A New Cluster Pair Method of Determining Absolute Single Ion Solvation Energies Demonstrated in Water and Applied to Ammonia

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Received: August 20, 2001; In Final Form: December 3, 2001

A new method of determining standard absolute solvation energies (enthalpies and Gibbs free energies) for individual ions is presented. This method originated from the cluster pair based approximation used in earlier work [Tissandier et al., *J. Phys. Chem. A* **1998**, *102*, 7787] and is called the cluster pair correlation scheme. Unlike the earlier approximation, the new scheme makes analysis possible in solvent systems for which bulk ion-solvation data are complemented by cluster ion data, either experimental or theoretical, for clusters containing only a single solvent molecule. The correlation scheme features linear plots of half the difference between standard conventional cluster solvation energies for anions and cations containing equal numbers of solvent molecules in the cluster vs their bulk counterparts. All of the correlation lines should intersect at a point whose ordinate defines the unknown shift between the conventional and absolute energy scales, the standard absolute energy of formation of the proton. The results obtained using this correlation scheme to analyze the available cluster ion data for water are in substantial agreement with the results reported earlier using the cluster pair based approximation. Preliminary values for the standard absolute enthalpy and Gibbs free energy of ammonation of the proton are obtained when the cluster pair correlation scheme is applied to ammonia, and a clear indication is obtained of what additional data are needed to improve these preliminary estimates.

I. Introduction

The purpose of this work is to develop and illustrate a method, based on earlier work,[1] of determining standard absolute single ion energies of formation and of solvation in liquid solvents such as water and ammonia. Experimentally, energies of formation and of solvation are known in solution only for electrically neutral systems. To facilitate the tabulation of individual ionic energies in water and ammonia, conventional sets are defined with arbitrary choices made for the standard conventional energies of formation of the solvated hydrogen ion as zero,[2] i.e., $\Delta B_f^{\circ,con}$ (H^+(solv)) = 0, where *B* may be enthalpy or free energy. To be useful the conventional quantities must give the same results as their absolute counterparts for electrically neutral systems. Accordingly for water,

$$\Delta B_f^{\circ,con}(M^+(aq)) + \Delta B_f^{\circ,con}(X^-(aq)) = \Delta B_f^{\circ}(M^+(aq)) + \Delta B_f^{\circ}(X^-(aq)) \quad (1)$$

where superscript “con” denotes a conventional quantity. For M = H, eq 1 reduces to

$$\Delta B_f^{\circ,con}(X^-(aq)) = \Delta B_f^{\circ}(X^-(aq)) + \Delta B_f^{\circ}(H^+(aq)) \quad (2)$$

so that all of the standard conventional energies of formation for univalent anions in solution are shifted from their absolute counterparts by the unknown standard single ion energy of formation of the aquated hydrogen ion. In order that eq 1 be maintained for neutral pairs, all of the standard conventional energies of formation for univalent cations in solution must be shifted by an equal amount in the opposite direction. Accordingly,

$$\Delta B_f^{\circ,con}(M^+(aq)) = \Delta B_f^{\circ}(M^+(aq)) - \Delta B_f^{\circ}(H^+(aq)) \quad (3)$$

so that adding eqs 2 and 3 regenerates eq 1, as it must. Corresponding hydration energies are similarly related because for a univalent ion Z

$$\Delta B_{aq}^{\circ}(Z) = \Delta B_f^{\circ}(Z(aq)) - \Delta B_f^{\circ}(Z(g)) \quad (4)$$

and

$$\Delta B_{aq}^{\circ,con}(Z) = \Delta B_f^{\circ,con}(Z(aq)) - \Delta B_f^{\circ}(Z(g)) \quad (5)$$

Consequently, the energies of formation in eq 2 are converted to energies of hydration simply by subtracting $\Delta B_f^{\circ}(X^-(g))$ from both sides of eq 2 to get

$$\Delta B_{aq}^{\circ,con}(X^-) = \Delta B_{aq}^{\circ}(X^-) + \Delta B_f^{\circ}(H^+(aq)) \quad (6)$$

which is the analogue of eq 2 for hydration energies. Similarly, the energies of formation in eq 3 are converted to energies of hydration by subtracting $\Delta B_f^{\circ}(M^+(g))$ from both sides of eq 3 to get

$$\Delta B_{aq}^{\circ,con}(M^+) = \Delta B_{aq}^{\circ}(M^+) - \Delta B_f^{\circ}(H^+(aq)) \quad (7)$$

which is the analogue of eq 3 for hydration energies. Obviously,

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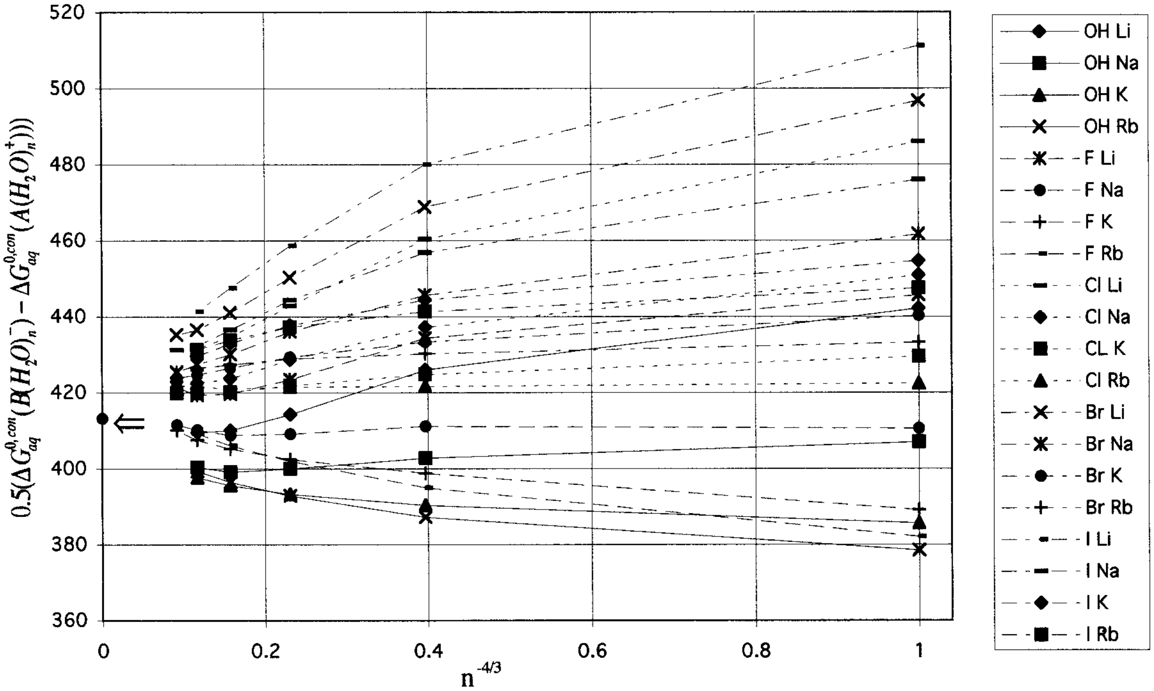

Figure 1. Half the difference between standard conventional Gibbs free energies of hydration of anions and of cations for cluster ions containing equal numbers of water molecules plotted as ordinate versus $n^{-4/3}$ as abscissa at 25.0 °C. Here, n is the number of water molecules in a cluster. These plots illustrate the apparent convergence of these differences toward the value of $\Delta G_f^{\circ}(H^+(aq))$ indicated on the y-axis at 413.2 kJ/mol.

adding eqs 6 and 7 yields the analogue of eq 1 for hydration energies,

$$\Delta B_{aq}^{o,con}(X^-) + \Delta B_{aq}^{o,con}(M^+) = \Delta B_{aq}^{\circ}(X^-) + \Delta B_{aq}^{\circ}(M^+) \tag{8}$$

Although this result is necessary and useful, it does not help in determining the absolute scale of hydration energies. For this purpose, half the difference between eqs 6 and 7,

$$\frac{1}{2}(\Delta B_{aq}^{o,con}(X^-) - \Delta B_{aq}^{o,con}(M^+)) = \frac{1}{2}(\Delta B_{aq}^{\circ}(X^-) - \Delta B_{aq}^{\circ}(M^+)) + \Delta B_f^{\circ}(H^+(aq)) \tag{9}$$

can be useful when the difference on the right-hand side (rhs) vanishes. This may occur, for example, when X^- and M^+ are spherically symmetric ions of the same size. These conditions are nearly satisfied when X^- and M^+ are large cluster ions. In fact, as noted by Klots[3]

$$\lim_{n\to\infty} it\{\Delta B_{aq}^{\circ}(B(H_2O)_n^{\,-}) - \Delta B_{aq}^{\circ}(A(H_2O)_n^{\,+})\} = 0 \tag{10}$$

so that taking the limit as $n \to \infty$ of eq 9 yields, because of eq 10,

$$\lim_{n\to\infty} it0.5\{\Delta B_{aq}^{o,con}(B(H_2O)_n^{\,-}) - \Delta B_{aq}^{o,con}(A(H_2O)_n^{\,+})\} = \Delta B_f^{\circ}(H^+(aq)) \tag{11}$$

Plots of half the difference between anions and cations of their standard conventional hydration Gibbs free energies, $0.5(\Delta G_{aq}^{o,con}(B(H_2O)_n^-) - \Delta G_{aq}^{o,con}(A(H_2O)_n^+))$, versus $n^{-4/3}$ are presented in Figure 1 to illustrate the apparent convergence of their values as n increases. (The equations used to determine $0.5(\Delta G_{aq}^{o,con}(B(H_2O)_n^-) - \Delta G_{aq}^{o,con}(A(H_2O)_n^+))$ are given in Tissandier et al.[1]) The value obtained for $\Delta G_f^{\circ}(H^+(aq))$ by using the analysis to be described is marked on the y-axis.

Note that for a given value of n in Figure 1, all of the points form a vertical line. Each of these lines passes through the value for $\Delta G_f^{\circ}(H^+(aq))$. Consequently, if the ordinates of the points in Figure 1 for each value of n could all be plotted against a common abscissa, which does not depend on n, they ought to form a family of curves, perhaps approximating straight lines, all passing through the same point whose ordinate is $\Delta G_f^{\circ}(H^+(aq))$. One of us, SM, discovered[4] such a common abscissa to be $0.5(\Delta G_{aq}^{o,con}(B^-) - \Delta G_{aq}^{o,con}(A^+))$. This common abscissa is suggested by the linear correlations shown in Figure 4 of our earlier work.[1] These are simply plots of $-(k(A^+) + k(B^-))/2 = 0.5(\Delta H_{aq}^{o,con}(B^-) - \Delta H_{aq}^{o,con}(A^+)) - \Delta H_f^{\circ}(H^+(g))$, a shifted (by $-\Delta H_f^{\circ}(H^+(g))$ version of the common abscissa used here for enthalpies, as ordinate vs the abscissas, $\Delta H_n^{\circ}(A^+) - \Delta H_n^{\circ}(B^-)$, used in the cluster pair based approximation.

Because

$$\Delta B_{aq}^{o,con}(Z(H_2O)_n) = \Delta B_{aq}^{o,con}(Z) - n\Delta B_{vap}^{\circ}(H_2O) - \sum_{i=1}^{n} \Delta B_{i-1,i}^{\circ}(Z) \tag{12}$$

for a univalent ion Z, where $\Delta B_{vap}^{\circ}(H_2O)$ is vaporization energy and $\Delta B_{i-1,i}^{\circ}(Z)$ are energies of the stepwise clustering reaction with water, the left-hand side (lhs) of eq 11 may be replaced by using eq 12 so as to lead to

$$0.5[\Delta B_{aq}^{o,con}(B^-) - \Delta B_{aq}^{o,con}(A^+) + \sum_{i=1}^{n}(\Delta B_{i-1,i}^{\circ}(A^+) - \Delta B_{i-1,i}^{\circ}(B^-))] = 0.5\sum_{i=n+1}^{\infty}(\Delta B_{i-1,i}^{\circ}(B^-) - \Delta B_{i-1,i}^{\circ}(A^+)) + \Delta B_f^{\circ}(H^+(aq)) \tag{13}$$

which is the analogue of eq 3 in ref 14 and may be converted to it by subtracting $\Delta B_f^{\circ}(H^+(g))$ from both sides. The utility of

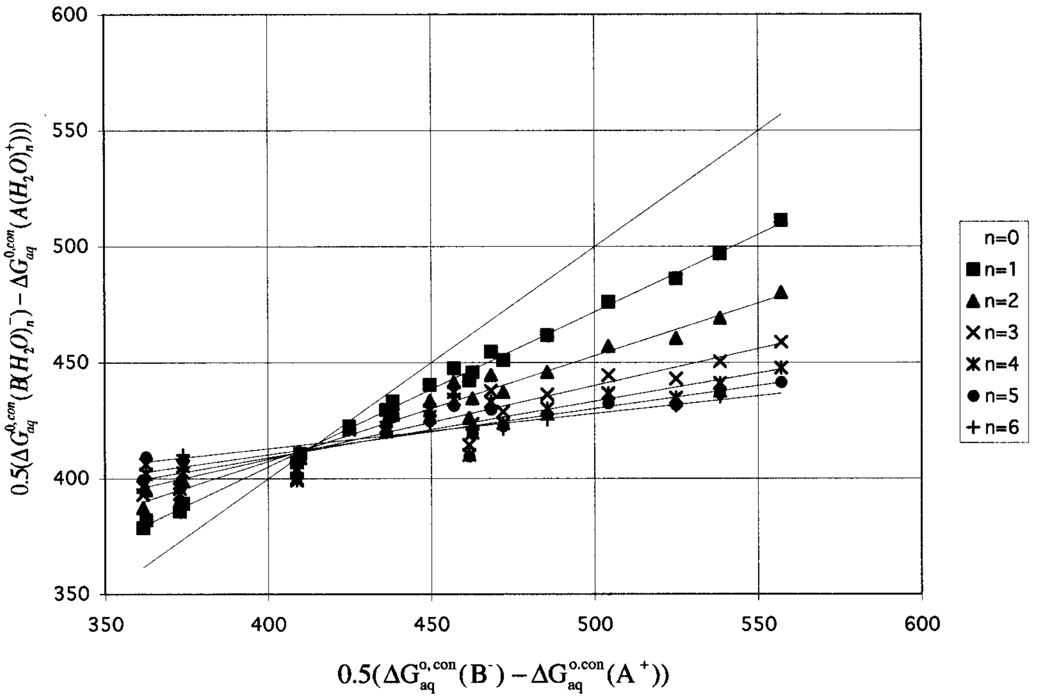

Figure 2. Half the difference between standard conventional Gibbs free energies of hydration of anions and of cations for cluster ions containing equal numbers of water molecules plotted as ordinate versus half the difference between standard conventional Gibbs free energies of hydration of anions and of cations for ions containing no water molecules at 25.0 °C.

eq 13 is two-fold. First it exhibits explicitly on its lhs the experimental quantities that determine the values that are plotted as ordinate in the cluster pair correlation scheme. Second, it exhibits on its rhs the quantity of interest, $\Delta B^{\circ}_{\mathrm{f}}(\mathrm{H}^+(\mathrm{aq}))$, with a residual sum quantifying just how much a given point deviates from it. When all the points for a fixed value of *n* are plotted, we may anticipate that the residual sum will change sign and that as a result the plotted line, whatever its form, will pass through the fixed value of $\Delta B^{\circ}_{\mathrm{f}}(\mathrm{H}^+(\mathrm{aq}))$. That this is indeed what happens for Gibbs free energies in water is substantiated through the visual inspection of Figure 1 invited above, for the point at which the residual sum changes sign is just when the line passes through $\Delta G^{\circ}_{\mathrm{f}}(\mathrm{H}^+(\mathrm{aq}))$.

Implicit in the above discussion is the fact that the chosen common abscissa, $0.5(\Delta B^{\mathrm{o,con}}_{\mathrm{aq}}(\mathrm{B}^-) - \Delta B^{\mathrm{o,con}}_{\mathrm{aq}}(\mathrm{A}^+))$, is not at all unique. As noted above, the common abscissa ought to be independent of *n*, yet any one of the differences, $\Delta B^{\circ}_{n}(\mathrm{B}^-) - \Delta B^{\circ}_{n}(\mathrm{A}^+)$, presumably could be chosen because the former differences are proportional to each of the latter. And the possibilities do not end there. Because of the well-known relationship between ionic solvation energies and ionic radii,[5-8] at least for spherically symmetric ions, $1/r_{\mathrm{A}^+} - 1/r_{\mathrm{B}^-}$ could be chosen. Given the wide variety of choice possible for a common abscissa for the correlation scheme, why choose the one that was chosen? Basically because the bulk solvation data are absolutely essential in order to implement the cluster pair correlation scheme for any given solvent, and because their use as a correlant does not imply any extrathermodynamic assumption or any special ionic shape in the scheme's implementation, as does a choice of differences of reciprocal ionic radii. True, a choice of other energy differences such as $\Delta B^{\circ}_{1}(\mathrm{B}^-) - \Delta B^{\circ}_{1}(\mathrm{A}^+)$ would also be free of the special implications just noted, but such experimental data need not be available, and even if available may not be as reliable as the differences involving bulk solvation data. Accordingly, although the choice of common abscissa that has been made is not unique it does seem to be well justified.

TABLE 1: Slopes and Intercepts of the Linear Least Squares Fits for Half the Standard, Conventional Cluster Ion Solvation Energy Differences vs the Corresponding Differences for the Bulk Solvent[a]

	free energies (kJ/mol)		enthalpies (kJ/mol)	
n	slope	intercept	slope	intercept
1	0.6679	137.9	0.6957	118.4
2	0.4545	225.6	0.5088	189.0
3	0.3180	281.1	0.3762	240.3
4	0.2431	311.8	0.2871	275.7
5	0.1987	330.8	0.2137	306.4
6	0.1514	352.3	0.2194	299.0

[a] $0.5(\Delta B^{\mathrm{o,con}}_{\mathrm{aq}}(\mathrm{B(H_2O)}_n^-) - \Delta B^{\mathrm{o,con}}_{\mathrm{aq}}(\mathrm{A(H_2O)}_n^+))$ are plotted as ordinates vs the common abscissa $0.5(\Delta B^{\mathrm{o,con}}_{\mathrm{aq}}(\mathrm{B}^-) - \Delta B^{\mathrm{o,con}}_{\mathrm{aq}}(\mathrm{A}^+))$. *B* is either Gibbs free energy, *G*, or enthalpy, *H*. The Gibbs free energy plots are shown in Figure 2. The straight line fits are referred to generically as cluster pair correlation fits.

II. Application of the Cluster Pair Correlation Scheme to Water

To test the efficacy of the new correlation scheme, it has been applied to water, for which reliable results are already available. Plots of half the difference between anions and cations of their standard conventional hydration Gibbs free energies for cluster ions versus those for $n = 0$ are shown in Figure 2. The plots for this cluster pair correlation scheme look very much like the plots for the earlier cluster pair based approximation, and the results obtained are essentially the same as those obtained previously. However, apart from the results, there are two notable differences in method. First, the abscissa for the plots is independent of *n* and second, a plot for $n = 0$ is added to those for $n = 1$ to 6. These features make the scheme applicable to systems for which sufficient cluster ion data are available for only $n = 1$, as is the case for ammonia.

The parameters characterizing the straight-line fits of Figure 2 for Gibbs free energies are given in Table 1 along with those for corresponding plots for enthalpies. The values of absolute standard Gibbs free energies and enthalpies of hydration of the

TABLE 2: Average Intersection Ordinate of the Ith Cluster Pair Correlation Straight Line with All of the Other Cluster Pair Correlation Straight Lines, Y_i, and Its Deviations from the Mean[a]

i	$Y_i(G)$	$\Delta Y_i(G)$	$W_i(G)$	$\Delta W_i(G)$	$Y_i(H)$	$\Delta Y_i(H)$	$W_i(H)$	$\Delta W_i(H)$
0	413.5	0.4	413.3	0.1	386.4	9.2	386.3	0.1
1	413.0	0.9	413.1	0.2	385.4	10.2	385.7	0.6
2	412.6	1.3	413.0	0.2	385.6	10.0	385.7	0.6
3	412.6	1.3	412.4	0.8	386.5	9.1	385.7	0.6
4	413.4	0.5	412.1	1.1	386.8	8.8	386.8	0.5
5	414.7	0.8	413.0	0.2	424.0	28.4	391.2	4.8
6	417.2	3.3	415.7	2.5	414.5	18.9	382.9	3.5
(a)[b]	413.9	1.2	413.2	0.7	395.6	13.5	386.3	1.5

[a] W_i and ΔW_i are corresponding weighted average and its deviation from the mean. The quantities in this table are calculated from the slopes and intercepts given in Table 1 with, in addition, $m_0 = 1$ and $b_0 = 0$, by using equations (A1) through (A5). [b] Each entry in row (a) is an average of the seven entries in the column above.

proton derived from the parameters in Table 1 are given in Appendix A, together with their counterparts obtained previously, for comparison (beginning with the paragraph starting just before eq A10). A notable feature of Figure 2, and of a corresponding one for enthalpies, though not shown, is that they are composed of straight lines whose slopes range from exactly one to, in the limit of $n \rightarrow \infty$, exactly zero. The former slope is exactly one because of its trivial origin of plotting a quantity against itself. The latter slope is exactly zero, but is experimentally inaccessible. Of course, every point on this straight line would have the same ordinate, equal to $\Delta B_f^\circ(H^+(aq))$, so that measurement of any point on it would yield an estimate of the quantity of interest. The lines correlating data for cluster ions appear to be straight lines (see Figure 2 for example). They exhibit positive slopes less than one (see Table 1) which values decrease monotonically with increasing n. The reversal of this trend between $n = 5$ and 6 for enthalpies is not statistically significant because the standard errors in these slopes of 0.027 and 0.062, respectively, far exceed the difference between them of 0.006. These straight-line correlations between cluster ion energy differences and their bulk counterparts, illustrated in Figure 2, lack and invite theoretical justification, but the results derived from the fitting procedure (see Table 2) do provide ample empirical justification for taking seriously our identification of the averaged ordinate (see Appendix A) of the intersection points as yielding reliable estimates of $\Delta B_f^\circ(H^+(aq))$, within experimental uncertainty.

The slopes of the linear plots in Figures 2 and 3 appear to arise because of proportionalities of absolute standard cluster ion energy differences between anions and cations to their bulk counterparts with the same slopes. The zero intercepts required by these proportionalities yield $\Delta G_f^\circ(H^+(aq)) = 413.5 \pm 1.2$ kJ/mol and $= 386.4 \pm 2.1$ kJ/mol, values which are virtually identical with the best average values from Table 2.

III. Application of the Cluster Pair Correlation Scheme to Ammonia

Even though cluster ion data for ammonia exist for anions only for $n = 1$, to go along with the data for $n = 0$, the cluster pair correlation scheme permits determination of absolute single ion standard enthalpies and Gibbs free energies, nonetheless. Had this been the case for water, the determination of the absolute quantities would have depended entirely on the intersection of the lines for $n = 0$ and $n = 1$. For water, the ordinate of this intersection for enthalpies, calculated using eq A2, is 389.1 kJ/mol, as compared to the best estimate from weighted averages in Table 2 of 386.2 kJ/mol. The analogous comparison for Gibbs free energies is between 415.2 kJ/mol from the single intersection point and 413.2 kJ/mol, the best estimate from Table 2. These comparisons suggest that even the single intersection point may be expected to provide an estimate of absolute energies within a few kJ/mol.

TABLE 3: Standard Conventional Enthalpies and Gibbs Free Energies of Ammonation for Ions and Cluster Ions in Ammonia in kJ/mol[a]

			$\Delta H_{am}^{\circ,con}(Z(NH_3))$		$\Delta G_{am}^{\circ,con}(Z(NH_3))$	
Z	$\Delta H_{am}^{\circ,con}(Z)$	$\Delta G_{am}^{\circ,con}(Z)$	expt.	calc.	expt.	calc.
H^+	−1536.2	−1516.9				
Li^+	−890.8	−874.5	−748.3	−742.8	−735.8	−731.1
Na^+	−768.8	−756.7	−666.9	−670.2	−661.3	−661.5
K^+	−683.7	−677.7	−619.5	−622.3	−616.6	−617.6
Rb^+	−653.3	−656.5	−594.9		−602.8	
F^-	(−202.0)	−75.8 (−87.8)	(−139.6)		(−13.4)	−25.7
Cl^-	−41.8	54.8	−27.3	−29.0	75.7	69.3
Br^-	−27.8	71.9	−15.4	−20.8	86.0	81.4
I^-	7.5	102.6	18.6			113.2

[a] The entries in columns 2 and 3 are calculated using eq 14 with Jolly's data[9] on the standard conventional energies of formation in ammonia and the standard energies of formation of the gas-phase ions from NBS tables.[2] The entries in columns 4, 5, 6, and 7 are calculated using eq 15 with the entries from columns 2 and 3, the enthalpy and Gibbs free energy of vaporization of ammonia at 25.0 °C of 19.8 kJ/mol and −5.7 kJ/mol, rspectively, and the relevant values of $\Delta B_{0,1}^\circ(Z;NH_3)$, experimental or calculated, given in Table 4. The parenthetical entries for F-containing species are estimates obtained by using empirical correlations (see Appendix B) of experimental data to interpolate and extrapolate the data.

The data needed to implement the cluster pair correlation scheme for ammonia[2,9−11] are collected in Table 3. The standard conventional enthalpies and Gibbs free energies of ammonation of the unclustered ions were computed using

$$\Delta B_{am}^{\circ,con}(Z) = \Delta B_f^{\circ,con}(Z(am)) - \Delta B_f^\circ(Z(g)) \qquad (14)$$

with Jolly's data[9] on the standard conventional energies of formation in ammonia and the standard energies of formation of the gas-phase ions from NBS tables.[2] The standard conventional enthalpies and Gibbs free energies of ammonation for the ammonia cluster ions[10,11] were computed using

$$\Delta B_{am}^{\circ,con}(Z(NH_3)) = \Delta B_{am}^{\circ,con}(Z) - \Delta B_{vap}^\circ(NH_3) - \Delta B_{0,1}^\circ(Z;NH_3) \qquad (15)$$

where $\Delta B_{0,1}^\circ(Z;NH_3)$ pertains to the reaction

$$Z(g) + NH_3(g) \rightarrow Z(NH_3)(g) \qquad (16)$$

Values for the standard enthalpy and Gibbs free energy of vaporization for ammonia[12] at 25.0 °C were determined to be 19.8 kJ/mol and −5.7 kJ/mol, respectively. Both experimental and calculated values for the standard enthalpies and Gibbs free energies of reaction 16 are collected in Table 4. The calculated enthalpy values were obtained with the hybrid DFT method with the 6-311++G** basis using Gaussian.[13] They include thermal and zero point energy corrections.

Cluster pair correlation plots for enthalpies in ammonia are given in Figure 3. The slopes and intercepts of the linear fits of three different sets of data points are given in Table 5 for both enthalpies and Gibbs free energies. Values of $\Delta H_f^\circ(H^+(am))$ and $\Delta G_f^\circ(H^+(am))$, as well as values of $\Delta H_{am}^\circ(H^+)$ and $\Delta G_{am}^\circ(H^+)$, calculated (see Appendix A) using these parameters are also given there.

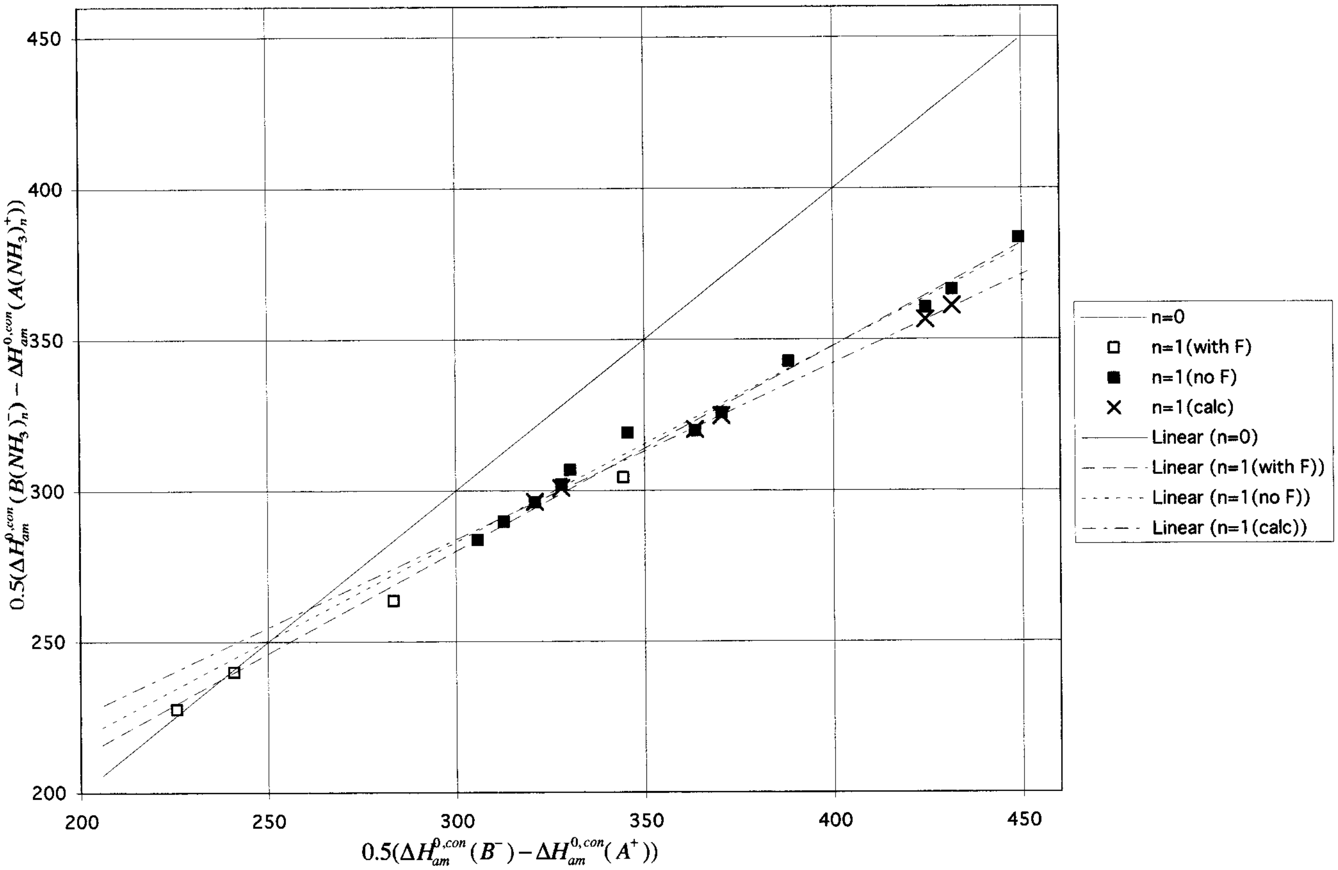

Figure 3. Half the difference between standard conventional enthalpies of ammonation of anions and of cations for cluster ions containing equal numbers of ammonia molecules plotted as ordinate versus half the difference between standard conventional enthalpies of ammonation of anions and cations for ions containing no ammonia molecules at 25.0 °C. The three dashed lines represent linear fits to different sets of data points. The line with short dashes is the linear fit to just the experimental data points which are the filled-in squares. The line with the long dashes is the linear fit to the experimental data points plus the four estimated points for fluoride which are the open squares. The line with the alternating dashes is the linear fit to the calculated data points which are represented by Xs.

TABLE 4: Experimental and Calculated Standard Enthalpies and Gibbs Free Energies for $Z(g) + NH_3(g) \rightarrow Z(NH_3)(g)$ at 25.0 °C in kJ/mol[10,11] [a]

	$\Delta H^\circ_{0,1}(Z;NH_3)$		$\Delta G^\circ_{0,1}(Z;NH_3)$	
Z	expt.	calc.	expt.	calc.
Li^+	−162.3	−167.8	−133.0	−137.7
Na^+	−121.8	−118.4	−89.7	−89.5
K^+	−84.1	−81.2	−55.4	−54.4
Rb^+	−78.2		−47.9	
F^-	(−46.0)	−72.4		−44.4
Cl^-	−34.3	−32.6	−15.1	−8.8
Br^-	−32.2	−26.8	−8.4	−3.8
I^-	−31.0			−4.9

[a] The parenthetical entry for F^- is an estimate not a measured value. It has not been used in any of our calculations. The experimental values for cations were taken from ref 10 and for anions from ref 11. The calculated enthalpy values were obtained with the hybridl DFT method B3LYP with the 6-311++G** basis using Gaussian.[13]

The three linear fits for $n = 1$ in Figure 3 pertain to different sets of data points. The set of data points depicted as filled-in squares is composed of all of the experimental points calculated using the data in Table 3. Points calculated using the estimates (the parenthetical entries in Table 3) for fluoride-containing species (see Appendix B) are represented by open squares in Figure 3. The computed data points are represented there by Xs.

The linear fit of just the experimental points, filled-in squares only, is the line made up of short dashes, $n = 1$ (no F) and excludes the estimates for F-containing species. The linear fit of the experimental points augmented by the estimates for F-containing species includes all of the square points, filled-in and open, is the line made up of long dashes, $n = 1$ (with F). The linear fit of the calculated data, marked by Xs, is the line composed of alternating long and short dashes, $n = 1$ (calc.).

Unfortunately, the calculated data set contains only six points. Even so, and despite the long extrapolation required to determine its intersection point, the resulting value of the standard absolute enthalpy of ammonation of the hydrogen ion is −1275 kJ/mol, just 10 kJ/mol above the value of −1285 kJ/mol, obtained from the much shorter extrapolation of the more numerous experimental data. When the cluster pair correlation scheme is used in conjunction with analogous calculated data in water, the magnitude of the absolute standard enthalpy of hydration is 14 kJ/mol less[14] than the 1150 kJ/mol for the magnitude of the experimental value.[1] In this light, the above comparison between calculated and experimental results for ammonia seems quite reasonable.

On the other hand, the experimental data augmented by the estimates for F-containing species yield a value of $\Delta H^\circ_{am}(H^+)$ of −1299 kJ/mol, which exceeds the experimental value in magnitude by 14 kJ/mol. Because of the uncertainties in the estimates for the F-containing species (see Appendix B) we do not conclude that this estimate of $\Delta H^\circ_{am}(H^+)$ is to be preferred over the experimental value of −1285 kJ/mol. Quite the opposite! The point to be made here is that the presence of the extra points for fluorides converts the extrapolation of the

TABLE 5: Parameters from Linear Fits of Cluster Pair Correlation Plots for Enthalpies and for Gibbs Free Energies in Ammonia. The Plots for Enthalpies Are Shown in Figure 3 (all energies are in kJ/mol)

	B = H			B = G		
	expt.[a]	expt. + F[b]	calc.[c]	expt.[a]	expt. + F[b]	calc.[c]
m_1(B)	0.6496	0.6789	0.5834	0.6165	0.6420	0.6370
b_1(B)	88.1	76,3	108.9	120.8	109.4	105.3
$\Delta B_f^\circ(H^+(am))$	251.4	237.6	261.3	315.0	305.7	290.1
$\Delta B_{am}^\circ(H^+)$	−1284.8	−1298.6	−1274.9	−1201.9	−1211.2	−1226.8

[a] Obtained from the fit of the experimental data only (filled-in squares in Figure 3 for enthalpies). [b] Obtained from the fit of the experimental data augmented by the estimates for fluoride (filled-in plus open squares in Figure 3 for enthalpies). [c] Obtained from the fit of the calculated data only (Xs in Figure 3 for enthalpies).

experimental points into an interpolation. This highlights the importance of getting actual experimental values for solution enthalpies of fluoride salts in ammonia as well as energies of clustering reactions like eq 16 for fluoride. As the results presented here clearly indicate, acquiring such data can make a substantial difference in the values obtained for standard absolute energies of formation and solvation by the application of the cluster pair correlation scheme.

In any event, these three estimates for the standard absolute enthalpy of ammonation, all using the cluster pair correlation scheme, are much greater in magnitude than the −1223 kJ/mol for this quantity obtained by adopting Jolly's assumption[15] that the absolute single ion enthalpies of Br^- and Rb^+ are equal in conjunction with the data in Table 3. A value of −1259 kJ/mol for the proton's absolute ammonation enthalpy, exceeding the above estimate in magnitude by 36 kJ/mol, results from combining Jolly's water → ammonia transfer enthalpy of −109kJ/mol with the proton's absolute hydration value of Tissandier et al.[1] of −1150 kJ/mol, but the transfer result relies on older thermodynamic data.[16] Schindewolf[17] provides an independent estimate of −1265 kJ/mol for the absolute standard enthalpy of ammonation of the proton at −40 °C. This estimate also relies on older thermodynamic data.[18] Correction of this value to 25.0 °C would no doubt produce a less negative value. The three values obtained by using the cluster pair correlation scheme span a range from −1274 kJ/mol to −1298 kJ/mol which excludes all of the earlier estimates. The most direct comparison between these two sets of results is between −1285 kJ/mol and −1223 kJ/mol, both of which have been obtained using the data given in Table 3. The former of these estimates was obtained using the cluster pair correlation scheme and the latter by using the assumption of equal absolute enthalpies of ammonation for the members of the Rb^+Br^- pair. If this assumption were correct, the cluster pair correlation plots should intersect at a point, whose ordinate is 313 kJ/mol, where B = Br and A = Rb. This is evidently not the case, as can be seen from Figure 3 in which the intersections occur well beyond all the experimental data points. In fact, the intersections occur in the neighborhood of the estimated point for B = F and A = K. Finally, the cluster pair correlation scheme yields a standard absolute enthalpy of transfer of a proton from water to ammonia of −135 kJ/mol, far in excess of the earlier estimate of −109 kJ/mol due to Jolly.[15]

Although considerable uncertainty remains in the value of $\Delta H_{am}^\circ(H^+)$ it seems reasonably certain that its true value is more negative than the value estimated by adopting Jolly's assumption.[15] For the time being, the value obtained by extrapolating the experimental data to the intersection point in Figure 3 is favored, yielding $\Delta H_{am}^\circ(H^+) = -1285 \pm 15$ kJ/mol. The corresponding absolute standard Gibbs free energy of ammonation of the proton is $\Delta G_{am}^\circ(H^+) = -1202$ kJ/mol. Evidently, reduction in the uncertainty of these energies, which may exceed 15 kJ/mol, must await the arrival of new experimental data, particularly pertaining to F^- and FNH_3^-. In addition it would be useful to have measured values of standard energy changes for the stepwise clustering reactions, $\Delta H_{n-1,n}^\circ(Z;NH_3)$ and $\Delta G_{n-1,n}^\circ(Z;NH_3)$, for anions for $n > 1$ to go along with those already measured for cations.[10] This would make possible more linear cluster pair correlation plots whose intersections contribute to determining values of the absolute energies.

Appendix A: Determination of Absolute Energies of Formation of the Hydrated Proton

Figure 2 is a graphic illustration of the application of the cluster pair correlation scheme to the Gibbs free energy data for water clusters. The data used in constructing Figure 2 was taken from ref 1. The slopes and intercepts of the straight line fits for Gibbs free energy differences in that figure are collected in Table 1 along with those for analogous straight line fits for enthalpy differences.

Representing the ordinates in these plots conveniently as y_i and the corresponding abscissas as x_i, the straight-line fits are simply written

$$y_i = m_i x_i + b_i \tag{A1}$$

where m_i and b_i are the constant slope and intercept, respectively. Values of the slopes and intercepts of the cluster pair correlation lines plotted in Figure 2 are given in Table 1. Values of the slopes and intercepts of the corresponding lines for enthalpies are also given there. The ith and jth straight lines intersect when $y_i = y_j$ and $x_i = x_j$. Imposing these conditions leads to

$$y_{ij} = (m_i b_j - m_j b_i)/(m_i - m_j) \tag{A2}$$

where y_{ij} is the ordinate of the intersection point. Each intersection point gives an estimate of the standard absolute energy of formation of the hydrated proton.

Average intersection ordinate of the ith straight line with all of the others is given by

$$Y_i(\mathrm{B}) = \frac{1}{6} \sum_{j \neq i=0}^{6} y_{ij}(\mathrm{B}) \tag{A3}$$

where B is either G or H. These average intersection ordinates with their average deviations are given in Table 2 for both Gibbs free energies and enthalpies. Also given in Table 2 are averages weighted to minimize excessive error introduced from intersections of nearly parallel lines. Note in particular the slopes for $n = 5$ and $n = 6$ for enthalpies in Table 1. The weighted averages are calculated using

$$W_i(\mathrm{B}) = \sum_{j\neq i=0}^{6} w_{ij} y_{ij}(\mathrm{B}) \tag{A4}$$

where

$$w_{ij} = |m_i - m_j| / \sum_{k=0}^{6} |m_i - m_k| \tag{A5}$$

Note that $\sum_{j=0}^{6} w_{ij} = 1$. Note also that weighting has little effect for Gibbs free energies where no near parallel lines are evident but that it does have a substantial effect for enthalpies where the $n = 5$ and $n = 6$ lines are almost parallel (see Table 2 and slopes in Table 1).

The best estimates for the absolute standard energies of formation of the aqueous proton are given in row a of Table 2:

$$\Delta G_\mathrm{f}^\circ(\mathrm{H^+(aq)}) = \frac{1}{7}\sum_{i=0}^{6} W_i(\mathrm{G}) = 413.2\ \mathrm{kJ/mol} \tag{A6}$$

with an average deviation from the mean of

$$\frac{1}{7}\sum_{i=0}^{6} \Delta W_i(\mathrm{G}) = 0.7\ \mathrm{kJ/mol} \tag{A7}$$

and

$$\Delta H_\mathrm{f}^\circ(\mathrm{H^+(aq)}) = \frac{1}{7}\sum_{i=0}^{6} W_i(\mathrm{H}) = 386.3\ \mathrm{kJ/mol} \tag{A8}$$

with an average deviation from the mean of

$$\frac{1}{7}\sum_{i=0}^{6} \Delta W_i(\mathrm{H}) = 1.5\ \mathrm{kJ/mol} \tag{A9}$$

The corresponding absolute Gibbs free energy of hydration is obtained from

$$\Delta G_\mathrm{aq}^\circ(\mathrm{H^+}) = \Delta G_\mathrm{f}^\circ(\mathrm{H^+(aq)}) + \Delta G_\mathrm{aq}^{\circ,\mathrm{con}}(\mathrm{H^+}) \tag{A10}$$

by using the value obtained above for the absolute energy of formation of the hydrated proton and the value of the conventional hydration Gibbs free energy of the proton used earlier,[1] i.e., $\Delta G_\mathrm{aq}^{\circ,\mathrm{con}}(\mathrm{H^+}) = -\Delta G_\mathrm{f}^\circ(\mathrm{H^+(g)}) = -1516.9$ kJ/mol to get

$$\Delta G_\mathrm{aq}^\circ(\mathrm{H^+}) = -1103.7 \pm 0.7\ \mathrm{kJ/mol} \tag{A11}$$

which is essentially the same as the value obtained using the cluster-pair based approximation[1] of −1104.5 kJ/mol with a standard deviation of the distribution of 0.7 kJ/mol.

Similarly, the corresponding absolute enthalpy of hydration of the proton is obtained from

$$\Delta H_\mathrm{aq}^\circ(\mathrm{H^+}) = \Delta H_\mathrm{f}^\circ(\mathrm{H^+(aq)}) + \Delta H_\mathrm{aq}^{\circ,\mathrm{con}}(\mathrm{H^+}) \tag{A12}$$

by using the value obtained above for the absolute enthalpy of formation of the hydrated proton and the value of the conventional hydration enthalpy of the proton used in the earlier work,[1] i.e., $\Delta H_\mathrm{aq}^{\circ,\mathrm{con}}(\mathrm{H^+}) = -\Delta H_\mathrm{f}^\circ(\mathrm{H^+(g)}) = -1536.2$ kJ/mol to get

$$\Delta H_\mathrm{aq}^\circ(\mathrm{H^+}) = -1149.9 \pm 1.5\ \mathrm{kJ/mol} \tag{A13}$$

which is essentially the same as the value obtained using the cluster-pair based approximation[1] of $\Delta H_\mathrm{aq}^\circ(\mathrm{H^+}) = -1150.1$ kJ/mol with a standard deviation of the distribution of 1.5 kJ/mol.

Appendix B: Method of Estimating Ammonation Energies for Fluoride-Containing Pairs of Ions

To obtain estimates of standard conventional energies of ammonation of F-containing species, advantage is taken of linear correlations that exist between hydration and ammonation energies for univalent atomic ions in electrically neutral systems. Explicitly, these linear correlations can be expressed as

$$\Delta B_\mathrm{am}^\circ(\mathrm{M^+ + X^-}) = m_n(\mathrm{B};+)\Delta B_\mathrm{aq}^\circ(\mathrm{M^+ + X^-}) + b_n(\mathrm{B};+) \tag{B1}$$

where n is the number of solvent molecules in the cluster. The linear correlations of eq B1 are used with eq 8 to obtain

$$\Delta B_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{F^-}) = m_0(\mathrm{B};+)\Delta B_\mathrm{aq}^\circ(\mathrm{A^+ + F^-}) + b_0(\mathrm{B};+) - \Delta B_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{A^+}) \tag{B2}$$

from which four separate values of $\Delta B_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{F^-})$ are obtained whose average is entered parenthetically in Table 3. Also, of course

$$\Delta B_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{FNH_3{}^-}) = m_1(\mathrm{B};+)\Delta B_\mathrm{aq}^\circ(\mathrm{AH_2O^+ + BH_2O^-}) + b_1(\mathrm{B};+) - \Delta B_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{ANH_3{}^+}) \tag{B3}$$

which provides four values of $\Delta B_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{FNH_3{}^-})$, whose average is also entered parenthetically in Table 3.

The standard error in the ordinate for these linear fits is ∼10 kJ/mol so that the estimates that are obtained cannot be considered to be very accurate. This is confirmed by the one direct comparison that can be made because $\Delta G_\mathrm{am}^{\circ,\mathrm{con}}(\mathrm{F^-})$ is known (see Table 3). Here the difference between the experimental value and the estimated value is 12 kJ/mol.

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