The Thermochemistry of Ammonium Compounds and the Energy Barrier opposing Ammonium Ion Reorientation

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There is a good linear correlation between the energy barrier opposing cation reorientation in a compound $(NH_4)_nX$ and the quantity $\Delta(X^{n-}) = \frac{1}{n}\{\Delta H_f^\circ[(NH_4)_nX, s] - \Delta H_f^\circ(Rb_nX, s)\}$. At zero barrier height, $\Delta(X^{n-}) = 143 \pm 3$ kJ mol^{-1}. There is a sense in which depressions below this threshold are a measure of cation–anion hydrogen bonding but this sense is an unconventional one. The estimated value of $\Delta H_f^\circ(NH_4^+, g)$ derived from the threshold is 638 ± 9 kJ mol^{-1}. The correlation is also used to improve literature thermodynamic data on ammonium and alkali-metal perrhenates, *e.g.* $\Delta H_f^\circ(NH_4ReO_4, s) = -965 \pm 5$ kJ mol^{-1}. Unknown enthalpies of formation of some ammonium and rubidium salts are also predicted, and the procedure is used to explore the thermodynamic stability of non-existent solid ammonium compounds. Both metallic ammonium and ammonium hydroxide are unstable at normal pressures. The former is most unlikely to be stabilized at high pressure, but it may be possible to synthesize the hydroxide in this way. The problem of the ionic radius of NH_4^+ is also discussed.

It was recently shown,[1] for a number of ammonium compounds, that the quantity $\Delta(X^{n-})$ [equation (1)] was constant to within

$$\Delta(X^{n-}) = \tfrac{1}{n}\{\Delta H_f^\circ[(NH_4)_nX, s] - \Delta H_f^\circ(Rb_nX, s)\} \quad (1)$$

±10 kJ mol^{-1}. Such constancy can be justified by a simple ionic model. By subtraction of the Born–Haber equations for the ammonium and rubidium compounds, one obtains expression (2) where $\Delta H_L^\circ(M_nX, s)$ is the standard enthalpy of reaction (3) at 298.15 K.

$$\Delta(X^{n-}) = [\Delta H_f^\circ(NH_4^+, g) - \Delta H_f^\circ(Rb^+, g)] - \tfrac{1}{n}\{\Delta H_L^\circ[(NH_4)_nX, s] - \Delta H_L^\circ(Rb_nX, s)\} \quad (2)$$

$$M_nX(s) \longrightarrow nM^+(g) + X^{n-}(g) \quad (3)$$

In the Appendix to this paper it is shown how a simple ionic model implies that, as X^{n-} is varied, $\frac{1}{n}\{\Delta H_L^\circ[(NH_4)_nX, s] - \Delta H_L^\circ(Rb_nX, s)\}$ should remain very small and nearly constant. It follows from equation (2) that $\Delta(X^{n-})$ will then remain nearly constant, and that this constant will be very close to $[\Delta H_f^\circ(NH_4^+, g) - \Delta H_f^\circ(Rb^+, g)]$. Here, the central assumption is that, in lattice-energy calculations, the ammonium ion may be treated as a spherical, alkali-metal-type cation with an ionic radius very close to that of Rb^+.

In some cases, however, this approximation leads to serious errors. The non-spherical nature of the ammonium ion generates a specific and detectable contribution to the lattice energy which cannot be present in the corresponding rubidium compounds. A gross instance is that of NH_4F where strong hydrogen-bonding occurs between the ammonium and fluoride ions. This leads to a structure identical with that of hexagonal ice,[2] and at the same time, $\Delta(F^-)$ is only 94 kJ mol^{-1}, compared with a typical $\Delta(X^{n-})$ figure of about 130 kJ mol^{-1}.

A more thoroughly investigated example of such hydrogen bonding occurs in the CsCl structure of ammonium chloride.[3] The potential-energy barrier for the torsional oscillation of the ammonium ion about the C_2 axis is approximately 20 kJ mol^{-1}. It may be regarded as a consequence of the cation–anion hydrogen bonding which tends to lock the ammonium ion in a particular position, and to resist thermal reorientation.

In the rest of this paper a recent compilation[4] is used to calculate a wider range of $\Delta(X^{n-})$ values than that studied in ref. 1. It is suggested that there is an upper, limiting threshold value which is appropriate for the 'spherical cation' case in which the ammonium ion is freely rotating at 298.15 K. For the most part, values fall below this threshold by an amount which can be closely correlated with the estimated energy barrier opposing cation reorientation in the ammonium compound.[5] The meaning of this observation is discussed and some possible uses of it are examined.

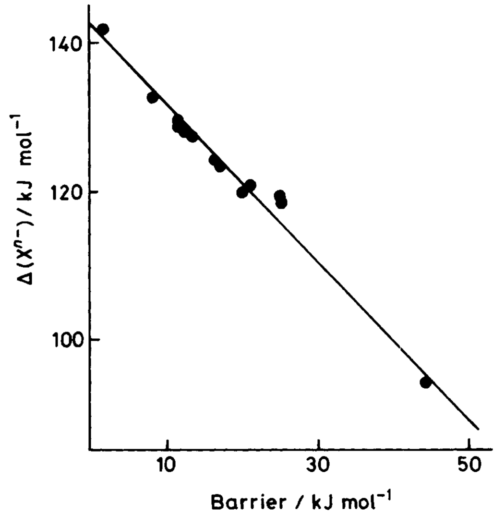

Figure. Correlation between $\Delta(X^{n-})$ and the energy barrier for cation rotation in ammonium compounds

Correlation of $\Delta(X^{n-})$ with the Energy Barrier opposing Ammonium Ion Reorientation.—Table 1 contains values of $\Delta(X^{n-})$, and of the energy barriers for cation reorientation in ammonium compounds. These data were selected using criteria given in ref. 5. The correlation is shown in the Figure. The extrapolation to zero barrier height gives $\Delta(X^{n-}) = 143$ kJ mol^{-1} which should therefore be an upper threshold. At zero barrier height, there is free rotation of the ammonium ion at normal temperatures, and the different orientations are

Table 1. Values of $\Delta(X^{n-})$ and the energy barriers to reorientation of the ammonium ion

Anion	$\Delta(X^{n-})$[a]	Energy barrier[b]	$[\Delta(T) - \Delta(X^{n-})]$[c]
		kJ mol^{-1}	
F^-	93.7	44	49
N_3^-	119.3	25	23
HF_2^-	119.7	25[d]	23
SeO_4^{2-}	119.8	20	23
Cl^-	120.9	21	22
CrO_4^{2-}	123.4	17	19
Br^-	123.8	17	19
SO_4^{2-}	127.4	14	15
I^- (1)[e]	128[f]	13	15
I^- (2)[g]	129[f]	12	14
NO_3^-	129.5	12	12
ReO_4^-	132[h]	9[i]	11
HSO_4^-	132.0	9	11
I^- (3)[j]	132.4	4	10
ClO_4^-	141.9	2	1

[a] All data from ref. 4 unless otherwise stated. [b] Ref. 3 unless otherwise stated. [c] $\Delta(T) = 143$ kJ mol^{-1}; see text. [d] E. C. Reynhardt, A. Watton, and H. E. Petch, *J. Chem. Phys.*, 1979, **71**, 4421. [e] Tetragonal low-temperature structure. [f] Data for the NaCl structure of NH_4I were corrected by the enthalpies of transition recommended in ref. 3. [g] The CsCl low-temperature structure. [h] See text. [i] See also ref. 22. [j] The NaCl structure.

energetically equivalent. In lattice-energy calculations one can then treat the cation as spherical, so the threshold value of $\Delta(X^{n-})$ is appropriate to the simple 'spherical cation' ionic model discussed earlier and used in the Appendix.

Interpretation of the correlation. The previous section implies that the spherical cation model of ammonium salts is only a limiting case for which $\Delta(X^{n-}) = 143$ kJ mol^{-1}. This threshold value will be denoted $\Delta(T)$. For the most part, the values of $\Delta(X^{n-})$ fall below it by varying amounts which are given in column 4 of Table 1 as $[\Delta(T) - \Delta(X^{n-})]$: the increase in $[\Delta(T) - \Delta(X^{n-})]$ from ClO_4^- to F^- corresponds to an increasing stabilization of the ammonium salt through an additional contribution to the lattice energy caused by the non-spherical nature of the cation. This contribution will be called ***the stabilization due to lowered cation symmetry*** (s.l.c.s.). In some cases the stabilized ammonium salt has a different crystal structure from that of the corresponding rubidium compound; in other cases, it does not. Different crystal structures occur most frequently when $[\Delta(T) - \Delta(X^{n-})]$ is large.

Table 1 shows that the values of $[\Delta(T) - \Delta(X^{n-})]$, and the energy barrier opposing cation reorientation, are usually very similar. This suggests that the s.l.c.s., and the depth of the librational potential well, are usually generated by the same types of interionic forces, and that the forces responsible for the s.l.c.s. are *comprehensively* disrupted during the librational reorientation of the cation. Comprehensive disruption is most likely if reorientation takes place by rotation about a C_2 axis. Such motion seems generally to be the case, especially in high barrier salts,[6] and in the CsCl-related structures of the ammonium halides.[3] Thus, in Table 1, the low-temperature CsCl-type forms of NH_4I satisfy the correlation, but the room-temperature rock salt structure NH_4I (3), which is not included in the Figure, does not. In NH_4I (3), an important component of the cation motion seems to be a large-amplitude libration about a single N-H $\cdots$ I axis.[7,8] It can therefore be argued that some hydrogen bonding is preserved throughout the libration, and that the energy barrier in NH_4I (3) is lower than the correlation would suggest. Further and more accurate thermodynamic data on low-barrier salts, where rotation about C_2 axes is less dominant, may reveal more departures of this kind. It is noticeable that an attempt at a linear correlation of energy barriers with $\nu_1(NH_3D^+)$ stretching frequencies breaks down when the barrier falls below about 10 kJ mol^{-1}.[9]

The suggestion that common forces contribute to the s.l.c.s. and the librational potential well does not imply that the common forces are always those of conventional hydrogen bonding. It may, for example, be possible to identify cases similar to those of the phosphonium halides where relatively high barriers of about 30 kJ mol^{-1} are said to be caused chiefly by the repulsive term in the dispersion energy.[10] The s.l.c.s. values will also include the small[11] differences in Madelung, repulsive, and dispersion energies for the real and hypothetical 'spherical cation' crystal structure, most obviously when, as discussed earlier, the two structures are different. Nevertheless, the s.l.c.s. does roughly vary in accordance with conventional expectations about relative hydrogen-bond strengths, a fact that I shall occasionally use to judge its possible size.

Although the present analysis explains why some sort of correlation between the s.l.c.s. and the energy barrier to reorientation might be expected, it is surprising that the two quantities are so nearly equal. Put another way, the *energetic* analogy between the ammonium ion at the saddle point of reorientation, and in the hypothetical spherical state, is unexpectedly close. Surprise at the quality of the correlation can only be increased by taking in the possibility of breakdowns of the NH_4I (3) type. For this reason, more extensive testing is desirable, notably on compounds for which data are either incomplete or less reliable than that of Table 1. To take a particular instance, $[\Delta(T) - \Delta(SH^-)] = 33$ kJ mol^{-1}, but the barrier to reorientation of the ammonium ion in NH_4SH is said to be only 8 kJ mol^{-1}.[12a] However, this barrier was calculated from an assignment of the librational frequency which, as the authors pointed out, was uncertain. I note here that if their assigned SH^- librational frequency is transferred to NH_4^+, and the calculation repeated, the barrier becomes 31 kJ mol^{-1} in excellent agreement with the Figure. An analysis of the temperature dependence of n.m.r. relaxation times in NH_4SH is in progress.[12b]

Applications.—The correlation in the Figure is now used to predict thermodynamic properties of both known and unknown compounds. Unless otherwise stated, all thermodynamic data are taken from ref. 4.

The value of $\Delta H^\circ_f(NH_4^+, g)$ *and of the proton affinity of ammonia.* Equation (2) is used with an estimate of the difference term $\frac{1}{n}\{\Delta H^\circ_L[(NH_4)_nX, s] - \Delta H_L(Rb_nX, s)\}$, for a specified anion. If we choose an anion for which $\Delta(X^{n-})$ is close to the spherical cation threshold, $\Delta(T)$, then the difference term has the merit of being small, and it is legitimate to estimate it by applying the simple ionic model in the Appendix. From Table 1, the obvious choice is perchlorate.

Equation (A3) is employed with an experimental value[13] of $(H^\circ_{298} - H^\circ_0)$ for NH_4ClO_4, and the figure 21.7 ± 0.6 kJ mol^{-1} for $RbClO_4$ which was obtained by interpolation of data for $KClO_4$ and $CsClO_4$. The cation radii are given in the Appendix, and the thermochemical radius of ClO_4^- is 240 pm.[14] This yields $[\Delta H^\circ_L(NH_4ClO_4, s) - \Delta H^\circ_L(RbClO_4, s)] = 6 \pm 8$ kJ mol^{-1}, where the error limits arise from an assumed possible difference of up to 10—15% in the repulsive energies. As expected, the estimated value is small. Then, from equation (2), $\Delta H^\circ_f(NH_4^+, g) = 638 \pm 9$ kJ mol^{-1} where, in line with ref. 4, the standard state of the gaseous electron is that of an ideal gas. The corresponding value of the proton affinity of ammonia, defined here as a standard (molar) enthalpy change at 298.15 K, is given in equation (4). Other recent stated or implied

$$NH_3(g) + H^+(g) \longrightarrow NH_4^+(g); \quad \Delta H^\circ_m = -852 \pm 9 \text{ kJ mol}^{-1} \qquad (4)$$

Table 2. Estimation of the standard enthalpies of formation of NH_4BF_4, NH_4PF_6, RbSCN, and CH_3CO_2Rb

X^-	Barrier	$\Delta(X^-)$[a]	$\Delta H^{\ominus}_{\mathrm{f}}(NH_4X, s)$[b]	$\Delta H^{\ominus}_{\mathrm{f}}(RbX, s)$[b]
	kJ mol^{-1}			
BF_4^-	*ca.* 2[c]	141	$-1\,739 \pm 18$[d]	$-1\,880 \pm 15$
PF_6^-	*ca.* 2[c]	141	$-2\,214 \pm 13$[d]	$-2\,354.8 \pm 8$
SCN^-	16[e]	126	-78.7 ± 8	-205 ± 13[f]
$CH_3CO_2^-$	33[g]	107	-616.1 ± 0.8	-723 ± 10[f]

[a] Estimated from column 2 using the correlation in the Figure. [b] From ref. 4 unless otherwise stated. [c] Taken to be very similar to the value for NH_4ClO_4 as suggested in ref. 3. [d] Estimated from the data in columns 3 and 5. [e] From ref. 3. [f] Estimated from the data in columns 3 and 4. [g] From ref. 6.

Table 3. U.S. National Bureau of Standards data on perrhenates[4] and recommended revised data in parentheses

Compound	State	$\Delta H^{\ominus}_{\mathrm{f}}$	$\Delta G^{\ominus}_{\mathrm{f}}$	$S^{\ominus}_{\mathrm{f}}$
		kJ mol^{-1}		J K^{-1} mol^{-1}
$KReO_4$	c	$-1\,097.0$	-994.5	167.82
		$(-1\,097.0 \pm 4)$	(-994.5 ± 4)	(167.8 ± 2)
$RbReO_4$	c	$-1\,102.9$	-996.1	167.4
		$(-1\,097 \pm 6)$	(-996 ± 5)	(184 ± 14)
NH_4ReO_4	c	-945.6	-774.7	232.6
		(-965 ± 5)	(-783 ± 5)	(193.1 ± 2)
ReO_4^-	aq	-787.4	-694.5	201.3
		(-787.4 ± 4)	(-694.5 ± 4)	(201.3 ± 2)

literature values of $\Delta H^{\ominus}_{\mathrm{f}}(NH_4^+, g)$/kJ mol^{-1} include 618 ± 6 (photoelectron spectroscopy[15]), 624 ± 8 (ion cyclotron resonance[16]), 630 ± 5 (*ab initio* molecular orbital theory[17]), 631 (lattice-energy calculations[18]), 631 ± 3 (from estimated ammonium halide hydration enthalpies[18]), 637 ± 12 (literature survey[19]), 638 ± 6 (photoionization studies[20]), and 643 ± 8 (mass spectrometry[21]). The uncertainties are those claimed by the authors. The present value lies within the upper half of this range.

Prediction of thermodynamic properties and the correction of literature data. If the correlation in the Figure is sound, then barries to reorientation in ammonium compounds can be used to estimate $\Delta H^{\ominus}_{\mathrm{f}}[(NH_4)_nX, s]$ or $\Delta H^{\ominus}_{\mathrm{f}}(Rb_nX, s)$ in cases when only one of these two standard enthalpies of formation have been experimentally determined. In Table 2, this is illustrated for the compounds NH_4BF_4, NH_4PF_6, CH_3CO_2Rb, and RbSCN.

This kind of exercise can also be used to identify suspect literature data. The energy barrier to ammonium ion reorientation in NH_4ReO_4 is about 9 kJ mol^{-1}.[3,22] The Figure then implies that $\Delta(ReO_4^-) = 133$ kJ mol^{-1}. Table 3 contains the U.S. National Bureau of Standards data[4] on potassium, rubidium, and ammonium perrhenates. They suggest that $\Delta(ReO_4^-) = 157$ kJ mol^{-1} which differs from my prediction by 24 kJ mol^{-1} and substantially exceeds the threshold limiting value of 143 kJ mol^{-1}. This discrepancy seems to be mainly due to an erroneous heat of solution derived by Smith and Long.[23] The value was obtained by plotting the solubility, rather than the solubility product, against $1/T$. The NBS data therefore need revision.

In Table 3, $\Delta H^{\ominus}_{\mathrm{f}}(KReO_4, s)$ is consistent with the calorimetric heat of solution found by Roth and Becker,[24] and $S^{\ominus}(KReO_4, s)$ is close to the recent figure obtained by Weir and Staveley.[25] No adjustment is therefore made to the $KReO_4$ data.

According to Smith and Long,[23] the solubility of NH_4ReO_4 at 298.15 K is 0.268 mol kg^{-1}. The activity coefficients for NH_4ClO_4 yield $\gamma_\pm = 0.631$ at this concentration,[26] so $\Delta G^{\ominus}_{\mathrm{m}} = 8.8 \pm 1$ kJ mol^{-1} for the process $NH_4ReO_4(s) \longrightarrow NH_4^+(aq) + ReO_4^-(aq)$. Weir and Staveley[25] give $S^{\ominus}(NH_4ReO_4, s) = 193.1 \pm 2$ J K^{-1} mol^{-1} so $\Delta H^{\ominus}_{\mathrm{m}} = 45.1 \pm 1.5$ kJ mol^{-1}. The data on $ReO_4^-(aq)$ then lead to the revised figures for NH_4ReO_4 in Table 3.

To recalculate data for $RbReO_4$, Smith and Long's solubility of 0.0379 mol kg^{-1} at 298.15 K is employed.[23] The activity coefficients of $TlClO_4$[26] then suggest that, at saturation, $\gamma_\pm \pm 0.815$, whence $\Delta G^{\ominus}_{\mathrm{m}} = 17.2 \pm 1$ kJ mol^{-1} for the solution reaction. An accurate heat of solution is not available. The solubilities[23] at 273.15, 303.15, and 323.45 K are therefore converted into solubility products by using the activity coefficients of $TlClO_4$ at 298.15 K, and then $\Delta H^{\ominus}_{\mathrm{m}}$ is determined from a plot of ln K against $1/T$. This gives $\Delta H^{\ominus}_{\mathrm{m}} = 58.5 \pm 4$ kJ mol^{-1}. The procedure ignores the significant variation of activity coefficients and $\Delta H^{\ominus}_{\mathrm{m}}$ with temperature, but when applied to $KReO_4$ and NH_4ReO_4 it yields heats of solution within less than 3 kJ mol^{-1} of my recommended values. Combining $\Delta G^{\ominus}_{\mathrm{m}}$ and $\Delta H^{\ominus}_{\mathrm{m}}$, $\Delta S^{\ominus}_{\mathrm{m}} = 139 \pm 14$ J K^{-1} mol^{-1}. These data on the solution reaction lead to the revised figures in Table 3. They imply that $\Delta(ReO_4^-) = 132 \pm 5$ kJ mol^{-1}, in very close agreement with the prediction using the Figure.

The NBS data on hexachlorotantalates(V) must also contain an error. They imply that $\Delta(TaCl_6^-) = 235$ kJ mol^{-1} which is nearly 100 kJ mol^{-1} above the present threshold value. The NBS value of $\Delta H^{\ominus}_{\mathrm{f}}(NH_4TaCl_6, s)$ suggests instability with respect to solid NH_4Cl and $TaCl_5$, and implies a $\Delta H^{\ominus}_{\mathrm{m}}$ value of only 60 kJ mol^{-1} for reaction (5). As $\Delta S^{\ominus}_{\mathrm{m}}$ should be of the order of the entropy of vaporization of $TaCl_5$ which, judging by the case of $NbCl_5$, is about 190 J K^{-1} mol^{-1}, this is refuted by the successful preparation[27] of NH_4TaCl_6 *via* the reverse reaction at about 600 K.

$$NH_4TaCl_6(s) \longrightarrow NH_4Cl(s) + TaCl_5(g) \qquad (5)$$

The thermodynamic stability of unknown ammonium compounds. Many ammonium compounds with well established alkali-metal analogues are unknown. The thermodynamic stability of these compounds can be investigated by using the relationships established in this paper. For example, with the spherical cation threshold value of $\Delta(X^-) = 143$ kJ mol^{-1}, data on rubidium analogues give, at 298.15 K, the values in equations (6)—(8). The entropy changes will be positive, and

$$NH_4H(s) \longrightarrow NH_3(g) + H_2(g); \quad \Delta H^{\ominus}_{\mathrm{m}} = -136 \text{ kJ mol}^{-1} \qquad (6)$$

$$NH_4NH_2(s) \longrightarrow 2NH_3(g); \quad \Delta H^{\ominus}_{\mathrm{m}} = -122 \text{ kJ mol}^{-1} \qquad (7)$$

$$NH_4O_2(s) \longrightarrow \tfrac{1}{2}N_2(g) + 2H_2O(l); \quad \Delta H^{\ominus}_{\mathrm{m}} = -436 \text{ kJ mol}^{-1} \qquad (8)$$

any stabilization due to hydrogen bonding should certainly be less than the $[\Delta(T) - \Delta(X^-)]$ value of 40—50 kJ mol^{-1} that I have estimated for NH_4F. It cannot therefore make the specified decompositions of these three unknown compounds thermodynamically unfavourable at room temperature and pressure.

I now turn to two unknown ammonium compounds of particular interest.

The stability of metallic ammonium. When concentrated ammonium chloride solutions are electrolysed with a mercury cathode, or treated with sodium amalgam, the mercurial phase turns black and spongy, and evolves ammonia and hydrogen gases in a 2:1 molar ratio.[28] This has been taken as a sign of the incipient formation of an amalgam of metallic ammonium, the

Table 4. Estimation of $\Delta H^{\ominus}_{m}(12)$ from $\Delta H^{\ominus}_{m}(11)$

Reaction	$\Delta H^{\ominus}_{m}$ [a]/kJ mol^{-1}
$NH_4(s, 0\ K) \longrightarrow NH_4^+(g, 0\ K) + e^-(g, 0\ K)$	493[b]
$NH_4^+(g, 0\ K) \longrightarrow NH_3(g, 0\ K) + H^+(g, 0\ K)$	846[c]
$H^+(g, 0\ K) + e^-(g, 0\ K) \longrightarrow \frac{1}{2}H_2(g, 0\ K)$	−1 528.0
$\frac{1}{2}H_2(g, 0\ K) \longrightarrow \frac{1}{2}H_2(s, 0\ K)$	−0.5[d]
$NH_3(g, 0\ K) \longrightarrow NH_3(s, 0\ K)$	−29.1[e]
$NH_4(s, 0\ K) \longrightarrow NH_3(s, 0\ K) + \frac{1}{2}H_2(s, 0\ K)$	−219[f]

[a] All data from ref. 4 unless otherwise stated. [b] Interpolated from a plot of $\Delta H^{\ominus}_{m}$ values for the analogous alkali-metal reaction at 0 K against ionic radius (see text). [c] From ref. 20; value is very close to that recommended in ref. 19 and identical with that estimated in this work. [d] From the sum of the fusion and vaporization enthalpies recommended by F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, National Bureau of Standards Circular 500, U.S. Government Printing Office, Washington, D.C., 1952. [e] Estimated by combining the enthalpies of condensation with enthalpy increments obtained from the plot of C_p *vs.* T given by R. Overstreet and W. F. Giauque (*J. Am. Chem. Soc.*, 1937, **59**, 254) with the $(H^{\ominus}_{298} - H^{\ominus}_{0})$ value for $NH_3(g)$ given by ref. 4. [f] Sum of the above.

Table 5. Various estimates of thermodynamic data for metallic ammonium, and for reaction (12) at 0 K

	$V^{\ominus}_{m}(NH_4, s, 0\ K)$	$\Delta H^{\ominus}_{m}(11)$	$\Delta H^{\ominus}_{m}(12)$[a]	$\Delta V^{\ominus}_{m}(12)$
Ref.	cm^3 mol^{-1}	kJ mol^{-1}		cm^3 mol^{-1}
33	28	563	−149	+4
34	52	521	−191	−19
34	57	517	−195	−24
35	63	499	−213	−32[b]
This work	50	493	−219	−19

[a] Calculated by combining the figures in the previous column with the auxiliary data of Table 4. [b] Using the molar volumes of $NH_3(s)$ and $H_2(s)$ recommended in the text.

pure metal being unstable at normal temperatures and pressures with respect to the reaction (9). Up until now, my

$$NH_4(s) \longrightarrow NH_3(g) + \tfrac{1}{2}H_2(g) \qquad (9)$$

estimation methods have been justified by an ionic model which cannot be applied to a metal. However, in the most general sense, they rely upon the idea that, except when there is reason to suppose that strong hydrogen bonding exists, the chemical bonding in the region of an ammonium ion resembles that of an alkali-metal cation with a radius close to that of Rb^+ when it is placed in the same environment. The spirit of the present estimation method can therefore be sustained by interpolating a plot of $\Delta H^{\ominus}_{m}(10)$ for the alkali metals against ionic radius. To

$$M(s) \longrightarrow M^+(g) + e^-(g) \qquad (10)$$

facilitate comparison with the results of other workers, the values of $\Delta H^{\ominus}_{m}(10)$ at 0 K will be used. The ionic radii are those of Shannon;[29] for NH_4^+, see the Appendix. The value $\Delta H^{\ominus}_{m}$ = 493 kJ mol^{-1} is then estimated for reaction (11). Likewise,

$$NH_4(s, 0\ K) \longrightarrow NH_4^+(g, 0\ K) + e^-(g, 0\ K) \quad (11)$$

by interpolating the low-temperature lattice parameters[30] of the alkali metals against cation radius, $V^{\ominus}_{m}(NH_4, s, 0\ K)$ = 50 cm^3 mol^{-1} is obtained. By adding $\Delta H^{\ominus}_{m}(11)$ to the $\Delta H^{\ominus}_{m}$ values of the other reactions in Table 4, $\Delta H^{\ominus}_{m}$ can be estimated for the process (12). The parameter $\Delta V^{\ominus}_{m}$ can also be obtained from the

$$NH_4(s, 0\ K) \longrightarrow NH_3(s, 0\ K) + \tfrac{1}{2}H_2(s, 0\ K) \quad (12)$$

molar volumes of solid ammonia (19.3 cm^3 mol^{-1})[31] and solid H_2 (22.9 cm^3 mol^{-1})[32] at 0 K. These estimates are the last set of data in Table 5. Table 5 also contains the results of quantum mechanical calculations: first those of Bernal and Massey,[33] then the two sets given by Stevenson,[34] and finally the values of Borshch.[35]

Bernal and Massey's work was prompted by the suggestion that metallic ammonium might be an important constituent of the interiors of Uranus and Neptune. Their results seemed to confirm this, because although $\Delta H^{\ominus}_{m}$ is negative, $\Delta V^{\ominus}_{m}$ is positive implying that, at least in the early stages of compression, the metallic phase is stabilized. Indeed, they concluded that the metal was the stable phase above a transition pressure in the 60—250 kbar range. Stevenson's and Borshch's results are quite different. The metallic phase is even less stable than predicted by Bernal and Massey, and $\Delta V^{\ominus}_{m}$ is negative. By incorporating his $\Delta H^{\ominus}_{m}$ and $\Delta V^{\ominus}_{m}$ values into estimated equations of state for the reactants and products in equation (12), Stevenson concluded that metallic ammonium could not be stabilized by pressure. My results support this, in as much as the $\Delta H^{\ominus}_{m}$ and $\Delta V^{\ominus}_{m}$ values agree quite closely with his and Borshch's.

These conclusions are consistent with failures to obtain metallic ammonium by the electrolysis of molten ammonium halides at pressures up to 200 kbar.[36] My estimates also lead to reasonable data for metallic ammonium in liquid ammonia. The parameter $\Delta G^{\ominus}_{f}(NH_4, s)$ is first computed. Comparison with the alkali metals suggests that $\Delta H^{\ominus}_{m}$ for the reaction (13) at

$$NH_4(s) \longrightarrow NH_4^+(g) + e^-(g) \qquad (13)$$

298.15 K is 5 kJ mol^{-1} greater than at 0 K. With $\Delta H^{\ominus}_{f}(NH_4^+, g)$ = 638 kJ mol^{-1}, $\Delta H^{\ominus}_{f}(NH_4, s)$ = 140 kJ mol^{-1}. By assuming that $S^{\ominus}(NH_4^+, g) = S^{\ominus}(CH_4, g)$ and interpolating $\Delta S^{\ominus}_{m}(10)$ for the alkali metals against ionic radius, we obtain $S^{\ominus}(NH_4, s)$ = 98 ± 15 J K^{-1} mol^{-1} and $\Delta G^{\ominus}_{f}(NH_4, s)$ = 217 kJ mol^{-1}. With auxiliary data[37–39] this yields $E^{\ominus}[NH_4^+(am)/NH_4(s)]$ = −2.37 V in liquid ammonia at 298.15 K, and $\Delta G^{\ominus}_{m}$ = −42 kJ mol^{-1} for the reaction (14). These values seem satisfactory. They

$$NH_4(s) \longrightarrow NH_4^+(am) + e^-(am) \qquad (14)$$

imply that metallic ammonium should be soluble in liquid ammonia, and are consistent with its absence during the decomposition of solutions of the ammoniated electron by ammonium ions. The figures are somewhat more negative than those for the alkali metals: for rubidium, the corresponding values[38,39] are −2.05 V and −12 kJ mol^{-1}. However, this is also reasonable because the ammonium ion in liquid ammonia should have its solvation energy enhanced by hydrogen bonding.

The stability of ammonium hydroxide. Solid ammonium hydroxide has not been prepared. If a liquid equimolar mixture of ammonia and water is cooled it freezes at 194.3 K to a crystalline solid[40] which contains discrete NH_3 and H_2O molecules linked together by hydrogen bonds. The formula can therefore be written as $NH_3{\cdot}H_2O(s)$. Below 194.3 K, ammonium hydroxide is presumably unstable, at 10^5 Pa, with respect to the process (15). Neglecting the s.l.c.s. in the

$$NH_4^+OH^-(s) \longrightarrow NH_3{\cdot}H_2O(s) \qquad (15)$$

ammonium compound, $\Delta H^{\ominus}_{f}(NH_4^+OH^-, s)$ = −275 kJ mol^{-1}. This figure is then combined with the data in Table 6 to obtain $\Delta H^{\ominus}_{m}(15)$ = −98 kJ mol^{-1} at the convenient temperature of 110 K. From this figure, and other data in Table 7, it is estimated that, at 110 K, $\Delta G^{\ominus}_{m}(15)$ = −98 kJ mol^{-1} and $\Delta V^{\ominus}_{m}(15) \approx$ 8 cm^3 mol^{-1}. As with metallic ammonium, the unknown compound is thermodynamically unstable at 10^5 Pa, but in this case the sign of $\Delta V^{\ominus}_{m}$ suggests that it might become stable if the pressure is

Table 6. Estimation of $\Delta H^{\ominus}_{\mathrm{m}}(15)$ at 110 K

Reaction[a]	$\Delta H^{\ominus}_{\mathrm{m}}$/kJ mol^{-1}
$NH_4{}^+OH(s) \longrightarrow NH_3{\cdot}H_2O(l)$	-86[b]
$NH_3{\cdot}H_2O(l) \longrightarrow NH_3{\cdot}H_2O(s, 110\ K)$	-26.3[c]
$NH_4{}^+OH^-(s, 110\ K) \longrightarrow NH_4{}^+OH^-(s)$	14[d]
$NH_4{}^+OH^-(s, 110\ K) \longrightarrow NH_3{\cdot}H_2O(s, 110\ K)$	-98[e]

[a] Temperatures are 298.15 K unless otherwise stated. [b] Using the value of $\Delta H_{\mathrm{f}}^{\ominus}(NH_4{}^+OH^-, s)$ estimated in the text. [c] D. L. Hildenbrand and W. F. Giauque, *J. Am. Chem. Soc.*, 1953, **75**, 28. [d] Estimated by adding the difference between the $(H^{\ominus}_{298} - H^{\ominus}_{110})$ values for NH_4ClO_4 and $KClO_4$ given in ref. 13, to that for KOH. [e] Sum of the figures above.

Table 7. Calculation of further data for reaction (15) at 110 K

$V^{\ominus}_{\mathrm{m}}(NH_4{}^+OH^-, s)$[a]/cm^3 mol^{-1}	28.4
$V^{\ominus}_{\mathrm{m}}(NH_3{\cdot}H_2O, s)$[b]/cm^3 mol^{-1}	36.8
$\Delta V^{\ominus}_{\mathrm{m}}(15)$[c]/cm^3 mol^{-1}	8.4
$\Delta G^{\ominus}_{\mathrm{m}}(15)$[d]/kJ mol^{-1}	-98

[a] By interpolation of the molar volumes of KOH and RbOH given by D. T. Amm, S. L. Segel, R. D. Heyding, and B. K. Hunter (*J. Chem. Phys.*, 1985, **82**, 2529) against the ionic radii of the Appendix, the result being corrected with a coefficient of linear expansion for KOH implied by R. G. Snyder, J. Kumamoto, and J. A. Ibers, (*J. Chem. Phys.*, 1960, **33**, 1171). [b] From ref. 40. [c] From the two preceding figures. [d] Value of $\Delta H^{\ominus}_{\mathrm{m}}$ given in the text, neglecting $T\Delta S^{\ominus}_{\mathrm{m}}$ at 110 K for the all-solid phase reaction.

increased. An estimated transition pressure can be obtained from equation (16) where P_1 = 1 bar (virtually zero) and P_2 is

$$\Delta G_{\mathrm{m}} = \Delta G^{\ominus}_{\mathrm{m}} + \int_{P_1}^{P_2} \Delta V_{\mathrm{m}} \mathrm{d}P \qquad (16)$$

the first-order transition pressure when $\Delta G_{\mathrm{m}} = 0$. As the dependence of the molar volumes of either phase on pressure is unknown, it is assumed that ΔV_{m} is constant up to pressure P_2. This yields a transition pressure in the region of 120 kbar.

The assumptions made in this calculation make it unlikely that the figure of 120 kbar has any precise significance, but because the transition pressure can be comfortably obtained in a laboratory, it suggests that the preparation of $NH_4OH(s)$ might not be out of the question. In this connection, it is interesting that the compression of water or ammonia in high-pressure adiabatic shock waves gives highly ionized fluids.[41] Consequently, the pressurized fluid 'ices', containing ammonia and water, which play a part in current models of the interiors of Uranus and Neptune,[42-44] are assumed to contain ammonium and hydroxide ions.[42]

Finally I turn to the potential sources of error in my calculation of the 120 kbar transition pressure. First, even if the crystal structures of the phases in equation (15) remain unchanged during compression, ΔV_{m} is more likely to decrease with pressure than to remain constant. A more serious objection is that the rather open structure of $NH_3{\cdot}H_2O(s)$[40] might collapse into a more compact hydrogen-bonded form at pressures below that at which proton transfer can occur. This happens with ice.[45] Both these things would tend to raise the transition pressure.

On the other hand, the failure of my assumption that the s.l.c.s. in $NH_4OH(s)$ is zero would have the opposite effect. With hydroxide anion, the s.l.c.s. would be expected to be substantial due to cation–anion hydrogen bonding, and $[\Delta(T) - \Delta(OH^-)]$ should be closer to the upper rather than the lower limit of the 0—50 kJ mol^{-1} range in Table 1. As noted earlier, $\Delta(SH^-) \approx$ 110 kJ mol^{-1}, and as cation–anion hydrogen bonding in NH_4OH is expected to be stronger than in NH_4SH, this suggests that $[\Delta(T) - \Delta(OH^-)]$ should exceed 30 kJ mol^{-1}. Such a stabilization would lower the transition pressure, an effect that would be compounded if the structure of NH_4OH could collapse to a more compact phase in which strong cation–anion hydrogen bonding were retained. This happens with NH_4F.[46]

Ultimately, therefore, the effect of increased pressure on $NH_3{\cdot}H_2O(s)$ is uncertain, but an investigation would be well worthwhile. Experiments of this type are difficult, and have so far been conducted only up to pressures of about 50 kbar.[47] They show that the melting point of $NH_3{\cdot}H_2O$ increases to about 360 K at 50 kbar, but no structural data have yet been published. Other preliminary studies suggest that, unfortunately, the material is a poor Raman scatterer.[48] Nevertheless, structural investigations of the substance at new and higher pressures are clearly a practical prospect. Even if it proved impossible to obtain a material containing NH_4 tetrahedra which justified the name, 'ammonium hydroxide', there remains the prospect of interesting new compact phases of ammonia hydrate.

Appendix

An Examination of Equation (2).—The quantity $\frac{1}{n}\Delta H_{\mathrm{L}}^{\ominus}(M_nX, s)$ can be related to the corresponding internal energy change at 0 K by the equation (A1). Unless otherwise stated, all

$$\tfrac{1}{n}\Delta H_{\mathrm{L}}^{\ominus}(M_nX, s) = \tfrac{1}{n}\Delta U_{\mathrm{L}}^{\ominus}(M_nX, s, 0\ K) + (H^{\ominus}_{298} - H^{\ominus}_{0})(M^+, g) + \tfrac{1}{n}(H^{\ominus}_{298} - H^{\ominus}_{0})(X^{n-}, g) - \tfrac{1}{n}(H^{\ominus}_{298} - H^{\ominus}_{0})(M_nX, s) \qquad (A1)$$

temperatures are 298.15 K. Subtracting the ammonium and rubidium equations, and assuming that $(H^{\ominus}_{298} - H^{\ominus}_{0})(NH_4{}^+, g) = (H^{\ominus}_{298} - H^{\ominus}_{0})(CH_4, g)$, yields equation (A2). The terms of

$$\begin{aligned}\tfrac{1}{n}\{\Delta H_{\mathrm{L}}^{\ominus}[(NH_4)_nX, s] - \Delta H_{\mathrm{L}}^{\ominus}(Rb_nX, s)\} &= \tfrac{1}{n}\{\Delta U_{\mathrm{L}}^{\ominus}[(NH_4)_nX, s, 0\ K] - \Delta U_{\mathrm{L}}^{\ominus}(Rb_nX, s, 0\ K)\} \\ &\quad - \tfrac{1}{n}\{(H^{\ominus}_{298} - H^{\ominus}_{0})[(NH_4)_nX, s] - (H^{\ominus}_{298} - H^{\ominus}_{0})(Rb_nX, s)\} \\ &\quad + 3.79\ \mathrm{kJ\ mol^{-1}} \qquad (A2)\end{aligned}$$

the type $\Delta U_{\mathrm{L}}^{\ominus}(M_nX, s, 0\ K)$ are lattice energies at 0 K. If these are approximated by two-term Kapustinskii equations,[11] equation (A3) is obtained. Here A and B are constants with the values 1.214×10^5 kJ mol^{-1} and 34.5 pm respectively.

$$\begin{aligned}\tfrac{1}{n}\{\Delta H_{\mathrm{L}}^{\ominus}[(NH_4)_nX, s] - \Delta H_{\mathrm{L}}^{\ominus}(Rb_nX, s)\} &= \left\{\frac{A(n+1)}{r(NH_4{}^+) + r(X^{n-})}\left[1 - \frac{B}{r(NH_4{}^+) + r(X^{n-})}\right] - \frac{A(n+1)}{r(Rb^+) + r(X^{n-})}\left[1 - \frac{B}{r(Rb^+) + r(X^{n-})}\right]\right\} \\ &\quad - \tfrac{1}{n}\{(H^{\ominus}_{298} - H^{\ominus}_{0})[(NH_4)_nX, s] - (H^{\ominus}_{298} - H^{\ominus}_{0})(Rb_nX, s)\} \\ &\quad + 3.79\ \mathrm{kJ\ mol^{-1}} \qquad (A3)\end{aligned}$$

For K^+, Rb^+, and Cs^+ in octahedral co-ordination, Shannon[29] recommends 138, 152, and 167 pm respectively. He declined to give a figure for $NH_4{}^+$ because of conflicting assessments by others, notably Khan and Baur.[49] However, Khan and Baur forced co-ordination numbers on the ammonium ion which were lower than those of the alkali-metal cation in an isostructural compound. For example, in KH_2PO_4, they allocated potassium a co-ordination number of eight due to eight oxygen atoms at distances in the range 282—289 pm. However in $NH_4H_2PO_4$, where the eight oxygen atoms lie 291—317 pm from the ammonium ion, they singled out the four nearest, and assign a co-ordination number of 4.[50] They thereby obtained what I believe to be artificially high values of $r(NH_4^+)$ at each listed co-ordination number. Comparisons of molar volumes of isostructural ammonium and rubidium salts[31] show that the values are very similar, but that in a substantial majority of cases that of the rubidium compound is slightly greater. This is consistent with an analysis of the cell parameters of cubic A_2MX_6 compounds[9] which gave a value of $r(NH_4^+)$ in twelve-co-ordination that was 1—5 pm less than that of Rb^+. Since a value for octahedral co-ordination is required, a figure is derived from the difference of 4 pm in the internuclear distances in the rock salt structures of ammonium and rubidium iodides.[31] With Shannon's value for Rb^+, this gives $r(NH_4^+) =$ 148 pm in octahedral co-ordination. With these radii, the first term in braces on the right-hand side of equation (A3) will be close to zero or, more precisely, will have a small positive value (with an anion radius of 200 pm, the figure is about 6 kJ mol^{-1}). Moreover, the sum of the remaining terms on the right-hand side is very small, typically within the range ±2 kJ mol^{-1} (for the bromides,[4,51] the figure is 0.14 kJ mol^{-1}). I conclude that if the ionic model represented by the two-term Kapustinskii equation is valid, then at 298.15 K, $\frac{1}{n}\{\Delta H_L^{\ominus}[(NH_4)_nX, s] - \Delta H_L^{\ominus}(Rb_nX, s)\}$ will have a small positive value which in practice will vary very little with X^{n-}.

This argument turns on equation (A3) which was derived by treating the lattice energies of ammonium and rubidium salts with the same ionic model. Because the internuclear distances or ionic radii in any pair of salts are similar, each bonding or antibonding contribution in $Rb_nX(s)$ is then matched by a very similar bonding or antibonding contribution in $(NH_4)_nX(s)$, and the two lattice energies turn out to be very nearly equal. In cases where the ammonium and rubidium salts are isostructural, such analyses can be made by extended classical calculation;[52] in cases where the salts are not isostructural, we can fall back, as here, on Kapustinskii equations,[11] when the central assumption is that in lattice-energy calculations the ammonium ion may be treated as a spherical, alkali-metal-type cation with an ionic radius very close to that of Rb^+. If, as in this Appendix, only those terms which are usually included in ionic model calculations are considered, this approximation seems a good one. Thus extended calculation of ammonium halide lattice energies with both spherical and non-spherical cation-charge distributions[18] gives values which differ by only 5—10 kJ mol^{-1}.

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