of $\Delta G^\ddagger$ include the possibility of a tunneling mechanism,[37] the involvement of a precursor complex of the type discussed in detail elsewhere,[2] or work terms which may include coulombic repulsion and solvent effects.[2,4] Although the reorganization of the inner coordination sphere prior to the electron transfer is not considered[38] to be as necessary for reactions of strongly negative ΔG° values as it is for reactions in which ΔG° is near zero, the observation that the limiting value of $\Delta G^\ddagger$ is found for reactions involving ions of a variety of properties suggests that solvent effects, possibly involving the secondary as well as the primary coordination sphere, may be involved.

The value of k_1 extrapolated to an ionic strength of zero is $7.08 \times 10^3\ M^{-1}\ \text{sec}^{-1}$, which is slightly less than half the value of $1.7 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ calculated from the Debye equation[39] for the diffusion-controlled limit for a reaction between two 3+ ions with an average radius of 4 Å. Although the derivation of the Debye equation assumes a structureless dielectric medium and will be only approximate, the above agreement may suggest that a diffusion-controlled limit is reached in the case of the U(III)–Co(III) reaction. An approach to a diffusion-controlled limit in a Co(III) reaction would be further evidence against the participation of a high-spin–low-spin preequilibrium.[40] However, the Debye equation involves the product (Z_1Z_2) of the charge carried by the reacting ions, and our observation that the limiting rates for the reactions of Co(III) with V(II), Eu(II), and Cr(II) as well as U(III) are all similar suggests that the value of the product Z_1Z_2 does not strongly influence the observed rate constant.

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Registry No. Co(III), 22541-63-5; U(III), 22578-81-0.

References and Notes

(1) G. Davis and B. Warnquist, *Coord. Chem. Rev.*, **5**, 349 (1970).
(2) I. Bodek and G. Davies, *Coord. Chem. Rev.*, **14**, 269 (1974).
(3) G. Davies, *Coord. Chem. Rev.*, **14**, 287 (1974).
(4) M. R. Hyde, R. Davies, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1838 (1972).
(5) (a) B. R. Baker, F. Basolo and H. M. Newman, *J. Phys. Chem.*, **63**, 371 (1959); (b) G. Davis, *Inorg. Chem.*, **10**, 1155 (1971).
(6) Calculated from E° values of −0.63 V for the U(III)–U(IV) couple [W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, New York, N.Y., 1952, p 304] and +1.85 V for the Co(III)–Co(II) couple [B. Warnquist, *Inorg. Chem.*, **9**, 682 (1970)].
(7) A. Ekstrom and Y. Farrar, *Inorg. Chem.*, **11**, 2610 (1972).
(8) A. Ekstrom, A. B. McLaren, and L. E. Smythe, *Inorg. Chem.*, **14**, 1035 (1975).
(9) E. B. Sandell "Colourimetric Determination of Traces of Metals", 3rd ed, Interscience, New York, N.Y., 1959.
(10) A. Moskowitz, J. Dasher, and H. W. Jamison, *Anal. Chem.*, **32**, 1362 (1960).
(11) W. J. Blaedel and M. A. Evenson, *Inorg. Chem.*, **5**, 944 (1966).
(12) L. E. Bennett and J. C. Sheppard, *J. Phys. Chem.*, **66**, 1275 (1962).
(13) A. Ekstrom, *Inorg. Chem.*, **13**, 2237 (1974).
(14) M. H. Lietzke, U.S. Atomic Energy Commission Report No. ORNL 3259, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed, Butterworths, London, 1959, p 468.
(16) Percent root-mean-square deviation, defined as $100[(1/n)\sum(k_{\text{obsd}} - k_{\text{calcd}})^2/k_{\text{obsd}}^2]^{1/2}$.
(17) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941, p 195.
(18) R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, **9**, 1590 (1970).
(19) J. C. Sullivan and R. C. Thompson, *Inorg. Chem.*, **6**, 1795 (1967).
(20) T. W. Newton and R. B. Fulton, *J. Phys. Chem.*, **74**, 2797 (1970).
(21) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).
(22) D. R. Rossinsky and M. J. Nicol, *J. Chem. Soc. A*, 1022 (1968).
(23) R. B. Fulton and T. W. Newton, *J. Phys. Chem.*, **74**, 1661 (1970).
(24) D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968).
(25) D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **91**, 599 (1969).
(26) T. W. Newton, *J. Phys. Chem.*, **74**, 1655 (1970).
(27) K. O. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **13**, 1712 (1974).
(28) D. R. Rossinsky and M. J. Nicol, *Trans. Faraday Soc.*, **64**, 2410 (1968).
(29) T. Newton and F. B. Baker, *J. Phys. Chem.*, **69**, 176 (1965).
(30) A. Ekstrom and D. A. Johnson, *J. Inorg. Nucl. Chem.*, **36**, 2557 (1974).
(31) O. J. Parker and J. H. Espenson, *Inorg. Chem.*, **8**, 185 (1969).
(32) D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2553 (1973).
(33) Some scatter would obviously be expected in such a wide variety of reactions. Furthermore, the determination of the activation parameters for the acid-independent, and often minor, reaction path is usually associated with large errors.
(34) B. Falcincella, P. D. Felgati, and G. S. Laurence, *J. Chem. Soc., Dalton Trans.*, 1 (1975).
(35) D. R. Rosseinsky, *J. Chem. Soc., Chem. Commun.*, 225 (1972).
(36) (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (b) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960); (c) D. R. Rosseinsky, *Chem. Rev.*, **72**, 215 (1972).
(37) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975).
(38) N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 119 (1966).
(39) P. Debye, *J. Electrochem. Soc.*, **82**, 268 (1942).
(40) The authors wish to thank one of the referees for drawing this point to their attention.

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Study of the Fused-Salt System Ammonium Chloride–Sodium Tetrachloroaluminate

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Experiments in which total vapor pressures generated by mixtures of ammonium chloride and sodium tetrachloroaluminate have been measured as a function of temperature have been used to derive information about the thermodynamic characteristics of this fused-salt system. At low mole fractions of NH_4Cl the principal component of the equilibrium vapor above the liquid at temperatures below 650 K is hydrogen chloride, with only small partial pressures of the ammine, NH_3AlCl_3, and ammonia present. Data correlate well when melts are treated as an ideal mixture of the ionic species with ammine molecules interspersed on adjacent cation–anion sites. Results are compared with an earlier study of the NH_4AlCl_4–NH_3AlCl_3 system. The reaction of ammonia with $NaAlCl_4$ has also been studied.

Introduction

In a recent study of the complex formed between ammonium chloride and aluminum chloride vaporization of NH_4AlCl_4 was found to occur by formation of the ammine, NH_3AlCl_3, and hydrogen chloride.[1,2] The ammine and the complex are miscible in the liquid phase over a significant concentration range at temperatures near the melting point of NH_4AlCl_4 (305°). Total pressures generated by the vaporization reaction

$$NH_4^+(l) + AlCl_4^-(l) = NH_3AlCl_3(g) + HCl(g) \qquad (1)$$

were found to correlate well by treating the liquid phase as an ideal mixture of the ammine, with each molecule presumed to occupy a combined cation and anion site, and the ionic complex. A preliminary study of such mixtures when an excess of NH_4Cl was also present suggested that the ionic solution model was still applicable although the "Henry's law" properties of liquid NH_4Cl at low concentrations in the complex liquid phase appeared somewhat different from those expected for pure liquid NH_4Cl.

The study of these interesting mixtures has now been extended to the NH_4Cl–$NaAlCl_4$ system and similar effects have been observed. In this case the overall vaporization reaction may be written

$$NH_4Cl(l) + NaAlCl_4(l) = NH_3AlCl_3(g) + HCl(g) + NaCl(s) \qquad (2)$$

when the amount of NaCl produced exceeds its solubility. Pure $NaAlCl_4$ melts at 151°;[3] the total pressures generated by mixtures of NH_4Cl and $NaAlCl_4$ were measured in the range 480–650 K. It is apparent from the results, when compared with predictions based on thermodynamic constants, that the ammine is also soluble in the $NaAlCl_4$ liquid phase. A correlation of the data in the form of eq 1, in the solvent $NaAlCl_4$, is compared with the earlier study in NH_4AlCl_4. An experimental study of the equilibrium

$$NH_3(g) + NaAlCl_4(l) = NH_3AlCl_3(g) + NaCl(s) \qquad (3)$$

was also carried out. In this system the behavior of $NaAlCl_4$–NH_3AlCl_3 solutions can be observed in the absence of hydrogen chloride. Since the properties of NaCl and NH_3 are well-known,[3] results give an indication of the difference in the thermodynamic properties of $NaAlCl_4(l)$ and $NH_3AlCl_3(g)$ and are compared with predictions based on an electrochemical study of $NaAlCl_4$ by Boxall, Jones, and Osteryoung[4] and our earlier work on the ammine.[11]

Experimental Part

Samples were prepared, transferred, and studied in all-Pyrex vacuum systems using vacuum "break-seal" techniques and a Pyrex diaphragm gauge pressure sensing device as described earlier.[1,2] A relatively large sample (ca. 5.6 g) of aluminum chloride, prepared by reaction of HCl [generated by reaction of H_2SO_4 (Allied Chemical reagent) with NaCl (Mallinckrodt AR) and Al (Baker Analyzed reagent)] was first isolated in a small preweighed Pyrex capsule. An equimolar amount of sodium chloride was introduced into a reaction vessel attached to the vacuum system and degassed ($<10^{-6}$ Torr at 450°) for 12 hr before the $AlCl_3$ capsule in the vacuum system was ruptured by dropping a glass-enclosed weight to bring the reactants into contact. Reaction occurred readily when the mixture was heated with a small hand torch; the melt was then held at 350° under high vacuum for 3 hr to remove excess aluminum chloride. The isolated evacuated reactor was then tilted and the hot liquid poured into an attached preweighed capsule which was sealed off. A small portion was left for analysis. Found: Na, 2.652×10^{-3} mol; Al, 2.600×10^{-3} mol; Cl, 1.050×10^{-2} mol. This corresponds to a mixture of 99.4 wt % $NaAlCl_4$ and 0.6 wt % NaCl.

The capsule containing the $NaAlCl_4$ was then inserted into a side arm attached to a Pyrex diaphragm gauge in which had been placed 1.6 g of sodium chloride. After degassing of the salt at 400° for 12 hr, the $NaAlCl_4$ capsule was ruptured; the sample was melted and allowed to run into the diaphragm gauge which was then sealed. No detectable pressure (<0.1 Torr) was observed when the gauge was heated to 375°. The vapor pressure of $NaAlCl_4$ and its decomposition pressure ($AlCl_3$ + NaCl) are not expected to be detectable in our apparatus below 400°.[5,6] After the series of equilibrium measurements the actual amount of $NaAlCl_4$ in the gauge was determined by analysis using a Perkin-Elmer atomic absorption spectrometer.

To study reaction 3, a break-seal attached to the gauge was then opened and a measured amount of ammonia (source: Matheson Anhydrous, 99.99%) admitted. Reaction did not occur at an appreciable rate until the $NaAlCl_4$ was liquefied. After the ammonia was taken up, the gauge was sealed and total pressures were measured (±0.2 Torr) as a function of temperature. Approach to equilibrium was slow; pressures changed slowly for several hours (as long as 24 hr at lower temperatures) before constant values were reached. Values were compared at a given temperature when the temperatures were increased between successive measurements and when they were decreased. After the first series was completed, the system was cooled, a second aliquot of ammonia was added, and measurements were repeated. The approach to equilibrium for this sample (no. 2) was exceedingly slow as the temperatures were increased (mixtures could not be stirred); results for descending temperatures were reproducible in two series of measurements and appeared to reach equilibrium more readily; these values were compatible with the limit approached in the ascending temperature series. Only the descending series values were used in the final analysis of the data. Boxall et al.[4] also noted a slow approach to equilibrium in their electrochemical study of the NaCl–$NaAlCl_4$ system, which they attributed to a slow rate of equilibrium with solid NaCl.

For the NH_4Cl–$NaAlCl_4$ experiments a large sample of $NaAlCl_4$ was again prepared. After introduction into the gauge, the sample was subjected to a cooling curve analysis to determine the melting point (151°) before addition of the ammonium chloride. Again the sample was found to develop no measurable gas pressure when heated to 380° in the sealed gauge. After cooling a small quantity of NH_4Cl, Baker Analyzed reagent (99.9%), previously vacuum sublimed, isolated, and weighed in a sealed capsule, was vacuum sublimed into the gauge. Total equilibrium pressures developed by this mixture were measured at various temperatures; the procedure was repeated after the addition of each of three more aliquots of NH_4Cl. Before each addition after the first, it was found necessary to pump out a small residual pressure of HCl (the amount was carefully measured) which had failed to recombine with NH_3AlCl_3 as the system was cooled. The rate of recombination was found to be very slow at lower temperatures. From the measured quantities of Na, Al, and Cl in the gauge, determined by final analysis, and the measured aliquots of NH_4Cl added and HCl removed, the composition of the system during each series of measurements was established.

Results and Discussion

Formation of the compound $NaAlCl_4$ has been well documented.[7-9] In mixtures with appreciable amounts of Cl^-, one concludes from the works of Fannin et al.[10] and of Boxall et al.[4] that the ion $AlCl_4^-$ is the major aluminum-containing species in melts; species such as $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ need only be considered when the melt composition is rich in aluminum chloride. In our studies mixtures were saturated or nearly saturated with NaCl.

The total equilibrium pressures developed in the study of reaction 3 were interpreted using eq 4–9 (the n's represent mole

$$n^0{}_{NH_3} = n_{NH_3(g)} + n_{NH_3AlCl_3(g)} + n_{NH_3AlCl_3(l)} \qquad (4)$$

$$n^0{}_{NaAlCl_4} = n_{AlCl_4^-(l)} + n_{NH_3AlCl_3(l)} + n_{NH_3AlCl_3(g)} \qquad (5)$$

$$n_g = PV/RT = n_{NH_3(g)} + n_{NH_3AlCl_3(g)} \qquad (6)$$

$$n_{NH_3AlCl_3(g)} = \frac{n_{NH_3AlCl_3(l)}n^0{}_{NH_3AlCl_3(g)}}{n_{NH_3AlCl_3(l)} + n_{Na^+(l)}} \qquad (7)$$

$$n_{Na^+(l)}n_{Cl^-(l)} = K_s(n_{NH_3AlCl_3(l)} + n_{Na^+(l)}{}^2 \qquad (8)$$

$$n_{Na^+(l)} = n_{AlCl_4^-(l)} + n_{Cl^-(l)} \qquad (9)$$

numbers of the species indicated by the subscripts). $n_{NH_3}{}^0$ and $n_{NaAlCl_4}{}^0$ represent the number of moles of the respective substances initially introduced into the diaphragm gauge, with volume V. P is the total pressure measured at T K. Liquid $NaAlCl_4$, containing a very small amount of dissolved NaCl, was assumed to form ideal mixtures with dissolved ammine molecules with the latter occupying adjacent cation and anion sites. Equation 7, used to relate the solubility of the ammine to its vapor pressure,[11] is Raoult's law in mole form: $n_{NH_3AlCl_3}{}^0$ represents the number of moles of ammine expected in the vapor volume if the liquid were pure ammine at the temperature of interest, i.e., $n^0 = P^0V/RT$ where P^0 is the vapor pressure of the pure ammine; correspondingly $n_{NH_3AlCl_3(g)} = P_{NH_3AlCl_3}V/RT$ where $P_{NH_3AlCl_3}$ is the partial pressure of the ammine in equilibrium with the liquid phase in which the mole fraction of the ammine is $n_{NH_3AlCl_3(l)}/n_{t(l)}$; $n_{t(l)} = n_{NH_3AlCl_3(l)} + n_{NaAlCl_4(l)} + n_{NaCl(l)} = n_{NH_3AlCl_3(l)} + n_{Na^+(l)}$.

The values of K_s in eq 8 were based on the solubility of NaCl in $NaAlCl_4$ reported by Torsi and Mamantov;[12] their data are in general agreement with the observations of Tremillon and Duchange.[13] These studies indicate a solubility of about one-third of that predicted on an ideal basis;[3] hence we have in effect assumed a "Henry's law ideal behavior" for these very dilute solutions of NaCl, i.e., $K_s = X_{Na^+(l)}X_{Cl^-(l)}$, which with $X_{Na^+(l)} = n_{Na^+(l)}/n_{t(l)}$ and $X_{Cl^-(l)} = n_{Cl^-(l)}/n_{t(l)}$ takes the form

Table I. Results Derived for Reaction 3

	Mole fractions (liquid phase)			Partial pressures, Torr			
T, K	$X_{NH_3AlCl_3}$	$X_{AlCl_4^-}$	X_{Cl^-}	$P_{NH_3AlCl_3}$	P_{NH_3}	K_3'	$K_3 = K_3'/K_s$
	Sample 1 ($n^0_{NaAlCl_4} = 0.0293$; $n^0_{NH_3} = 2.01 \times 10^{-3}$; $V = 0.0500$ l.)						
545	0.066	0.910	0.024	1.8	0.07	0.7	32
571	0.065	0.905	0.030	3.7	0.1	1.2	43
596	0.063	0.900	0.037	6.8	0.3	0.9	26
613	0.062	0.897	0.041	9.8	1.2	0.4	10
629	0.060	0.894	0.047	13.8	1.4	0.5	11
645	0.057	0.891	0.052	18.5	2.5	0.4	8
613	0.061	0.897	0.042	9.9	1.1	0.4	10
608	0.062	0.898	0.040	8.9	0.8	0.5	13
596	0.063	0.900	0.037	6.8	0.5	0.6	18
538	0.067	0.911	0.022	1.5	0.1	0.4	19
	Sample 2 ($n^0_{NaAlCl_4} = 0.0293$; $n^0_{NH_3} = 6.38 \times 10^{-3}$; $V = 0.0480$ l.)						
621	0.193	0.756	0.051	36.7	5.6	0.4	10
620	0.193	0.756	0.051	36.4	5.4	0.5	12
619	0.194	0.755	0.051	36.1	4.1	0.6	15
602	0.199	0.756	0.045	24.5	3.4	0.4	11
551	0.209	0.761	0.030	6.8	0.3	0.9	39
512	0.213	0.767	0.020	2.1	0.1	0.5	31
637	0.187	0.755	0.057	52.0	5.4	0.7	15
583	0.204	0.757	0.039	15.8	0.8	1.0	32
533	0.211	0.764	0.025	4.1	0.1	1.3	65

of (8) shown. This treatment neglects any effect the presence of the ammine may have on the solubility of NaCl. The ionic electroneutrality requirement is expressed in eq 9. The six equations shown were solved simultaneously to obtain values for the six mole numbers for each experimental value of P and T. Mole fractions in the liquid phase and partial pressures derived are listed in Table I. The mole fraction of the ammine in the second mixture is about 3 times that in the first. Temperatures are listed in the order measured for sample 1. As discussed in the Experimental Section, only pressures measured when equilibrium was approached from the high-pressure side were used for sample 2.

The data derived indicate that reaction 3 proceeds nearly to completion. Total pressures are only slightly higher than the predicted partial pressures of the ammine. These values are compared graphically in Figure 1; the slope of the plot of log P vs. $1/T$ corresponds closely to the heat of vaporization of the ammine, as expected if the vapor is nearly pure ammine, if the ideal solution model is a reasonably good approximation, and if the $X_{NH_3AlCl_3}$ changes only slightly with temperature.

When $P_{NH_3AlCl_3}$ is close to the total pressure, values derived for P_{NH_3} are subject to large experimental error. Hence, values derived for $K_3' = P_{NH_3AlCl_3}X_{Cl^-}/P_{NH_3}X_{AlCl_4^-}$ (Table I) show substantial scatter and no systematic variation with temperature is apparent. An average of 0.5 is obtained when data points with indicated pressures of ammonia less than 1 Torr are discounted because of their larger relative uncertainty. Division of K_3' by K_s gives K_3, the equilibrium constant for reaction 3. The conclusion that the equilibrium for reaction 3 lies far to the right under our reaction conditions is not particularly sensitive to the estimated values for the solubility of sodium chloride and hence to the validity of the assumptions involved in eq 8. By eq 7, $P_{NH_3AlCl_3}$ is fixed by $X_{NH_3AlCl_3(l)}$; hence the equilibrium constant for (3) depends basically on the ratio $X_{NH_3AlCl_3}/X_{NaAlCl_4}$ which is not very sensitive to moderate changes in the small values of X_{Cl^-}. This was verified by calculations in which the latter was varied from near zero to the ideal saturation limit.

A separate experiment was conducted to examine the composition of the equilibrium vapor. A liquid mixture, which subsequent analysis showed to have a composition corresponding to $X_{NaAlCl_4} = 0.84$ and $X_{NH_3AlCl_3} = 0.16$, was held at 683 K in a small bulb connected by 3-mm i.d. tubing to a 0.2 l. volume held at 723 K. After 4 hr the volume holding the vapor was sealed off. The vapor condensate was found to contain 5.093×10^{-4} mol of Al (presumably as NH_3AlCl_3 and $NaAlCl_4$) and 7.48×10^{-6} mol of Na (presumably as $NaAlCl_4$). The condensate was found to melt at 129–130°, which corresponds closely to the melting point of the ammine.[11] A small pressure (ca. 2 Torr) of residual gas, presumably NH_3, was detected when the vapor vessel was opened through a break-seal to a manometer at room temperature. These quantities indicate ammine and ammonia pressures at the equilibration temperature of 110 Torr (predicted from eq 7, 80 Torr) and 4.5 Torr, respectively, and a K_3 value around 30. In view of the uncertainties associated with the thermal

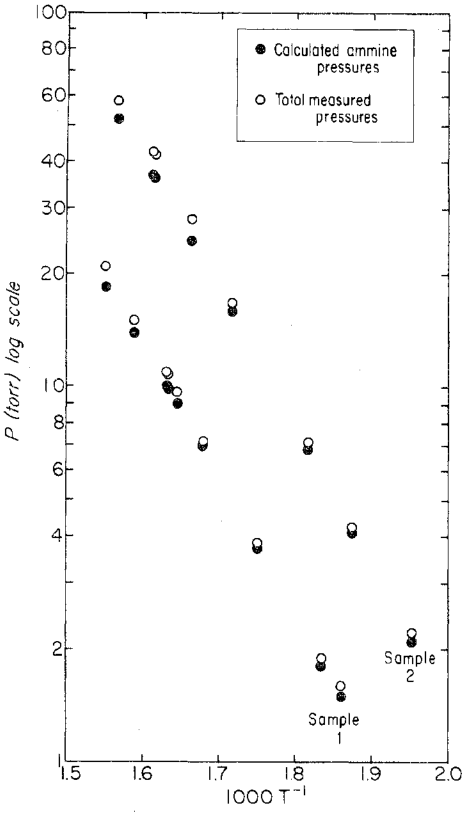

Figure 1. Comparison of measured total pressures (○) and predicted partial pressures of NH_3AlCl_3 (●) for samples 1 and 2 in the study of reaction 3.

Table II. Thermodynamic Constants Derived for Reaction 3 at 600 K

	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}	$\Delta G°$, kcal mol^{-1}	K_3 (range)
Present study	5.5 ± 3	−3.9 ± 2	−3.7 ± 1.3	14 (8–65)
Ref 3, 4, 11	2.4 ± 3	−11.3 ± 3	4.4 ± 5	0.025 (4 × 10^{-4}–1.6)

gradients and flame seal-off procedure and possible problems with adsorption in this experiment, these observations seem in reasonable accord with the diaphragm gauge results.

It is clear that the results in Table I can only be expected to give a rough estimate of the thermodynamic constants for reaction 3. Yet the range of the values derived for K_3 is substantially different from that predicted by combining our earlier data for the ammine[11] with those of the electrochemical study of $NaAlCl_4$ by Boxall et al.[4] The comparison is shown in Table II. The uncertainties indicated for the present study are based on the scatter of calculated values of K_3 and do not reflect the uncertainties of the ideal model. The range of K_3 values (Table I) was used as a basis to estimate the uncertainty in $\Delta G°$ and $\Delta S°$; that for $\Delta H°$ reflects the range of reasonable slopes that might be drawn through a van't Hoff plot of the data. The uncertainties for results derived from ref 3, 4, and 11 are based on the combined uncertainties reported by the respective authors. The two values of the projected enthalpy change fall within the combined experimental errors; however the entropy (and free energy) values differ somewhat more than expected. We can only suggest that further work on the ammine and on $NaAlCl_4$ would be helpful to confirm the values of the constants used. Undoubtedly the ideal solution model used to analyze the present data is an oversimplification and this may account for the difference; however the study of the NH_4Cl–$NaAlCl_4$ system, to be discussed in following paragraphs, provides additional evidence that the model gives a surprisingly good approximation to the vapor pressures generated by these mixtures. In both cases the correlation covers a substantial liquid-phase concentration range.

The JANAF tables[3] also include estimated properties for $NaAlCl_4(s)$, based on early heat of solution measurements of Baud[14] and estimated heat capacities; $\Delta H°$ of $NaAlCl_4(s)$ at 600 K is listed as −270.6 kcal mol^{-1}. Our present results indicate a value for the liquid of −273 ± 3 kcal mol^{-1} and those of Boxall et al.[4] a value of −276 ± 1 kcal mol^{-1}, both of which suggest that to give a reasonable heat of fusion the enthalpy of formation of $NaAlCl_4(s)$ must be considerably more negative than the JANAF value.

The system represented by reaction 2 may be considered similar to that of reaction 3 with the behavior of the latter modified by the presence of HCl. The experimental observations indicate that the reaction

$$NH_4Cl + NaAlCl_4 = NH_4AlCl_4 + NaCl \tag{10}$$

goes virtually to completion and, since the solubility of NaCl in $NaAlCl_4$ is relatively small, solid NaCl was precipitated in most of our experiments. It was assumed that the NH_4AlCl_4 produced forms an ionic ideal solution with $NaAlCl_4$; the predicted mole fractions of the NH_4^+ ion for the four mixtures studied range from 0.004 to 0.2. Reaction 1 may then be considered to generate the equilibrium vapor phase, and for the conditions under which these mixtures were studied the ammine is sufficiently soluble in the melt so that the vapor is virtually all HCl.

As indicated in the experimental section some HCl was removed when the system was opened to add new aliquots of NH_4Cl; this leaves some condensed ammine in the system. Hence in treating the experimental data, the moles of NH_4Cl added were treated as equivalent numbers of moles of NH_3 and HCl; the total quantity of HCl could then be conveniently corrected for the amounts pumped out of the system. The six equations (4–9) were modified to include the presence of NH_4^+ and HCl and used together with the relationships

$$n^0_{HCl} = n_{HCl(g)} + n_{NH_4^+(l)} \tag{11}$$

$$K_3' = 0.5 = P_{NH_3AlCl_3}X_{Cl^-}/P_{NH_3}X_{AlCl_4^-} \tag{12}$$

to solve for the eight unknown mole numbers. The meaning of the symbols in (11) and (12) will be clear from the previous discussion. Equation 12 incorporates the results of the study of reaction 3 (Table I) to estimate the partial pressures of NH_3. A total of 12 data points were measured for sample 1, 15 for sample 2, 16 for sample 3, and 14 for sample 4. Of these representative sets of four for each sample at similar temperatures are displayed in Table III for comparison and to illustrate the range of mole fractions derived (liquid phase). It will be observed that ammonia and the ammine appear to be only minor components of the vapor. In sample 1 the amount of chloride ion generated is sufficiently small to remain in solution; for the other mixtures, X_{Cl^-} is limited by K_s; i.e.,

Table III. Equilibrium Characteristics Derived for NH_4Cl–$NaAlCl_4$–NH_3AlCl_3 Mixtures

	Partial pressures, Torr			Mole fractions (liquid phase)				
T, K	P_{HCl}	P_{NH_3}	$P_{NH_3AlCl_3}$	$X_{AlCl_4^-}$	X_{Cl^-}	$X_{NH_4^+}$	$X_{NH_3AlCl_3}$	log K$_1$ (atmos)^2
Sample 1 ($n^0_{NaAlCl_4} = 0.0200$; $n^0_{NH_3} = 1.96 \times 10^{-4}$; $n^0_{HCl} = 1.96 \times 10^{-4}$; $V = 0.0497$ l.)								
512.4	17.8	0.0003	0.01	0.989	0.0097	0.0083	0.0014	−4.29
551.0	33.7	0.002	0.08	0.988	0.0097	0.0073	0.0024	−3.20
600.6	61.0	0.009	0.50	0.986	0.0097	0.0057	0.0040	−2.05
644.1	94.4	0.04	1.80	0.985	0.0097	0.0039	0.0057	−1.12
Sample 2 ($n^0_{NaAlCl_4} = 0.0200$; $n^0_{NH_3} = 1.13 \times 10^{-3}$; $n^0_{HCl} = 1.11 \times 10^{-3}$; $V = 0.0477$ l.)								
506.2	45.4	0.001	0.03	0.980	0.016	0.051	0.0041	−4.28
550.5	83.9	0.01	0.20	0.969	0.025	0.049	0.0064	−3.20
601.1	164.8	0.10	1.30	0.952	0.038	0.044	0.011	−2.05
641.1	264.2	0.50	4.60	0.934	0.050	0.038	0.015	−1.23
Sample 3 ($n^0_{NaAlCl_4} = 0.0200$; $n^0_{NH_3} = 1.94 \times 10^{-2}$; $n^0_{HCl} = 1.88 \times 10^{-3}$; $V = 0.0457$ l.)								
506.7	36.8	0.002	0.05	0.977	0.017	0.090	0.0058	−4.46
555.6	96.9	0.02	0.35	0.964	0.027	0.085	0.0093	−3.15
600.4	197.3	0.10	1.70	0.946	0.039	0.079	0.015	−2.10
643.9	349.8	0.80	6.80	0.925	0.053	0.070	0.021	−1.20
Sample 4 ($n^0_{NaAlCl_4} = 0.0200$; $n^0_{NH_3} = 4.16 \times 10^{-3}$; $n^0_{HCl} = 4.08 \times 10^{-3}$; $V = 0.055$ l.)								
506.4	55.7	0.003	0.07	0.972	0.019	0.195	0.0087	−4.44
552.0	130.0	0.030	0.50	0.956	0.030	0.188	0.014	−3.23
603.7	291.4	0.30	3.1	0.930	0.045	0.174	0.024	−2.01
643.7	492.1	1.50	11.0	0.905	0.060	0.160	0.035	−1.19

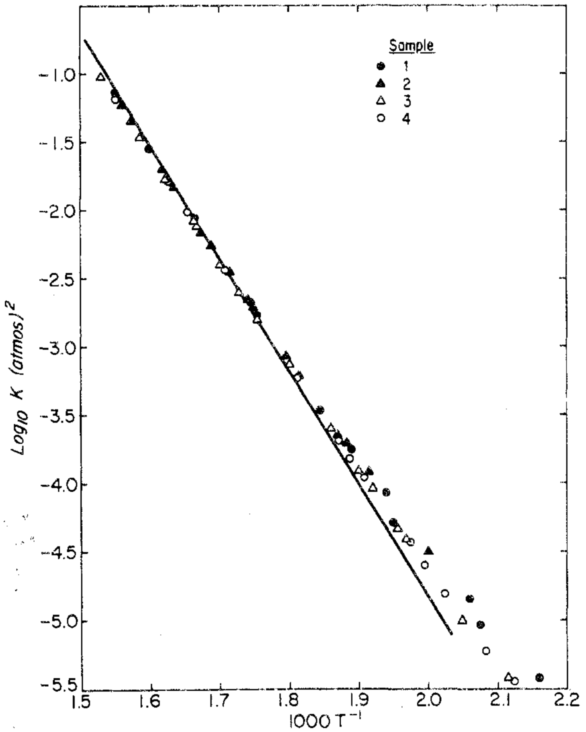

Figure 2. Values of $K_1 = P_{NH_3AlCl_3}P_{HCl}/X_{NH_4^+}X_{AlCl_4^-}$ derived from total equilibrium pressure and composition data for various mixtures of NH_4Cl-$NaAlCl_4$-NH_3AlCl_3. Solid line represents values of K_1 derived in an earlier study of NH_4AlCl_4-NH_3AlCl_3 mixtures.[1,2]

the calculation predicts that solid NaCl is precipitated. The mole fraction of the ammine in the liquid phase is relatively small in all mixtures, less than 0.04.

To test the correlation of the data, values of K_1

$$K_1 = P_{NH_3AlCl_3}P_{HCl}/X_{NH_4^+}X_{AlCl_4^-} \tag{13}$$

were calculated. The results for all of the data points are displayed in Figure 2. The agreement of the four sets of data is remarkably good. Even more remarkable, particularly considering the ideal solution approximations and the fact that NH_4AlCl_4 and the ammine in the present study are present at relatively low concentrations in $NaAlCl_4$ as the solvent, is the close correspondence of the values of K_1 derived in the present study with the line drawn which reflects the values of K_1 and its temperature dependence based on data measured in the earlier study of the pure complex NH_4AlCl_4 and its mixtures with NH_3AlCl_3.[1] It should be noted that the correlation of the data in the form of K_1 does not provide a real test of the accuracy of K_3', since the ammine and NH_3 pressures are so small as to contribute little to the total pressure.

One may also examine values for the equilibrium constants predicted by the data in Table III for the vaporization of "liquid ammonium chloride" from its dilute solution in the $NaAlCl_4$ melt mixture (designated as liq I).

$$NH_4^+(\text{liq I}) + Cl^-(\text{liq I}) = NH_3(g) + HCl(g) \tag{14}$$

It can easily be seen that K_{14} is equivalent to K_1/K_3', which, subject to the large uncertainty of K_3', corresponds to $2K_1$. These values are about one-ninth of those derived in the earlier study of NH_4Cl in NH_4AlCl_4 melts (liq II). This difference may in part (recognizing the large experimental uncertainty in the predicted value of K_{14}) reflect a difference in the "Henry's law" behavior of the chloride ion in the two different solvent systems. One tends to conclude, from the observation that the K_1 values derived are virtually identical in liquid I and liquid II, that the NH_4^+ and Na^+ sublattice mixtures do indeed behave nearly ideally. (It does appear (Figure 2) that a divergence of the K_1 values for the two solvent systems is developing at lower temperatures.) Nonideal effects for mixing Cl^- and $AlCl_4^-$, which have appreciably different ionic volumes, may be expected to be more substantial. The chloride ion mole fractions appear relatively small; the Cl^- activity coefficients could be substantially different in the two melts without significant effect on K_1; however, since ionic volume effects alone should be comparable in the two solvent systems, cation–anion specific interactions may be responsible. A more careful comparison of the equilibrium characteristics of reaction 14 in liquids I and II is needed to gain a real insight into this question.

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Registry No. NH_4Cl, 12125-02-9; $NaAlCl_4$, 7784-16-9; NH_3AlCl_3, 15550-69-3; NH_3, 7664-41-7.

References and Notes

(1) W. C. Laughlin and N. W. Gregory, *Inorg. Chem.*, **14**, 1263 (1975).
(2) W. C. Laughlin, Doctoral Dissertation, University of Washington, Seattle, Wash. 98195, 1974.
(3) D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971).
(4) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, **120**, 223 (1973).
(5) A. I. Morozov and I. S. Morozov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **18**, 520 (1973).
(6) E. W. Dewing, *J. Am. Chem. Soc.*, **77**, 2639 (1955).
(7) J. E. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).
(8) W. Fischer and A. L. Simon, *Z. Anorg. Allg. Chem.*, **306**, 1 (1960).
(9) C. R. Boston, *Adv. Molten Salt Chem.*, **1**, Chapter 3 (1971).
(10) A. A. Fannin, L. A. King, and D. W. Seegmiller, *J. Electrochem. Soc.*, **119**, 801 (1972).
(11) W. C. Laughlin and N. W. Gregory, *J. Chem. Eng. Data*, **20**, 137 (1975).
(12) G. Torsi and G. Mamantov, *Inorg. Chem.*, **10**, 1900 (1971).
(13) B. Tremillon and J. P. Duchange, *J. Electroanal. Chem. Interfacial Electrochem.*, **44**, 395 (1973).
(14) E. Baud, *Ann. Chim. Phys.*, [8] **1**, 8 (1904).