

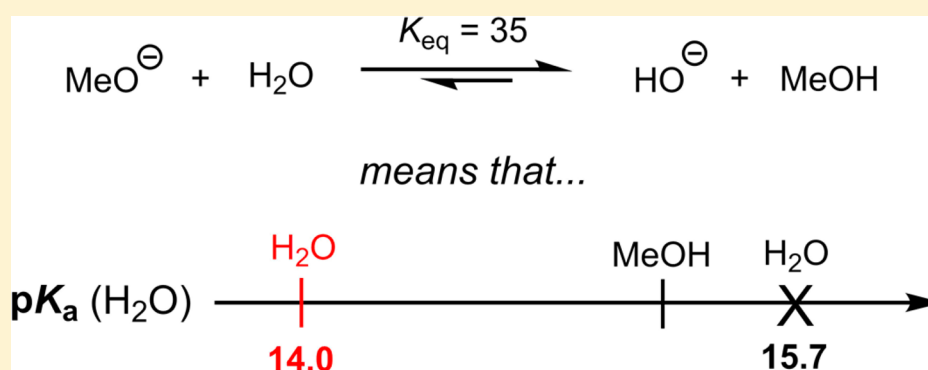
pK_a Values in the Undergraduate Curriculum: What Is the Real pK_a of Water?

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S Supporting Information



ABSTRACT: Since at least the 1960s, organic chemistry textbooks have featured pK_a tables for organic acids that include values for H_2O and H_3O^+ (15.74 and -1.74 , respectively) that are thermodynamically and chemically indefensible. Here we trace this error back to Brønsted's early contributions in the 1920s to the Brønsted–Lowry Theory of acids and bases. Organic chemists generally defend the use of these values by citing measurements of the equilibrium constant for the water + methoxide acid–base reaction that suggested that methanol ($pK_a = 15.54$) is a stronger acid than water; from this, organic chemists have concluded that pK_a of water must be 15.74 rather than 14.00. Here we discuss the problems that invalidate this conclusion, the most important being that it is based on the use of the pure liquid standard state (mole fraction = 1) that is quite different from the standard state for acidities determined in dilute solution (molality = 1). Using the latter standard state, the equilibrium constant for the water/methoxide reaction ranges from 4 to 70, showing water to be a *stronger* acid than methanol, and justifying the use of the thermodynamically correct value, $pK_a(\text{H}_2\text{O}) = 14.00$.

KEYWORDS: First-Year Undergraduate/General, Second-Year Undergraduate, History/Philosophy, Physical Chemistry, Organic Chemistry, Misconceptions/Discrepant Events, Textbooks/Reference Books, Brønsted–Lowry Acids/Bases, Water/Water Chemistry, Aqueous Solution Chemistry

INTRODUCTION

Acid–base reactions are so important in most branches of chemistry that they are discussed at length in all first-year chemistry courses. After covering the pH scale and acid–base strength, first-year chemistry textbooks generally introduce the concept of the acid ionization equilibrium and its associated equilibrium constant, K_a .

Two Different pK_a Values for Water

The acid ionization equilibrium applies to dilute aqueous solution. The solvent water also ionizes (eqs 1 and 7); however, due to its high concentration (i.e., mole fraction close to 1), the solution-based thermodynamics of water ionization must be treated differently than those of dilute solute acids. This has led over the past century to the promulgation of two different pK_a s for water and aqueous H^+ . Organic chemistry texts feature $pK_a = 15.74$ for water and -1.74 for $\text{H}^+(\text{aq})$, whereas the respective values cited in almost all other chemistry texts are 14.00 and

0.00. In this paper we trace the source of these two pairs of pK_a values back at least as far as Brønsted, who, in his seminal 1928 review,¹ devoted attention to the acidity of the solvent water, as well as the influence of solvent polarity on solute acidity and pK_a . Here we explore Brønsted's original arguments, revisit and reinterpret subsequent literature that bears on the acidity of the aqueous solvent, and make recommendations for changes in the first-year and organic chemistry courses. We have additional studies underway to assess the latter issue, the influence of solvent polarity on solute acidity and pK_a .

In his 1928 discussion of the pK_a of H_2O , Brønsted distinguished 15.74, the “rational” value, from 14.00, the “conventional” value.^{1,2} Similarly, he cited both “rational” and “conventional” pK_a 's for aqueous H^+ (-1.74 and 0.00,

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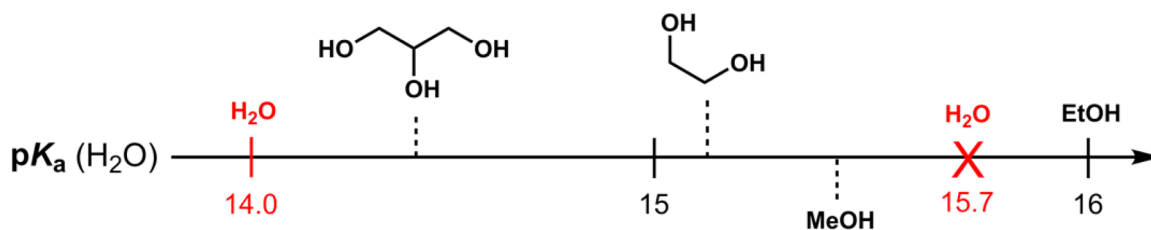


Figure 1. pK_a values for several alcohols, as determined by Ballinger and Long.⁴ Values for water are thermodynamic ($pK_w = 14.00$) or calculated (15.74), not measured. (Levine's physical chemistry textbook²⁷ includes a similar K_a figure, 11.1 on p 333, but it gives only the thermodynamically incorrect "rational" pK_a of water.)

respectively). In this *Journal*, the issue of these two different pairs of pK_a values was first raised in 1986 by Starkey et al.,³ who cited a seminal 1960 paper in *J. Am. Chem. Soc.*⁴ In this paper, Ballinger and Long concluded (erroneously, as we shall prove) that methanol (pK_a 15.54) is a stronger acid than water; hence, the pK_a of water must be 15.74 and not 14.00 (see Figure 1). On the basis of Ballinger and Long's (invalid) conclusion, Starkey et al. asserted that Brønsted's "rational" values (15.74 and -1.74) were "correct" and the "conventional" ones (14 and 0) "incorrect". Over the next two decades, several contributors to this *Journal*^{5–9} opposed Starkey et al, arguing that the rational values are in fact thermodynamically untenable. Meister et al. published a comprehensive paper in 2014 presenting this point of view from several different perspectives.¹⁰

pK_a Tables in Chemistry Textbooks

Soon after Ballinger and Long published their work in 1960, a split developed in the K_a and pK_a tables published in first-year and organic chemistry textbooks:¹¹ First-year chemistry texts either used Brønsted's "conventional" values of 14 and 0, or omitted water and the hydronium ion from the table; on the other hand, organic chemistry textbooks uniformly used Brønsted's "rational" values of 15.74 and -1.74 . For example, Cram listed the "rational" values in his 1965 monograph *Fundamentals of Carbanion Chemistry*,¹² citing Ballinger and Long; from there, they made their way into the seminal 1970 edition of Hendrickson, Cram, and Hammond's *Organic Chemistry* (3rd ed.)¹³ and into a number of reference works, including *CRC Handbooks*.¹⁴ Similarly, the commonly used Evans¹⁵ and Bordwell¹⁶ pK_a tables both list the "rational" values and cite Ballinger and Long.

The status today is similar to that in the 1970s. A random sampling of 16 first-year chemistry textbooks published within the past decade showed 10 that omitted H_2O and H_3O^+ from their K_a tables, 5 that used the thermodynamically correct "conventional" values of 14 and 0, and only 1¹⁷ that used the "rational" values of 15.74 and -1.74 . On the other hand, almost all organic chemistry textbooks and pedagogical papers¹⁸ still use Brønsted's "rational" values (but see Schwarzenbach et al.¹⁹). Also, this is by no means only a textbook problem: Just this year, this *Journal* published an article¹⁶ that includes the "rational" -1.74 pK_a value for $H^+(aq)$, and another article²⁰ that makes the related error of using solvent molarity in the equilibrium constant expression.

Our analysis of textbooks above shows that organic chemists have been the main supporters^{21–24} of the Starkey et al. contention that Brønsted's "rational" pK_a values are the "correct" ones. Their primary supporting argument^{11,23–26} mirrors that originally stated by Ballinger and Long,⁴ who compared their experimentally determined alcohol pK_a s (14.4–

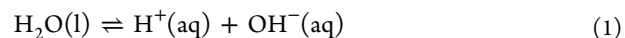
15.5 for methanol, glycerol, and ethylene glycol) to the "rational" value of 15.74 for water, and concluded that the alcohols were stronger acids than water (Figure 1).

There are two important fallacies with this argument, as we shall demonstrate below: (1) Ballinger and Long calculated their alcohol pK_a s relative to water's "conventional" pK_a (14.0); hence, comparison to the "rational" value (15.74) is inappropriate. (2) Also, a careful examination of Ballinger and Long's calculations shows that they used an inappropriate standard state for the solute alcohols (mole fraction = 1), which in turn invalidated their conclusion that water is less acidic than the three alcohols. It is our fervent hope that after readers consider our review of the thermodynamic arguments against Brønsted's "rational" pK_a values for water and H^+ , as well as our critique of the results and conclusions in Ballinger and Long's seminal 1960 *J. Am. Chem. Soc.* paper, that the non-thermodynamic "rational" values will be banished once and for all from modern chemistry textbooks and chemical literature.

DISCUSSION

pK_a of H_2O and H_3O^+ : Brønsted's "Rational" versus "Conventional" Values

Why do almost all organic chemistry textbooks list the "rational" pK_a 's of $H^+(aq)$ and H_2O , -1.74 and 15.74, respectively, and how do these values arise? Brønsted explained the source of the "rational" and "conventional" pairs of values by considering the autoionization of water (sometimes called autoprotolysis):



The "conventional" (and generally accepted) value comes from solution equilibrium thermodynamics, in which the reactant water species in the denominator of the equilibrium constant expression has an activity of 1:

$$\begin{aligned} K_w &= \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} = a_{H^+} \cdot a_{OH^-} \cong \frac{[H^+]}{c^\circ} \cdot \frac{[OH^-]}{c^\circ} \\ &= 1.00(10^{-7}) \cdot 1.00(10^{-7}) = 1.00(10^{-14}) \end{aligned} \quad (2)$$

Here, a_i refers to the activity of solution component i , and $c^\circ = 1$ M, the standard concentration. Recall that the activity of a pure compound in its standard state is 1, and solute activity relates to the more common concentration terms (e.g., molarity, molality, mole fraction) via an activity coefficient (γ): $a_i = \gamma_i \cdot (\text{concentration of } i)$. The value of the activity coefficient is unity for ideal solutions. For most reactions in aqueous solution, the assumption is made that concentrations are sufficiently dilute that molarity is a reasonable proxy for molality, and activity coefficients are close to 1, making the

activity-based K_{eq} approximately equal to the concentration-based ratio (eq 3); all molar concentrations c_i are divided by $c^\circ = 1 \text{ M}$.

$$K_{\text{eq}} = \frac{\prod_{\text{prods}} a_{\text{prods}}^{\nu_{\text{prods}}}}{\prod_{\text{rcts}} a_{\text{rcts}}^{\nu_{\text{rcts}}}} \cong \frac{\prod_{\text{prods}} c_{\text{prods}}^{\nu_{\text{prods}}}}{\prod_{\text{rcts}} c_{\text{rcts}}^{\nu_{\text{rcts}}}} \quad (3)$$

The “conventional” value of K_w , sometimes referred to as the “ion-product” or “activity-based” value, is $1.00(10^{-14})$ at 25°C (eq 2); the negative log of this value yields $\text{p}K_a(\text{H}_2\text{O}) = 14.00$. On the contrary, the “rational” (or “concentration-based”) value comes from using a concentration of 55.33 M for the reactant water species:

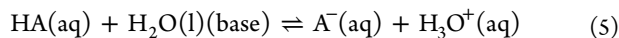
$$K_w' = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}^*} \approx \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{1.00 \times 10^{-14}}{55.33} = 1.81 \times 10^{-16} \quad (4)$$

[In this and future equilibrium constant expressions, the division of each molar concentration by the standard concentration ($c^\circ = 1 \text{ M}$) is understood, and omitted from the expression.]

The “rational” $K_w' = 1.81(10^{-16})$ then leads to $\text{p}K_a'(\text{H}_2\text{O}) = 15.74$. (In this paper we will distinguish the “conventional” and “rational” values by priming the “rational” symbol, e.g., $\text{p}K_a'$.) It is important to point out that common thermodynamic practice for an activity-based equilibrium constant expression approximates the activity of the solvent water as ≈ 1 , or essentially pure; this approximation is included in eq 2. On the other hand, eq 4 approximates the activity of solvent water ($a_{\text{H}_2\text{O}}^*$) as $\approx 55 \text{ M}$. Hence, eq 4 is thermodynamically incorrect, which raises the question of why Brønsted felt justified in presenting the “rational” K_w' and $\text{p}K_a'$ of water as acceptable values.

Acid Ionization Equilibrium

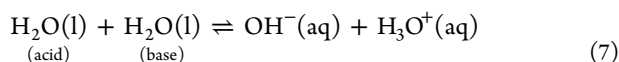
In order to do this, Brønsted used a version of the general acid ionization equilibrium in which a single solvent water molecule serves as the proton-accepting base (eq 5). This depiction of the reaction envisions the product aqueous proton as being bound to a single water molecule in the hydronium ion (H_3O^+); although this depiction is now known to be incorrect,²⁸ it is still widely used as a “shorthand” description of $\text{H}^+(\text{aq})$.



The activity-based equilibrium constant expression for the acid ionization reaction depicted in eq 5 leads to a molarity-based expression (eq 6) in which the product proton concentration is expressed as either $[\text{H}^+]$ or $[\text{H}_3\text{O}^+]$, and the reactant water molecule does *not* appear in the denominator:

$$K_a \equiv \frac{a_{\text{A}^-} a_{\text{H}_3\text{O}^+}}{a_{\text{HA}} a_{\text{H}_2\text{O}}} \approx \frac{a_{\text{A}^-} a_{\text{H}_3\text{O}^+}}{a_{\text{HA}} \cdot 1} \approx \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \quad (6)$$

In eq 5, a single water molecule acts as the base; analogously, Brønsted¹¹ presented the autoionization of water in terms of two water molecules,²⁹ one behaving as acid and the other as base (eq 7).



In his “rational” approach, Brønsted treats similarly the *solvent water acting as base* in both eq 5 (solute acid ionization)

and eq 7 (water autoionization).¹ Specifically, of the two reactant water molecules in eq 7, only the one acting as base is assigned an activity of ≈ 1 ; the water molecule acting as acid is assigned its molar concentration of pure water, 55.33 M :

$$K_w' \equiv \frac{a_{\text{OH}^-} a_{\text{H}_3\text{O}^+}}{a_{\text{H}_2\text{O}}(\text{acid}) \cdot a_{\text{H}_2\text{O}}(\text{base/solvent})} = \frac{a_{\text{OH}^-} a_{\text{H}_3\text{O}^+}}{a_{\text{H}_2\text{O}}(\text{acid}) \cdot 1} \approx \frac{[\text{OH}^-][\text{H}^+]}{55.33 \cdot 1} = 1.81 \times 10^{-16} \quad (8)$$

Meister et al.¹⁰ have pointed out that one cannot assign the two water molecule reactants in eqs 7 and 8 *different* activities (or concentrations); hence, K_w' and $\text{p}K_a'(\text{H}_2\text{O}) = 15.74$ are inconsistent with a thermodynamic description of solution-phase equilibrium.

In his discussion of the acidity of the aqueous proton, Brønsted repeated this error of treating two water molecules differently. In Section I of the Supporting Information, we summarize how this leads to the (erroneous) “rational” values of $K_a' \approx 55.33$ and $\text{p}K_a' = -1.74$ for the aqueous proton.

Brønsted does not explain in any of his early papers^{1,29,30} why he thought it necessary to propose two sets of $\text{p}K_a$ s for water and the aqueous proton, one set of which is thermodynamically indefensible; perhaps he did this in order to align his newly proposed acid–base theory with prior literature and usage, which was split between the two different sets of values. This split has persisted to the present time, almost 90 years later. Brønsted himself was inconsistent in his use of the rational versus conventional $\text{p}K_a$ values. He stated clearly¹ that, for solute acids, the “conventional” K_a with its water activity of 1 was preferred.³ However, for the solvent water, Brønsted usually defaulted to the “rational” K_a' values for H_2O and H_3O^+ .^{31,32}

In summary, the thermodynamically acceptable approximation of the activity of water as ≈ 1 leads to the activity-based “conventional” value of $K_w = 1.00(10^{-14})$, and the “conventional” $\text{p}K_a$ s of 14 and 0 for water and $\text{H}^+(\text{aq})$. The concentration-based “rational” value of $K_w' = 1.81(10^{-16})$ stems from assigning water its thermodynamically unacceptable molar concentration of 55 M , leading to the “rational” $\text{p}K_a'$ values of 15.74 and -1.74 for water and $\text{H}^+(\text{aq})$. In other words, “conventional” and “rational” values are based on different conventions for the concentration of solvent water. To our knowledge, *all chemistry textbooks cite the activity-based value of $K_w = 1.00(10^{-14})$, and none cite the concentration-based K_w' value; hence, textbook authors have confirmed the activity-based convention. Because all texts accept K_w , only “conventional” $\text{p}K_a$ values for water and $\text{H}^+(\text{aq})$ are valid.*

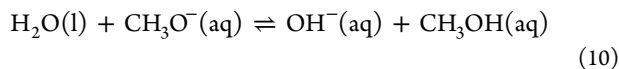
Ballinger and Long: Experimental Systems and Calculations

In spite of the thermodynamic argument above, modern organic chemists continue to use Brønsted’s rational $\text{p}K_a'$ values for water and $\text{H}^+(\text{aq})$, citing Ballinger and Long’s experimental results.⁴ Ballinger and Long measured the acidities of alcohols dissolved in water, employing conductance measurements to determine the equilibrium constant of alcohol/hydroxide reactions (eq 9) of a dozen different alcohols:



Using the K_{eq} values for these reactions, Ballinger and Long then calculated the $\text{p}K_a$ of each alcohol. For example, to determine the $\text{p}K_a$ of methanol, they equilibrated hydroxide

with different concentrations of aqueous methanol (eq 10), and then calculated the equilibrium constant, $K_b(\text{MeO}^-)$, using eq 11:



$$K_b(\text{MeO}^-) = \frac{a_{\text{OH}^-} a_{\text{MeOH}}}{a_{\text{MeO}^-} a_{\text{H}_2\text{O}}} \approx \frac{[\text{OH}^-][\text{MeOH}]}{[\text{MeO}^-]} \quad (11)$$

It is important to note that several approximations typical of dilute solutions are made in eq 11: $a_{\text{H}_2\text{O}} \approx 1$ (water is essentially pure), the activity coefficient of methanol is close to 1, and the ratio of the activity coefficients of the two anions is approximately 1. In their oft-cited 1960 paper,⁴ Ballinger and Long determined $K_b(\text{MeO}^-)$ to be 34.6 ± 2.7 , showing the forward reaction in eq 10 to be spontaneous; in other words, water is a *stronger* acid than methanol. $K_a(\text{MeOH})$ was then calculated from $K_b(\text{MeO}^-)$ and the “conventional” auto-ionization constant for water ($K_w = 1.00 \times 10^{-14}$ at 25 °C), using the well-known eq 12:

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{34.6} = 2.89 \times 10^{-16} \\ \Rightarrow \text{p}K_a(\text{MeOH}) = 15.54 \quad (12)$$

It is crucial to point out that, in eq 12, the K_a of the solute alcohol is calculated relative to the “conventional” K_w of water; for this reason, the $\text{p}K_a$ of the alcohol *must* be compared to the “conventional” $\text{p}K_a$ of water, 14.00, and *not* to the “rational” value. Unfortunately, Ballinger and Long made this very error. When comparing their experimentally determined alcohol $\text{p}K_a$'s to that of water, they used Brønsted's “rational” $\text{p}K_a'$, stating that water's “ion product [was] referred to [a] hypothetical one molar solution.” In other words, Ballinger and Long divided K_w , the conventional “ion product”, by 55.33 M to calculate the rational “concentration-based” K_w' , as shown in eq 8.

Supporters of the “rational” $\text{p}K_a$ of water have often cited this phrase from Ballinger and Long's abstract: “the relative acidities of methanol, water, and ethanol are found to be in the ratio 3:2:1 in the solvent water.”⁴ The methanol/ethanol 3:1 relative acidity is correct, stemming from their experimentally determined $\text{p}K_a$'s: $10^{(16.0-15.54)} = 10^{0.46} = 2.9$. However, the methanol/water 3:2 ratio is incorrect; here, Ballinger and Long inappropriately compared the $\text{p}K_a$ of methanol to the $\text{p}K_a'$ of water (15.54 vs 15.74), to calculate that methanol is 1.5-fold more acidic ($10^{0.2} = 1.58$). Authors who cited Ballinger and Long's conclusion generally made two errors: (1) Some assumed that Ballinger and Long actually measured the $\text{p}K_a'$ of water, when in fact they only calculated it, and (2) other “rational” $\text{p}K_a$ supporters cited Hine and Hine's measured relative acidities of glycerol > ethylene glycol > methanol > water to support the conclusion that methanol is more acidic than water. However this is not valid, because Hine and Hine's measurements were made in the solvent isopropanol.³³

K' versus $K_b(\text{MeO}^-)$: Which Best Expresses Relative Acidity?

In addition to the two very different values for the relative acidities of methanol and water discussed above (from the abstract, methanol is 1.5-fold more acidic than water, based on comparing $\text{p}K_a$'s; from experimental measurements of $K_b(\text{MeO}^-)$, water is 35-fold more acidic than methanol), Ballinger and Long also calculated a third value. This mole-fraction-based value, which they denoted as K' , suggested that

water and methanol are almost equally acidic ($K' = 0.96$). Because K' is quite common in the historical literature, in Section II of the Supporting Information we clearly outline why and how this value is calculated from $K_b(\text{MeO}^-)$. For our purposes, the key conclusions are that K' is essentially a form of $K_b(\text{MeO}^-)$ that is calculated from eq 11, but by using the mole-fraction-based activity of methanol, instead of its molality/molarity-based activity as shown in eq 11. This, along with the mole-fraction-based activity coefficient of methanol, leads to a value of $K' = 0.96$ (eq 13).

$$K' = 0.0277 \cdot K_b(\text{MeO}^-) = 0.0277 \cdot 34.6 = 0.960 \quad (13)$$

Literature values tabulated in Section III of the Supporting Information show that K' averages to 0.6 ± 0.6 , ranging from 0.1 to 2.0. Although it seems statistically reasonable to conclude that K' is essentially 1, previous authors used the overall average K' value to conclude that methanol is a stronger acid than water by a factor of 1.5–3.¹¹

This raises two important questions: (1) Is K' (or $K_b(\text{MeO}^-)$) a reasonable proxy for the spontaneity of the methanol/hydroxide acid–base reaction? And (2) how can the same reaction have two different equilibrium constants, one of which is greater than 1, and the other less than 1?

Choice of Concentration Units Affects Standard Conditions and K_{eq}

The equilibrium constant is a proxy for reaction spontaneity under standard conditions because it is related to the standard reaction free energy: $K_{\text{eq}} = e^{-\Delta G^\circ/RT}$. The magnitude of K_{eq} (>1 vs <1) tells us which direction the reaction goes when starting from standard conditions; hence, its value depends on the choice of standard conditions. In turn, the choice of concentration units dramatically alters standard chemical potential, μ° , as discussed in most undergraduate physical chemistry textbooks (see for example ref 27). In short, the choice of concentration units alters μ° , which in turn alters ΔG° and K_{eq} .

In Section IV of the Supporting Information we discuss in detail the two common standard state conventions, and their effect on μ° and K_{eq} . Summarizing here, convention I is used for miscible liquids (e.g., methanol in water), and takes the pure liquid (mole fraction = 1) as standard state. Convention II is used for solid or gaseous solutes dissolved in liquid solvents (e.g., aqueous acids), and chooses the standard state such that activity coefficients go to 1 in the limit of infinite dilution. The difference between solute standard states in conventions I versus II corresponds to the different standard states used in the calculation of K' (convention I: pure methanol) versus $K_b(\text{MeO}^-)$ (convention II: $\gamma_{\text{MeOH}} = 1$ in 1 M methanol). Because all tabulated $\text{p}K_a$ (and $\text{p}K_b$) values are calculated using convention II under standard conditions of 1 M solute, K_b (and not K') is the appropriate equilibrium constant to use to characterize the acidity of methanol.

Clearly, K_b and K' differ because K_b uses molarity and a standard state of 1 M, whereas K' uses mole-fraction-based activity and a standard state of 1 (i.e., pure compound). One may picture this difference using distance: If you set out for Los Angeles, travel 3000 miles west, and your kids ask “are we almost there yet?”, the answer depends very much on where you started (cf., standard state). If you started from New York, then the answer is yes, but if you started from London, the answer is no. For the case of acidity measurements, because K_a is by convention measured and calculated using solute molarity

and standard state of 1 M, any comparisons to the acidity of water must be made using the molarity-based K_b , and not the activity-based K' .

The net result of our critical examination of Ballinger and Long's three published estimates of the relative acidity of methanol versus water is that the only correct one is their value of $K_b(\text{MeO}^-) = 34.6$, showing that water is 35-fold more acidic than methanol. The average $K_b(\text{MeO}^-)$ from 12 published studies (Table S1, Supporting Information), $K_b(\text{MeO}^-) = 20 \pm 23$, matches what one would expect from comparing the average $\text{p}K_a(\text{MeOH}) = 15.3 \pm 0.5$ to $\text{p}K_a(\text{H}_2\text{O}) = 14.0:10^{1.3} = 20$.

CONCLUSIONS

One might be inclined to view the decision as to which $\text{p}K_a(\text{H}_2\text{O})$ to use, the "rational" versus the "conventional" value, as unimportant. As we see it, there are three reasons why it is important to get this value right. The obvious problem is that because $\text{p}K_a$ values for all solute acids are calculated relative to the "conventional" $\text{p}K_a$ of water, any calculations that use the "rational" $\text{p}K_a'$ of water (or aqueous H^+) will be off by more than 50-fold ($10^{1.74}$). In other words, the correct "conventional" $\text{p}K_a$ of water = 14.00 shows water to be a 55-fold stronger acid than the incorrect "rational" value of 15.74. Similarly, the correct "conventional" $\text{p}K_a$ of $\text{H}^+(\text{aq}) = 0.00$ shows $\text{H}^+(\text{aq})$ to be a 55-fold weaker acid than the incorrect "rational" value of -1.74 .

The second reason why it is important to get this right is that students (and organic chemists!) *must* realize that thermodynamics applies to organic chemistry just as it applies to the first-year chemistry course, and indeed to all of chemistry, biology, and physics. The thermodynamic reasons that justify use of the "conventional" $\text{p}K_a$ values in one course *must* apply as well to organic chemistry. Students are justly confused when they see $\text{p}K_a(\text{H}_2\text{O}) = 14.00$ in their first-year chemistry textbook, and $\text{p}K_a(\text{H}_2\text{O}) = 15.74$ in their organic chemistry text. Only one of these values can be correct, assuming that the standard states are the same.

Finally, it is interesting that this controversy arose so long ago, in the 1920s, at the dawn of the Bronsted–Lowry approach to acid–base chemistry, and seemed to be supported by experimental measurements made over six decades (1927–1990). Our historical analysis of these published results has shown that the definition of the standard state of the solute organic acid differed in different literature reports. The importance of using a uniform, commonly accepted standard state has been discussed,³⁴ but our historical analysis of this controversy shows that this issue deserves closer attention.

Accordingly, we encourage organic chemistry textbook authors to remove the nonthermodynamic "rational" $\text{p}K_a$ values from their $\text{p}K_a$ tables, and replace them with the thermodynamic "conventional" values. Furthermore, the 25 °C $\text{p}K_a$ of 14.00 for water should be followed by a footnote explaining that the $\text{p}K_a$ of the solvent should not directly be compared to those of dilute solutes, due to the different standard states of solvated species vs solvent.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00623.

Additional calculation details and equilibrium values (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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