THE DISSOCIATION CONSTANT OF AMMONIUM NITRATE AND ITS DEPENDENCE ON TEMPERATURE, RELATIVE HUMIDITY AND PARTICLE SIZE

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Abstract—The dissociation constant of NH_4NO_3(c, IV) is determined from the evaluation of literature data from a variety of sources. Three different methods of calculation using five independent data sets lead to accurate values of the dissociation constant; these are in excellent agreement with each other. The recommended value of the standard free energy of dissociation of NH_4NO_3(c, IV) to NH_3(g) and HNO_3(g) is 93.4 ± 0.3 kJ mol^{-1}. Over the temperature range for which crystalline phase IV is stable (-17 to $32°C$), the temperature dependence of the dissociation constant (in units of nb^2) is given to within $\pm 12\%$ by

$$\ln(K_p) = 118.87 - \frac{24084}{T} - 6.025 \ln(T).$$

Equations are also given for the computation of the dissociation constant of NH_4NO_3(aq) to NH_3(g) and HNO_3(g) as a function of temperature and either solution concentration or equilibrium relative humidity. For saturated solutions these equations are consistent with the results for the solid, and for dilute solutions they are consistent with data on dilute solutions of NH_3(aq) and HNO_3(aq). For particles with radii less than 0.1 μm, the Kelvin effect has a substantial effect on the dissociation constant. However, particle size has little effect on the deliquescence point.

Key word index: Dissociation constant, ammonium nitrate, gas–particle exchange, aerosol equilibria.

INTRODUCTION

NH_4NO_3 is often a significant component of atmospheric particles in polluted areas. If NH_3 and HNO_3 can exchange readily between the gas and particle phases then an equilibrium should exist between atmospheric NH_4NO_3(s), NH_3(g) and HNO_3(g). The gas-phase concentrations of NH_3 and HNO_3 would then be limited by this equilibrium. Furthermore, the rate of evaporation of NH_4NO_3 from particles should depend on its dissociation (or solid–vapour equilibrium) constant. The evaporation rate affects the dry deposition of NH_3 and HNO_3 since the deposition velocities depend upon whether these species are in the gas or particle phase (Huebert et al., 1988; Brost et al., 1988). Possible artifacts in measuring NH_3 and HNO_3 also depend on the rate of gas–particle exchange (Durham et al., 1987). The interpretation of experimental measurements of this evaporation rate (Harrison et al., 1990) also requires a knowledge of the equilibrium constant.

Values of the $NH_3 NO_3$ dissociation constant that appear in the atmospheric chemistry literature vary by about a factor of two. Stelson and Seinfeld (1982) recommended a value for the equilibrium constant (at 298.15 K) of 30 nb^2; this was based on tabulated thermodynamic data. Stelson et al. (1979) arrived at a value of 41 nb^2 from slightly different thermodynamic data and a value of 54 nb^2 from extrapolating the vapour pressure data of Brandner et al. (1962).

Wexler and Seinfeld (1991) use tabulated data to arrive at a value of 59 nb^2. These dissociation constants correspond to standard free energies of dissociation, ΔG°_{298} (a standard state of 1 b at 298.15 K will be used here), of 94.3, 93.5, 92.8 and 92.6 kJ mol^{-1}, respectively.

Several studies of atmosphere concentrations of NH_3(g) and HNO_3(g) have been made (Stelson et al., 1979; Allen et al., 1989, and references therein). When sufficient NH_3(g) and HNO_3(g) are present at temperatures above 5°C, the product of the partial pressures was found to be in rough agreement with the NH_4NO_3 dissociation constants recommended by Stelson et al. (1979) and consistently somewhat larger than the values recommended by Stelson and Seinfeld (1982). At lower temperatures the partial pressures tend to be considerably higher than expected from the dissociation constant; this has been attributed to kinetic factors (Harrison and MacKenzie, 1990; Wexler and Seinfeld, 1992).

Jaffe (1988) has questioned the validity of the recommended dissociation constants. He argued that the thermodynamic data are probably based on the vapour pressure measurements and that the extrapolation of the vapour pressure measurements over a wide temperature range could result in errors of more than an order of magnitude in the dissociation constant. If this constant is indeed off by this much, the atmospheric measurements of NH_3(g) and HNO_3(g) cited above would have to be reinterpreted

and the effect of gas–particle exchange on dry deposition and on measurements of gas-phase concentrations would have to be reassessed.

In fact, the available thermodynamic data on this system is much better than is implied by the factor of two range implied by the work cited above. It will be shown in the following that the dissociation constant, K_p, may be determined to within $\pm 12\%$. Values of ΔG^o_{diss} and $K_p(298)$, derived from several independent sets of measurements, are summarized in Table 1 and discussed individually in the following.

EXTRAPOLATION OF VAPOUR PRESSURE MEASUREMENTS

Feick (1954) has measured the vapour pressure of liquid NH_4NO_3 and Brandner et al. (1962) have measured the vapour pressure of solid and liquid NH_4NO_3 at elevated temperatures. Jaffe (1988) has criticized the extrapolation of this data to lower temperatures, largely because of the sensitivity of the extrapolation to small changes in the slope or intercept. Such errors come from two sources. First, in fitting the data to obtain the entropy and enthalpy of vaporization, each parameter can partially compensate for errors in the other. Errors in the experimental measurement then become magnified in the extrapolation. Second, the enthalpy and entropy of vaporization are themselves functions of temperature. If this is not accounted for in the extrapolation, the results will not be reliable. Jaffe also mentions several possible sources of systematic error in the experiments of Brandner et al. (1962). It should be noted that Brandner et al. (1962) took steps to avoid these errors.

Errors due to the temperature dependence of the enthalpies and entropies can be essentially eliminated by using heat capacity and enthalpy of phase transition data. Furthermore, if these data are available to a sufficiently low temperature then the absolute entropy change of the reaction may be determined. This eliminates the first source of error described above. In effect, a determination of the dissociation constant at any one temperature becomes a measurement of ΔG^o_{diss}. When vapour pressure measurements are available over a range of temperatures they constitute a set of replicate measurements of this one quantity.

Accurate thermodynamic data for NH_3, HNO_3 and NH_4NO_3 over the required temperature range are available in the literature. For NH_4NO_3, Stephenson et al. (1955) and Nagatani et al. (1967) report low temperature heat capacity and enthalpy of transition data that are in excellent agreement with each other. Eichenauer and Liebscher (1965) report data that differ somewhat, especially in the value of the entropy at 298 K. Nagatani et al. (1967) attribute the discrepancy to an incomplete phase transition. For the calculations presented here, I will use the data of Nagatani et al. (1967) since it extends to the highest temperature, 410 K, and appears to be the most thorough study. For calculations above 410 K, I have extrapolated Nagatani et al.'s (1967) heat capacity data for crystalline phase I to the melting point at 442.75 K (Dellien, 1982), used the value of the heat of fusion of $6.20 \pm 0.20 \, kJ \, mol^{-1}$ reported by Dellien (1982), and used the liquid phase heat capacity $(0.191 \, J \, mol^{-1} \, K^{-1})$ measured by Feick (1954). Data for $NH_3(g)$ were taken from Haar (1968) while data for $HNO_3(g)$ were taken from the JANAF tables (Chase et al., 1985).

The standard free energy of dissociation was determined from two sets of vapour pressure measurements; those of Feick (1954) over the liquid at 442.8–522.3 K and those of Brandner et al. (1962) over the solid at 349.2–438.2 K and over the liquid at 443.2–513.2 K. Each reported vapour pressure was used to determine the dissociation constant at that temperature from the formula $K_p = (P_{vap}/2)^2$. These were then used to compute ΔG^o_{diss} at 298.15 K using the tabulated thermodynamic data. The individual data points are plotted in Fig. 1; the agreement between these points is good. Since the two data sets agree well an average of all the points was taken; this average is reported in Table 1; error limits were estimated as twice the standard error of the mean. The actual uncertainty should be somewhat larger due to possible systematic errors in the measurements and uncertainties in the data used to adjust the values to 298 K. The resulting value of $K_p(298)$ is only slightly larger than that recommended by Stelson et al. (1979).

Table 1. Values of the standard Gibbs free energy of dissociation and the dissociation constant at 298.15 K

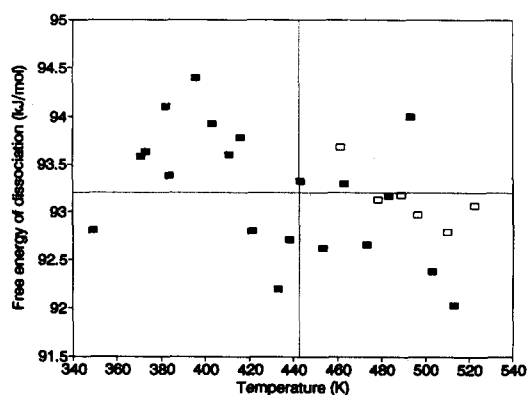| Method	S^o from Nagatani et al. (1967)		S^o from Eichenauer and Liebscher (1965)	
	ΔG^o_{diss} (kJ mol^{-1})	K_p (nb^{-2})	ΔG^o_{diss} (kJ mol^{-1})	K_p (nb^{-2})
Vapour pressure	93.20 ± 0.25	47 ± 5	93.84 ± 0.22	36 ± 3
Vapour–solution equilibria	93.26 ± 0.27	46 ± 5	93.26 ± 0.27	46 ± 5
Calorimetry (heats of formation)	94.11 ± 0.56	33 ± 7	92.76 ± 0.56	56 ± 13
Calorimetry (heats of solution)	93.51 ± 0.22	41 ± 4	92.16 ± 0.22	71 ± 6
Weighted average	93.39	43	93.05	50

Fig. 1. Values of $\Delta G^{\circ}_{\text{diss}}$ determined from vapour pressure measurements as a function of the temperature of the measurement. The horizontal line is the average of all points and the vertical line indicates the melting point of NH_4NO_3. ■ Data of Brandner et al. (1962), □ data of Feick (1954).

A close examination of Fig. 1 shows a slight downward trend in $\Delta G^{\circ}_{\text{diss}}$ with increasing temperature of the measurement. Although this trend accounts for only about 20% of the total variance, it is statistically significant at the 95% confidence level. One possible source of this trend would be an error in the value of $\Delta S^{\circ}_{\text{diss}}$ since this would change the temperature dependence of $\Delta G^{\circ}_{\text{diss}}$. This trend may be almost completely eliminated if the value of $S^{\circ}(NH_4NO_3)$ reported by Eichenauer and Liebscher (1965) is used instead of the value reported by Nagatani et al. (1967). Table 1 includes values of $\Delta G^{\circ}_{\text{diss}}$ based on both values of S° (NH_4NO_3).

Additional vapour pressure measurements have been reported by Dionne et al. (1986). These do not appear to be of as high a quality as the earlier measurements. First, Dionne et al. (1986) do not seem to have conducted any tests to ensure that vapour–solid equilibrium was achieved. Also, only the partial pressure of $HNO_3(g)$ was measured and it is not clear if the reported "vapour pressure" is the total vapour pressure or only this partial pressure. The data were reported in the form of a Clausius–Clapeyron equation; the results suggest a dissociation consant that is somewhat smaller, with a weaker temperature dependence, than the other measurements.

de Kruif (1982) has reported vapour effusion results that suggest that NH_4NO_3 is only partially dissociated in the gas phase at 352 K. His reported vapour pressure at this temperature agrees with the results of Brandner et al. (1962). However, de Kruif's (1982) data appear to be incorrectly analysed since he did not account for the effect of differing rates of effusion on the vapour-phase concentrations of the various species. When his equations are modified to account for this, the results are no longer physically possible.

CALCULATION OF THE DISSOCIATION CONSTANT FROM VAPOUR–SOLUTION EQUILIBRIA

For a solution of NH_4NO_3 in water, we may define a concentration-dependent dissociation constant, K^*_p, by

$$K^*_p = P(NH_3)P(HNO_3), \qquad (1)$$

where $P(NH_3)$ and $P(HNO_3)$ are the equilibrium partial pressures of NH_3 and HNO_3 over the solution. We also note that

$$P(NH_3) = \frac{a(NH_3)}{H(NH_3)} \qquad (2)$$

and

$$P(HNO_3) = \frac{a(HNO_3)}{H(HNO_3)}, \qquad (3)$$

where a is the activity of the solute and H is the Henry's law constant. As long as activities are used, these expressions are valid for both concentrated and dilute solutions. Similarly, we may express the acid dissociation constants for NH_4^+ and HNO_3 as

$$K_a(NH_4^+) = \frac{a(NH_3)a(H^+)}{a(NH_4^+)} \qquad (4)$$

and

$$K_a(HNO_3) = \frac{a(NO_3^-)a(H^+)}{a(HNO_3)}. \qquad (5)$$

Finally, we note that for a solution of NH_4NO_3 in water

$$a(NH_4^+)a(NO_3^+) = (\gamma_{\pm}m)^2, \qquad (6)$$

where $\gamma_{\pm}$ is the mean activity coefficient and m is the molality of $NH_4NO_3(aq)$. Now Equations (2)–(6) may be substituted into Equation (1) to give

$$K^*_p = \frac{(\gamma_{\pm}m)^2 K_a(NH_4^+)}{K_a(HNO_3)H(HNO_3)H(NH_3)}. \qquad (7)$$

K^*_p may be related to K_p by

$$K^*_p = (\gamma_{\pm}m)^2 \frac{K_p}{K_{sp}}, \qquad (8)$$

where K_{sp} is the solubility product constant for $NH_4NO_3(s)$. For a saturated solution, $K_{sp} = (\gamma_{\pm,\text{sat}}m_{\text{sat}})^2$. Then $K^*_p = K_p$; that is, the solution is in equilibrium with the solid and the vapour pressure product is therefore the same as for the solid. Thus, combining (7) and (8) for the saturated solution:

$$K_p = \frac{(\gamma_{\pm,\text{sat}}m_{\text{sat}})^2 K_a(NH_4^+)}{K_a(HNO_3)H(HNO_3)H(NH_3)}. \qquad (9)$$

Published data exist for all the quantities on the right-hand side of Equation (9). For a saturated solution, $\gamma_{\pm,\text{sat}} = 0.1317$ and $m_{\text{sat}} = 25.954$ molal (Wishaw and Stokes, 1953). The product $K_a(HNO_3)H(HNO_3)$ has a value of $(2.59 \pm 0.20) \times 10^6$ mol^2 kg^{-2} b^{-1} (Clegg

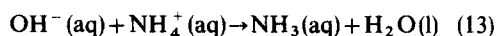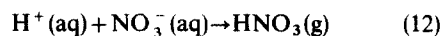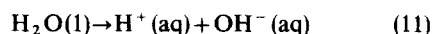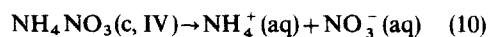and Brimblecombe, 1990; Tang et al., 1988). Dasgupta and Dong (1986) have measured the solubility of NH_3 in water over the temperature range 279–291 K and have corrected the results for the effects of ionic strength and for equilibrium with NH_4^+. They also provide a discussion of earlier measurements on this system; these other measurements do not seem to be as suitable for a thermodynamic calculation (infinitely dilute solution, zero ionic strength). Extrapolating their results to 298 K yields $H(NH3) = 55.3 \pm 4$ mol kg^{-1} b^{-1}. This extrapolation is over a small enough temperature range that ΔC_p may be neglected since its effect on ΔH and ΔS will nearly cancel in ΔG. Finally, $K_a(NH_4^+) = 5.69 \times 10^{-10}$ mol kg^{-1} (Bates and Pinching, 1950). Substituting these values into Equation (9) yields $K_p(298) = 46.5 \pm 5$ nb^2 and $\Delta G^\circ_{diss} = 93.2 \pm 0.3$ kJ mol^{-1}.

CALORIMETRIC DETERMINATION OF THE FREE ENERGY OF DISSOCIATION

Standard enthalpies of formation and standard absolute entropies for $NH_4NO_3(c, IV)$, $NH_3(g)$ and $HNO_3(g)$ have been determined from calorimetric measurements. The values are summarized in Table 2. The references review earlier measurements. For ΔH_f° ($HNO_3(g)$) the value given by Forsythe and Giauque (1942) was used, instead of that in the JANAF tables, since the latter is an average of values from several sources that are neither independent of each other nor of the data used elsewhere in this paper. Combining these data yields $\Delta H^\circ_{diss} = 186.00 \pm 0.56$ kJ mol^{-1}. Using the data of Nagatani et al. (1967), $\Delta S^\circ_{diss} = 308.36$ J mol^{-1} K^{-1}, whereas the data of Eichenauer and Liebscher (1965) yield $\Delta S^\circ_{diss} = 312.73$ J mol^{-1} K^{-1}. The resulting values of ΔG°_{diss} are given in Table 1.

Additional, independent, calorimetric data are available for heats of solution. A cycle, equivalent to the dissociation reaction, may be constructed from the reactions

$$NH_4NO_3(c, IV) \rightarrow NH_4^+(aq) + NO_3^-(aq) \quad (10)$$

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq) \quad (11)$$

$$H^+(aq) + NO_3^-(aq) \rightarrow HNO_3(g) \quad (12)$$

$$OH^-(aq) + NH_4^+(aq) \rightarrow NH_3(aq) + H_2O(l) \quad (13)$$

$$NH_3(aq) \rightarrow NH_3(g). \quad (14)$$
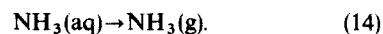
Standard enthalpies of reaction are given in Table 2. The papers by Vanderzee and King (1962) and Vanderzee et al. (1972, 1980a, b) provide comparisons with earlier results. A comparison of data on HNO_3 solubility given by Tang et al. (1988) suggests that the data of Forsythe and Giauque (1942) are not reliable. However, the discrepancies appear to be due to the estimate used for $S^\circ(298, NO_3^-, aq)$ and an arithmetic error in computing ΔG from ΔH and ΔS, rather than in the heat of solution. For the dissociation reaction, this cycle yields $\Delta H^\circ_{diss} = 185.40 \pm 0.22$ kJ mol^{-1}. Combining this with the entropy data gives the values of ΔG°_{diss} listed in Table 1.

RECOMMENDED VALUES OF DISSOCIATION CONSTANT AND FREE ENERGY OF FORMATION

The results summarized in Table 1 show that when the absolute entropy determined by Nagatani et al. (1967) is used there is excellent agreement among the standard free energies of dissociation of $NH_4NO_3(c, IV)$ as determined by several methods. The value determined from the heat of formation data differs somewhat from the others but it is also the most uncertain. The difference may be due to an error in the value for ΔH_f° ($HNO_3(g)$) given by Forsythe and Giauque (1942). Cox et al. (1989) recommend $\Delta H_f^\circ(HNO_3(g)) = -134.2 \pm 0.4$ kJ mol^{-1}; using this value would yield $\Delta G^\circ_{diss} = 93.75$ kJ mol^{-1}, in much better agreement with the other measurements. This value was not used in the present analysis since it relies on much of the data used in the other methods and is therefore not independent of them.

Table 2. Calorimetric data used to determine the standard free energy of dissociation. Enthalpies are in kJ mol^{-1}, entropies in J mol^{-1} K^{-1}

Quantity	Value	Reference
$\Delta H_f^\circ(NH_4NO_3(c, IV))$	-365.61 ± 0.32	Cox et al. (1979)
$\Delta H_f^\circ(NH_3(g))$	-45.77 ± 0.19	Vanderzee and King (1972)
$\Delta H_f^\circ(HNO_3(g))$	-133.84 ± 0.4	Forsythe and Giauque (1942)
$S^\circ(NH_4NO_3(c, IV))$	150.81	Nagatani et al. (1967)
$S^\circ(NH_4NO_3(c, IV))$	146.44	Eichenauer and Liebscher (1965)
$S^\circ(NH_3(g))$	192.77	Haar (1968)
$S^\circ(HNO_3(g))$	266.40	Chase et al. (1985)
$\Delta H^\circ_{rxn}(10)$	25.54 ± 0.03	Vanderzee et al. (1980b)
$\Delta H^\circ_{rxn}(11)$	55.88 ± 0.05	Pitzer (1937)
$\Delta H^\circ_{rxn}(12)$	72.48 ± 0.2	Forsythe and Giauque (1942)
$\Delta H^\circ_{rxn}(13)$	-3.85 ± 0.04	Vanderzee et al. (1972)
$\Delta H^\circ_{rxn}(14)$	35.35 ± 0.06	Vanderzee and King (1972)

These measurements are independent except that the determinations other than that based on the vapour–solution equilibria all depend on the absolute entropies at 298 K. An error in this quantity would cause the values of ΔG^o_{diss} calculated from the vapour pressure measurements to increase or decrease systematically as the temperature of the measurement changes. Such a trend does occur if the data of Nagatani et al. (1967) are used (Fig. 1) but not if the data of Eichenauer and Liebscher (1965) are used. However, there are several arguments against using the later data. First, as may be seen in Table 1, this data leads to substantial disagreements between the results of the different methods. Second, the data of Nagatani et al. appear to be of higher quality and are confirmed by the measurements of Stephenson et al. (1955). Finally, the small trend in Fig. 1 could be due to systematic error in the measurements rather than an error in ΔS^o_{diss}.

A weighted average of the values in Table 1 based on the absolute entropy given by Nagatani et al. yields a recommended value of 93.4 ± 0.3 kJ mol^{-1} for ΔG^o_{diss}. The corresponding value of $K_p(298)$ is 43 ± 5 nb^2 and $\Delta H^o_{diss} = 185.3$ kJ mol^{-1}.

TEMPERATURE AND RELATIVE HUMIDITY DEPENDENCE

At atmospheric pressure, $NH_4NO_3(c, IV)$ is stable with respect to other crystalline phases over the temperature range 256.2–305.4 K (Dellien, 1982). Over this limited range, the heat capacities may be taken as constant and the dissociation constant may be calculated from the integrated form of the van't Hoff equation:

$$\ln(K_p) = \frac{\Delta S^o_{diss} - \Delta C_{p, diss}}{R} - \frac{\Delta H^o_{diss} - T_o \Delta C_{p, diss}}{RT}$$
$$+ \frac{\Delta C_{p, diss}}{R} \ln\left(\frac{T}{T_o}\right), \tag{15}$$

where $T_o = 298.15$ K. With data from the sources described above, this becomes

$$\ln(K_p) = 118.87 - \frac{24084}{T} - 6.025 \ln(T). \tag{16}$$

The dissociation constants calculated from Equation (16) should be accurate to within $\pm 12\%$. This equation predicts dissociation constants that are about 50% larger than those predicted by the equation of Stelson and Seinfeld (1982).

To obtain the temperature dependence of K_p^* (Equation 8), we first note that the temperature dependence of K_{sp} is given by

$$\ln(K_{sp}) = \frac{\Delta S^o_{soln} - \Delta C_{p, soln}}{R} - \frac{\Delta H^o_{soln} - T_o \Delta C_{p, soln}}{RT}$$
$$+ \frac{\Delta C_{p, soln}}{R} \ln\left(\frac{T}{T_o}\right), \tag{17}$$

where ΔS^o_{soln}, ΔH^o_{soln} and $\Delta C_{p, soln}$ are for the process of passing from the solid to the solution in its standard state (infinite dilution). The standard free energy of solution is determined from

$$\Delta G^o_{soln} = -2RT_o \ln(\gamma_{\pm, sat} m_{sat}). \tag{18}$$

Using the data of Wishaw and Stokes (1953) for the saturated solution, $\Delta G^o_{soln} = -6.09$ kJ mol^{-1}. From Vanderzee et al. (1980b), $\Delta H^o_{soln} = 25.54$ kJ mol^{-1}. Stelson and Seinfeld (1982) give an equation for the partial molal heat capacities; evaluating this at $m = 0$ and combining the result with the data cited above for the gas-phase species yields $\Delta C^o_{p, soln}/R = 11.208$.

The temperature dependence of the activity coefficients is given by (Lewis et al., 1961, p. 392):

$$\ln(\gamma_\pm^2) = \ln(\gamma_{\pm, o}^2) - \frac{\bar{L}_o}{RT_o} + \frac{\bar{J}}{R} + \frac{\bar{L}_o - \bar{J}T_o}{RT}$$
$$- \frac{\bar{J}}{R} \ln\left(\frac{T}{T_o}\right), \tag{19}$$

where $\gamma_\pm$ is the mean activity coefficient, $\bar{L}_o$ is the relative partial molal enthalpy, and $\bar{J}$ is the relative partial molal heat capacity. Subscript o indicates the value at $T = T_o$. These quantities are for the solute at a fixed molality m and 298 K. Note that Equation (19) applies to $\gamma_\pm^2$ since it is this quantity, and not $\gamma_\pm$, that is proportional to the activity of $NH_4NO_3(aq)$. The corresponding equation given by Stelson and Seinfeld (1982) is incorrect in this respect.

Equations (17), (19) and (15) may be substituted into Equation (8) to give

$$\ln(K_p^*) = \frac{\Delta S^o_m - \Delta C_{p, m}}{R} - \frac{\Delta H^o_m - T_o \Delta C_{p, m}}{RT}$$
$$+ \frac{\Delta C_{p, m}}{R} \ln\left(\frac{T}{T_o}\right), \tag{20}$$

where

$$\Delta S^o_m = \Delta S^o_{diss} - \Delta S^o_{soln} + 2R \ln(\gamma_{\pm, o} m) - \frac{\bar{J}}{T_o} \tag{21}$$

$$\Delta H^o_m = \Delta H^o_{diss} - \Delta H^o_{soln} - \frac{\bar{L}_o}{R} \tag{22}$$

and

$$\Delta C_{p, m} = \Delta C_{p, diss} - \Delta C_{p, soln} - \bar{J}. \tag{23}$$

These quantities are for the evaporation of equal amounts of $NH_3(g)$ and $HNO_3(g)$ from a solution with the specified molality, m.

Hamer and Wu (1972) have fit the data of Wishaw and Stokes (1953) to obtain an analytic expression for $\gamma_{\pm, o}$ as a function of m. Stelson and Seinfeld (1982) have provided expansions, in half powers of m, for $\bar{L}_o$ and $\bar{J}$ based upon the data of Vanderzee et al. (1980a) and Roux et al. (1978). These expressions were used (with a small modification as described in the

Table 3. Expansion coefficients for Equations (24) and (26)

i	a_i	b_i	c_i
0	−9.293	15876	11.208
1	33.983	1259.4	−5.223
2	45.4557	2867.7	−6.318
3	−28.5816	−1704.56	4.013
4	5.9599	378.94	−0.822
5	−0.44257	−36.144	0.0564
6	0.003962	1.2071	0.0

following) in Equation (20) to obtain

$$\ln(K_p^*) = 2\ln(m) - \frac{2.3523\sqrt{m}}{1+0.925\sqrt{m}}$$

$$+ \sum_{i=0}^{6}\left[a_i - \frac{b_i}{T} + c_i\ln T\right]m^{i/2}. \quad (24)$$

The coefficients for Equation (24), with K_p^* in nb^2, are given in Table 3. Equation (24) may also be applied to an ideal solution by dropping the Debye–Huckel term (the 2nd term on the right-hand side) and setting all the expansion coefficients for $i>0$ equal to zero.

The relative humidity at which a solution of a given molality is in equilibrium with water vapour is given by the water activity. The water activity, a_w, at any temperature, T, may be related to the activity, $a_{w,o}$, for a solution of the same composition at $T_o = 298.15$ K by the equation

$$\ln(a_w) = \ln(a_{w,o}) - \frac{\bar{L}_w - \bar{C}_{p,w}T_o}{R}\left[\frac{1}{T_o} - \frac{1}{T}\right]$$

$$- \frac{\bar{C}_{p,w}}{R}\ln\left[\frac{T}{T_o}\right]. \quad (25)$$

The partial molal enthalpy, $\bar{L}_w$, and heat capacity, $\bar{C}_{p,w}$, for water may be obtained from those of the solute by use of the Gibbs–Duhem equation. This gives us, for the osmotic coefficient, ϕ,

$$\phi = 1 - \frac{1.4861}{m}\left[D - 2\ln D - \frac{1}{D}\right] + \sum_{i=1}^{6}\frac{i}{2(i+2)}$$

$$\times \left[a_i - \frac{b_i}{T} + c_i\ln T\right]m^{i/2}, \quad (26)$$

where

$$D = 1 + 0.925\sqrt{m} \quad (27)$$

and

$$\ln(a_w) = \frac{-2m\phi}{55.51}. \quad (28)$$

The coefficients for Equation (26) are the same as for Equation (24) and are given in Table 3.

Equations (24) and (26) allow the calculation of K_p^* and a_w as functions of composition and temperature. Together, they provide an implicit equation for K_p^* as a function of temperature and relative humidity. The validity of these equations can be tested as

follows. Linke and Seidel (1965) provide data on the solubility of NH_4NO_3 in water as a function of temperature. Over the temperature range for which the solid is in phase IV, these data can be fit by the expression

$$\ln(m_{sat}) = 9.771 - \frac{1935}{T}. \quad (29)$$

Equations (24) and (26) can be used to evaluate $K_{p,sat}^*$ and $a_{w,sat}$ (i.e. the relative humidity at the deliquescence point) along this saturation line. Figure 2a shows the ratio of the resulting values of $K_{p,sat}^*$ to the value of K_p evaluated for the solid using Equation (16). Figure 2b compares the calculated values of $a_{w,sat}$ to the experimental points of Dingemans (1941) from 10 to 32°C and the value determined by Wishaw and Stokes (1953) at 25°C. This later value should be more reliable since it was determined by the isopiestic method rather than by measurement of the total vapour pressure. Although the calculated values of $a_{w,sat}$ are systematically larger (by 1–2%) than the data of Dingemans, they agree well with the value of Wishaw and Stokes. The calculated values may be
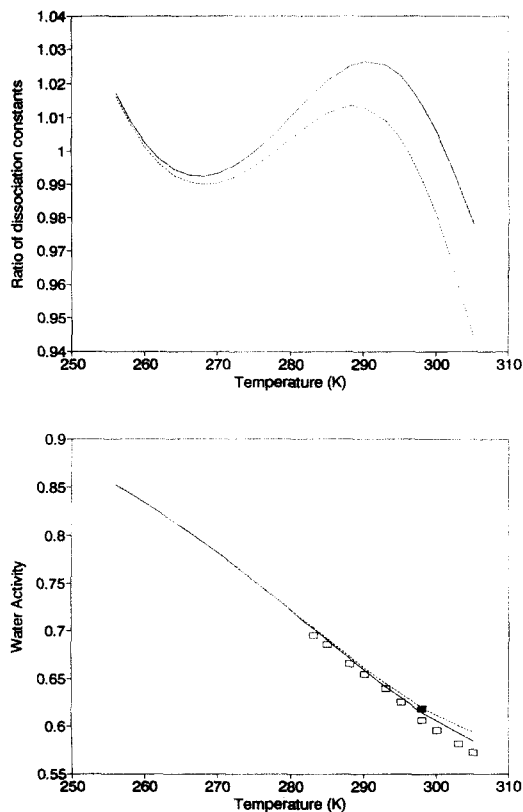

Fig. 2. (a) Ratio of K_p^* for the saturated solution to K_p for the solid as a function of temperature. (b) Comparison of calculated and measured water activities for saturated solutions. □ Data of Dingemans (1941), ■ data of Wishaw and Stokes (1953). (a, b) - - - calculated using the parameters given by Hamer and Wu (1972); ——— using slightly modified parameters (see text).

represented to within 2% by the equation

$$\ln(a_{w,sat}) = -2.551 + \frac{618.3}{T}. \qquad (30)$$

This equation differs significantly from those given by Stelson and Seinfeld (1982) and Wexler and Seinfeld (1991) except at temperatures near 25°C.

The broken lines in Fig. 2 were calculated using the parameters given by Hamer and Wu (1972). It can be seen that the results begin to deviate rapidly above 298 K. This is not surprising. The parameters were based on a fit of data up to saturation (25.95 molal) at 25°C. Calculations on the saturated solutions at higher temperatures require an extrapolation (to 31 molal at 32°C) of an equation that has no physical basis. In fact, the calculated activity coefficients of Hamer and Wu (1972) begin to diverge from the experimental values (Wishaw and Stokes, 1953) above 24 molal. Accordingly, the coefficient of the cubic term in the equation given by Hamer and Wu (1972) was adjusted from -1.9075×10^{-5} to -1.8814×10^{-5}. This amounts to using the solubility data to determine the activity coefficients above 27 molal and results in the solid lines in Fig. 2. The coefficients in Table 3 are based on this adjusted parameter. The smoothly varying nature of the remaining deviations is probably due to the deficiencies of using a polynomial to fit the data; the remaining errors ($\pm 2\%$) are within the uncertainty of the measurements. The agreement between the results for the saturated solutions and the solid may also be seen in Fig. 3. This is in contrast to the results of Stelson and Seinfeld (1982) who found large discrepancies between K_p and K_p^* for the saturated solution.

Although the extrapolation of the modified equation of Hamer and Wu gives good results up to saturation at temperatures up to 32°C, at lower temperatures the calculated value of K_p^* passes through

a maximum at a concentration somewhat above saturation. Thus, these equations are not suitable for supersaturated solutions.

The values used for $\bar{L}_o$ and $\bar{J}$ (and therefore also for $\bar{L}_w$ and $\bar{C}_{p,w}$) above 25 molal were also based on extrapolations of data from lower concentrations. However, since these high concentrations will only occur for temperatures near 25°C, these terms will have relatively little effect. An error of 1 kJ mol^{-1} in $\bar{L}_o$ or $\bar{L}_w$ will only change K_p^* or a_w by 1% at 32°C. Since these parameters only change by only 5.1 and 2.6 kJ mol^{-1}, respectively, over the range of the extrapolation the errors should not be more than 1 or 2%. The effect of errors in partial molal heat capacities are negligible over such a small temperature range.

These equations may also be tested by applying them to very dilute (ideal) solutions. In this case, we obtain from Equations (7) and (24), with $\gamma_{\pm} = 1$:

$$\frac{K_a(NH_4^+)}{K_a(HNO_3)\,H(HNO_3)\,H(NH_3)}$$

$$= \exp\left[a_o - \frac{b_o}{T} + c_o\right]. \qquad (31)$$

The ratio of the left-hand to the right-hand side may now be evaluated as a function of temperature; the results are shown in Fig. 4. For the product $K_a(HNO_3)\,H(HNO_3)$ the equation of Clegg and Brimblecombe (1990) was used. For $K_a(NH_3)$ the data of Bates and Pinching (1950) may be fit to 0.2% by

$$\ln(K_{NH_4^+}) = -0.227 - \frac{6279}{T}. \qquad (32)$$

Although these data are for the temperature range 0–50°C, the quality of the data and the fit are such that a value of ΔC_p greater than R can be excluded. The error in the extrapolation to 256 K should then
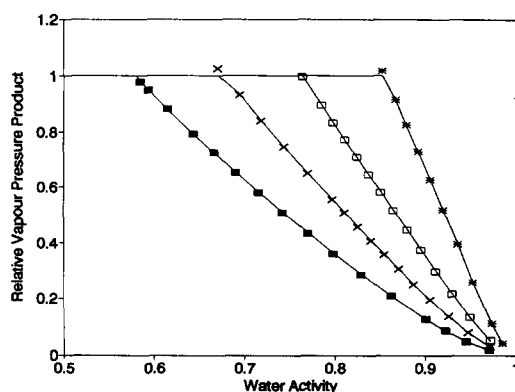

Fig. 3. Temperature and relative humidity dependence of the equilibrium vapour pressure product, K_p^*. Values are plotted relative to the dissociation constant, K_p, of the solid. Points are calculated from Equations (24) and (26); ∗ -17°C, □ 0°C, × 15°C, ■ 32°C. The lines are calculated from Equation (34).
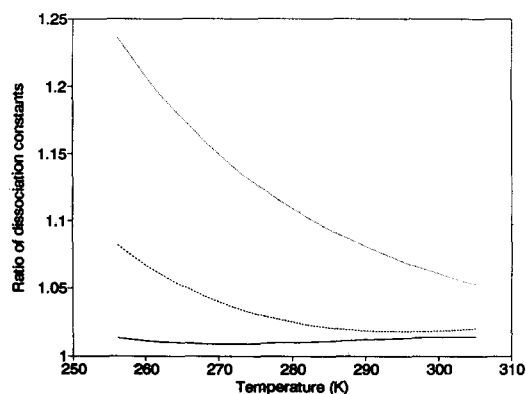
Fig. 4. The ratio of K_p^* calculated from Equation (7) to that from Equation (24) for ideal solutions. The various curves are for the temperature dependence of the Henry's law constant for NH_3 calculated from the data of Dasgupta and Dong (1986) (. . .), Vanderzee and King (1972) with $\Delta C_p = 0$ (— — —), and Vanderzee and King (1972) with $\Delta C_p = 5R$ (———).

be no more than 2%. When the expression given by Dasgupta and Dong (1986) is used for the temperature dependence of $H(NH_3)$, the dotted line in Fig. 4 results. Since this equation is based on a fit of data over a limited temperature range and the data were only fit to an accuracy of a few per cent, it should not be surprising if it should result in relatively large errors in an extrapolation. Vanderzee and King (1972) give values of ΔH° and ΔG° for Reaction (14) but ΔC_p does not seem to have been measured for this reaction. Using this data and setting ΔC_p equal to zero results in the dashed line in Fig. 4. Setting ΔC_p equal to $5R$ (the value for $H_2O(g) \rightarrow H_2O(l)$) yields

$$\ln(H(NH_3)) = -43.70 + \frac{5746}{T} + 5\ln(T) \quad (33)$$

and results in the solid line in Fig. 4. It is clear that the temperature dependencies are consistent to within the uncertainty of the thermodynamic parameters for Reaction (14).

Having established the validity of these equations, we may now use them to determine the temperature and relative humidity dependence of K_p^*. Equations (24) and (26) may be used to calculate both K_p^* and a_w as functions of molality and temperature. The results of such a calculation were used to generate the points in Fig. 3. The solid lines in Fig. 3 were calculated from the equation

$$K_p^* = (P_1 - P_2(1 - a_w) + P_3(1 - a_w)^2)$$
$$\times (1 - a_w)^{1.75} K_p, \quad (34)$$

where

$$\ln(P_1) = -135.94 + \frac{8763}{T} + 19.12\ln(T) \quad (35)$$

$$\ln(P_2) = -122.65 + \frac{9969}{T} + 16.22\ln(T) \quad (36)$$

and

$$\ln(P_3) = -182.61 + \frac{13875}{T} + 24.46\ln(T). \quad (37)$$

These smooth curves fit the calculated points to within 1% for relative humidities less than 94% (concentrations greater than 2.5 molal) and to within 4% for r.h. <99.7% (>0.1 molal). Equation (34) is not consistent with the Debye–Huckel equation and so does not provide accurate results for dilute solutions.

DEPENDENCE OF DISSOCIATION CONSTANT AND DELIQUESCENCE POINT ON PARTICLE SIZE

As the size of a particle of solid NH_4NO_3 becomes smaller, the value of K_p will increase because of the Kelvin effect according to the formula (Lewis et al., 1961, p. 483):

$$K_p(a) = K_p(\text{bulk}) \exp\left(\frac{2\sigma\bar{v}}{aRT}\right), \quad (38)$$

where σ is the surface tension of the particle, $\bar{v}$ is the molar volume of NH_4NO_3, a is the particle radius (i.e. the radius of a sphere with the same volume as the particle), R is the gas constant and T is the absolute temperature. At 25°C, $\sigma = 113$ dynes cm^{-1} (Kodas et al., 1986) and $\bar{v} = 46.5$ cm^3 mol^{-1} (Mellor, 1964, p. 518), so $K_p(a)$ is 4.3% larger than the bulk value for a particle radius of 0.1 μm and 53% larger for $a = 0.01$ μm.

This decrease in the stability of the solid will also increase its solubility. This will be partially offset by the fact that K_p^* for the solution droplet will increase in the same manner as K_p. In this case the surface tension and radius of the solution drop and the partial molal volume of $NH_4NO_3(aq)$ must be used in Equation (38). The surface tension of the solution as a function of concentration is given in the International Critical Tables (Washburn, 1928, vol. 4, p. 464). The difference, $\Delta\sigma$, between the surface tension on the solution and that of pure water is independent of temperature and may be fit by

$$\Delta\sigma = \frac{m}{1 + 0.034 m} \quad (39)$$

which is of the general form suggested by Eberhart (1966). The data for the density of the solution (Mellor, 1964, p. 520) may be fit by assuming a constant partial molal volume of 51.2 cm^2 mol^{-1} for $NH_4NO_3(aq)$. This also implies that the partial molal volume of H_2O is constant at 18.07 cm^3 mol^{-1}, the same as for pure water. Using this data, the solution drop size and the value of K_p^* may be calculated as a function of concentration; the saturated solution will be the one for which $K_p^* = K_p$. This calculation requires extrapolating the activity coefficients to concentrations that are supersaturated with respect to the bulk. As noted previously, the equation of Hamer and Wu (1972) is not suitable for this purpose. However, for concentrations above 20 molal, the osmotic coefficient varies linearly with molality (Wishaw and Stokes, 1953). This linear behaviour was assumed to continue for supersaturated conditions and thus the activity coefficients from the Gibbs–Duhem equation were determined. An iterative solution of the equation $K_p^* = K_p$ then reveals that the solubility (at 25°C) increases to 26.5 molal for a dry particle radius of 0.1 μm and 31.3 molal for $a = 0.01$ μm. The ratio of the radius of the saturated solution drop to that of the dry particle decreases from 1.246 to 1.215 over this same range.

Finally, the deliquescence point of the salt will also be affected by particle size. There are two opposing effects here. First, the vapour pressure of water will be decreased because of the increase in solute concentration at saturation. Second, the vapour pressure will increase because of the Kelvin effect, Equation (38). The result is that particle size has little effect on the deliquescence point. The deliquescence point for a dry particle of 0.1 μm radius is 62.0% and is 63.7% for

a radius of 0.01 μm. Thus the only significant effect of particle size will be to increase the value of K_p and this will only be substantial for radii below 0.1 μm. Although the surface tensions of the solid and of the solutions are not very well known, these conclusions are not very sensitive to the exact values used.

CONCLUSIONS

Thermodynamic data relevant to the system $NH_4NO_3/NH_3/HNO_3$ from a variety of sources have been examined. These include calorimetric data, measurements of the vapour pressure of the solid and liquid, data on dilute solutions of $NH_3(aq)$ and $HNO_3(aq)$, isopiestic and thermal data on aqueous solutions of varying concentration, and data on the concentrations and vapour pressures of saturated solutions. The data are found to be highly consistent and are sufficient to determine the dissociation constant of solid and aqueous NH_4NO_3 as a function of temperature and relative humidity with errors of 15% or less. The results may be expressed in terms of reasonably convenient equations. The dissociation constants are significantly increased when particle radii are less than 0.1 μm. More accurate data on the temperature dependence of the Henry's law constant for NH_3 would be helpful in fully accessing the accuracy of this equation.

The results obtained here are similar to those obtained by Stelson and Seinfeld (1982), although the recommended value of K_p is about 50% larger. However, their analysis suggests that there are larger discrepancies both between values of the dissociation constant of the solid as obtained from various sources and between the dissociation constant of solid NH_4NO_3 and saturated solutions of NH_4NO_3. The present analysis shows that those discrepancies are not inherent in the data.

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