



Chemical Education

A CHIMIA Column

Teaching the Correct Values of the Acidity Constants of Water and the Hydrogen Ion in Water is Important

The pK_a Values of Water in Water: A Long-Standing, Tiresome, yet Soon Forgotten Issue?

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Abstract: The pK_a values of water and the hydrogen ion (proton) in water are 14 and 0, respectively. Yet, many textbooks of general, organic, and, to a lesser extent, inorganic chemistry provide the incorrect values 15.74 and -1.74, respectively. This column briefly introduces the long-standing issue of these two different pairs of values, the consequences it bears when teaching general chemistry, and expresses the hope that it may be solved soon.

Keywords: Acid-base equilibria · Activity · General chemistry · pK_a of H^+ · pK_a of water · Thermodynamics

A sense of incredulity and astonishment pervades the audience of ca. 250 students when I present the data in Table 1 in my General Chemistry I (Inorganic Chemistry) course. This happens usually during the third week of the first semester in the curriculum for the students of chemistry, chemical engineering, biochemistry, and interdisciplinary sciences at ETH Zurich. There are two equilibrium constants concerning the acid-base behaviour of such a fundamental compound as water, and two different pairs of values for $pK_a(H_2O)$ and $pK_a(H^+_{aq})$, depending on which textbook one consults. I consider this to be not only confusing for the students, but also embarrassing for the chemical community as a whole. Let me get it straight from the beginning: the correct values are $pK_a(H_2O) = 14$ and $pK_a(H^+_{aq}) = 0$. There are three publications that convincingly show how the correct values can be derived by applying quite simple, yet proper thermodynamic criteria, *i.e.* most importantly, the correct standard state for water and activities instead of molar concentrations. The first one, published in 2014, is from a group of authors (including myself) who have taught and still partly teach general chemistry at ETH,^[1] the second one has been authored by Silverstein and Heller in 2017,^[2a] and the third one is a more recent contribution to Libretexts Chemistry by Neils and Schaertel.^[3] Thus, the interested reader – including high school teachers – is invited to consult these three articles for details I will no longer present here. Note, however, that the issue at stake has been discussed long before in the literature.^[4]

The textbooks in Table 1 represent a random choice of books I happen to have, or had, in my office. However, a more extensive number of textbooks have also been listed by others, according to the specific criterion of the pK_a values of water.^[5] It is important to note that several other general chemistry textbooks do not provide these values at all in their pK_a tables, possibly out of prudence. It has also been pointed out^[2,3] that the incorrect values are mainly to be found in organic chemistry textbooks, as a consequence of an influential 1960 paper by Ballinger and Long in

JACS.^[4f] While this is most likely true, a notable case for inorganic chemistry, at least for books written in German, is the renowned Riedel/Janiak (Table 1, entry 7). On the other hand, the famous March's Advanced Organic Chemistry features for the first time the correct values in its 8th edition in 2020, though the erroneous values are still given in brackets (entry 4). Finally, the important monograph by Bell (entry 9) listed the incorrect values back in 1959 (and in the 2nd edition of 1973 as well).

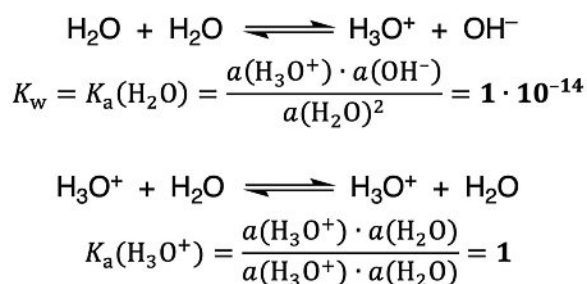
Table 1. Different pairs of values for $pK_a(H_2O)$ and $pK_a(H^+_{aq})$ in a random selection of various textbooks.

Textbook	$pK_a(H_2O)$	$pK_a(H^+_{aq})$
1. Oxtoby, Gillis, Butler, <i>Principles of Modern Chemistry</i> , 8 th Ed., 2016, p.623	14	0
2. Baars, Christen, <i>Allgemeine Chemie</i> , 1. Auflage, 2008, S. 207	14	0
3. Holleman, Wiberg, <i>Anorganische Chemie</i> , 103. Auflage, 2017, p. 268	14	0
4. Smith, <i>March's Advanced Organic Chemistry</i> , 8 th Ed., 2020, pp. 341-345	14 (15.7)	0 (-1.74)
5. March, <i>Advanced Organic Chemistry</i> , 4 th Ed., 1992, Table 8.1, pp. 250-252	15.74	-1.74
6. Anslyn, Dougherty, <i>Modern Physical Organic Chemistry</i> , 2006, pp. 272, 281	15.57	-1.74
7. Riedel, Janiak <i>Anorganische Chemie</i> , 10. Auflage, 2022, S. 350	15.74	-1.74
8. Dickerson, Gray, Darensbourg, <i>Chemical Principles</i> , 4 th Ed., 1984, p.170	15.76	0
9. R.P. Bell, <i>The Proton in Chemistry</i> , 1 st Ed., Methuen, London, 1959, p. 92	15.7	-1.7

In the specific case of my course, taking into account that my students do not yet have a detailed knowledge of thermodynamics to understand a thorough treatment of the problem, how do I go about explaining why the pair of values 15.74 and -1.74 is incorrect? I need to rely on simple chemical arguments and partly even on intuitive ones. The two differences from the correct values amount in absolute terms to 1.74, which corresponds to $\log_{10} 55.5$, and 55.5 is the molar concentration of water in water. The fact that the concentration of the solvent in itself should account for significant differences in the magnitude of two equilibrium constants is intuitively somewhat suspicious, isn't it? However, on a more solid ground, if one formulates an equation for the dissociation of water in water, *i.e.* for its behaviour as an acid, it is self-evident that the same equation describes the self-ionization of water with an accepted equilibrium constant $K_w = 1 \cdot 10^{-14}$ at 25 °C, hence $pK_w = 14$ (Scheme 1). Accordingly, since we are dealing here with one and the same reaction/equilibrium, there are no rational reasons to assume two different equilibrium constants under the exact same conditions. After all, even simple thermodynamics is not an opinion!

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Scheme 1. The fundamental equilibria for the self-ionization of water, the acid behaviour of H_2O and H_3O^+ , and their correct thermodynamic equilibrium constants, under standard conditions.

Before I come to the second constant, 0 vs -1.74 for the $\text{p}K_a$ value of H^+_{aq} , and how I explain it to my students, it is important to realize that the hydrated nature of the hydrogen ion H^+ (proton) in water is more complex than the common representation as H_3O^+ implies. In fact, it has been shown by Stoyanov, Reed and coworkers^[6] that $\text{H}(\text{H}_2\text{O})_6^+$ is the unique form of H^+ in aqueous solutions of ionized acids. Thus, the more appropriate notation of the hydrogen ion in water should be H^+_{aq} rather than H_3O^+ , contrary to what is still adopted in many textbooks and taught in high school and in undergraduate courses. Nonetheless, there are many examples in the literature of simple salts of the solvated proton $\text{H}(\text{H}_2\text{O})_n^+$ that have been isolated in pure form and characterized by X-ray crystallography for $n = 1, 2, 3,$ and 4 . Three of them are shown in Fig. 1. The first one, $(\text{H}_3\text{O})\text{NO}_3$, hydronium nitrate, has been reported as *nitric acid monohydrate*, thereby reflecting the stoichiometry of the compound which crystallizes from equimolar mixtures of nitric acid and water at low temperature.^[7] Values between -1.3 and -1.5 can be found in the literature for the $\text{p}K_a$ of nitric acid.^[8] This value is higher (less negative) than the purported value of -1.74 for H_3O^+ . The very fact that hydronium nitrate exists as such indicates that water is more basic than the nitrate ion, thus retaining the proton in the solid state. This makes it very plausible that H_3O^+ will be a weaker acid than nitric acid in solution as well, meaning that its $\text{p}K_a$ cannot be -1.74 .

Furthermore, the basicity of the hexafluoroantimonate anion in the other two salts in Fig. 1 is extremely low because the conjugate acid HSbF_6 is actually a superacid.^[9] Thus, SbF_6^- can be viewed as a totally innocent counterion, though it engages in the solid state in hydrogen bonding with H_3O^{+10} and H_5O_2^+ (Zundel ion),^[11] respectively. Nonetheless, these two salts are the available pure forms of the monohydrated and dihydrated hydrogen ion, respectively, the latter containing H_3O^+ and H_2O in a 1:1 ratio, forming the strongly hydrogen-bonded H_5O_2^+ ion. Thus, one can in principle imagine to use either one of these two salts as suited starting materials for the preparation of a corresponding

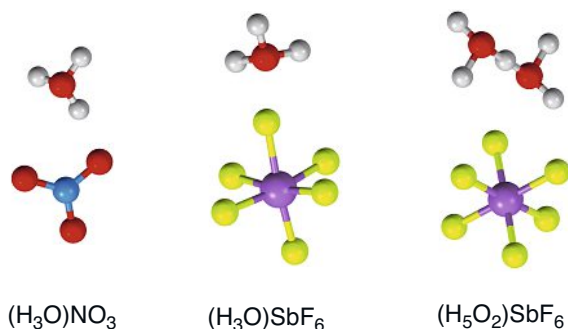


Fig. 1. Representations of the X-ray crystal structures of $(\text{H}_3\text{O})\text{NO}_3$ (CCDC 1591869), $(\text{H}_3\text{O})\text{SbF}_6$ (CCDC 1628625), and $(\text{H}_5\text{O}_2)\text{SbF}_6$ (CCDC 1725516).

buffer having $\text{pH} = \text{p}K_a$ by applying the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]}$$

Caution: What follows is sort of a *reductio ad absurdum*, or apagogical argument, that $\text{p}K_a(\text{H}^+_{\text{aq}})$ can never be -1.74 . Still, for the advocates of this value, and systematically using molar concentrations instead of activities, such a hypothetical buffer would display a $\text{pH} = \text{p}K_a = -1.74$ only in the case of equal molar concentrations of 55.5 M for both H_3O^+ and its conjugate base H_2O . However, such a concentration is only possible for pure water, meaning that this buffer is chemically and physically a non-existent entity, *i.e.* an absurdity that appears to be quite convincing for the students.

By way of a conclusion, it is comforting that the authoritative *Journal of the American Chemical Society* has recently taken up the issue in one of its JACS Video Bytes,^[12] unmistakably explaining that the correct values at stake are $\text{p}K_a(\text{H}_2\text{O}) = 14$ and $\text{p}K_a(\text{H}^+_{\text{aq}}) = 0$. It will be interesting to see how long it takes until the incorrect values are completely eradicated from both textbooks, high school and undergraduate chemistry courses.

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