The Proton's Absolute Aqueous Enthalpy and Gibbs Free Energy of Solvation from Cluster-Ion Solvation Data

Michael D. Tissandier, Kenneth A. Cowen, Wan Yong Feng, Ellen Gundlach, Michael H. Cohen, Alan D. Earhart, and James V. Coe*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1173

Thomas R. Tuttle, Jr.

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254-9110

Received: June 16, 1998; In Final Form: July 27, 1998

A method is presented to determine the absolute hydration enthalpy of the proton, $\Delta H_{aq}°[\text{H}^+]$, from a set of cluster-ion solvation data without the use of extra thermodynamic assumptions. The absolute proton hydration enthalpy has been found to be ∼50 kJ/mol different than traditional values and has been more precisely determined (by about an order of magnitude). Conventional ion solvation properties, based on the standard heat of formation of $\text{H}^+(aq)$ set to zero, have been devised that may be confusing to the uninitiated but are useful in thermochemical evaluations because they avoid the unnecessary introduction of the larger uncertainties in our knowledge of absolute values. In a similar strategy, we have motivated the need for a reassessment of $\Delta H_{aq}°[\text{H}^+]$ by the trends with increased clustering in conventional cluster-ion solvation enthalpy differences for pairs of oppositely charged cluster ions. The consequences of particular preferred values for $\Delta H_{aq}°[\text{H}^+]$ may be evaluated with regard to cluster-ion properties and how they connect to the bulk. While this approach defines the problem and is strongly suggestive of the currently determined proton value, it requires extra thermodynamic assumptions for a definitive determination. Instead, a unique reassessment has been accomplished without extra thermodynamic assumptions, based on the known fraction of bulk absolute solvation enthalpies obtained by pairs of oppositely charged cluster ions at particular cluster sizes. This approach, called the cluster-pair-based approximation for $\Delta H_{aq}°[\text{H}^+]$, becomes exact for the idealized pair of ions that have obtained the same fraction of their bulk values at the same cluster size. The true value of $\Delta H_{aq}°[\text{H}^+]$ is revealed by the linear deviations of real pairs of ions from this idealized behavior. Since the approximation becomes exact for a specific pair of oppositely charged ions, the true value of $\Delta H_{aq}°[\text{H}^+]$ is expected to be commonly shared on plots of the approximation vs the difference in cluster-ion solvation enthalpy for pairs of ions sharing the same number of solvating waters. The common points on such plots determine values of -1150.1 ± 0.9 kJ/mol (esd) for $\Delta H_{aq}°[\text{H}^+]$ and -1104.5 ± 0.3 kJ/mol (esd) for $\Delta G_{aq}°[\text{H}^+]$. The uncertainties (representing only the random errors of the procedure) are smaller than expected because the cluster data of 20 different pairings of oppositely charged ions are folded into the determination.

I. Introduction

With the advent of large-cluster experiments and nanosynthetic methods,[1,2] it is currently technologically and scientifically important to characterize the variation of chemical and physical properties of clusters from small gas-phase monomers to bulk. It is important to establish in what ways cluster properties are both similar and different from their bulk counterparts. Our first step in connecting the properties of small clusters to bulk is to obtain the best bulk parameters available. The issue of absolute values for single-ion solvation properties[3] is a long-standing problem in electrochemistry for which there are a great number of proposed solutions.[4–10] In the next sections it will be shown that current literature values for the proton's absolute hydration enthalpy are likely to be inconsistent with constraints imposed by the cluster-ion thermochemical data set.

Traditional bulk measurements are performed on inherently neutral, dilute, electrolytic solutions and basically characterize the thermochemistry of pairs of oppositely charged ions. Cluster-ion experiments circumvent the bulk limitation by examining the properties of isolated single ions. In this and other cluster-ion-based work, the adopted value for the absolute solvation free energy or enthalpy of the proton is required to be consistent with both the body of cluster-ion data and bulk thermochemistry. There have been a number of observations[4,11–14] regarding the connection of stepwise cluster-ion thermochemistry to single-ion bulk solvation thermochemistry. The present work builds on these observations but avoids making assumptions that may have prevented general acceptance of the cluster-ion constrained results.

Definition of Conventional and Absolute Enthalpies and Gibbs Free Energies of Solvation. Using tabulated heats and Gibbs free energies of formation,[15,16] good values of bulk solvation free energies and enthalpies have been computed for pairs of oppositely charged ions as given in Table 1. The problem of determining absolute values can be restated as uncertainty about the fractional contribution of each member of the ion pair to the corresponding entry in Table 1. As a result, we usually find single-ion hydration enthalpies tabulated as conventional values $\Delta H_{aq}°^{,con}$ rather than absolute $\Delta H_{aq}°$. The

TABLE 1: Solvation Free Energy, $\Delta G_{aq}°(A^+ + B^-)$ (kJ/mol) = $\Delta G_{aq}°(A^+) + \Delta G_{aq}°(B^-)$, and Solvation Enthalpy, $\Delta H_{aq}°(A^+ + B^-)$ (kJ/mol) = $\Delta H_{aq}°(A^+) + \Delta H_{aq}°(B^-)$, to Place a Pair of Separate, Oppositely Charged, Gas Phase Ions into Water at 25 °C[a]

positive ion	negative ion				
	OH^-	F^-	Cl^-	Br^-	I^-
	$\Delta G_{aq}°(A^+ + B^-)$ (kJ/mol)				
H^+	−1535.3	−1533.4	−1408.7	−1382.0	−1344.6
Li^+	(−960.2)	−958.1	−833.8	−807.0	−769.5
Na^+	(−854.6)	−852.6	−728.0	−701.2	−663.9
K^+	(−782.8)	−780.8	−656.2	−629.4	−592.1
Rb^+	(−760.1)	−758.2	−633.6	−606.8	−569.4
	$\Delta H_{aq}°(A^+ + B^-)$ (kJ/mol)				
H^+	−1622.7	−1613.8	−1469.9	−1438.9	−1396.8
Li^+	−1050.7	−1041.8	−897.8	−866.8	−828.8
Na^+	−936.1	−927.3	−783.3	−752.3	−710.2
K^+	−852.7	−844.0	−700.0	−669.0	−627.0
Rb^+	−827.1	−818.9	−674.9	−643.9	−601.9

[a] Entries corresponding to strong electrolytes come from the free energies and enthalpies of formation of the corresponding salt minus that of the gas-phase ions (refs 15, 16, 28, 29, and 31). The H^+,OH^- pair corresponds to a weak electrolyte and is treated differently (ref 30). The values in parenthesis were not directly available from data in refs 15 and 16. They were determined from the differences (Table 2) that were available.

TABLE 2: Bulk Average Differences between Similarly Charged Ions from Differences in Table 1 Entries such as $\Delta G_{aq}°(A^+ + B^-) - \Delta G_{aq}°(C^+ + B^-)$ to Give $\Delta G_{aq}°(A^+) - \Delta G_{aq}°(C^+)$ (kJ/mol)

$\Delta G_{aq}°(H^+) - \Delta G°_{aq}(A^+)$			
H^+, Li^+	H^+, Na^+	H^+, K^+	H^+, Rb^+
−575.1	−680.7	−752.5	−775.2
$\Delta G_{aq}°(OH^-) - \Delta G_{aq}°(B^-)$			
OH^-, F^-	OH^-, Cl^-	OH^-, Br^-	OH^-, I^-
−2.0	−126.6	−153.4	−190.8
$\Delta H_{aq}°(H^+) - \Delta H_{aq}°(A^+)$			
H^+, Li^+	H^+, Na^+	H^+, K^+	H^+, Rb^+
−571.2	−686.6	−769.9	−795.1
$\Delta H_{aq}°(OH^-) - \Delta H_{aq}°(B^-)$			
OH^-, F^-	OH^-, Cl^-	OH^-, Br^-	OH^-, I^-
−8.7	−152.7	−183.7	−224.9

relation between absolute and conventional hydration enthalpies involves the hydrated proton's absolute formation enthalpy $\Delta H_f°[H^+(aq)]$. The formation enthalpy of $H^+(aq)$ can be broken into two steps, the formation of $H^+(g)$ and its subsequent solvation to make $H^+(aq)$:

$$\Delta H_f°[H^+(aq)] = \Delta H_f°[H^+(g)] + \Delta H_{aq}°[H^+] \quad (1)$$

The conventional energy scale is defined by $\Delta H_{aq}°^{,con}[H^+(aq)] = 0$ which is equivalent to an assignment of the conventional absolute proton hydration value to $-\Delta H_f°[H^+(g)] = -1536.2$ kJ/mol. Therefore,

$$\Delta H_{aq}°^{,con}[A^+] = \Delta H_{aq}°[A^+] - \Delta H_f°[H^+(aq)] \quad (2)$$

Using eq 1, the conventional value can be rewritten as the known difference between the bulk values for the ion and H^+ (see Table 2) and the known heat of formation[15] of $H^+(g)$ (1536.2 kJ/mol):

$$\Delta H_{aq}°^{,con}[A^+] = (\Delta H_{aq}°[A^+] - \Delta H_{aq}°[H^+]) - 1536.2 \text{ kJ/mol} \quad (3)$$

Therefore, the conventional hydration enthalpies of H^+, Li^+, Na^+, K^+, and Rb^+ are −1536.2, −965.0, −849.6, −766.3, and −741.1 kJ/mol, respectively. Similarly, for Gibbs free energies,

$$\Delta G_{aq}°^{,con}[A^+] = (\Delta G_{aq}°[A^+] - \Delta G_{aq}°[H^+]) - 1516.9 \text{ kJ/mol} \quad (4)$$

The conventional hydration Gibbs free energies for H^+, Li^+, Na^+, K^+, and Rb^+ are −1516.9, −941.8, −836.2, −764.4, and −741.7 kJ/mol, respectively.

Since the combination of positive and negative conventional ion quantities must give the same results for neutral systems as absolute ion quantities, the conventional quantities for the anions must be shifted so as to compensate for the conventional shifts of the cations, i.e., the sign of $\Delta H_f°[H^+(aq)]$ changes in the relation between conventional and absolute anion solvation enthalpy:

$$\Delta H_{aq}°^{,con}[B^-] = \Delta H_{aq}°[B^-] + \Delta H_f°[H^+(aq)] \quad (5)$$

Using eq 1, adding zero in the form of $\Delta H_{aq}°[OH] - \Delta H_{aq}°[OH^-]$, and pairing up the solvation enthalpy of H^+ and OH^- (to get a quantity available in Table 1) gives the anion conventional solvation enthalpy:

$$\Delta H_{aq}°^{,con}[B^-] = \Delta H_{aq}°[B^-] + \Delta H_f°[H^+(g)] + \Delta H_{aq}°[H^+ + OH^-] - \Delta H_{aq}°[OH^-] \quad (6)$$

where $\Delta H_{aq}°[H^+ + OH^-]$ is the sum of the bulk solvation enthalpies of H^+ and OH^-. Noting the literature value of $\Delta H_f°[H^+(g)]$ and the value of $\Delta H_{aq}°[H^+ + OH^-]$ available in Table 1, the conventional anion hydration enthalpy can be written in terms of a known difference between the bulk values of the anion and OH^- (Table 2) and a constant:

$$\Delta H_{aq}°^{,con}[B^-] = (\Delta H_{aq}°[B^-] - \Delta H_{aq}°[OH^-]) - 86.5 \text{ kJ/mol} \quad (7)$$

Therefore, the conventional hydration enthalpies of the OH^-, F^-, Cl^-, Br^-, and I^- anions are −86.5, −77.8, +66.2, +97.2, and +138.4 kJ/mol. Similarly, the conventional Gibbs free energies of hydration of the anions are

$$\Delta G_{aq}°^{,con}[B^-] = (\Delta G_{aq}°[B^-] - \Delta G_{aq}°[OH^-]) - 18.4 \text{ kJ/mol} \quad (8)$$

where the OH^-, F^-, Cl^-, Br^-, and I^- anions have values of −18.4, −16.4, +40.1, +66.9, and +104.3 kJ/mol, respectively. Conventional hydration enthalpies and Gibbs free energies are well-defined in the bulk and for many purposes can be used to avoid the unnecessary introduction of the larger errors associated with our limited knowledge of absolute values. The monomer-ion conventional quantities determined in this section provide one important quantity in the determination of the corresponding conventional quantities for the cluster ions.

Conventional Hydration Enthalpies of Clusters. It is instructive to consider the absolute vs conventional relations in view of cluster ions to see how the cluster data constrain the problem of the absolute solvation enthalpy of the proton. Uncertainty in absolute values is avoided in this exercise by

Cluster-Ion Solvation Data

J. Phys. Chem. A, Vol. 102, No. 40, 1998 **7789**

TABLE 3: Bulk Solvation Free Energy and Enthalpy of Various Ions[a] Relative to H^{+} Giving the $k(Z^{\pm})$ Constants of eq 19

ion	$\Delta G_{aq}°$ (kJ mol^{-1})	$\Delta H_{aq}°$ (kJ mol^{-1})
H^{+}	X	Y
Li^{+}	575.1+X	571.2 + Y
Na^{+}	680.7 + X	686.6 + Y
K^{+}	752.5 + X	769.9 + Y
Rb^{+}	775.2 + X	795.1 + Y
OH^{−}	−(1535.3 + X)	−(1622.7 + Y)
F^{−}	−(1533.3 + X)	−(1614.0 + Y)
Cl^{−}	−(1408.7 + X)	−(1470.0 + Y)
Br^{−}	−(1381.9 + X)	−(1439.0 + Y)
I^{−}	−(1344.5 + X)	−(1397.8 + Y)
H₃O^{+}		∼647[b]+Y

[a] All values except the last are from heats and free energies of formation in refs 15 and 16 as made available in Tables 1 and 2. [b] Assuming a thermal proton affinity of 7.16 eV.

considering the difference in properties of a pair of oppositely charged cluster ions in terms of their conventional solvation properties. As clusters ions get large, the ionic subcomponents become essentially fully solvated, leaving nothing to be accomplished by further solvation and no further differences between different ions. As noted by Klots:[4]

$$\lim_{n\to\infty}\{\Delta H_{aq}°[B^-(H_2O)_n(g)] - \Delta H_{aq}°[A^+(H_2O)_n(g)]\} = 0 \quad (9)$$

In terms of conventional values, by virtue of eqs 5, 2, and 1, the absolute hydration enthalpy of $B^-(H_2O)_n$ is $\Delta H_{aq}^{°,con}[B^-(H_2O)_n] - \Delta H_f°[H^+(g)] - \Delta H_{aq}°[H^+]$ and that of $A^+(H_2O)_n$ is $\Delta H_{aq}^{°,con}[A^+(H_2O)_n] + \Delta H_f°[H^+(g)] + \Delta H_{aq}°[H^+]$. Substituting these relations into eq 9 and solving for $\Delta H_{aq}°[H^+]$ (upon simplification, division by two, and notice of terms not dependent on clustering) produces a relation for the absolute proton solvation enthalpy in terms of the limiting difference of oppositely charged cluster-ion conventional hydration enthalpies:

$$1/2\lim_{n\to\infty}\{\Delta H_{aq}^{°,con}[B^-(H_2O)_n] - \Delta H_{aq}^{°,con}[A^+(H_2O)_n]\} - \Delta H_f°[H^+(g)] = \Delta H_{aq}°[H^+] \quad (10)$$

Cluster-ion conventional hydration enthalpies relate to the monomer-ion (Z) conventional value by

$$\Delta H_{aq}^{°,con}[Z(H_2O)_n] = \Delta H_{aq}^{°,con}[Z] - n\Delta H_{vap}°(H_2O) - \sum_{i=1}^{n}\Delta H_{i-1,i}°(Z) \quad (11)$$

where $\Delta H_{vap}°(H_2O)$ is the heat of vaporization of water and $\Delta H_{i-1,i}°(Z)$ is the stepwise enthalpy for the addition of H_2O to the cluster $Z(H_2O)_{i-1}$ to make $Z(H_2O)_i$. The $\sum_{i=1}^{n}\Delta H_{i-1,i}°(Z)$ term is a summation of stepwise enthalpies, sometimes called a partial sum. Partial sum values for different ions and cluster sizes are presented in Table 4. Conventional cluster solvation enthalpies were computed using eq 11, the data from Table 4, and the previously computed monomer conventional quantities for all of the ions under consideration.

By virtue of eq 10, it is useful to observe the behavior of $^1/_2\{\Delta H_{aq}^{°,con}[B^-(H_2O)_n] - \Delta H_{aq}^{°,con}[A^+(H_2O)_n]\} - \Delta H_f°[H^+(g)]$ vs cluster size (*n*) for various pairs of ions to see how this quantity approaches $\Delta H_{aq}°[H^+]$ as cluster size increases. A plot of this quantity vs $n^{-1/3}$ for the 20 different pairings of Li^{+}, Na^{+}, K^{+}, Rb^{+} with OH^{−}, F^{−}, Cl^{−}, Br^{−}, I^{−} is given in Figure 1. The parameter $n^{-1/3}$ was chosen because linear trends in single-

TABLE 4: Cluster-Ion Solvation Free Energy and Enthalpy Partial Sums of Various Ions vs Cluster Size[a]

ion	n = 1	2	3	4	5	6
		$\sum_{i=1}^{n}\Delta G_{i-1,i}$ (kJ mol^{-1})				
Li^{+}	−113.8	−192.9	−248.5	−279.9	−298.7	−309.2
H₃O^{+}	−100.7	−155.6	−193.6	−216.6	−233.3	−245.4
Na^{+}	−78.5	−133.7	−171.4	−196.2	−211.3	−223.4
K^{+}	−49.5	−86.7	−113.1	−131.5	−144.9	−154.5
Rb^{+}	−41.0	−70.3	−91.2	−107.1	−118.8	
OH^{−}	−74.7	−121.4	−153.6	−176.6	−194.2	
F^{−}	−79.8	−136.2	−169.9	−193.9	−211.9	−226.6
Cl^{−}	−35.9	−63.6	−84.2	−99.2	−111.9	−121.6
Br^{−}	−30.6	−53.9	−72.3	−85.1	−94.9	−102.8
I^{−}	−22.0	−38.8	−51.6	−60.7	−67.2	
H₂O	0	+6.7	+11.3	+14.6	(+16.9)[b]	(+18.5)[b]
		$\sum_{i=1}^{n}\Delta H_{i-1,i}$ (kJ mol^{-1})				
Li^{+}	−142.3	−250.2	−336.8	−405.4	−463.6	−514.2
H₃O^{+}	−144.0	−230.5	−302.0	−356.8	−407.0	−454.3
Na^{+}	−104.6	−187.4	−251.8	−307.0	−355.1	−399.9
K^{+}	−75.7	−143.1	−198.3	−247.7	−292.5	−334.3
Rb^{+}	−66.9	−123.8	−174.8	−221.7	−265.6	
OH^{−}	−109.6	−188.3	−257.7	−317.1	−376.1	
F^{−}	−97.5	−172.4	−233.1	−290.4	−344.0	−389.6
Cl^{−}	−60.2	−113.8	−162.8	−208.4	−248.1	−284.9
Br^{−}	−54.4	−104.6	−152.3	−198.3	−243.4	−286.5
I^{−}	−43.9	−84.6	−123.5	−162.0	−199.7	
H₂O	0.0	−15.7	−29.1	−45.7	(−66.4)[b]	(−88.7)[b]

[a] Ion values are averaged from data in refs 11−14. [b] Values in parentheses are estimated from the expected trend to the known bulk value of the entries up to n = 4.
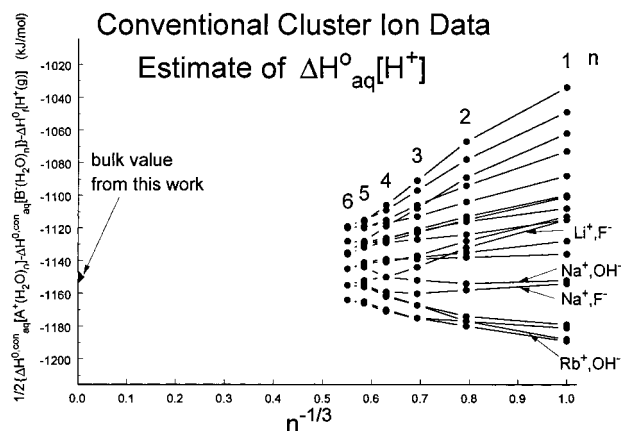

Figure 1. Plot of one-half the difference in conventional cluster hydration enthalpies minus the heat of formation of H[+](g) vs $n^{-1/3}$ for various pairs of oppositely charged cluster ions. This quantity approaches $\Delta H_{aq}°(H^+)$ in the limit as *n* goes to infinity or as $n^{-1/3}$ goes to 0 with a limiting slope of zero, so the plotted quantities can be considered estimates of the bulk $\Delta H_{aq}°(H^+)$ value which get better with increased clustering. This exercise illustrates the constraints imposed on the problem of the absolute hydration enthalpy of the proton without introducing uncertainties in the absolute single-ion quantities. It characterizes our expectations and motivates the desire for an approach without assumptions about the trends. Considerable progress is demonstrated by *n* = 6. All of the pairs of ions exhibit either increasing or decreasing monotonic trends (within 1 kJ/mol) except the Na^{+},OH^{−} and Na^{+},F^{−} pairs which exhibit flat trends. When these trends are considered with the absolute proton value of −1150 kJ/mol determined later in this paper (without extra thermodynamic assumptions about the trends), it suggests that there is gradual, steady, and predictable progress toward the bulk value and limiting slope of zero. If one preferred a bulk value near −1100 kJ/mol, for example, then there would have to be a dramatic change in the exhibited trends, which is unlikely for reasons described in the text.

ion solvation energetics are expected[17] in the large cluster size regime (at about *n* > 100 or $n^{-1/3}$ < 0.21). Upon inspection, we note: (1) rapid reduction in the range of $\Delta H_{aq}°(H^+)$ estimates

as n increases from 1 to 6 (this range in n corresponds to a bit less than one-half of the total $n^{-1/3}$ space and the single ions have obtained roughly one-half of their bulk values), (2) the range of $\Delta H_{aq}°(H^+)$ estimates at $n = 6$ are all of larger magnitude than values typically offered in the literature[18] [$\Delta H_{aq}°(H^+) \approx -1100$ kJ/mol], and (3) with the exception of the Na$^+$,OH$^-$ and Na$^+$,F$^-$ pairs which have flat trends, all of the pairs of ions exhibit either a monotonic decrease or increase of the $\Delta H_{aq}°(H^+)$ estimate (to within ~1 kJ/mol) as n increases from 1 to 6.

Hypothesis Based on the Trends of Cluster-Pair Differences Using Conventional Cluster-Ion Hydration Enthalpies. The general monotonicity of the present observations is suspected to arise from the similar functionality in the stepwise hydration of the different ions under consideration, as observed and described by Lee, Keesee, and Castleman.[14] Noting that single-ion trends have been characterized over the whole cluster size range for Gibbs free energies of solvation for a few simple ions,[17] it is observed that by taking the difference in solvation enthalpy between a pair of cluster ions vs $n^{-1/3}$, any features common to both ions are subtracted away, leaving much less structure in the trends toward the bulk than would be observed in the individual ions. In the limit of large cluster size, the solvation enthalpies (and free energies) of all ions must exhibit the same $n^{-1/3}$ slope based on the dielectric properties of the solvent,[17] so the limiting behavior of ion-pair differences upon approaching bulk in Figure 1 is a flat line with a slope of zero. If monotonic behavior toward the limiting trend has been obtained by pairing oppositely charged ions (excluding the flat trends which may have already obtained the limiting slope), then the lowest value obtained by decreasing differences (from the Li$^+$,F$^-$ pair) establishes an approximate upper bound on $\Delta H_{aq}°[H^+]$ of -1155 kJ/mol and the highest value obtained by increasing differences (from the Rb$^+$,OH$^-$ pair) establishes an approximate lower bound of -1154 kJ/mol. These two limits are (barely) mutually exclusive unless one accounts for errors in the measurements and that the trends are not complete at $n = 6$. When these results are coupled with the observation of flat trends for Na$^+$,OH$^-$ and Na$^+$,F$^-$ in the vicinity of -1150 kJ/mol, it suggests that serious attention should be given to values of $\Delta H_{aq}°(H^+)$ around -1150 kJ/mol.

Upon increased clustering, the data in Figure 1 display gradual, monotonic trends with a diminishing slope, suggesting steady and predictable progress toward the bulk slope of zero. If one prefers a bulk proton hydration value of -1100 kJ/mol, then a very different set of expectations arises. There would have to be a dramatic change in the exhibited trends. Such a change would have to be due to important generic differences in the solvation energetics (not just structures) between positive and negative ions, i.e., differences due to the sign of the charge and not the individual chemical identity of the ion. Such a change could not happen at very large cluster sizes because the limiting slope is zero. Such a change is not evident at the smallest cluster sizes. Such a change would have to happen in the intermediate cluster size regime, although no such generic differences are evident in the small cluster data. It is our supposition that such a dramatic change in the intermediate cluster size regime is unlikely. Furthermore, with increased clustering, we hypothesize that the range of absolute proton hydration estimates smoothly diminishes and that the diminished ranges of larger cluster sizes will fall inside the ranges of smaller cluster sizes.

It is the latter part of our hypothesis that motivates serious consideration of absolute bulk proton hydration values in the

vicinity of -1150 kJ/mol. We are aware of only one previously published value[6] for $\Delta H_{aq}°$ of -1153 ± 6 kJ/mol in this region. This method used the fraction of bulk solvation enthalpy obtained by pairs of oppositely charged ions at a common cluster size to predict relative differences in single-ion solvation enthalpy between oppositely charged ions at bulk. The relative differences were then commonly scaled back into a physically meaningful range at bulk in a manner consistent with the known bulk summed quantities of Table 1. The cluster-pair-based scaling and the projection back into a meaningful bulk range were assumed to be linear operations, so the final result of the work in ref 6 was conditioned on the truth of that assumption. Similarly, one could make some extra thermodynamic assumptions about the smoothness or monotonicity of the trends of the data in Figure 1 and determine a bulk proton value conditioned on those assumptions. In this work, we attempt to avoid such assumptions. The present work (1) demonstrates the linearity of the cluster-pair-based scaling, (2) makes no extra thermodynamic assumptions about cluster trends toward bulk, (3) better explains how the cluster data determine absolute bulk hydration values for the proton, (4) includes a treatment for free energies, and (5) obtains enthalpic and free energy results that are optimally compatible with the best thermochemical tabulations. Before the method can be presented, it is necessary to explain how the literature energetics on stepwise addition of solvent to ion clusters are converted to solvation energies for placing ions within neutral water clusters, i.e., the property which directly connects to a bulk solvation energy.

Converting the Energetics of Stepwise Solvent Addition to Cluster Ions into Cluster-Ion Solvation Energetics Analogous to Bulk. To compare bulk solvation values to cluster data, the extensive literature[19-24] on the energetics of stepwise addition of solvent molecules to ion−solvent clusters via

$$Z(H_2O)_{i-1} + H_2O \rightarrow Z(H_2O)_i \qquad \Delta H_{i-1,i}°(Z) \quad (12)$$

where $i = 1, 2, 3 ...$, together with a similar relation for water clusters

$$(H_2O)_{i-1} + H_2O \rightarrow (H_2O)_i \qquad \Delta H_{i-1,i}°(H_2O) \quad (13)$$
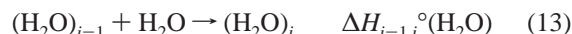
must be converted to a solvation enthalpy for placing the ion within a water cluster of size n [$\Delta H_n°(Z)$] for the following process

$$Z + (H_2O)_n \rightarrow Z(H_2O)_n \qquad \Delta H_n°(Z) \quad (14)$$
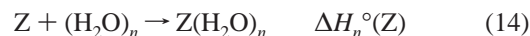
Clearly, the cluster solvation enthalpy [$\Delta H_n°(Z)$] is found by summing the stepwise enthalpies of eq 12 to build a $Z(H_2O)_n$ cluster ion with subtraction of the stepwise enthalpies to build an $(H_2O)_n$ cluster

$$\Delta H_n°(Z) = \sum_{i=1}^{n} \Delta H_{i-1,i}°(Z) - \sum_{i=1}^{n} \Delta H_{i-1,i}°(H_2O) \quad (15)$$

The summations of stepwise enthalpies (or analogously Gibbs free energies) that appear in eq 15 are called partial sums. They are given in Table 4 and are averaged results accumulated from literature values.[19-24] Note that $\Delta H_{0,1}(H_2O) = 0$ with this indexing scheme.

The neutral water cluster partial sums for $n = 2-4$ are experimental results obtained from the equilibrium measurements of Kell and McLaurin[25] on small water clusters in steam by extrapolation down to 300 K from the 425−725 K range of their measurements. For $n = 5$ and 6, the extrapolation formulas

that previously were found[6] to connect the calculated stepwise energies of Buffey and Brown[26] in an averaged way to bulk were used

$$\Delta H_{n-1,n}°[\text{H}_2\text{O}] \text{ (kJ/mol)} =$$
$$-44.0 + (57.6 \pm 8.1)[n^{2/3} - (n-1)^{2/3}] \quad (16)$$

$$\Delta G_{n-1,n}°[\text{H}_2\text{O}] \text{ (kJ/mol)} =$$
$$-8.59 + (26.6 \pm 0.5)[n^{2/3} - (n-1)^{2/3}] \quad (17)$$

The constant values -44.0 and -8.59 kJ/mol are the bulk heat and free energy of vaporization of water.[15] The other parameters were found by fitting the cluster data of Kell and McLaurin.[25] Note that the stepwise free energies for adding a water cross over from unfavorable to favorable at some intermediate cluster size (ca. $n = 10$). To get a cluster-ion solvation enthalpy [$\Delta H_n°(\text{Z})$] or free energy [$\Delta G_n°(\text{Z})$], one simply subtracts the Table 4 entry for water from the Table 4 entry for the ion of interest at the cluster size of interest. The method to be presented is not very sensitive to the water partial sum values, but their use allows for a simple comparison to bulk.

The bulk single-ion solvation enthalpy [$\Delta H_{aq}°(\text{Z})$] is the limit of the cluster value [$\Delta H_n°(\text{Z})$] as n goes to infinity

$$\Delta H_{aq}°(\text{Z}) = \lim_{n \to \infty} \Delta H_n°(\text{Z}) \quad (18)$$

In practice, the available cluster data are limited to $n < 10$ and usually $n \leq 6$, so that use of eq 18 to directly obtain absolute single-ion hydration energies is not currently possible. In the next section, a cluster-pair-based approximation is presented which enables the proton's absolute enthalpy and free energy of solvation to be determined from the cluster-ion data set.

II. Results

Finding the Best Absolute Proton Hydration Enthalpy and Free Energy: A Cluster-Pair-Based Approximation. Given the conventional monomer ion solvation enthalpies and free energies computed in the Introduction section, eqs 2 and 5 taken with the relation in eq 1 show that any absolute single-ion hydration enthalpy can be written in terms of a known constant determined from the literature and the absolute value of the proton. Therefore, the determination of the absolute value for one ion effectively determines all of the rest. In the manner of Klots,[4] the constants denoted $k(\text{Z}^\pm)$ which express the absolute bulk single-ion enthalpies (or free energies) of the various ions in terms of the unknown absolute solvation enthalpy (or free energy) of the proton are given in Table 3

$$\Delta H_{aq}°(\text{Z}^\pm) = \pm[\Delta H_{aq}°(\text{H}^+) + k(\text{Z}^\pm)] \quad (19)$$

The difference between the absolute bulk hydration enthalpy of a positive ion (A^+) and a negative ion (B^-) can be related to the bulk absolute proton value and the Table 3 constants as

$$\Delta H_{aq}°(\text{H}^+) =$$
$$\frac{1}{2}[\Delta H_{aq}°(\text{A}^+) - \Delta H_{aq}°(\text{B}^-) - k(\text{A}^+) - k(\text{B}^-)] \quad (20)$$

Knowledge of the bulk difference between any pair of oppositely charged ions would be sufficient to determine the bulk proton hydration value.

In cluster-based work,[4,6] cluster-ion solvation data are used to indicate what these differences will be at bulk. In the work of Klots,[4] it was assumed that cluster data at the size $n = 5$

was sufficient to determine the bulk difference, $\Delta H_{aq}°(\text{A}^+) - \Delta H_{aq}°(\text{B}^-)$, for certain chosen pairs of ions. Although this assumption is better than would appear upon initial inspection, it is unlikely to be valid over the set of ions with which it was employed in view of our current expectations[17] about how cluster solvation free energies proceed to bulk. More recent cluster work[6] has avoided this assumption by taking the cluster-ion solvation differences for pairs of oppositely charged ions as a relative or proportional indication of the differences at bulk. The current work expands, justifies, and more rigorously develops this strategy.

The quantity, $\Delta H_{aq}°(\text{A}^+) - \Delta H_{aq}°(\text{B}^-)$, is the key quantity missing in the bulk data, but it can be determined in a generalized fashion from the behavior of cluster-ion solvation differences over many pairs of oppositely charged ions. The above equation can be given in terms of cluster-ion quantities by defining coefficients (c_n) which represent the fraction of the bulk solvation enthalpy obtained by an ion (Z) at cluster size n

$$c_n(\text{Z}) = \frac{\Delta H_n°(\text{Z})}{\Delta H_{aq}°(\text{Z})} \quad (21)$$

where the cluster-ion solvation enthalpy [$\Delta H°_n(\text{Z})$] is defined in eqs 14 and 15. Using this relation to substitute for the bulk solvation enthalpies of eq 20 gives

$$\Delta H_{aq}°(\text{H}^+) = \frac{1}{2}\left[\frac{\Delta H_n°(\text{A}^+)}{c_n(\text{A}^+)} - \frac{\Delta H_n°(\text{B}^-)}{c_n(\text{B}^-)} - k(\text{A}^+) - k(\text{B}^-)\right] \quad (22)$$

We do not know the c_n values for the individual ions, but we do know comparable ratios for the sums of pairs of oppositely charged ions. Let the known coefficient for a pair of oppositely charged ions be given by

$$c_{n,n}(\text{A}^+,\text{B}^-) = \frac{\Delta H_n°(\text{A}^+) + \Delta H_n°(\text{B}^-)}{\Delta H_{aq}°(\text{A}^+) + \Delta H_{aq}°(\text{B}^-)} \quad (23)$$

where the denominator comes from Table 1 and the numerator from eq 15 and Table 4. The cluster-pair-based approximation to the proton solvation enthalpy can be obtained by substituting $c_{n,n}(\text{A}^+,\text{B}^-)$ for $c_n(\text{A}^+)$ and $c_n(\text{B}^-)$ in eq 22, such that

$$\Delta H_{aq}°(\text{H}^+) \approx \frac{1}{2}\left[\frac{\Delta H_n°(\text{A}^+) + \Delta H_n°(\text{B}^-)}{c_{n,n}(\text{A}^+,\text{B}^-)} - k(\text{A}^+) - k(\text{B}^-)\right] \quad (24)$$

Note that if $c_n(\text{A}^+) \neq c_n(\text{B}^-)$, one must be larger than $c_{n,n}(\text{A}^+,\text{B}^-)$ and one must be smaller. If the ordering of the bulk solvation enthalpies for A^+ and B^- is indicated at the cluster size examined, then eq 24 represents a rigorous upper or lower limit on the value of the proton solvation enthalpy, depending on only the sign of the cluster difference. However, we do not make this assumption even though it would be a good one. Most importantly, if $c_n(\text{A}^+) = c_n(\text{B}^-) = c_{n,n}(\text{A}^+,\text{B}^-)$, then eq 24 becomes an exact relation.

In the following section, we discover the circumstances in which the $c_n(\text{A}^+) = c_n(\text{B}^-) = c_{n,n}(\text{A}^+,\text{B}^-)$ condition is true which, by eq 24, provides a best value of $\Delta H_{aq}°(\text{H}^+)$. The systematic and linear deviations of the $\Delta H_{aq}°(\text{H}^+)$ cluster-pair-based approximation for various pairs of real ions are used to infer the $\Delta H_{aq}°(\text{H}^+)$ value at which it would be true. A statistical or least-squares approach is employed in recognition
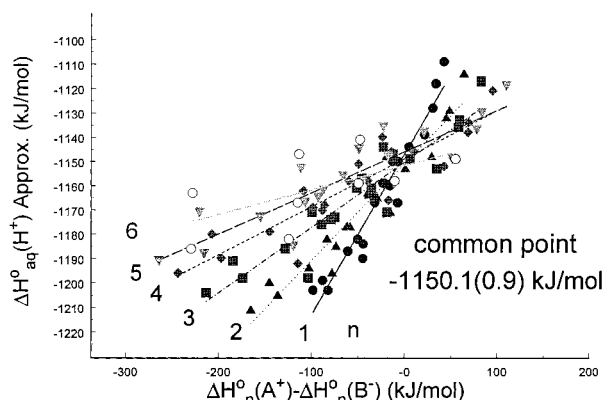
Figure 2. Cluster pair-based $\Delta H_{aq}°(H^+)$ approximation vs the difference in cluster-ion solvation enthalpy for various cluster sizes. The $\Delta H_{aq}°(H^+)$ approximation is good at only one particular pair of ions, so each data set at a particular cluster size, can be expected to share the good value in common. At each cluster size the data have been fit to a line by the method of least squares (see Table 5). The spread in these fitted lines vs the difference in cluster-ion solvation enthalpy was used to determine a most common value of -1150.1 ± 0.9 kJ/mol (esd) without invoking extra thermodynamic assumptions or upper-bound/lower-bound arguments. This value represents the best cluster-constrained value of the absolute proton hydration enthalpy and a significant reassessment of most literature values.

of the fact that there does not need to an actual pair of ions that satisfies the $c_n(A^+) = c_n(B^-) = c_{n,n}(A^+,B^-)$ relation, although there are some real pairs that come close (Na^+,F^- and Na^+,OH^-). When the approximation is examined vs cluster size, an approach independent of extra thermodynamic assumptions emerges. The results are illustrated primarily with the enthalpies, but equivalent procedures have also been carried out for the free energies.

Effect of Cluster Size on the Cluster-Pair-Based Approximation for $\Delta H_{aq}°(H^+)$ and $\Delta G_{aq}°(H^+)$: The Common Point. One interesting aspect of the cluster-pair-based approximation (eq 24) is that it does not get better as the clusters get bigger; rather it is an approximation that is good for a specific pair of oppositely charged ions (indicated statistically even if such a pair of ions does not actually exist). This consideration suggests that plots of the cluster-pair-based approximation for the proton solvation enthalpy vs cluster solvation enthalpy difference for the various pairs of oppositely charged ions at specific cluster sizes will intersect at the true $\Delta H_{aq}°(H^+)$ value (i.e., a common point) where the approximation is best. Such plots are presented in Figure 2 for the experimental cluster data out to $n = 6$ and in Figure 3 for the Gibbs free energies. The slopes and intercepts of the least-squares fitted lines are given in Table 5. The following observations have been made: (1) the cluster pair-based approximations for $\Delta H_{aq}°(H^+)$ and $\Delta G_{aq}°(H^+)$ show good linear correlations with the difference in cluster solvation enthalpy or free energy for specific cluster sizes, just as assumed in ref 6, and (2) the fitted lines for each cluster size intersect at a shared common point where the approximation becomes good.

Since there are errors in the data and the least-squares fitted lines representing the data, we must use a statistical criterion for the determination of the most common $\Delta H_{aq}°(H^+)$ approximation value. At any value of $\Delta H_n°(A^+) - \Delta H_n°(B^-)$, there are six values of the $\Delta H_{aq}°(H^+)$ approximation from each different size cluster curve (see Table 5). The magnitude of the standard deviation of these six values statistically characterizes how deviant these values are from their average. A plot of the standard deviation vs $\Delta H_n°(A^+) - \Delta H_n°(B)$ is parabolic

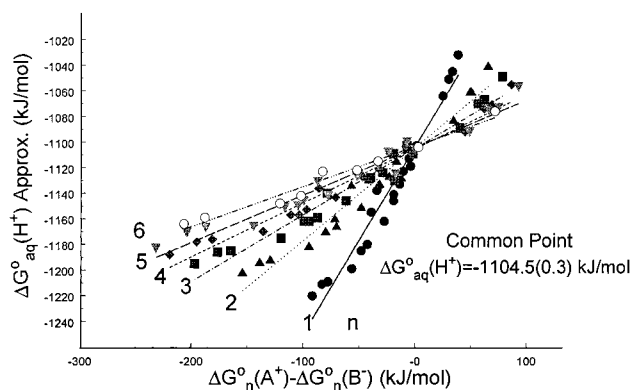**Figure 3.** Cluster-pair-based $\Delta G_{aq}°(H^+)$ approximation vs the difference in cluster-ion solvation free energy for various cluster sizes. The $\Delta G_{aq}°(H^+)$ approximation curves for different cluster sizes share a common point where the approximation is best. The common point determines an absolute proton hydration free energy of -1104.5 ± 0.3 kJ/mol (esd) without invoking extra thermodynamic assumptions or upper-bound/lower-bound arguments. This value compares favorably to the center-of-weight of previous determinations.

TABLE 5: Slopes and Intercepts of the $\Delta H_{aq}°(H^+)$ and $\Delta G_{aq}°(H^+)$ Approximations vs the Difference in Cluster Solvation Enthalpy or Free Energy for Different Cluster Sizes, n^a

	enthalpies		free energies	
n	slope	intercept (kJ/mol)	slope	intercept (kJ/mol)
1	0.659(0.039)	−1147.2(1.8)	1.455(0.072)	−1104.3(3.1)
2	0.397(0.026)	−1150.9(2.0)	0.725(0.034)	−1104.5(2.5)
3	0.268(0.024)	−1150.4(2.3)	0.520(0.025)	−1105.0(2.3)
4	0.198(0.021)	−1148.9(2.3)	0.423(0.018)	−1105.3(2.1)
5	0.169(0.019)	−1146.0(2.3)	0.371(0.018)	−1104.4(1.9)
6	0.101(0.048)	−1151.7(6.2)	0.314(0.021)	−1103.4(2.4)

^{a} Estimated standard deviations are given in parenthesis.

TABLE 6: Absolute Single-Ion Bulk Solvation Free Energies, $\Delta G_{aq}°$ (kJ/mol), and Enthalpies, $\Delta H_{aq}°$ (kJ/mol), Determined with the Cluster-Pair-Based Approximation^a

ion	$\Delta G_{aq}°$ (kJ/mol) this work^b	$\Delta H_{aq}°$ (kJ/mol) this work^b	$\Delta H_{aq}°$ (kJ/mol) ref 6
H^+	−1104.5(0.3)	−1150.1(0.9)	−1152.6(6.0)
Li^+	−529.4	−578.9	−576.1(5.5)
H_3O^+		−503^c	−513.4(7.1)
Na^+	−423.8	−463.5	−466.5(3.0)
OH^-	−430.8	−472.6	−479.5(4.9)
F^-	−428.8	−463.9	−456.9(10.6)
K^+	−352.0	−380.2	−381.3(3.9)
Rb^+	−329.3	−355.0	−357.9(4.3)
Cl^-	−304.2	−319.9	−316.3(8.1)
Br^-	−277.4	−288.9	−282.7(9.3)
I^-	−240.0	−247.7	−245.9(8.0)
σ (kJ/mol)	0.1	0.8	5.6^d

^{a} The σ value given at the bottom represents the standard deviation of comparison of each data set when the oppositely charged ions are paired for comparison to the entries in Table 1. ^{b} Single-ion values from this work should be cited with uncertainties of about ±8 kJ/mol by comparison to the more rigorous error analysis of ref 6. ^{c} Calculated using current the NIST web page value of 691 kJ/mol for the room-temperature proton affinity of water. ^{d} This value was 2.4 kJ/mol with the alternative bulk set used in ref 6.

with a minimum at $\Delta H_n°(A^+) - \Delta H_n°(B) = -3$ kJ/mol, which is only slightly shifted from the intercept. The best or most common $\Delta H_{aq}°(H^+)$ approximation value is the average of the six values with the smallest standard deviation. The six $\Delta H_{aq}°$-(H^+) approximation values at $\Delta H_n°(A^+) - \Delta H_n°(B) = -3$ kJ/

Cluster-Ion Solvation Data

J. Phys. Chem. A, Vol. 102, No. 40, 1998 **7793**

mol, are -1149.2, -1152.1, -1151.2, -1149.5, -1146.5, and -1152.0 kJ/mol for *n* values of $1-6$, respectively. The average of these values is -1150.1 kJ/mol with a minimum standard deviation of 2.1 kJ/mol and a standard deviation of the mean of $2.1/\sqrt{6} \approx 0.9$ kJ/mol. We take -1150.1 ± 0.9 kJ/mol (esd) as our best determination of the proton hydration enthalpy. The free energies show an even more consistent behavior than the enthalpies, exhibiting a minimum standard deviation of $0.7/\sqrt{6}$ kJ/mol at a $\Delta G_{aq}°(H^+)$ approximation value of -1104.5 kJ/mol and $\Delta G_n°(A^+) - \Delta G_n°(B) = 0$ kJ/mol, i.e., no offset from the intercept. The value of -1104.5 ± 0.3 kJ/mol (esd) is taken as our best value of the absolute proton hydration free energy.

Why the $\Delta H_{aq}°(H^+)$ Cluster-Pair-Based Approximation Works: The $-[k(A^+) + k(B^-)]/2$ Correlation with Cluster Solvation Enthalpy Differences. In this work, the behavior of the summed solvation energies of a pair of oppositely charged ions relative to the known sum of the bulk quantities is used as an indication of the cluster behavior of each individual member of the pair. The linearity of the deviations of the approximation from the true proton values reveals the point at which the approximation is best, i.e., the method reveals the deviations of real pairs of ions from the idealized pair of oppositely charged ions that make equal fractional contributions to their bulk values at equal cluster sizes. The quality of the cluster-pair-based approximation actually has very little impact on the results determined in this work. A plot of $1/c_{n,n}(A^+,B^-)$ vs $\Delta H_n°(A^+) - \Delta H_n°(B^-)$ is basically constant, although a different constant exists for any particular value of *n*. Therefore, the first term in eq 24 is simply linear in $\Delta H_n°(A^+) - \Delta H_n°(B^-)$ and will contribute a value of zero to the $\Delta H_{aq}°(H^+)$ approximation at the intercept, which is very close to the common point. The determination of the best $\Delta H_{aq}°(H^+)$ value comes almost entirely from the latter terms in eq 24 consisting of $-[k(A^+) + k(B^-)]/2$. These constants are well-known bulk values, are made available in Table 3, and are not determined by the cluster data. To demonstrate this, the quantity $-[k(A^+) + k(B^-)]/2$ is plotted against $\Delta H_n°(A^+) - \Delta H_n°(B^-)$ in Figure 4 revealing very linear relations whose intercepts essentially determine the proton's hydration enthalpy. Using least-squares fitted lines to characterize the data sets at each cluster size, the most common point is found to be -1150.2 ± 0.8 kJ/mol at a position offset by only 1.8 kJ/mol in the difference in cluster solvation enthalpy. This is essentially the same value obtained by the full cluster-pair-based approximation. Therefore, it is the correlation of the known parts (the $k(Z)$ constants from Table 3) of the single-ion hydration enthalpies with the difference in cluster solvation enthalpies that determines the proton's value, not the cluster approximation, i.e., the cluster approximation makes a zero contribution to $\Delta H_{aq}°(H^+)$ at the point where the approximation is valid. The cluster approximation simply allows these correlations to be made evident.

III. Discussion

The value of $\Delta H_{aq}°[H^+] = -1150.1 \pm 0.9$ kJ/mol (esd reflecting random errors only) obtained by the cluster-pair-based approximation is greater in magnitude than most literature values and constitutes an important reassessment of this value. This value was obtained without extra thermodynamic assumptions, including assumptions about the smoothness or monotonicity of the trends in Figure 1 (data based on the difference in conventional cluster-ion solvation enthalpies). It implies that there are no surprises in the larger cluster size trends in Figure 1 and that the bulk value falls comfortably within the range of estimates at $n = 6$ as hypothesized. The pairing of oppositely
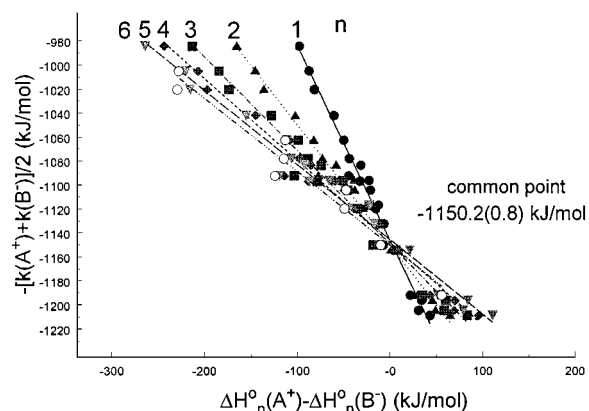

Figure 4. Dependence of the bulk constants, $-[k(A^+) + k(B^-)]/2$, on the difference in cluster solvation enthalpy at different cluster sizes. The cluster-pair-based approximation employed in this work involves only the first term of eq 24, which is essentially zero at the common point, so the proton's absolute value is determined almost entirely by the behavior of the bulk constants from Table 3 vs the difference in cluster solvation enthalpy. Notice the linearity of the data sets at particular cluster sizes and the shared common point at -1150.2 ± 0.8 kJ/mol, which is the same as the value determined by the full cluster-pair-based approximation for the proton's absolute hydration enthalpy. The fitted lines have slopes of $-1.615(0.050)$, $-0.998(0.034)$, $-0.782(0.030)$, $-0.685(0.025)$, $-0.622(0.022)$, and $-0.613(0.049)$ for $n = 1-6$, respectively, and intercepts of $-1146.4(2.3)$, $-1150.5(2.6)$, $-1149.9(2.9)$, $-1148.5(2.7)$, $-1145.8(2.6)$, and $-1150.6(6.4)$ kJ/mol for $n = 1-6$, respectively, with estimated first standard deviations in parentheses.

charged ions subtracts a fair amount of common energetic behavior, producing gradual, generally monotonic trends with diminishing slope and steady predictable progress toward the bulk value and the limiting slope of zero in Figure 1. There are a number of literature values of $\Delta H_{aq}°[H^+]$ near -1100 kJ/mol,[18] which would require dramatically different behavior in the intermediate cluster size regime. The presently determined value is not inconsistent with several other literature values if an attempt is made to estimate their uncertainties. Any set of single-ion hydration enthalpies can be compared to bulk by adding the values of oppositely charged pairs in the set for comparison to the summed values in Table 1. The standard deviation of comparison to Table 1 of literature single-ion data sets has been used as an estimate of the error in the corresponding absolute proton value. Keeping in mind that the errors are from the above stated criteria and not the cited work, the present result can be compared to the values of -1129 ± 32 kJ/mol from Friedman and Krishnan[7] and -1136 ± 9 kJ/mol from Klots.[4] The present result is in excellent agreement with the value of -1153 ± 6 kJ/mol determined by Coe[6] in which the cluster-pair scaling was assumed (rather than demonstrated) to be linear. These results agree even though ref 6 employed an alternative enthalpic bulk data set based on lattice enthalpies, heats of solution, and bond dissociation enthalpies, as opposed to the heat of formation tables. Finally, the experimental enthalpic data set of Randles[10] shows a standard deviation of comparison to Table 1 of 12 kJ/mol. Each of Randles' single-ion enthalpy values has been used to determine an absolute solvation enthalpy of the proton whose average value with the above standard deviation estimate suggest a value of -1131 ± 12 kJ/mol for the proton's hydration enthalpy. The experiment does not account for the surface potential of water (~ 13 kJ/mol[27]), but if it is considered, the present results and experiment are in good agreement, i.e., the current results taken with Randle's data suggest a surface potential of water of 19 ± 12 kJ/mol.

The presently obtained value of $\Delta G_{aq}°[H^+] = -1104.5 \pm 0.3$ kJ/mol (esd reflecting random errors only) obtained by the cluster-pair-based approximation compares favorably to the center of weight of determinations in the chronological survey of Friedman and Krishnan (see Figure 5 in ref 7, Chapter 1, p 25). Again, using the standard deviation of comparison to Table 1 of literature single-ion data sets as an estimate of the error in the corresponding absolute proton value, the present result can be compared to -1059 ± 43 kJ/mol from Gomer and Tryson,[8] -1066 ± 8 kJ/mol from Conway,[9] and -1098 ± 9 kJ/mol from Klots[4] (to pick just a few). In general, there is less information available for the free energy determinations than for enthalpies. Unlike the enthalpies, there exists no alternative set of free energy tabulations that allows one to check the data. Also, some of the bulk free energy entries in Table 1, the ones given in parentheses, are missing from the presently used free energy of formation tabulations.[15,16] They have been determined from the differences in Table 1 as presented in Table 2. In view of these considerations, it is reassuring that the common point of the cluster-pair-based approximation for the proton's absolute Gibbs free energy of hydration is even better determined than that of the enthalpies.

It is noteworthy that the same common point (or bulk proton value) is obtained (see Figures 2 and 4) by the cluster-pair-based common point method even when the cluster ion term of eq 24 is ignored! Clearly, the cluster-ion term goes to zero when the approximation becomes good. Furthermore, it is the correlation between the bulk constants, $-[k(A^+) + k(B^-)]/2$, from Table 3 and the difference in cluster-ion solvation enthalpy or free energy that critically determines the absolute proton value. The cluster pair-based approximation is different than other cluster approaches since it does not get better with increased cluster size. In contrast, it becomes good for one idealized pair of oppositely charged ions (ones that have obtained the same fraction of their bulk hydration values at a given cluster size). The linear deviations from this ideal exhibited by real pairs of ions allow the idealized behavior to be deduced. It is the Na^+, F^- and Na^+, OH^- pairs that are closest to this idealized pair and these pairs are also the ones showing flat trends in Figure 1.

The cluster-pair-based method successfully determines the proton's absolute enthalpy and Gibbs free energy of hydration without invoking extra thermodynamic assumptions. The presently determined set of single-ion values is (1) consistent with experiment when surface potentials are considered, (2) completely consistent with bulk thermochemical tabulations as only literature heats and free energies of formation have been employed, and (3) maximally consistent with the cluster data. It is hoped that these values will find utility in the increasingly important activity of connecting cluster ion data to bulk.

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(28) Ion-pair entries corresponding to strong electrolytes were determined from $\Delta H_f°[AB(aq)] - \Delta H_f°[A^+(g)] - \Delta H_f°[B^-(aq)]$ where $\Delta H_f°[A^+(g)]$ is 1536.2(0.1), 685.7(1.0), 609.5(0.7), 514.0(0.8), and 490.1(0.8) kJ/mol for H^+, Li^+, Na^+, K^+, and Rb^+, respectively, and $\Delta H_f°[B^-(g)]$ is −143.5, −255.0(0.3), −233.5(0.1), −218.9(0.2), and −194.6(0.1) for OH^-, F^-, Cl^-, Br^-, and I^-, respectively. These values are in excellent agreement with the values in the 1982 NBS tables (ref 16): $\Delta H_f°[A^+(g)]$ is 1536.2, 685.8, 601.4, 514.3, and 490.1 kJ/mol for H^+, Li^+, Na^+, K^+, and Rb^+, respectively, and $\Delta H_f°[B^-(g)]$ is −143.5, −255.0, −233.5, −218.9, and −194.6 for OH^-, F^-, Cl^-, Br^-, and I^-, respectively.

(29) $\Delta G_f°[A^+(g)]$ is 1516.9, 648.6, 574.3, 481.1, and 457.7 kJ/mol for H^+, Li^+, Na^+, K^+, and Rb^+, respectively, and $\Delta G_f°[B^-(g)]$ is −138.7, −262.3, −239.3, −238.9, and −223.9 kJ/mol for OH^-, F^-, Cl^-, Br^-, and I^-, respectively. These values were determined from data in the 1982 NBS tables (ref 16) and calculations of the gas-phase entropies (ref 31).

(30) Since water is a weak electrolyte, the H^+, OH^- value was determined by $\Delta H_{aq}°(H^+ + OH^-) = \Delta H_f°[H_2O(l)] - \Delta H_f°[OH^-(g)] - \Delta H_f°[H^+(g)] + \Delta H°[H_2O(l) \rightarrow H^+(aq) + OH^-(aq)]$, where the last term is 55.8 kJ/mol for enthalpy and 80.0 kJ/mol for free energy.

(31) Standard entropies of formation in J mol^{-1} K^{-1} for the gas-phase ions were determined using $\Delta S_f°[X(g)] = 108.8555 + 12.4716 \ln(M) -v^*S(X^*) \pm S[e^-(g)]$, where M is the molar mass in grams, v^* is $1/2$ for H^+ and the anions and 1 for the alkali ions, $S(X^*)$ is the element's absolute entropy in the standard state, and $S[e^-(g)]$ is the absolute entropy of the gaseous electron. It is added for cations, subtracted for anions, and determined by using $108.8555 + 12.4716 \ln(M)$ with $M = 5.4858 \times 10^{-4}$ and adding $R[\ln(2)]$ for the spin degeneracy to obtain the value 20.980 J mol^{-1} K^{-1}.