3692 *J. Phys. Chem. A* **2004,** *108,* 3692−3694

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

Matthew W. Palascak and George C. Shields*

Department of Chemistry, Hamilton College, 198 College Hill Road, Clinton, New York 13323

Received: January 7, 2004; In Final Form: February 17, 2004

Accurate experimental values for the free energies of hydration, or the free energies of solvation, of the H^+, OH^-, and H_3O^+ ions are of fundamental importance. By use of the most accurate value for the free energy of solvation of H^+, the known value for the free energy of solvation of water, and the known values for the gas phase and aqueous phase deprotonation of water, the corresponding experimental free energy of solvation for OH^- is −106.4 ± 0.5 kcal/mol. Similarly, by use of the known values for $\Delta G_f{}^0$ for H_3O, H_2O^+, and OH^-, the known values for ΔG_s for H^+ and OH^-, and the known value for the aqueous phase autoionization of water, we obtain an experimental free energy of solvation value for H_3O^+ of −103.4 ± 0.5 kcal/mol. These values are in excellent agreement with the commonly accepted values and with the value for $\Delta G_s(OH^-)$ obtained from embedding clusters of $OH^-(H_2O)_n$ in a dielectric continuum.

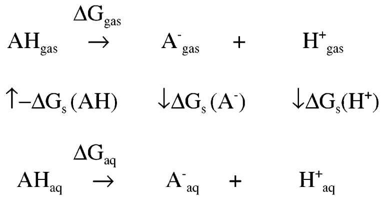
Introduction

Accurate experimental values for the free energy of hydration, or the free energy of solvation, of the H^+, OH^-, and H_3O^+ ions are of fundamental importance. The free energy of hydration of H^+ serves as the benchmark reference for the determination of free energies of hydration of ions, since experiments only allow for the determination of the sum of the free energies of solvation for a pair of oppositely charged ions.[1] Yet the most common method for determining the free energy of hydration of H^+, which is measured from the standard hydrogen potential, results in values that range from −254 to −261 kcal/mol.[2] This range results in an uncertainty of 7 kcal/mol for determination of the free energy of hydration of other ions. The standard hydrogen potential cannot be obtained by measurement alone but requires an independent quantity to determine an absolute half-cell potential.[2,3] This large uncertainty is unacceptable at a point in time when state-of-the-art computational methods (model chemistry, continuum methods)[4−6] allow for the accurate calculation of pK_a values in solution using thermodynamic cycle 1.[7,8] Since an error of 1.4 kcal/mol in ΔG_{aq} yields an error of 1 pK_a unit, an accurate value for $\Delta G_s(H^+)$ is absolutely essential to obtain accurate pK_a values.[2,7−14] We have shown that accurate values for ΔG_{aq} can be determined for carboxylic acids and phenols using compound model chemistry gas-phase calculations[15−18] to evaluate ΔG_{gas} and CPCM continuum calculations[6] to evaluate ΔG_s.[7,8,10] The major uncertainty in this procedure is the accurate calculation of ΔG_s for ionic species.[7,8,19] To obtain the most accurate calculated values for the free energy of hydration of various ions, it is imperative that method developers have access to the most reliable experimental information.

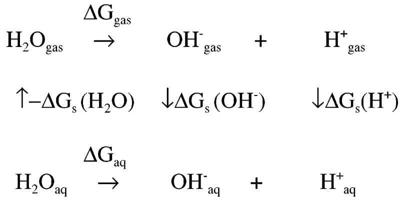
The free energy of hydration for H^+, $\Delta G_s(H^+)$, has been the focus of much study over the past five years.[1,7,8,20−23] Tissandier et al. have used a cluster-pair approximation approach to obtain an experimental value of −263.98 ± 0.07 kcal/mol for $\Delta G_s(H^+)$.[1] Coe et al. have reviewed the cluster ion data and obtain a value of −263.67 kcal/mol from their plots.[22] Most recently, Tuttle et al. have updated their previous work and obtain a value of −263.98 ± 0.2 kcal/mol from the cluster-pair approximation.[23] We have used the experimental values for ΔG_{gas} for the dissociation of acetic acid, ΔG_s(acetic acid), and ΔG_s(acetate ion) to derive an experimental value of −264.61 kcal/mol using thermodynamic cycle 1.[7,8] Calculated values for $\Delta G_s(H^+)$ have converged on −264.1 to −264.3 kcal/mol, when the standard state is 1 M.[20,21] In this paper, we use the value for $\Delta G_s(H^+)$ of −264.0 kcal/mol to obtain the experimental values for $\Delta G_s(H_3O^+)$ and $\Delta G_s(OH^-)$ that are consistent with this most reliable value for $\Delta G_s(H^+)$.

Results

By use of thermodynamic cycle 2 and the known values for ΔG_{gas}, $\Delta G_s(H^+)$, $\Delta G_s(H_2O)$, and $\Delta G_{aq}(H_2O_{aq} \rightarrow H^+_{aq} + OH^-_{aq})$, we can determine an experimental value for $\Delta G_s(OH^-)$. The known value of ΔG_{gas} is 383.70 ± 0.3 kcal/mol,[24−26] for a standard state of 1 atm, or 385.59 kcal/mol for a standard state of 1 M. The known value for $\Delta G_s(H_2O)$ is −6.32 kcal/mol,[10] the most reliable estimate for the experimental value for $\Delta G_s(H^+)$ is −264.0 kcal/mol, and the known value for ΔG_{aq} is 21.4762 kcal/mol.[27] These values allow us to solve for the experimental value for $\Delta G_s(OH^-)$, for a 1 M standard state, which is −106.44 ± 0.5 kcal/mol.



Thermodynamic Cycle 1



Thermodynamic Cycle 2

10.1021/jp049914o CCC: $27.50

TABLE 1: Experimental Values for $\Delta G_s(OH^-)$ and $\Delta G_s(H_3O^+)$ Consistent with Thermodynamic Cycles 2 and 3 and the Indicated Values for $\Delta G_s(H^+)$[a]

$\Delta G_s(H^+)$	$\Delta G_s(OH^-)$	$\Delta G_s(H_3O^+)$
−263.67	−106.77	−103.12
−264.0	**−106.44**	**−103.45**
−264.61	−105.83	−104.06

[a] All values are in kcal/mol, for a standard state of 1 M and 298.15 K. The best values, based on the most accurate experimental determination of $\Delta G_s(H^+)$, are in bold, with an estimated uncertainty of ±0.5 kcal/mol.

Similarly, we use thermodynamic cycle 3 to solve for $\Delta G_s(H_3O^+)$. In this case, we determine ΔG_{gas} using the standard Gibbs free energies of formations, $\Delta G_f{}^0$, for H_2O (−54.6324 kcal/mol), H_3O^+ (144.9843 kcal/mol), and OH^- (−33.1496 kcal/mol).[28] For thermodynamic cycle 3, we have that $\Delta G_{gas} = 221.0995$ kcal/mol for a standard state of 1 atm and for a standard state of 1 M, since Δn_{gas} equals zero. From K_w and the concentration of water at 298.15 K, $[H_2O] = 55.34$ M, we have $\Delta G_{aq} = 23.8541$ kcal/mol. By use of a value of $\Delta G_s(H^+)$ of −264.0 and a value for $\Delta G_s(OH^-)$ of −106.44 kcal/mol, we derive a value for $\Delta G_s(H_3O^+)$ of −103.45 kcal/mol. Table 1 summarizes the values of $\Delta G_s(OH^-)$ and $\Delta G_s(H_3O^+)$ obtained from various values of $\Delta G_s(H^+)$.

$$\begin{tikzcd}
H_2O_{gas} + H_2O_{gas} \arrow[r, "\Delta G_{gas}"] & OH^-_{gas} \arrow[d, "\Delta G_s(OH^-)"] & + & H_3O^+_{gas} \arrow[d, "\Delta G_s(H_3O^+)"] \\
H_2O_{aq} + H_2O_{aq} \arrow[u, "-2\Delta G_s(H_2O)"] \arrow[r, "\Delta G_{aq}"] & OH^-_{aq} & + & H_3O^+_{aq}
\end{tikzcd}$$

Thermodynamic Cycle 3

Discussion

Because $\Delta G_s(H^+)$ is a number close to −264 kcal/mol, $\Delta G_s(OH^-)$ must be close to −106.4 kcal/mol, and $\Delta G_s(H_3O^+)$ must be close to −103.4 kcal/mol (Table 1). On the basis of the agreement between experimental and theoretical approaches for determining $\Delta G_s(H^+)$, we estimate error bars on the numbers listed in boldface type in Table 1 of ±0.5 kcal/mol. With these values in hand, we can evaluate the values reported in the literature for $\Delta G_s(OH^-)$ and $\Delta G_s(H_3O^+)$.

Zhan and Dixon have used clusters of $OH^-(H_2O)_n$ embedded in a dielectric continuum to calculate a value of $\Delta G_s(OH^-)$ of −104.5 kcal/mol, for a standard state of 1 M.[29] Our prediction is in excellent agreement with their prior calculation. Pliego and Riveros have used Monte Carlo simulations and free-energy pertubation to estimate the absolute free energy of hydration of OH^- in aqueous solution to be −108.0 kcal/mol.[30] Pliego has also used Tissandier's value of −264.0 kcal/mol for $\Delta G_s(H^+)$[1] and a combination of experimental and theoretical values for proton affinities, aqueous acidity constants, and solvation free energies of neutral species, to calculate a value for $\Delta G_s(OH^-)$ of −105.0 kcal/mol.[31] This value is 1.4 kcal/mol more positive than our estimate, a result stemming from the approximation that the gas-phase proton affinities of all negatively charged species have constant entropy terms ($T\Delta S$) equal to 7.5 kcal/mol.[32−34] Mejías and Lago have calculated the value for $\Delta G_s(H^+)$ and $\Delta G_s(OH^-)$ using a combination of DFT and a polarizable continuum model.[35] Their results for $\Delta G_s(H^+)$, −274.9 kcal/mol, appear to be relatively inaccurate given the convergence of other computed numbers with similar procedures,[20,21] and the most reliable available experimental results.[1,22,23] Similarly, the value obtained for $\Delta G_s(OH^-)$, −95.6 kcal/mol, is again off by 10 kcal/mol.[35] The authors speculate that their method is not suitable for a highly accurate determination of entropic effects, as their values for ΔH_s are in better agreement with experiment. [35]

Our results predict a range for the value for $\Delta G_s(H_3O^+)$ of −103 to −104 kcal/mol, with the best estimate being −103.4 kcal/mol. Pliego and Riveros have determined $\Delta G_s(H_3O^+)$ from a three-step process: vaporization of water, formation of the H_3O^+ ion in the gas phase, and solvation of the H_3O^+ species. They use the equation $\Delta G_s(H_3O^+) = \Delta G_s(H^+) + \Delta G^0_{bas}(H_2O) + \Delta G_{vap}(H_2O)$. They use the best experimental value for $\Delta G_s(H^+)$, −264.0 kcal/mol, a value of 155.6 kcal/mol for $\Delta G^0_{bas}(H_2O)$, and a value of 2.0 kcal/mol for $\Delta G_{vap}(H_2O)$.[31] The value for $\Delta G^0_{bas}(H_2O)$ was determined from the approximate relationship, $\Delta G^0_{bas} \approx \Delta H^0_{PA} - 7.5$ kcal/mol, using the experimental value of 165.0 ± 0.5 kcal/mol for the proton affinity.[36] We believe that most of the 7 kcal/mol discrepancy between Pliego and Riveros' value of −110.4 and our value of −103.4 is attributable to inconsistencies in standard states and their value of 155.6 kcal/mol for the basicity of water.

We can estimate an accurate value for the basicity of water using the complete basis set atomic-pair natural orbital (CBS-APNO) method.[37,38] By use of CBS-APNO calculations for H_3O^+ and H_2O, we obtain absolute free energies of −76.428190 and −76.690657 Hartrees at 298.15 K. By use of $G_{gas}(H^+) = -6.28$ kcal/mol,[7,8] we obtain a ΔG_{gas} of −158.4 kcal/mol for a standard state of 1 atm. Converting to a standard state of 1 M yields −160.3 kcal/mol, which differs from the Pliego value for the basicity of water by 5 kcal/mol. Using the CBS-APNO calculated value of −160.3 yields a value of −105.7 kcal/mol for $\Delta G_s(H_3O^+)$. Thus the CBS-APNO value is 2.3 kcal/mol more negative than the best estimate using the best available experimental numbers (Table 1) but is still 5 kcal/mol more positive than the calculated value of Pliego and Riveros.

It has been previously demonstrated that the value of 2.0 kcal/mol for the vaporization of water represents the transition of liquid water in the reference state of 55.34 M, 298.15 K to gaseous water in the reference state of 1 atm, 298.15 K.[10] As the relationship between intermolecular interactions and free energies of transfer between phases is most direct when using the same standard concentration for both phases, the usual reference state is 1 M at the given temperature.[39] Thus the value of 2.0 kcal/mol for the vaporization of 55.34 M water at 298.15 K to 1 atm gaseous water is equivalent to 6.32 kcal/mol when both the water and gas standard states are 1 M.[10] This idea has been recognized by Pliego in a recent paper, where the validity of our calculation of standard states[10] has been affirmed.[32]

The usual quoted experimental values for $\Delta G_s(OH^-)$ and $\Delta G_s(H_3O^+)$ are −106 and −104 kcal/mol, respectively.[31,40] Our values provide a slight correction and are within half a kcal/mol of the usual numbers. We note that these numbers are generally not believed to be very accurate, given the assumptions made in their derivation and the previously mentioned difficulties in assigning the value for $\Delta G_s(H^+)$ from the standard hydrogen potential. In fact, the range of reported experimental values for $\Delta G_s(OH^-)$ is extremely wide, from −90.6 to −110.0 kcal/mol.[35,41,42] This unfortunate situation makes it difficult for scientists to assess their own work when using these values. It is reassuring that the most widely quoted values are in agreement with our more accurate determinations presented in this paper.

Conclusion

We have shown that, by use of the most accurate value for the free energy of solvation of H^+, −264.0 kcal/mol, the known value for the free energy of solvation of water, −6.32 kcal/mol, and the known values for the gas-phase and aqueous-phase deprotonation of water, the corresponding experimental free energy of solvation for OH^- is −106.4 kcal/mol. Similarly, by use of the known values for $\Delta G_f{}^0$ for H_2O, H_3O^+, and OH^-, the values for ΔG_s for H^+, OH^-, and H_2O, and ΔG_{aq} for the dissociation of water into $OH^-{}_{aq}$ and $H_3O^+{}_{aq}$, we obtain an experimental free energy of solvation value for H_3O^+ of −103.4 kcal/mol. These values are in excellent agreement with the commonly accepted values[40] and with the value for $\Delta G_s(OH^-)$ obtained from embedding clusters of $OH^-(H_2O)_n$ in a dielectric continuum.[29] These accurate experimental values for $\Delta G_s(H^+)$, $\Delta G_s(OH^-)$, and $\Delta G_s(H_3O^+)$, for the standard state of 1 M and 298.15 K, can now be used to reevaluate values of ΔG_s for all of the anions and cations reported in the literature. In addition, these values can be used with confidence for assessing the ability of various computational methods to reproduce the free energy of solvation of these important ions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the NIH, to the Dreyfus Foundation, and to Hamilton College for support of this work. This project was supported in part by NSF Grant CHE-0116435 as part of the MERCURY supercomputer consortium (http://mars.hamilton.edu). M.W.P acknowledges support from the Camille & Henry Dreyfus Foundation.

References and Notes

(1) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R. *J. Phys. Chem. A* **1998**, *102*, 7787−7794.

(2) Lim, C.; Bashford, D.; Karplus, M. *J. Phys. Chem.* **1991**, *95*, 5610−5620.

(3) Reiss, H.; Heller, A. *J. Phys. Chem.* **1985**, *89*, 4207−4213.

(4) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299−11308.

(5) Pople, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1894−1902.

(6) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995−2001.

(7) Liptak, M. D.; Shields, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 7314−7319.

(8) Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6421−6427.

(9) Toth, A. M.; Liptak, M. D.; Phillips, D. L.; Shields, G. C. *J. Chem. Phys.* **2001**, *114*, 4595−4606.

(10) Liptak, M. D.; Shields, G. C. *Int. J. Quantum Chem.* **2001**, *85*, 727−741.

(11) Kallies, B. M. R. *J. Phys. Chem. B* **1997**, *101*, 1089−5647.

(12) Shapley, W. A. B.; George B.; Warr, G. G. *J. Phys. Chem. B* **1998**, *102*, 1938−1944.

(13) Li, J. F.; Cindy, L.; Chen, J. L.; Bashford, D.; Noodleman, L. *Inorg. Chem.* **1996**, *35*, 4694−4702.

(14) Topol, I. A.; Tawa, G. J.; Burt, S. K.; Rashin, A. A. *J. Phys. Chem. A* **1997**, *101*, 10075−10081.

(15) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1995**, *103*, 4192−4200.

(16) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Baboul, A. G.; Pople, J. A. *Chem. Phys. Lett.* **1999**, *314*, 101−107.

(17) Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900−5909.

(18) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822−2827.

(19) Cramer, C. J.; Truhlar, D. G. *Chem. Rev.* **1999**, *99*, 2161−2200.

(20) Tawa, G. J.; Topol, I. A.; Burt, S. K.; Caldwell, R. A.; Rashin, A. A. *J. Chem. Phys.* **1998**, *109*, 4852−4863.

(21) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2001**, *105*, 11534−11540.

(22) Coe, J. V. *Int. Rev. Phys. Chem.* **2001**, *20*, 33−58.

(23) Tuttle, T. R.; Malaxos, S.; Coe, J. V. *J. Phys. Chem. A* **2002**, *106*, 925−932.

(24) Bartmess, J. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, March 2003; http://webbook.nist.gov.

(25) Smith, J. R.; Kim, J. B.; Lineberger, W. C. *Phys. Rev. A: At., Mol., Opt. Phys.* **1997**, *55*, 2036−2043.

(26) Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153−1165.

(27) $\Delta G_{aq} = -RT \ln K_c = -(8.314/4184)(298.15)\ln(10^{-14}/55.3436) = 21.4762$ kcal/mol.

(28) Chase, M. *NIST-JANAF Thermochemical Tables*, 4th ed.; American Institute of Physics, 1998.

(29) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2002**, *106*, 9737−9744.

(30) Pliego, J. R.; Riveros, J. M. *J. Phys Chem. B* **2000**, *104*, 5155−5160.

(31) Pliego, J. R.; Riveros, J. M. *Chem. Phys. Lett.* **2000**, *332*, 597−602.

(32) Pliego, J. R. *Chem. Phys. Lett.* **2003**, *367*, 145−149.

(33) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046−6056.

(34) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 318−329.

(35) Mejías, J. A.; Lago, S. *J. Chem. Phys.* **2000**, *113*, 7306−7316.

(36) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839−7848.

(37) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys.* **1996**, *104*, 2598−2619.

(38) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570−10579.

(39) Winget, P.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *J. Phys Chem. B* **2000**, *104*, 4726−4734.

(40) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109−6114.

(41) Zhu, T.; Li, J.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *J. Chem. Phys.* **1998**, *109*, 9117−9133.

(42) Friedman, H. L.; Krishnan, C. V. *Thermodynamics of Ionic Hydration, Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 3, pp 1−118.