_{NH_3AlCl_3(l)}$$

$$n_{AlCl_3} = n_{NH_3AlCl_3(l)} + n_{NH_3AlCl_3(g)} + n_{NH_4AlCl_4(l)}$$

$$n_g = PV/RT = n_{HCl} + n_{NH_3(g)} + n_{NH_3AlCl_3(g)}$$

$$n_{HCl(g)} = n_{NH_3(g)} + n_{NH_3AlCl_3(g)} + n_{NH_3AlCl_3(l)}$$

$$n_{NH_3AlCl_3(g)} = X_3 n^0_{NH_3AlCl_3}$$

In the last equation n represents the number of moles in the vapor-phase volume corresponding to the ammine partial pressures above the solution and n^0 the corresponding number above pure liquid ammine. We also have for reaction 2

$$\frac{K_2}{(RT/V)^2} = \frac{n_{HCl(g)} n_{NH_3AlCl_3(g)}}{X_{NH_4}^+ X_{AlCl_4}^-}$$
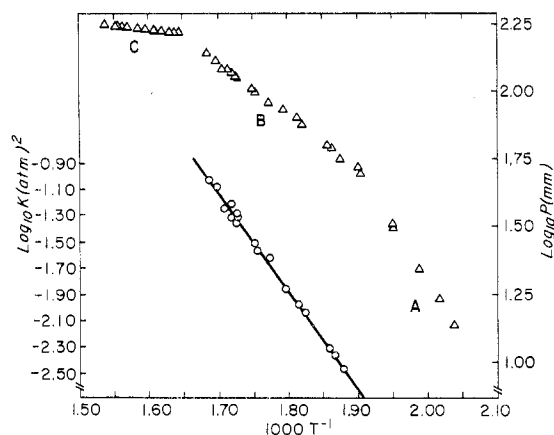
and the mole fraction relationship

Figure 5. Total pressures represented by the open triangles (using the ordinate scale on the right) developed at various temperatures above a mixture of 2.26×10^{-5} mol of $AlCl_3$ and 5.5×10^{-5} mol of NH_4Cl in a diaphragm gauge of volume 25.3 cm³. See text for discussion of regions A, B, and C. The open circles represent the same data in region B plotted (using the ordinate scale on the left) as the equilibrium constant for the reaction $NH_4^+(l) + Cl^-(l) \rightleftarrows NH_3(g) + HCl(g)$.

$$X_{NH_4^+} = X_{AlCl_4^-} + X_{Cl^-} = 1 - X_3$$

These equations are sufficient to define the system. The mole fraction of the ammine derived for the liquid phase varied from 0.6 at 531°K to 0.2 at 570°K. An equilibrium constant for the vaporization of "NH_4Cl" from the liquid phase can now be considered, i.e., reaction 4

$$\frac{K_4}{(RT/V)^2} = \frac{n_{HCl(g)}n_{NH_3(g)}}{X_{NH_4^+}X_{Cl^-}}$$

log K_4 values so derived are plotted vs. $1/T$ in Figure 5. The least-squares line leads to a $\Delta H°$ value of 34.3 ± 1.0 kcal mol⁻¹ and $\Delta S°$ of 53.3 ± 1.3 cal mol⁻¹ deg⁻¹.

No direct study of the vaporization equilibrium for pure liquid NH_4Cl has been found for comparison. The melting point under pressure is reported to be 793°K.[4] If the present results are combined with sublimation data, without correction

for temperature or pressure differences, values for fusion of 5.3 ± 1.0 kcal mol⁻¹ and 8.6 ± 1.3 cal deg⁻¹ mol⁻¹ are derived. The latter predict a melting point of 609°K; however, the uncertainties are large and values can be varied within the range indicated so as to yield the reported melting point.

One expects that use of the mole fraction in the treatment described will tend to underestimate the entropy of the mixture. In the dilute solution range (calculted Cl⁻ mole fractions range between 0.05 and 0.4) chloride ions were assumed to mix ideally with $AlCl_4^-$ ions, which are substantially larger. Because of the different ionic volumes the effective partial molar entropy of Cl⁻ in such a solution should be larger than it is in pure liquid NH_4Cl. A simple free volume ratio of 4 would provide a correction of 2.7 cal mol⁻¹ deg⁻¹ which overcorrects the entropy in the direction of predicting the correct melting point. An attempt to treat the data using volume fractions led to an intractable equation (seventh power) and results were apparently not sufficiently precise to give a meaningful solution. The simple solution model seems, however, to give a surprisingly good basis for correlating the vapor pressures generated by this mixture.

References and Notes

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Electronic Structure and Optical Properties of Manganese(V) Oxytrichloride, MnOCl3

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The electronic absorption spectrum of manganese(V) oxytrichloride, MnOCl3, in the gas phase has been measured in the energy region from 12,000 to 52,000 cm⁻¹. The ground-state molecular orbital energy levels and transition-state energies have been calculated by the SCF–Xα scattered-wave method. Good agreement between the observed bands in the optical spectrum and the excitations from the transition-state Xα calculation is observed.

Introduction

A number of studies of the electronic structures of tetrahedral oxy anions containing Mn(V)[1-11] have been made. The most successful of these have centered around the polarized optical spectrum of MnO_4^{3-} doped into various crystalline tetrahedral hosts. Polarized optical spectra have helped to provide information which allows for a theoretical interpretation of the electronic structure of these systems.

Little is known, however, about the electronic structure of

the symmetry-reduced oxyhalide analogs of the hypomanganate ion. In an effort to provide an explanation of the electronic structure of these analogs, we wish to report for the first time the optical absorption spectrum of manganese oxide trichloride, MnOCl3, in the gas phase.

Calculational Method

In the past few years the SCF–Xα scattered-wave method has been used to describe the electronic structure of many systems, generally with good results. We have applied this method recently to CrO_2X_2 (X = F, Cl),[12] MnO_3X (X = F, Cl),[13] and MnO_2Cl_2[14] in an effort to explain the electronic

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