Table III. Calorimetric Parameters

Compound	Series	Mass, g	ml_{NaOH}	E_{ign}, J	T, °C	T_{max}	E_s, J/°C
Standardization							
BA (6) (benzoic acid)	A	1.120314	5.92	6.51	1.48809	25.75	19929.7 ± 3.7
BA (6)	B	1.067590	5.94	7.83	1.41630	26.62	19956.5 ± 4.5
							$E°_{comb}$, J/g
Determination							
DCFO (6)	A	1.427027	13.17	7.00	1.08324	25.89	15043.2 ± 7.4
HIP (1) (hippuric acid)	A	0.909139	8.03	7.39	1.07628	26.48	23482.3
DCFOB (4)	B	1.278989	12.01	7.44	0.92769	25.79	14349.2 ± 20.9
DCFA (2)	B	1.300227	12.76	6.68	1.11257	26.25	16935.4 ± 46.0
HIP (1)	B	1.213106	10.50	7.28	1.432216	26.57	23452.7

Quality of Data

As seen from the precision of benzoic acid sort standardization data, our calorimetric system is capable of producing research quality data (±0.02%). However, it was intended for this project that good quality calorimetric data would be obtained as part of the characterization program; then, if one or more compounds were selected as storable fuels for the gas dynamic laser, research quality data would be determined for that compound or compounds. Unfortunately, all of the compounds here reported were, for one reason or another, excluded from consideration before research quality data were required.

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Equilibrium Vapor Pressures and Vapor-Phase Dissociation of Monoammine of Aluminum Chloride

William C. Laughlin and Norman W. Gregory[1]
Department of Chemistry, University of Washington, Seattle, Wash. 98195

The vapor pressures in equilibrium with liquid NH_3AlCl_3 and equilibrium constants for the vapor-phase dissociation of the ammine into ammonia and aluminum chloride are studied in Pyrex diaphragm gauge experiments. An enthalpy of formation of -190.5 kcal mol^{-1} and a standard entropy of 85.0 cal mol^{-1} deg^{-1} are derived for $NH_3AlCl_3(g)$ at 25°.

This work was undertaken to establish the vaporization thermodynamics of the monoammine of aluminum chloride, NH_3AlCl_3. In addition to an inherent interest in these properties, the information was needed as part of a more general study of the vaporization characteristics of the complex compound ammonium tetrachloroaluminate. A substantial amount of information about the ammoniates of aluminum chloride has been published (*4*). Klemm and collaborators (*7, 8*) report compounds containing 1, 3, 5, 7, and 14 moles of ammonia, respectively, for each mole of aluminum chloride. They report a heat of formation for the monoammine, based on heat of solution experiments; this value, together with the low melting point, 125°, and relatively large molar volume of the solid, is said to be suggestive of a molecular lattice. Vapor-pressure data for the liquid, determined from diaphragm gauge and transpiration studies, were reported; dissociation of the ammine in the equilibrium vapor phase was estimated to be less than 1% below 400°.

Results of a more recent study of the equilibrium vapor pressure have been reported by Yurlova and coworkers (*14*) and do not agree well with those of Klemm et al. The present work was undertaken in part to resolve this discrepancy. We have measured vapor pressures in equilibrium with the liquid phase in a Pyrex diaphragm gauge; pressures developed by a known quantity of the unsaturated vapor indicate a slight dissociation of the ammine into ammonia and aluminum chloride. Apparent equilibrium constants for the dissociation reaction have been derived and used to evaluate thermodynamic properties of $NH_3AlCl_3(g)$.

Experimental

Samples were studied in a Pyrex envelop containing a thin Pyrex membrane as a pressure-sensing device (*1*).

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[1] To whom correspondence should be addressed.

Deflections of a slender pointer attached to the membrane (diaphragm) were magnified and focused onto a ground glass plate and observed through a telescope. The device was used as a null point instrument, with a measured pressure of air used to produce a detectable displacement of the pointer from the null position. An accuracy of 0.1 torr could be achieved in a series of readings in which the gauge was neither moved nor subjected to an excessive stress (less than 10 torr). The null position was independent of temperature below 460°.

Because of the reactivity of the aluminum halides toward water, samples were produced in all Pyrex systems, isolated in sealed-off capsules, and introduced into the diaphragm gauge via Pyrex "break-seals" which could be ruptured inside the vacuum system by dropping a magnetically controlled glass enclosed weight. The gauge system was heated by a specially wound electric furnace, designed to insure a temperature uniform within 1° over all parts of the gauge. Four calibrated thermocouples placed strategically around the gauge were used to monitor the temperature. For vapor-pressure measurements, the measuring couple at a position close to the surface of the liquid was used as an indicator of the equilibrium temperature. Pressure-temperature dependence was determined both by increasing or decreasing the temperature between successive measurements.

The ammine was prepared by reaction of aluminum chloride with anhydrous ammonia. Two sources of aluminum chloride were used: Allied Chemical anhydrous reagent (99%), samples of which were introduced into the vacuum system and resublimed several times before isolation in an attached capsule; and a product formed by reaction of Baker analyzed reagent aluminum wire (ACS specifications) with anhydrous hydrogen chloride; this material was also vacuum sublimed several times before collection of the sample.

Matheson Gas Products anhydrous ammonia (99.99%) was used as a source of ammonia; samples were admitted to a bulb attached to the vacuum system and repeatedly distilled from Dry Ice to liquid nitrogen temperatures with intermittent pumping as appropriate to remove air and moisture. The amount of ammonia introduced into the gauge or an alternative reactor was calculated from its measured pressure in a calibrated volume. The amount of aluminum chloride was estimated by difference in weight of the capsule container before and after introduction of the sample or, in some cases, by preliminary measurement of the pressure of the completely vaporized sample in the diaphragm gauge. The quantity of aluminum in the gauge was finally determined after completion of a particular series of measurements by analysis of the contents for aluminum, with a Perkin-Elmer atomic absorption spectrophotometer.

Ten different mixtures of $AlCl_3$ and NH_3 were studied. For the first six, the size of the total sample was small enough ($10^{-5} - 10^{-4}$ mole) so that complete vaporization occurred in the gauge at relatively low temperatures, ca. 350°. The samples were prepared by introduction of the reactants directly into the gauge and were used to study the vapor-phase dissociation reaction. One sample had a 3 mol % excess of NH_3; the others all had small excesses of aluminum trichloride, which in one case was as high as 20 mol %. Although initial reaction of NH_3 and $AlCl_3$ at room temperature was rapid, the first series of pressure-temperature measurements in the liquid-vapor region in each case was often not in agreement with succeeding ones. It is suggested that a nonequilibrium mixture containing higher ammines may form initially; however, once the sample had been completely vaporized, reproducible pressure-temperature behavior was observed.

To prepare the seventh sample, approximately 5 grams of $AlCl_3$ was introduced into a reaction vessel. An equimolar amount of ammonia measured into a calibrated volume was condensed into a finger cooled with Dry Ice, and the vapor (at ca. 30 torr) allowed to react with the $AlCl_3$ at room temperature. After the NH_3 had been absorbed, the mixture was sealed off and then held at 350° for 16 hr. The capsule was then opened in the vacuum system, and ca. 1 gram of the ammine sublimed out in an effort to insure removal of any small excess of either reactant. The melting point of the resulting sample, 127° ± 2°, agreed well with the accepted value (*2*). The remaining material was all distilled into the diaphragm gauge.

After measuring the equilibrium vapor pressure at a series of temperatures, a small reservoir at the bottom of the gauge holding the excess liquid was sealed off (electrically) while the entire system was held at 300°, isolating the small amount of the equilibrium vapor in the upper part of the gauge. This vapor was then cooled, and the equilibrium vapor pressure of the condensed liquid again measured at lower temperatures. Values were in excellent agreement with those obtained above the large sample (Figure 3). Pressures generated by this sample at higher temperatures were also used for study of the vapor-phase dissociation reaction.

Sample 8 was prepared in the same manner and was of comparable initial size to sample 7; however, sample 8 was not fractionated at the end of the series of vapor-pressure measurements. Sample 9 (ca. 1.5 gram) was prepared by decomposition of NH_4AlCl_4, prepared from NH_4Cl and $AlCl_3$, into the ammine and hydrogen chloride (*9*). The HCl released when liquid NH_4AlCl_4 is heated was condensed into a finger cooled by liquid nitrogen; the remaining monoammine condensed on the glass wall just outside the heating furnace. The ammine was isolated and redistilled in vacuum several times before it was vaporized into the diaphragm gauge. Melting points observed for samples 7, 8, and 9 were 127°, 127°, and 126°, respectively. Equilibrium vapor-pressure data for the liquid were obtained from these three samples.

A tenth sample was prepared from aluminum chloride and ammonia and used in a Knudsen cell quadrupole mass spectrometer study of the vapor. The apparatus has been described earlier (*12*).

Results and Discussion

Vapor-phase dissociation. The pressure-temperature behavior of the unsaturated vapor of NH_3AlCl_3 suggests only a small degree of dissociation in the range studied (60–253 torr for various samples; 313–457°), ranging up to ca. 4 mol %. An effort to study the dissociation at temperatures above 550° in a quartz diaphragm gauge was frustrated by irreversible generation of gas, possibly associated with a breakdown of the ammine to form AlN(s) and HCl (*11*). Similar difficulties were not encountered in the Pyrex system.

Total pressures ranged from ca. 15 to 65% of saturation values in the data used to calculate equilibrium constants for the dissociation reaction. One cannot be certain of the relative importance of gas imperfection and adsorption effects on the total pressure; however, calculated equilibrium constants, assuming perfect gas behavior and attributing the abnormal increase in pressure to dissociation, were remarkably consistent for the various samples. In this treatment only two reactions were assumed significant:

$$NH_3AlCl_3(g) = NH_3(g) + AlCl_3(g) \quad (1)$$

$$2AlCl_3(g) = Al_2Cl_6(g) \quad (2)$$

Mass spectral analysis of vapors effusing from a Knudsen cell containing the ammine at 174° was in qualitative agreement with this assumption. The only shutter dependent mass peaks observed were identified with the following ions: NH_3^+, Al^+, Cl^+, HCl^+, $AlCl^+$, NH_3AlCl^+, $AlCl_2^+$, $NH_3AlCl_2^+$ (most intense), and $NH_3AlCl_3^+$. Although ions indicating the presence of Al_2Cl_6 were not observed, this species is well known to play a dominant role in the vapor of aluminum chloride at moderate temperatures (*6*). The sensitivity of the instrument was such that failure to detect dimer peaks at the low partial pressure predicted in the effusion cell was not unexpected. HCl is assumed generated by hydrolysis because of slight contamination of the sample on transfer to the mass spectrometer Knudsen cell and/or reaction of the sample with traces of water vapor in the vacuum system.

Thus, in the diaphragm gauge studies, the total pressure measured was attributed to the contributions of the ammine, ammonia, and the monomer and dimer of aluminum chloride. Equilibrium constants relating the partial pressures of the latter two species were evaluated from data published in the JANAF tables (*6*). Hence, from the amount of aluminum in the gauge, determined by analysis of the contents after the measurements, the known amount of ammonia admitted to the gauge and the total pressure, the partial pressure of each component may be calculated and the equilibrium constant K for Reaction 1 evaluated. Data were correlated in the form $\log_{10} K = A - BT^{-1}$ by least-squares analysis; results derived independently for each sample are shown in Table I together with the associated mean deviation for each constant. Least-squares values for A and B when all data points were combined are shown in the equation:

$$\log K \text{ (atm)} = 7.91 - 8730\, T^{-1} \quad (3)$$

A computer-generated graphical display of every sixth data point from a listing of the combined data for all samples is shown in comparison with the least-squares line in Figure 1. The constants in Equation 3 correspond to values of $\Delta H°_{653} = 39.9 \pm 1.3$ kcal and $\Delta S°_{653} = 36.2 \pm 1.9$ cal deg^{-1} for Reaction 1. The uncertainties correspond to the least-square mean deviations derived for the constants.

Using JANAF values for the entropies of ammonia and $AlCl_3(g)$, a standard entropy of 106.8 cal mol^{-1} deg^{-1} is calculated for $NH_3AlCl_3(g)$ at 653K. This may be compared with the entropy predicted by evaluation of partition functions. For the rotational contribution, moments of inertia were based on interatomic distances given by Gerding and Hontgraaf (*3*) and tetrahedral bond angles for the joined NH_3 and $AlCl_3$ groups (symmetry of the ammine has been reported to be C_{3V}) (*12*).

Vibration frequencies were taken from assignments of Gerding and Hontgraaf (*3*) and Goubeau and Siebert (*5*) [as an aid the values published for NH_3BF_3 were used as a guide (*9*, *13*)]. The total contribution without inclusion of the degree of freedom anticipated for internal rotation of the ammonia and $AlCl_3$ groups was 103.6 eu. For the internal rotation degree of freedom to contribute the remaining 3.2 eu, the tables of Pitzer and Gwinn (*10*) indicate a barrier height of 1950 cal mol^{-1}. While this seems not unreasonable, it is clear that the uncertainty of the interpretation and the entropy is too large, particularly in comparison with the predicted contribution of this degree of freedom, to permit anything more than a conclusion

Table I. Vapor-Phase Dissociation Data for NH_3AlCl_3

Sample	A	Mean dev, %	B	Mean dev, %
1	7.76	9.6	8660	7.0
2	7.84	4.8	8710	3.5
3	8.01	3.9	8840	2.6
4	7.91	3.7	8730	2.5
5	7.96	3.4	8760	2.5
6	7.93	2.2	8740	1.4
7	7.89	1.4	8720	0.8

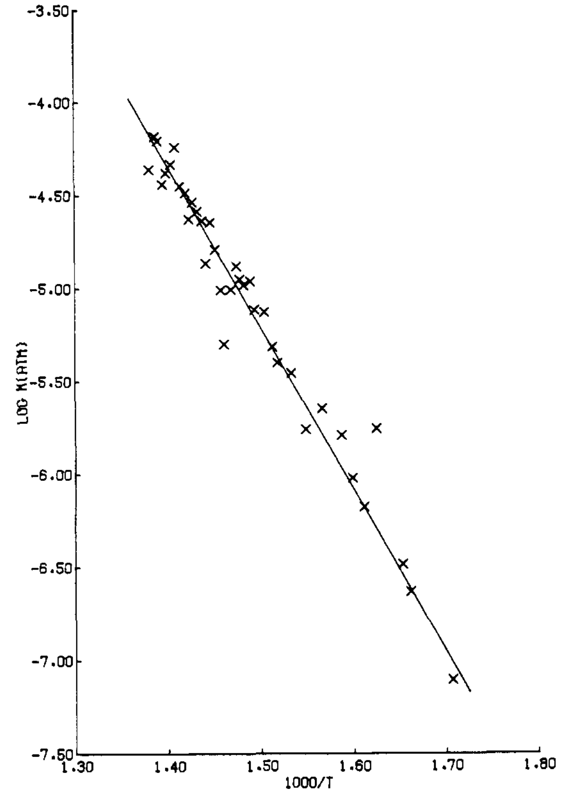

Figure 1. Equilibrium constants for reaction $NH_3AlCl_3(g) \rightarrow NH_3(g) + AlCl_3(g)$. $K = P(NH_3)P(AlCl_3)/P(NH_3AlCl_3)$

Every sixth point from complete table of pressures (*9*) from all samples listed in order measured was selected to give representative graphical display

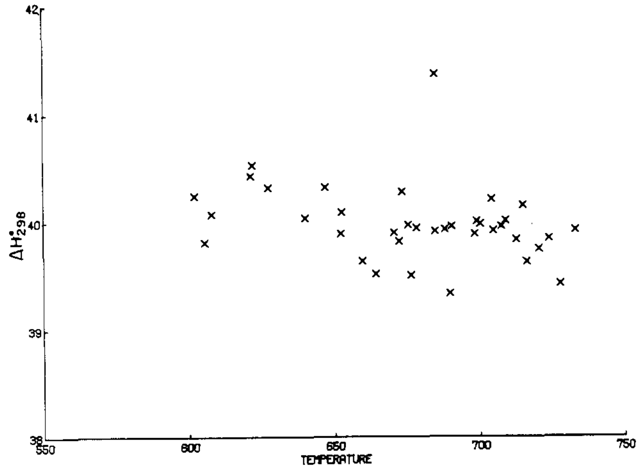

Figure 2. $\Delta H°_{298}$ values from partition functions and equilibrium constants displayed in Figure 1

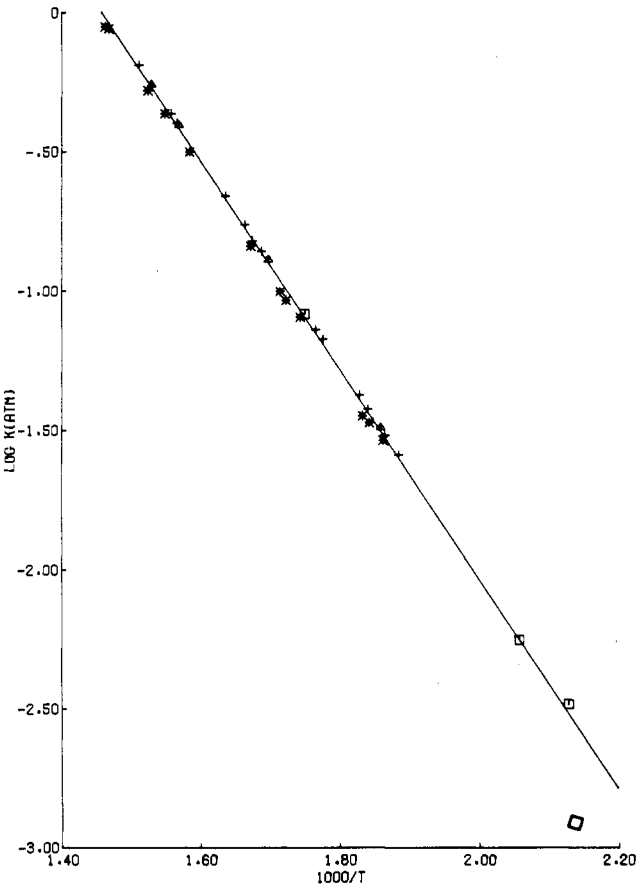

Figure 3. Equilibrium constants for $NH_3AlCl_3(l) \rightarrow NH_3AlCl_3(g)$. $K = P(NH_3AlCl_3)$ (atm)

Only every fifth point from complete table of measured pressures (*9*) is shown. ▲, sample 7, 1st series; ⊡, sample 7, 2nd series; +, sample 8; *, sample 9

that the entropy derived seems generally consistent with molecular properties reported for NH_3AlCl_3.

The enthalpy change for Reaction 1 derived from the van't Hoff treatment, together with JANAF values for ammonia and $AlCl_3$, leads to an enthalpy of formation of $NH_3AlCl_3(g)$ of -190.5 ± 1.2 kcal mol^{-1} at 298K. The correction to room temperature was made with relative enthalpy functions based on the partition functions discussed above, including a contribution for internal rotation indicated by the entropy comparison. Similarly, free energy functions may be used together with equilibrium constants to derive a value for $\Delta H°_{298}$ for Reaction 1:

$$\Delta H°_{298} = T(-R \ln K - \Delta(G° - H°_{298})/T)$$

Figure 2 shows a plot (of every sixth data point) of $\Delta H°_{298}$ values calculated in this way at various temperatures. The mean value based on all data is 40.0 kcal, which corresponds closely to that derived from the van't Hoff slope (40.2 kcal, corrected to 298K). This value also agrees within experimental error with that derived by Klemm and Tanke, 41 ± 2 kcal, from their heat of solution and vapor-pressure data (*8*). The standard entropy of $NH_3AlCl_3(g)$ at 298° is calculated to be 85.0 cal mol^{-1} deg^{-1}.

Equilibrium vapor pressures above liquid NH_3AlCl_3. From the total equilibrium vapor pressure measured when an excess of liquid ammine was present in the diaphragm gauge, it is possible to evaluate the equilibrium constant for the process:

$$NH_3AlCl_3(l) = NH_3AlCl_3(g) \tag{4}$$

from the relationships:

$$P_{\text{total}} = P_{NH_3AlCl_3} + P_{NH_3} + P_{AlCl_3} + P_{Al_2Cl_6}$$
$$P_{NH_3} = P_{AlCl_3} + 2P_{Al_2Cl_6}$$

and the equilibrium constants for Reactions 1 and 2. Data obtained from samples 7, 8, and 9 were correlated by least-squares analysis in the form $\log_{10} P(NH_3AlCl_3)$ (atm) $= A - BT^{-1}$. The least-squares line is shown in Figure 3 in comparison with a selection of every fifth data point from a combination of results from all samples. The standard enthalpy and entropy changes for Reaction 4 derived at the mean experimental temperature of 500K were 17.2 ± 0.2 kcal and 24.9 ± 0.3 cal deg^{-1}, respectively. The corresponding constants reported by Klemm and Tanke (*8*), 17.6 kcal and 25.2 cal deg^{-1}, were determined without allowance for dissociation for the ammine. The effect of the latter is small; however, if data measured in the present study are treated similarly, for example, values of 17.4 and 25.0 are obtained.

It is clear that our results agree very well with those of Klemm. On the other hand, Yurlova and coworkers (*14*) report an enthalpy of vaporization of only 9.5 kcal mol^{-1}, and their melting point (194°) is much higher, and apparent boiling point much lower than observed in our work. A possible explanation for the disparity may be the presence of substantial amounts of higher ammines in their samples.

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