

The K_a Values of Water and the Hydronium Ion for Comparison with other Acids

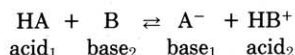
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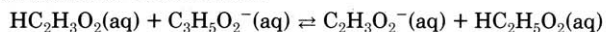
There appears to be considerable debate among chemists regarding the correct values to use for the K_a of water and of the hydronium ion. In *this Journal*, Starkey, Norman, and Hintze (1) proposed using the values of 1.8×10^{-16} for water and 55.3 for the hydronium ion. They "derived" these values by treating the water as a solute and invoking a Henry's law standard state despite its solvent environment. This derived K_a for water appears to be accepted on a wide basis (1-12) despite being derived using an unconventional standard state. As a rebuttal to the derivation by Hinze et al., Baldwin and Burchill (13) derive the conventionally correct K_a values for H_2O (1.0×10^{-14}) and the hydronium ion (1.0) by treating the water as the solvent and using a Raoult's law standard state.

Since the values derived by Baldwin and Burchill are thermodynamically rigorous, the question arises as to why so many chemists prefer the unconventionally derived values. Certainly it is not from ignorance of thermodynamic principles since many of these individuals are distinguished chemists who have devoted a good part of their careers to acid/base chemistry. The answer appears to lie in water's "intrinsic" acidity; water does not act like a compound with a K_a of 1.0×10^{-14} ; it acts like an acid with an ionization constant of about 100 times less. For instance, the K_a 's of small aliphatic alcohols are known to be approximately 10^{-16} . In comparing the acidity of water in the gas phase with that of a number of alcohols, water was found to be a weaker acid than all the alcohols studied (14), inconsistent with a comparison of the K_a 's. Furthermore, arguments based on thermodynamic (15, 16) and kinetic (17) data also support a K_a value on the order of 10^{-16} .

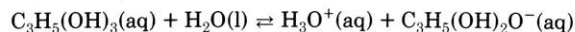
A primary interest in establishing the correct K_a values for water and the hydronium ion is to be able to compare the strengths of these species acting as acids with the strengths of other compounds acting as acids. Thus, in theory, by comparing the K_a of a compound with the K_a of water (or the hydronium ion), one would be able to classify a compound as either a stronger or a weaker acid than water (or the hydronium ion). However, in order for this comparison to be valid, the acids must be treated on an "equal" basis. The problem is whether it is appropriate to compare the acidity of an acid acting as the solute in solution with that of the primary component acting as the solvent. When one compares acid strength, it is common to look at the reaction:



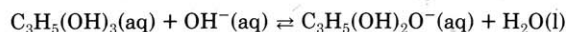
Starting with each of the reactants and products in their standard states, if the reaction proceeds to the right, then acid_1 is stronger than acid_2 , whereas, if the reaction proceeds from right to left, then acid_2 would be considered a stronger acid than acid_1 . Using this criterion for two solutes, this method gives a straightforward and unambiguous result for acid strength. For example, using the K_a 's of acetic acid (1.75×10^{-5}) and propionic acid (1.34×10^{-5}), the equilibrium constant for the reaction:



is determined to be 1.3. Thus, with each of the reactants and products initially in their standard states, the reaction would proceed to the right unambiguously showing that acetic acid is a stronger acid than propionic acid in aqueous solution. In this case, the acids are on "equal terms", and a comparison of the K_a 's for these acids yields a valid result. However, when one compares a compound's acid strength with that of water or the hydronium ion in aqueous solution, then the fact that we are comparing a property of the solute with that of the solvent means that the two species are inherently on "unequal terms", i.e., the properties of a species in a dilute environment can be drastically different than its properties when it is in a very concentrated environment. As an example, let us attempt to compare the acid strength of glycerin ($K_a = 6 \times 10^{-15}$) to that of water. If one looks at the equilibrium system:



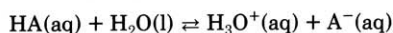
and solves for the equilibrium concentrations of the species in a 1.0 F glycerin solution, then one finds that the $[\text{H}_3\text{O}^+]$ and $[\text{C}_3\text{H}_5(\text{OH})_2\text{O}^-]$ at equilibrium are 1.3×10^{-7} M and 5×10^{-8} M, respectively. Using percent ionization as a measure of acidity, the water would be considered the weaker acid since the percent ionization of the autoionized water (using a value of 55 M for the molar concentration of water) is $1.4 \times 10^{-7}\%$ while that of glycerin is $5 \times 10^{-6}\%$. However, if one looks at the reaction:



the equilibrium constant of 0.6 indicates that, with each of the reactants and products in their standard states, the reaction would proceed from right to left, indicating that water is the stronger acid. Which is the correct interpretation? Clearly, percent ionization is not a valid measure of acidity in this case since it is well established that % ionization varies significantly with concentration, and in this instance we are trying to compare one species that is at a concentration 55 times that of the other. But is the second interpretation really "correct" since in comparing the solute using a Henry's law standard state with the solvent using a Raoult's law standard state we are not treating the two species in an equal manner? For the purpose of comparing acid strengths, we support the view that the K_a 's proposed by Hintze et al. represent a more valid representation of the relative acidity of water. The following treatment uses "labeled" water in an aqueous solution to analyze the "acidity" of water acting as a solute and thus yields an ionization constant on a more equal basis for comparison with other acids.

Consider the generic weak acid, HA. Prepare an m molal solution of the weak acid by adding m mol of HA to 1 kg of water. The neutral HA molecules interact with the solvent species (which are in much greater abundance) and a certain fraction of the HA solute ionize; a few solvent molecules becoming protonated in the process. For simplicity, we are ignoring the production of higher hydrates of the proton

beyond the formation of the hydronium ion. The reaction that occurs is as follows:



and the thermodynamic equilibrium constant expression is:

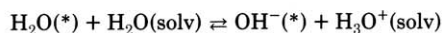
$$K_{\text{th}} = a_{\text{A}^-} a_{\text{H}_3\text{O}^+} / a_{\text{HA}} a_{\text{H}_2\text{O}}$$

where the conventional standard states are chosen for solute and solvent, i.e., solutes are defined to have a standard state of ideal 1 *m* concentration and solvent is defined to have a standard state of the ideal mole fraction concentration. In the low concentration limit where ideality is approached, the solvent mole fraction approaches unity, and the solute species' activities approach their molalities. Extensive tables of ionization constants for various acids based on this treatment have been published.

This type of system is interesting and unusual in that the solvent not only hosts but also participates in the reaction. Circumstances become even more complicated, however, for the $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ system.

Consider a system in which one can distinguish between a solute water molecule and a solvent water molecule. Such a system can be prepared by using "labeled" water (designated by an "*"); unlabeled solvent will be designated with "solv". A solution of *m* molal "labeled" water can be prepared experimentally by dissolving *m* mol of H_2^{18}O in 1 kg of H_2^{16}O solvent, or one can run a "thought" experiment by simply "labeling" the *m* mol of introduced water. In either case it must be assumed that the reactivity of the "labeled" water is identical to that of conventional water.

The objective is to determine the appropriate K_{th} for the interaction of this "labeled" water with the solvent, i.e.,



where the introduced solute is acting as an acid through protonation of the solvent. This system is strictly analogous to the case of the "typical" weak acid treated previously; i.e., the thermodynamic equilibrium constant expression is:

$$K_{\text{th}} = a_{\text{H}_3\text{O}^+(\text{solv})} a_{\text{OH}^-(\text{aq})} / a_{\text{H}_2\text{O}^*(\text{aq})} a_{\text{H}_2\text{O}(\text{solv})}$$

Introduction of *m* mol of "labeled" water into 55.3 mol of water indicates that $m/(m + 55.3)$ of the resulting species OH^- , H_2O , and H_3O^+ will also be of the "labeled" variety. Now, at equilibrium, it is well known that the total OH^- concentration at 25 °C is 1.0×10^{-7} , i.e.,

$$1.0 \times 10^{-7} = m_{\text{OH}^-(*)} + m_{\text{OH}^-(\text{solv})}$$

assuming a complete mixing of the labeled species at equilibrium. Thus, the activity of the labeled OH^- , which is equal to its molality in the dilution limit, is given by

$$\begin{aligned} a_{\text{OH}^-(*)} &= \lim_{m \rightarrow 0} m_{\text{OH}^-(*)} \\ &= \lim_{m \rightarrow 0} \{m/(m + 55.3)\} \times 1.0 \times 10^{-7} \\ &= (m/55.3) 1.0 \times 10^{-7} \end{aligned}$$

The same argument applies to the activity of H_3O^+ at equilibrium,

$$\begin{aligned} a_{\text{H}_3\text{O}^+(\text{solv})} &= \lim_{m \rightarrow 0} m_{\text{H}_3\text{O}^+(\text{solv})} \\ &= \lim_{m \rightarrow 0} \{1 - (m/(m + 55.3))\} \times 1.0 \times 10^{-7} \\ &= 1.0 \times 10^{-7} \end{aligned}$$

For the labeled solute H_2O and unlabeled solvent H_2O , the activities are given by

$$\begin{aligned} a_{\text{H}_2\text{O}^*(\text{aq})} &= \lim_{m \rightarrow 0} m_{\text{H}_2\text{O}^*(\text{aq})} \\ &= \lim_{m \rightarrow 0} \{m - (m/m + 55.3) \times 1.0 \times 10^{-7}\} \\ &= m \\ a_{\text{H}_2\text{O}(\text{solv})} &= \lim_{m \rightarrow 0} \chi\{\text{H}_2\text{O}(\text{solv})\} \\ &= \lim_{m \rightarrow 0} \{55.3/(m + 55.3)\} \\ &= 1 \end{aligned}$$

Hence, the value of K_{th} obtained is:

$$K_{\text{th}} = \{(m/55.3) \times 1.0 \times 10^{-7} \times 1.0 \times 10^{-7}\} / m$$

which simplifies to

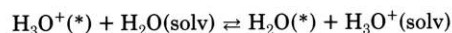
$$K_{\text{th}} = 1.0 \times 10^{-14} / 55.3 = 1.8 \times 10^{-16}$$

The factor 55.3 arises in this derivation from the fact that the labeled water is being treated with the same standard state as other solutes, i.e., unit molality. Removing the label at this point gives rise to the general statement that the ionization constant of water is 1.8×10^{-16} when used as a measure of acid strength to compare to other weak acids using the conventional solute standard state.

This derivation avoids the inappropriate use of assigning the activity of the water to be 55.3 when it is considered as a reactant in the reaction. In the dilution limit where a Henry's law standard state for a solute can properly be invoked, the activity of the "labeled" water approaches its molality. In this special case, however, the "labeled" water experiences the same environment in the dilution limit as it does in the full 55.3 *m* treatment. For this reason, it appears that the activity of the water can be represented as 55.3, whereas this treatment gives a better accounting of the activity.

Finally, consider the acid H_3O^+ . Prepare an *m* molal solution of "labeled" H_3O^+ by dissolving *m* mol in 1 kg of unlabeled aqueous solvent. At equilibrium, the labeling will distribute itself throughout the species H_3O^+ and H_2O . Again, as for the second case above, the fraction of these species that will be of the labeled variety is $m/(55.3 + m)$.

Thus, for the acid reaction (analogous to those treated above)



the following must hold in the dilution limit:

$$\begin{aligned} a_{\text{H}_2\text{O}^*(\text{aq})} &= m\{55.3/(m + 55.3)\} \rightarrow m \\ a_{\text{H}_3\text{O}^+(\text{solv})} &= m\{1 - m/(m + 55.3)\} \rightarrow m \\ a_{\text{H}_3\text{O}^*(\text{aq})} &= \{m/(m + 55.3)\}m \rightarrow m^2/55.3 \\ a_{\text{H}_2\text{O}(\text{solv})} &= \{55.3/(m + 55.3)\} \rightarrow 1 \end{aligned}$$

Hence, the value of the thermodynamic equilibrium constant is

$$K_{\text{th}} = (m)(m)/(m^2/55.3) = 55.3$$

Once again the treatment of the labeled solute leads to an equal comparison of the equilibrium constant that differs from conventional standard state approaches by a factor of 55.3. The treatment presented above, although yielding the same results as those in ref 1, is preferable since this treatment does not require a "last minute" distinguishing between water as a solvent or as a product of the protonation process. Of course, when the abundant species is treated according to the conventional solvent standard state approach, regardless of its source, the K_{th} becomes unity. Both values are appropriate for the standard states chosen. For

the purpose of comparing acid strengths, however, it is clear that the approach presented above is the most consistent. It enables one to invoke the conventional standard states and the limits in which these standard states are easily treated.

Finally, it is possible to show that acids with conventional ionization constants greater than 55.3 are stronger acids than H_3O^+ , at least in the sense of their propensity to donate protons to the surrounding solvent. For example, consider a 0.10 M H_3O^+ solution prepared using "labeled" H_3O^+ . Using the K_a of 55.3, the percent ionization of the labeled hydronium ions is calculated to be 99.82%. In other words, the original "labeled" H_3O^+ (which represents about 0.1 parts in 55.3) has redistributed its donated protons among the other "unlabeled" water molecules, leaving 0.1/55.3 of the original hydronium un-ionized. An unusual feature of this particular acid, however, is that other measures of acid strength, e.g., pH, do not distinguish between the labeled and unlabeled species. Hence, 0.1 M H_3O^+ exhibits a pH of 1.000 instead of 1.008, which would be calculated from consideration of "another" acid with a K_a of 55.3. Acids with conventional ionization constants greater than 55.3 are stronger acids than hydronium in the sense that they will exhibit a greater percent ionization than that of the "labeled" hydronium. For example, the percent ionization of a 0.1 M permanganic acid ($K_a = 178$) solution is calculated to be 99.94%, higher than the case

of the "labeled" hydronium above. However, a comparison of the pH's of the two solutions shows that the permanganic acid solution exhibits a pH of 1.0002, which is "less acidic" than the 1.0000 calculated for the 0.1 M hydronium solution. The pH's in this case are not indicative of acid strength, which is normally defined in terms of the propensity of the species to donate protons to the solvent.

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