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COMMENTS

Comment on “Accurate Experimental Values for the Free Energies of Hydration of H^+, OH^-, and H_3O^+”

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Palascak and Shields[1] claim to have derived accurate experimental values for the hydration free energies of H^+, OH^-, and H_3O^+. The purpose of this Comment is to alert the community that, in fact, their values are less accurate than the values they are meant to replace. In what follows we show the errors Palascak and Shields made and, by example, give practical advice on how to ensure correct assignment of standard states for reactions with water as a reactant or product in gas and solution phases.

Palascak and Shields begin the derivation of hydration free energies of OH^- and H_3O^+ by asserting that the most reliable estimate of the experimental value for hydration of a proton is −264 kcal/mol.[2,3] They use this value as if the reference standard states are 1 M for both gas and aqueous phases, i.e., $\Delta_s G^*(H^+)$.[4,5] This practice is wrong. Tissander et al.[2] and Tuttle et al.[3] derive the hydration free energy of a proton by correlating ion−water cluster data, referenced to standard gas phase conditions (1 bar, 298 K), with free energies of hydration of the anion−cation pairs that are derived from gas phase reaction energies referenced to the 1-bar standard state and aqueous reactions referenced to 1-*m* standard state. Therefore, the recommended value (−264 kcal/mol) for the hydration of a proton represents the conventional process with standard states essentially equal to 1 atm for gas and 1 M for solution. To convert from the 1-atm gas phase/1-*m* solution standard state to the 1-M gas/1-M solution standard state, one must subtract 1.9 kcal/mol,[6] such that $\Delta_s G^*(H^+) = -265.9$ kcal/mol.[7,8] Bartels and coworkers[9] have recently reproduced this result to within 0.2 kcal/mol and derived values for temperatures up to 648 K using the SUPCRT92 software package.[10] Solvation energies of ions based on $\Delta_s G^*(H^+) = -265.9$ kcal/mol have been widely adopted.[11] This benchmark experimental value should not be changed unless/until it is superseded by better measurements.[12−14] Accordingly, Palascak’s and Shields’ determination of $\Delta_s G^*(OH^-)$ is too negative by 1.9 kcal/mol. With this correction, the value is $\Delta_s G^*(OH^-) = -104.5$ kcal/mol, which is in good agreement with the value previously determined by Pliego and Riveros.[15]

Not converting $\Delta_s G^\circ(H^+)$ to number density standard states is just one of the problems with Palascak’s and Shields’ paper. A more serious problem arises in the derivation by Palascak and Shields of the hydration free energy of H_3O^+. Their value is several kcal/mol less negative than the value previously derived by Pliego and Riveros.[15] Although Pliego and Riveros and Palascak and Shields use different thermochemical cycles, such a large discrepancy should not arise.

Pliego and Riveros use thermochemical cycle 1 with the gas phase basicity of water, $\Delta_b G^\circ = 157.7$ kcal/mol, free energy of vaporization, $\Delta_{vap} G^\circ(H_2O) = 2.05$ kcal/mol, and hydration free energy of the proton, $\Delta_s G^\circ(H^+) = -264$ kcal/mol, to calculate $\Delta_s G^\circ(H_3O^+) = -108.4$.[16] This value is referenced to the 1-atm gas phase, 1-M aqueous phase standard states. Converting to the 1-M gas phase standard state, the value is $\Delta_s G^*(H_3O^+) = -110.2$ kcal/mol.

$$\begin{tikzcd}
H_2O(g) & +\,H^+(g) \arrow[r, "\Delta_r G^\circ_{gas}"] & H_3O^+(g) \arrow[d, "\Delta_s G^\circ"] \\
H_2O(l) \arrow[u, "\Delta_{vap} G^\circ"] & +\,H^+(aq) \arrow[u, "-\Delta_s G^\circ"] \arrow[r, "\Delta_r G^\circ_{aq}"] & H_3O^+(aq)
\end{tikzcd}$$

Thermochemical Cycle 1

Palascak and Shields use the auto-ionization reaction of water (thermochemical cycle 2) to derive $\Delta_s G^*(H_3O^+)$. They obtained −103.45 kcal/mol for the hydration free energy of H_3O^+, having derived the hydration free energy of OH^- from the ionic dissociation of water.[17] Had they used $\Delta_s G^*(H^+) = -265.9$ kcal/mol in their work, a value −105.3 kcal/mol would have been obtained.

$$\begin{tikzcd}
2\,H_2O(g) \arrow[r, "\Delta_r G^*_{gas}"] & H_3O^+(g) \arrow[d, "\Delta_s G^*"] & +\,OH^-(g) \arrow[d, "\Delta_s G^*"] \\
2\,H_2O(aq) \arrow[u, "-2\Delta_s G^*"] \arrow[r, "\Delta_r G^*_{aq}"] & H_3O^+(aq) & +\,OH^-(aq)
\end{tikzcd}$$

Thermochemical Cycle 2

Palascak and Shields attribute the discrepancy “to inconsistencies in standard states [used by Pliego and Riveros] and their value of 155.6 for the [gas phase] basicity of water.” We find no inconsistencies in the standard states used by Pliego and Riveros. For the basicity of water, Pliego and Riveros initially used 157.5,[15a] but then subsequently used 157.7,[15b] which is the value recommended by Hunter and Lias[18] and available currently online at the NIST Chemistry Webbook site.[19] Either value is within experimental error (±0.5 kcal/mol). They also agree with ab initio values of 158.4 calculated by Palascak and Shields and a “best estimate” of 157.3 by Zhan and Dixon.[13] Instead, we trace the discrepancy to Palascak and Shields having used the NIST-JANAF[20] gas phase thermochemical data to calculate 221.1 kcal/mol for the gas phase free energy of the auto-ionization of water.

The NIST-JANAF data for H_3O^+ are derived from a value of 169 kcal/mol[21] for the proton affinity of water to which thermal corrections are applied to obtain $\Delta_r G^\circ_{298}(H^+ + H_2O \rightarrow H_3O^+) = -170$ kcal/mol.[20] However, this value has been superseded by measurements that are well supported by high level ab initio calculations such that the accepted 298 K value is −165 kcal/mol.[18,19,22] Therefore, $\Delta_r G^\circ(2H_2O \rightarrow H_3O^+ + OH^-) = 226$ kcal/mol is the preferred value. Using

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TABLE 1: Standard States, Equilibrium Constants, and Free Energies for Transfer of H_2O from Solution to Gas at 298 K[a]

standard states				
solution	gas	K_{eq}	$\Delta_{eq}G$, kcal/mol	comment
$X = 1$	1 atm	0.0316 atm/mole fraction	2.05	conventional free energy of vaporization, $\Delta_{vap}G°(g)$
1 M	1 atm	$0.0316/55.3 = 5.72 \times 10^{-4}$ atm/M	4.42	
1 M	1 M	$1.29 \times 10^{-3}/55.3 = 2.4 \times 10^{-5}$ M/M	6.32	standard free energy of hydration, Δ_sG^*

[a] Concentration of water at 298.2 K is 55.34 M.[19]

this value in cycle 2 yields $\Delta_sG^*(H_3O^+) = -110.2$ kcal/mol, the same value derived by Pliego's and Riveros's cycle 1.

We surmise that underlying the errors made by Palascak and Shields is confusion about the reference standard states for the free energies of vaporization and hydration of water: $-\Delta_{vap}G°(H_2O) = -2.05$ kcal/mol and $\Delta_sG^*(H_2O) = -6.32$ kcal/mol, respectively. This confusion, which may arise whenever water appears as a reactant or product, is shared by others[23] and has been a source of controversy in the literature.[24-26] $-\Delta_{vap}G°(H_2O)$ is obtained by definition from $RT \ln(K_{vap})$ given the vapor pressure of pure water, $p_w = 0.0316$ atm, at 298 K.[27] Accordingly, $-\Delta_{vap}G°(H_2O)$ is referenced to the 1-atm gas phase standard state and mole fraction, $X = 1$, liquid standard state. As Ben-Naim teaches,[8] this value converts to $\Delta_sG^*(H_2O)$ by correcting the reference states to number density states. We summarize the determination of these values in Table 1. Inspection of Table 1 shows that the reference standard states correspond directly to the units of the equilibrium constant from which ΔG is obtained. Therefore, with knowledge of the units of the equilibrium constant for a physical/chemical process, one can confidently assign the standard states of reactants and products.

In summary, Palascak and Shields claim to have derived accurate experimental values for OH^- and H_3O^+. We disagree with Palascak and Shields, because (1) they adopt -264 kcal/mol for $\Delta_sG^*(H^+)$ instead of the actual experimental value of -265.9 kcal/mol and (2) they use outdated and inaccurate data to derive the reaction free energy for the gas phase autoionization of water. Correcting these two errors brings the values calculated by Palascak's and Shields' thermodynamic cycles into agreement with the values calculated by Pliego and Riveros where $\Delta_sG^*(OH^-) = -104.6$ and $\Delta_sG^*(H_3O^+) = -110.2$ kcal/mol. We favor these values and recommend them to community.

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(7) Following the convention of Ben-Naim[8] we use the asterisk to designate the solvation energy when the reference states of the solution and gas phase are both expressed in number density units, e.g., moles/liter.

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(12) Though Palascak and Shields point out that recent ab initio calculations[13,14] converge to $\Delta_sG^* \sim -264$ kcal/mol, the result should not be taken to be superior to experimental measurements in this case. Despite using accurate quantum methods, the calculations suffer approximate methods that, though making the calculations tractable, also limit their accuracy. Accurate computation of single ion solvation energies is still a challenge; e.g., see discussions in: (a) Grabowski, P.; Riccardi, D.; Gomez, M. A.; Asthagiri, D.; Pratt, L. R. *J. Phys. Chem. A* **2002**, *106*, 9145−9148. (b) Asthagiri, D.; Pratt, L. R.; Ashbaugh, H. S. *J. Chem. Phys.* **2003**, *119*, 2702−2708. (c) Grossfield, A. *J. Chem. Phys.* **2005**, *122*.

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(16) Pliego and Riveros[15] use the gas phase basicity value referenced to the conventional gas phase standard (298 K, 1 atm). Therefore, they use $-\Delta_{vap}G°(H_2O)$ in their determination of $\Delta_sG°(H_3O^+)$. The standard state of liquid water in this case is mole fraction, $X = 1$, such that $\Delta_rG°[H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)] = 0$.

(17) In cycle 2, Palascak and Shields define the equilibrium constant for auto-ionization of water in the condensed phase as $K_w/[H_2O]^2$. This definition of the equilibrium constant requires the solute state (1 M) for water so that $\Delta_sG^*(H_2O)$ can be used. As Palascak and Shields point out, the gas phase free energy for auto-ionization reaction is the same for either the 1-M or 1-atm standard.

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(23) A reviewer asked that we comment on the nature of the aqueous, 1-M standard state of water. To this end, we quote Pliego,[24b] "this is only a reference state and any other state can be reached from this reference." Indeed, to predict solution properties such as pK_a or $E°$ using Δ_sG^* values

either derived from experimental data[8,15] or computed with quantum mechanical continuum solvation models,[5] the $\Delta_s G^*$ values for reactants and products must be corrected to values that are referenced to conventional standard states. For thorough discussion of such standard state issues, see ref 11i.

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