REVIEW

Confusing Quantitative Descriptions of *Brønsted–Lowry* Acid–Base Equilibria in Chemistry Textbooks – A Critical Review and Clarifications for Chemical Educators

by **Erich C. Meister**[a]), **Martin Willeke**[b]), **Werner Angst**[c]), **Antonio Togni**[a]), and **Peter Walde***[b])

[a]) Department of Chemistry and Applied Biosciences (D-CHAB), ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich

[b]) Department of Materials (D-MATL), ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich
(e-mail: peter.walde@mat.ethz.ch)

[c]) Department of Environmental Systems Science (D-USYS), ETH Zürich, Universitätstrasse 16, CH-8092 Zürich

In chemistry textbooks, the pK_{a,H_2O} value of water in the solvent water at 25 °C is sometimes given as 14.0, sometimes as 15.7. This is confusing. The particular chemical reaction considered is the one in which water as *Brønsted–Lowry* acid reacts with water as *Brønsted–Lowry* base in water as solvent to yield equal concentrations of hydrated oxonium and hydroxide ions, H_3O^+(aq) and HO^-(aq), respectively. This reaction is also known as the 'self-ionization' of water for which the equilibrium constant is abbreviated as K_w with its known value of $10^{-14.0}$ at 25 °C, *i.e.*, $pK_w(25 °C) = 14.0$. Identical values for pK_{a,H_2O} and pK_w at a fixed temperature appear reasonable, since K_{a,H_2O} and K_w refer to one and the same reaction. Therefore, reasons for the apparent disagreement between the 'thermodynamically correct' pK_a value for water (14.0 at 25 °C) and the value reported in most organic chemistry textbooks (15.7) should be discussed when teaching acid–base chemistry. There are good arguments for introducing, from the very beginning, the concepts of activity and thermodynamic standard states when teaching quantitative aspects of chemical equilibria. This also explains in a straightforward way why all thermodynamic equilibrium constants, including K_w, are dimensionless, and why $pK_{H_3O^+}(25 °C) = 0$.

1. Introduction. – The treatment of chemical reaction equilibria – in particular the equilibrium that exists if a *Brønsted–Lowry* acid reacts with water as a base, or if a *Brønsted–Lowry* base reacts with water as an acid – is part of *all* general chemistry textbooks that are used, *e.g.*, at universities for first-year students of chemistry, biology, and other related disciplines (*Fig. 1*). The reasons for this are obvious: *i*) the description and understanding of chemical reaction equilibria is an essential part of the fundament on which chemistry or biology as scientific disciplines are built; and *ii*) the treatment of *Brønsted–Lowry* acid–base reactions in aqueous solution is a particularly important application of the general concepts of chemical equilibria which are usually first outlined in a chemistry course for reactions taking place in the gas phase, *i.e.*, in the absence of any solvent.
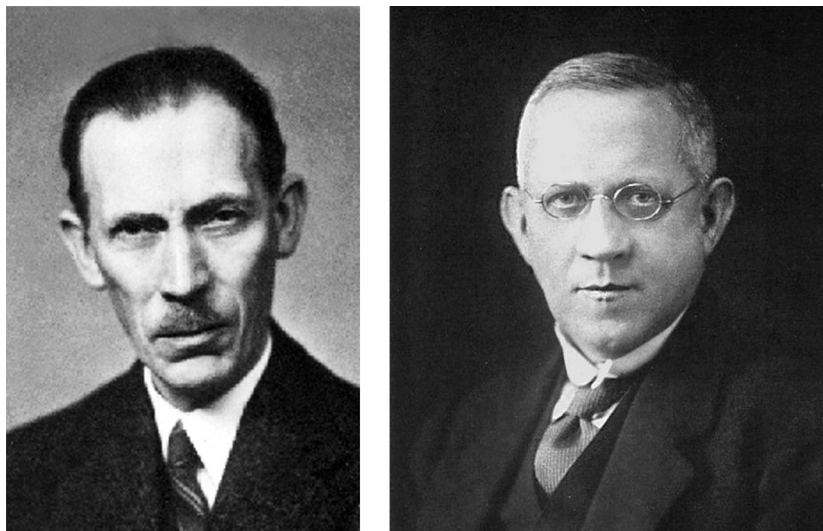
Fig. 1. *According to* Johannes Nicolaus Brønsted (1879–1947; *left*) *and* Thomas Martin Lowry (1874–1936; *right*)*, an acid is a molecule that is able to donate* (release) *a proton, and a base is a molecule that is able to accept* (bind) *a proton* [1][2]. This is the definition of a *Brønsted–Lowry* acid and a *Brønsted–Lowry* base (see [3]). Photographs from Encyclopedia Britannica Online, accessed February 22, 2013, http://www.britannica.com (*Brønsted*); and from *Trans. Faraday Soc.* **1936**, *32*, 1657 (*Lowry*).

Since many years, there exists an apparent inconsistency between the pK_a value of H_2O as *Brønsted–Lowry* acid in water as solvent, if tabulated values reported in some of the general-chemistry textbooks are compared with the values given in organic-chemistry textbooks. Arbitrarily chosen examples of general-chemistry textbooks report that $pK_{a,H_2O}(25\,^\circ C) = 14.0$ (see [4–11]). Apart from notable exceptions [12], organic-chemistry textbooks generally report a pK_a value for H_2O at $25\,^\circ C$ of 15.7 or 15.74, (see, *e.g.*, [13–22]). This is confusing, and even more so, if in one and the same textbook both values are given, a value of 14.0 in the chapter on '*Acid and Base Strength*' and a value of 15.7 in the chapter '*Structure and Reactivity: Organic Acids and Bases*' [23].

The aim of this review is to clarify this dissatisfying apparent discrepancy which was pointed out and discussed previously in a number of articles and personal statements published in chemical education journals [3][24–39]. In only a few textbooks, *e.g.*, [40][41], the authors make the critical readers aware of the '*existence of different pK_a values*' for water: a thermodynamically meaningful value ($pK_{a,H_2O}(25\,^\circ C) = 14.0$) which is fully compatible with the standard *Gibbs* free energy for the reaction (see below in *Sects. 3* and *4* (*Fig. 2*), and a value (15.7 or 15.74) which originally was calculated by taking into account the value of $K_w(25\,^\circ C)$ and the molar concentration of water; see *Appendix*). This latter approach has its roots in those years when the *Brønsted–Lowry* acid–base concepts were applied to '*carbon acids*' and to other weakly acidic organic molecules with low water solubility, on the estimation of their acidity, and the concomitant development of relative acidity scales [43–46].
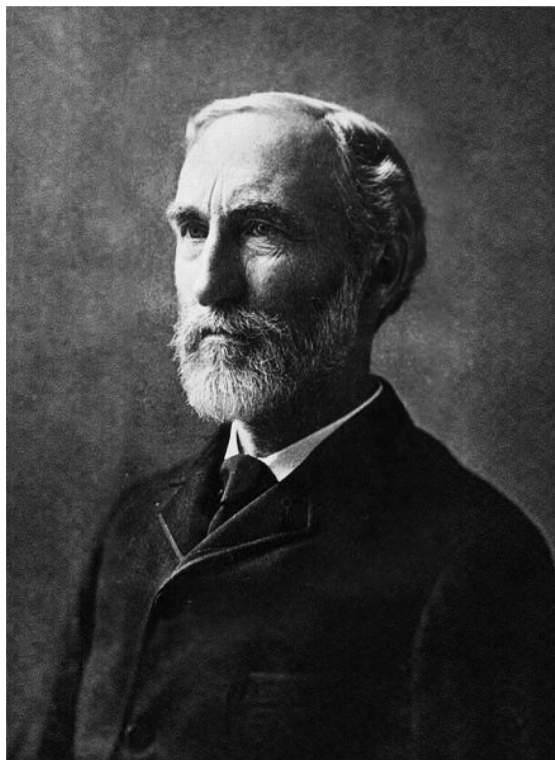
Fig. 2. *The work of* Josiah Willard Gibbs (1839 – 1903) *was fundamental for the development of chemical thermodynamics and for a large part of physical chemistry.* One of the most important publications of *Gibbs* was [42]. Photograph from C. S. Hastings, '*Biographical memoir of Josiah Willard Gibbs 1839 – 1903*', *Natl. Acad. Sci. U.S.A., Biogr. Mem.* **1909**, *6*, 373 – 393.

One of the reasons for the different reported pK_a values are the different conventions used when defining K_a, and the different standard states used for the solvent water in its liquid state, $H_2O(l)$. They are either *i*) pure water ('thermodynamically correct', *i.e.*, compatible with tabulated thermodynamic data), which is consistent with $pK_{a,H_2O}(25\,^\circ C) = 14.0$, or *ii*) one mole water per liter total volume (1M). Similarly, a straightforward 'thermodynamically correct' treatment of $H_3O^+(aq)$ as *Brønsted – Lowry* acid in water yields $pK_{a,H_3O^+} = 0$, while in many organic chemistry textbooks a value of -1.7 or -1.74 is given, which again is not compatible with tabulated thermodynamic data.

An additional inconsistency and confusion currently exists about the dimension of the equilibrium constant K_w as reported in chemistry textbooks, irrespective whether the textbook is on general or organic chemistry. The 'thermodynamically correct' constant $K_w(25\,^\circ C) = 10^{-14.0} = K_{a,H_2O}(25\,^\circ C)$ is dimensionless, as all thermodynamic equilibrium constants, including K_a for any type of *Brønsted – Lowry* acid. This is immediately obvious if one applies the straightforward thermodynamic conventions. It is difficult to understand why these well-elaborated thermodynamic conventions are

not used in contemporary chemistry textbooks, or why reference to the thermodynamic conventions is only made in side remarks, often in such a way that they appear dubious and more irritating than useful (see *Appendix*).

In this contribution, we describe different conventions used in chemistry textbooks for the quantitative thermodynamic description of *Brønsted–Lowry* acid–base reaction equilibria. Particularly, we outline the clear and convincing advantages of introducing and applying 'thermodynamically correct' conventions from the very beginning when teaching this important topic of general chemistry.

For some of the readers, we may be occasionally a bit too trivial, for which we apologize. However, we always try to be clear, dealing with arguments that are straightforward, always based on scientifically reasonable grounds, and hopefully easy to understand. With this, we try to contribute to an improved and consistent teaching of *Brønsted–Lowry* acid–base equilibria. We are convinced that clarifications in textbooks would help avoiding all the on-going confusion and unnecessary discussions that exist in this area of chemistry education since several decades. It is time to reconsider and to rewrite and improve certain chapters in chemistry textbooks, as it would be for the benefit of those students who are interested in chemistry and for the benefit of chemistry as scientific discipline as a whole.

2. The Classical Example: Acetic Acid Dissolved in Water as Solvent. – Before discussing the particular case in which water reacts as *Brønsted–Lowry* acid with water as *Brønsted–Lowry* base, we will discuss in detail the behaviour of acetic acid in water, the classical example which is frequently used in chemistry textbooks to outline the *Brønsted–Lowry* acid–base concepts. This example refers to the reaction that occurs if a small amount of acetic acid is added to water, typically 3.0 g (50 mmol) acetic acid dissolved in a total volume of 1 l at an assumed – and usually not explicitly mentioned – pressure of 1 bar or 1 atm. If the acetic acid molecules (CH_3COOH) come into contact with the water molecules (H_2O), a reaction between the acetic acid molecules (a *Brønsted–Lowry* acid) and the water molecules takes place in such a way that the water molecules act as *Brønsted–Lowry* base. This results in a net transfer of a proton (H^+) from a small part of the CH_3COOH molecules to some of the H_2O molecules, so that acetate ions (CH_3COO^-) and an equal amount of oxonium ions form (H_3O^+; also called hydronium ions). The net proton transfer process is very fast and often described with *Lewis* formula (*Figs. 3* and *4*)[1].

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[1]   Curved arrows are often used to indicate the formal 'electron flow', the movement of an electron pair bound to a H_2O molecule to a H-atom bound to a CH_3COOH molecule, as shown in *Fig. 4,a*, on the left hand side. With this 'curved arrow' convention [13][18][19][52–56], also called 'arrow pushing' [55][57] or 'pushing electrons' convention [46], the formal attack of the acid by the base is illustrated. The convention is that the curved arrow begins where the electrons are originally localized, at the nucleophilic, electron-rich part of the base (H_2O for the forward reaction), and points towards the electrophilic center of the acid (the H-atom of the carboxy group for the forward reaction). While a new O–H bond is formed to yield H_3O^+, the existing O–H bond in CH_3COOH is cleaved, again indicated with a curved arrow. The curved arrows on the right hand side of the reaction in *Fig. 4,a*, show the formal electron flux for the backward reaction (from right to left). Using arrows in *opposite direction*, *i.e.*, from the proton of the *Brønsted–Lowry* acid to the *Brønsted–Lowry* base (see for example [9][58–60]), is not recommended as it does not agree with
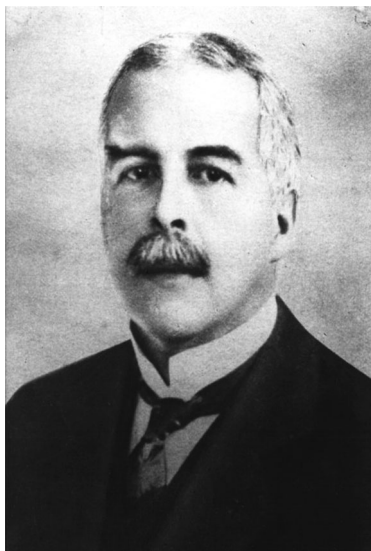
Fig. 3. *In addition to his contributions to 'chemical thermo-dynamics' and the general concept of 'activities'* [47][48], Gilbert Newton Lewis (1875–1946) *introduced a very useful convention for representing chemical structures, in particular organic molecules, whereby pairs of dots indicate electron pairs.* Usually pairs of electrons forming a covalent bond are drawn as line, and lone pairs (non-bonding) are either drawn as pairs of dots or as lines [49–51]. See also [50][51]. Photograph from http://www.msu.edu, accessed February 22, 2013.

In the reaction considered in *Fig. 4,a*, the H_2O molecules are assumed to be present in large excess with respect to the CH_3COOH molecules and with respect to the formed CH_3COO^- and H_3O^+ ions, *i.e.*, water is at the same time *Brønsted–Lowry* base as well as solvent. In the role of solvent, the H_2O molecules hydrate all the dissolved molecules, CH_3COOH, CH_3COO^-, and H_3O^+, forming an aqueous shell around them. This is usually emphasized by writing $CH_3COOH(aq)$, $CH_3COO^-(aq)$, and $H_3O^+(aq)$, indicating that the species actually are dissolved in water and do not form a separate phase. If we consider a closed system without any material exchange with the environment, at any time at a temperature between 0 and 100 °C, the vast majority of the H_2O molecules in this dilute solution is present as liquid water. This means that, at 25 °C, water is a liquid, indicated as $H_2O(l)$, *i.e.*, the standard state of water is liquid. The molar concentration of $H_2O(l)$ is $c_{H_2O} = 55.33$ M at 25 °C (with density $\varrho_{H_2O} = 0.9970$ g/cm³ and molar mass $M_{H_2O} = 18.02$ g/mol). Since the concentrations of the

the mentioned curved arrow formalism which is usually used for describing organic reaction mechanisms. Another generally accepted convention is that the reaction equilibrium is represented with two half arrows (*Fig. 4,a*). In contrast, a single arrow with two heads is used to indicate existence of mesomeric structures (also called 'resonance structures'; *Fig. 4,b*). The two reasonable mesomeric structures of the CH_3COO^- ion shown in *Fig. 4,b*, are of equal energy, and, therefore, contribute equally to the 'real' situation. The curved arrow convention is sometimes also used to indicate how one obtains from one mesomeric structure another one [41][55][61], as indicated in *Fig. 4,b*. This may help students to understand how the different mesomeric structures can be obtained formally.
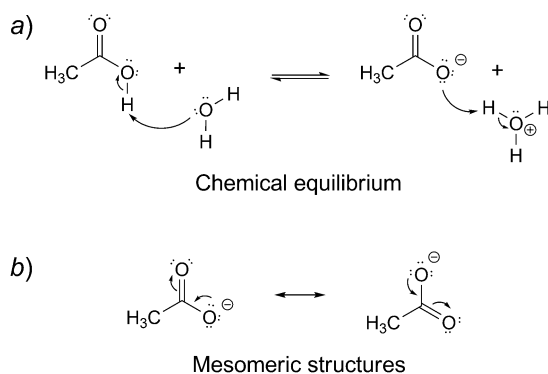
Fig. 4. a) *Chemical formula of the relevant chemical species present at equilibrium upon dissolving* CH_3COOH *in* H_2O. In the forward reaction, CH_3COOH molecules react with H_2O to yield CH_3COO^- and H_3O^+ ions; the formal electron flow for the forward reaction is shown with curved arrows on the left hand side, and for the backward reaction on the right hand side. The two straight arrows with half heads indicate that the system is a chemical equilibrium, *i.e.*, the forward as well as the backward reactions take place. b) *Illustration of the two mesomeric structures of the* CH_3COO^- *ion.* The curved arrows indicate here how one can arrive from one mesomeric structure to the other, by formally delocalizing electron pairs.

dissolved species are negligibly small, the concentration of $H_2O(l)$ in the reaction mixture is always almost the same as the concentration of water in pure water[2]).

The chemical reaction occurring in water between $CH_3COOH(aq)$ and $H_2O(l)$ and the resulting equilibrium situation is usually represented as shown in *Eqn. 1*:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad (1)$$

Another way of describing exactly the same reaction is given in *Eqn. 1′*:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \qquad (1')$$
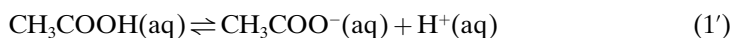
In *Eqn. 1′*, the solvent, $H_2O(l)$, is not explicitly mentioned. The specification '(aq)' indicates that the solvent is water. Note that *Eqns. 1* and *1′* indicate that the concentrations of $H_3O^+(aq)$ and $H^+(aq)$ are the same, although the two species $H_3O^+(aq)$ and $H^+(aq)$ are, from a molecular point of view, not identical and not even the only ones present (*e.g.*, $H_5O_2^+(aq)$ or $H_7O_3^+(aq)$ and so on). Therefore, they all have different standard *Gibbs* energies of formation (see below).

Note that, in principle, the equilibrium of any chemical reaction can be quantitatively 'specified' by using any type of 'rules' to yield an equilibrium constant which has a defined numerical value for the particular stoichiometric reaction

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[2]) For the sake of simplicity, in introductory chemistry textbooks, discussions of the reactions between *Brønsted–Lowry* acids and *Brønsted–Lowry* bases, and their quantitative treatment are often limited to room temperature, *i.e.*, to 25°C. Furthermore, it is assumed that the pressure p is constant, $p = 1$ bar, the standard pressure, although this is not always specifically emphasized.

considered at the particular temperature and pressure. The numerical values of such equilibrium constants then not only depend on the stoichiometry of the reaction, but also on how the equilibrium constant is actually defined, *i.e.*, on the conventions used. Therefore, the numerical value of the equilibrium constant depends on the used measure of the composition (*i.e.*, molar concentrations, mass fractions, *etc.*), and whether relation to a particular reference state of the different species is made. If the conventions applied are not clearly communicated, a correct interpretation and comparison of the equilibrium constants is not possible. With different conventions different equilibrium constants are obtained, with different numerical values and different meanings. Depending on what one intends to express and to compare with a certain equilibrium constant, some of the conventions used are more useful than others. Confusion arises if equilibrium constants obtained using different conventions are compared. This is actually the main reason for the apparent 'water pK_a value problem' which is mentioned in *Sect. 1*, and which led to the writing of this review.

3. The Thermodynamic Acidity Constant of Acetic Acid in Water, K_{a,CH_3COOH}, and Its Negative Logarithm, pK_{a,CH_3COOH}. – On the basis of the definitions and conventions of classical equilibrium thermodynamics developed for ideal gases and ideal solutions (*Raoult*'s law and *Henry*'s law; see [62–64]), for the particular reaction in *Eqns. 1* and *1′*, the relevant quantities which define the thermodynamic equilibrium constant are the *activities*, $a_{i,c}$ of $CH_3COOH(aq)$, $CH_3COO^-(aq)$, $H_3O^+(aq)$ or $H^+(aq)$, and $a_{i,x}$ of $H_2O(l)$. The activity is a quantity which is dependent on the concentrations of all species $A_{1...n}$ in the reaction mixture. For a given reaction between species listed in the stoichiometric equation, the thermodynamic equilibrium constant K is defined by taking the activities of these species into account. The numerical value for the particular equilibrium constant at fixed pressure only depends on temperature.

Before proceeding with the definition of K for the reaction in *Eqns. 1* and *1′*, an alternative and useful formalism is first mentioned, *i.e.*, *Eqns. 2* and *2′*:

$$- CH_3COOH(aq) - H_2O(l) + CH_3COO^-(aq) + H_3O^+(aq) = 0 \qquad (2)$$

$$- CH_3COOH(aq) + CH_3COO^-(aq) + H^+(aq) = 0 \qquad (2')$$
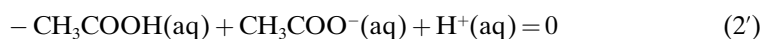
In such type of equations, the sign of the stoichiometric coefficients ν_i is emphasized. It is negative for all species on the left hand side in *Eqns. 1* and *1′* and positive for all species on the right hand side of *Eqns. 1* and *1′*, *i.e.*, ν_i is -1 for $CH_3COOH(aq)$, -1 for $H_2O(l)$, $+1$ for $CH_3COO^-(aq)$, and $+1$ for $H_3O^+(aq)$.

A generalized formalism for any type of chemical reaction, including the discussed reaction in *Eqns. 2* and *2′*, is given in *Eqn. 3* (see *e.g.*, [63]):

$$\sum_{i=1}^{n} \nu_i A_i = 0 \qquad (3)$$

Here, A_i ($A_1, A_2, ... A_n$) represents the n various chemical species appearing in the stoichiometric reaction equation. The stoichiometric coefficient ν_i of the species A_i is

defined as above, with $\nu_i < 0$ for species on the left hand side of the reaction equation (reactants) and $\nu_i > 0$ for species on the right hand side (products), respectively. *Eqns. 2, 2′*, and *3* are simple and useful for a straightforward mathematical treatment of equilibrium equations.

The thermodynamic equilibrium constant K for the general reaction described in *Eqn. 3* follows from the general equilibrium condition for a closed system and is defined as given in [63][3]):

$$K = \prod_{i=1}^{n} a_i^{\nu_i} \tag{4}$$

whereby a_i is the equilibrium activity of species A_i, as mentioned above.

Applying the definition for K in *Eqn. 4* to the reaction formulated with *Eqns. 1* and *2*, one obtains for K the following expression:

$$K_{Eqn.1} = K_{Eqn.2} = a_{CH_3COOH(aq),c}^{-1} \cdot a_{H_2O(l),x}^{-1} \cdot a_{CH_3COO^-(aq),c}^{+1} \cdot a_{H_3O^+(aq),c}^{+1}$$

$$= \frac{a_{CH_3COO^-(aq),c} \cdot a_{H_3O^+(aq),c}}{a_{CH_3COOH(aq),c} \cdot a_{H_2O(l),x}} \tag{5}$$

This is the correct form of the thermodynamic acidity constant for CH_3COOH in water, abbreviated as $^{H_2O}K_{a,CH_3COOH}$ or simply K_{a,CH_3COOH}, without explicit indication that the solvent is water[4]). If not stated otherwise, the solvent is always water, and the pressure is assumed to be $p = 1$ bar. Note, that the activity of the solvent is referred to its standard state which is the pure liquid (see below).

Applying the definition for K in *Eqn. 4* to the reaction in *Eqns. 1′* and *2′* leads to *Eqn. 5′*:

$$K_{Eqn.1'} = K_{Eqn.2'} = a_{CH_3COOH(aq),c}^{-1} \cdot a_{CH_3COO^-(aq),c}^{+1} \cdot a_{H^+(aq),c}^{+1} = \frac{a_{CH_3COO^-(aq),c} \cdot a_{H^+(aq),c}}{a_{CH_3COOH(aq),c}} \tag{5'}$$

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[3]) In a closed system, the equilibrium condition requires that the stoichiometric sum of the chemical potentials of the species vanishes, *i.e.*,

$$\sum_{i=1}^{n} \nu_i \mu_i = 0$$

The chemical potentials are given by $\mu_i = \mu_i^\circ + RT \ln a_i$, with the standard chemical potentials μ_i° and the activities a_i. Note that these latter quantities depend on the choice of the standard state. Upon substitution, we arrive at *Eqn. 4*.

[4]) If water as solvent is replaced with another solvent, *i.e.*, dimethyl sulfoxide (DMSO, $(CH_3)_2SO$), the chemical reaction considered is different as well as the equilibrium constant, $^{DMSO}K_{a,CH_3COOH}$. In this case, CH_3COOH as *Brønsted–Lowry* acid reacts with DMSO as *Brønsted–Lowry* base in DMSO as solvent according to the chemical reaction: $- CH_3COOH(dmso) - (CH_3)_2SO(l) + CH_3COO^-(dmso) + (CH_3)_2SOH^+(dmso) = 0$, whereby '(dmso)' indicates that the dissolved species are solvated by DMSO, in analogy to '(aq)' in the case of aqueous solutions.

Now, let us turn to the *definition of the activities*. Within the thermodynamic convention that is compatible with tabulated thermodynamic data for chemical compounds (see below), the activities of the *dissolved species*, *i.e.*, the activities of $CH_3COOH(aq)$, $CH_3COO^-(aq)$, and $H_3O^+(aq)$ or $H^+(aq)$, are related to the molar concentrations of the dissolved species c_i and the standard concentration c° (1 mol/l = 1M) according to *Eqn. 6* [62–64]:

$$a_{i,c} = \gamma_{i,c} \cdot \frac{c_i}{c^\circ} \tag{6}$$

whereby $\gamma_{i,c}$ is the dimensionless activity coefficient of A_i on the basis of molar concentration. The activity coefficient can be interpreted as an adjustment factor that relates the actual, real behavior of a species to the ideal behavior. In most general-chemistry textbooks, the molar concentration c_i of species A_i is denoted with square brackets, *i.e.*, $c_{CH_3COOH(aq)} = [CH_3COOH(aq)]$. Note, however, that chemistry-textbook authors, when dealing with *Brønsted–Lowry* acid–base equilibria, often use the brackets for both molar concentrations as well as for molar concentrations divided by 1 mol/l. Therefore, in one and the same textbook, even within the same chapter, $[CH_3COOH(aq)]$ may stand for a quantity with the unit mol/l, or it may stand for a dimensionless quantity – which is another point of potential confusion.

In this treatise, c_i stands for the molar concentration of species A_i and it has the unit mol/l = M, while c_i/c° is dimensionless. For strongly diluted, ideal solutions, $\gamma_{i,c} = 1$ is valid and, therefore, $a_{i,c} = c_i/c^\circ$. Here, and in most of the general-chemistry textbooks, this ideal, diluted state is assumed to prevail, since it simplifies all further discussions and calculations ($\gamma_{i,c} = 1$). There is, however, no conceptual problem at all to consider for all equations and calculations values of $\gamma_{i,c} \neq 1$, although the situation becomes more complicated. For example, in electrolyte solutions one has to deal with average, and not individual, activity coefficients due to the interdependence of oppositely charged dissolved species. This is usually outlined in detail in physical-chemistry textbooks and is highly relevant in chemistry courses dedicated to students of environmental sciences, since the concentrations of acids and bases, and other dissolved species in 'natural waters', *e.g.*, sea water, may be so high that considering them as 'diluted solutions' would be inappropriate [12]. Again, for the sake of simplicity, as it is done in most general-chemistry textbooks, we assume here that $\gamma_{i,c} = 1$.

It is very important to note that the thermodynamic standard states of dissolved species and of the solvent *are different*, and this has to be taken into account whenever activities and equilibrium constants are used. Furthermore, since these quantities are related to other thermodynamic properties such as, *e.g.*, the *Gibbs* energies of formation of the solvated species and of the solvent, which are tabulated according to defined standard states, the thermodynamic conventions have to be applied accordingly. Arbitrariness and sloppiness in this subject are the key points for all the confusing discussions in the literature.

To be compatible with tabulated thermodynamic data (*Table*), the activity of the *liquid solvent*, *i.e.*, the activity of $H_2O(l)$ for the reaction considered here, corresponds to the convention given in *Eqn. 7*.

$$a_{\text{solvent},x} = \gamma_{\text{solvent},x} \cdot x_{\text{solvent}} \tag{7}$$

whereby $\gamma_{\text{solvent},x}$ is the dimensionless activity coefficient of the solvent on the basis of mole fraction (for ideal solutions, $\gamma_{\text{solvent},x} = 1$ for all concentrations); and x_{solvent} is the mole fraction of the solvent ($x_{\text{solvent}} = n_{\text{solvent}}/n_{\text{total,solution}}$; n_{solvent} being the amount of solvent and $n_{\text{total,solution}}$ the total amount of species in the solution). For highly diluted solutions, $x_{\text{solvent}} = 1$ is an appropriate assumption. Therefore, with this convention and assuming diluted solutions, the activity of the solvent is $a_{\text{H}_2\text{O(l)},x} = 1$. This is what should be kept in mind.

Table. *Values for the Standard* Gibbs *Energy of Formation, $\Delta_f G_i^\circ(25\,^\circ C)$, for Selected Species A_i in Their Standard States, as Used in This Treatise, from* [5][11][62]

Species A_i	Standard state	$\Delta_f G_i^\circ(25\,^\circ C)$ [kJ/mol]
$CH_3COOH(aq)$	solution, $c = 1\text{M}$	-396.46
$CH_3COO^-(aq)$	solution, $c = 1\text{M}$	-369.31
$H_2O(l)$	pure solvent, $x = 1$	-237.13
$H^+(aq)$	solution, $c = 1\text{M}$	0
$H_3O^+(aq)$	solution, $c = 1\text{M}$	-237.13
$HO^-(aq)$	solution, $c = 1\text{M}$	-157.24

Taking into account the two definitions in *Eqns. 6* and *7*, and assuming that $\gamma_{i,c} = 1$ for all dissolved species and $\gamma_{\text{H}_2\text{O(l)},x} = 1$ for the solvent, one obtains with *Eqns. 5* or *5′* the expression given in *Eqn. 8* for the thermodynamic equilibrium constant $K = K_{\text{a,CH}_3\text{COOH}}$ for the *Brønsted–Lowry* acid–base reaction formulated with *Eqns. 1* or *1′*:

$$K_{\text{a,CH}_3\text{COOH}} = \frac{\dfrac{c_{\text{CH}_3\text{COO}^-(aq)}}{c^\circ} \cdot \dfrac{c_{\text{H}_3\text{O}^+(aq)}}{c^\circ}}{\dfrac{c_{\text{CH}_3\text{COOH}(aq)}}{c^\circ}} = \frac{\dfrac{c_{\text{CH}_3\text{COO}^-(aq)}}{c^\circ} \cdot \dfrac{c_{\text{H}^+(aq)}}{c^\circ}}{\dfrac{c_{\text{CH}_3\text{COOH}(aq)}}{c^\circ}} \tag{8}$$

Obviously, $K_{\text{a,CH}_3\text{COOH}}$ is dimensionless. Furthermore, both reactions in *Eqns. 1* and *1′* yield the same equilibrium constant, since $c_{\text{H}_3\text{O}^+(aq)} = c_{\text{H}^+(aq)}$. This is reasonable since both chemical reactions describe the same equilibrium reaction and are formulated with the same stoichiometry.

Note that the numerical value of the molar concentration of the solvent water, $c_{\text{H}_2\text{O(l)}} = 55.33\text{M}$ at $25\,^\circ C$, must not be considered in the equilibrium expression (*Eqn. 8*), since the thermodynamic standard state of the solvent is the pure solvent, *i.e.*, $x_{\text{H}_2\text{O(l)}} = 1$ rather than $c_{\text{H}_2\text{O(l)}} = 1\text{M}$.

With the definition

$$pK = -\log_{10} K = -\log K \tag{9}$$

and, accordingly, $pK_{\text{a,CH}_3\text{COOH}} = -\log K_{\text{a,CH}_3\text{COOH}}$, *Eqn. 8* can be transformed to *Eqn. 10:*

$$\log K_{a,CH_3COOH} = -pK_{a,CH_3COOH} = \log\left(\frac{\dfrac{c_{CH_3COO^-(aq)}}{c^\circ} \cdot \dfrac{c_{H_3O^+(aq)}}{c^\circ}}{\dfrac{c_{CH_3COOH(aq)}}{c^\circ}}\right)$$

$$= \log\left(\frac{\dfrac{c_{CH_3COO^-(aq)}}{c^\circ}}{\dfrac{c_{CH_3COOH(aq)}}{c^\circ}}\right) + \log\left(\frac{c_{H_3O^+(aq)}}{c^\circ}\right)$$

$$= \log\left(\frac{c_{CH_3COO^-(aq)}}{c_{CH_3COOH(aq)}}\right) + \log\left(\frac{c_{H_3O^+(aq)}}{c^\circ}\right) \qquad (10)$$

Again, it is assumed that all activity coefficients are $\gamma_i = 1$, as mentioned above.

The pH value is *defined* as the negative logarithm to base 10 of the activity of $H_3O^+(aq)$ or $H^+(aq)$ [62–64] (see *Eqn. 11* and [65]).

$$pH = -\log\left(a_{H_3O^+(aq),c}\right) = -\log\left(\gamma_{H_3O^+(aq),c} \cdot \frac{c_{H_3O^+(aq)}}{c^\circ}\right) = -\log\left(\gamma_{H^+(aq),c} \cdot \frac{c_{H^+(aq)}}{c^\circ}\right) \quad (11)$$

For $\gamma_{H_3O^+(aq),c} = 1$ and $\gamma_{H^+(aq),c} = 1$ (see above), one obtains *Eqn. 12*:

$$pH = -\log\left(\frac{c_{H_3O^+(aq)}}{c^\circ}\right) = -\log\left(\frac{c_{H^+(aq)}}{c^\circ}\right) \qquad (12)$$

With the definition of pH in *Eqn. 12*, *Eqn. 10* yields the well-known equation of *Henderson* and *Hasselbalch* (*Fig. 5*), which relates the acidity constant and the equilibrium concentrations to the pH value:

$$pH = pK_{a,CH_3COOH} + \log\left(\frac{c_{CH_3COO^-(aq)}}{c_{CH_3COOH(aq)}}\right) \qquad (13)$$

with $c_{CH_3COO^-(aq)} + c_{CH_3COOH(aq)} = c_{CH_3COOH,total}$, the constant pK_{a,CH_3COOH} can be determined experimentally through simple titration experiments, in which an aqueous acetic acid solution is titrated with a solution of a strong base, typically a solution of hydroxide ions, $HO^-(aq)$, obtained by previously dissolving $NaOH(s)$ in water (see *Fig. 6*). The pH value is measured as a function of added amount of NaOH. The pK_{a,CH_3COOH} value is the pH value of the solution at which the equilibrium concentration of $CH_3COOH(aq)$ and $CH_3COO^-(aq)$ are equal, *i.e.*, $c_{CH_3COO^-(aq)}/c_{CH_3COOH(aq)} = 1$, which means that $\log(c_{CH_3COO^-(aq)}/c_{CH_3COOH(aq)}) = 0$. Since the entire experimental titration curve in *Fig. 6* can be fitted with *Eqn. 13*, experiments and theory are in full agreement with each other, confirming that the assumptions made are reasonable, *i.e.*, $\gamma_i = 1$. An
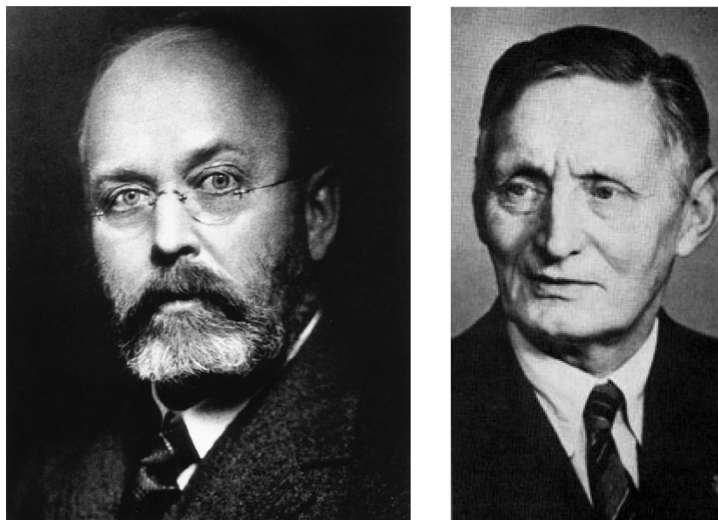
Fig. 5. Lawrence Joseph Henderson (1878 – 1942; *left*) *and* Karl Albert Hasselbalch (1874 – 1962; *right*). See also [66 – 68]. Photographs from J. W. Severinghaus, P. Astrup, J. F. Murray, '*Blood gas analysis and critical care medicine*', *Am. J. Respir. Crit. Care Med.* **1998**, *157*, S114 – S122 (*Henderson*); and F. Sgambato, S. Prozzo, E. Sgambato, R. Sgambato, L. Milano, '*Il centenario del pH (1909 – 2009) – parte seconda. Ma era proprio necessario sostituire l'equazione di Henderson con quella di Henderson-Hasselbalch?*', *Ital. J. Med.* **2011**, *5*, 215 – 226 (*Hasselbalch*).
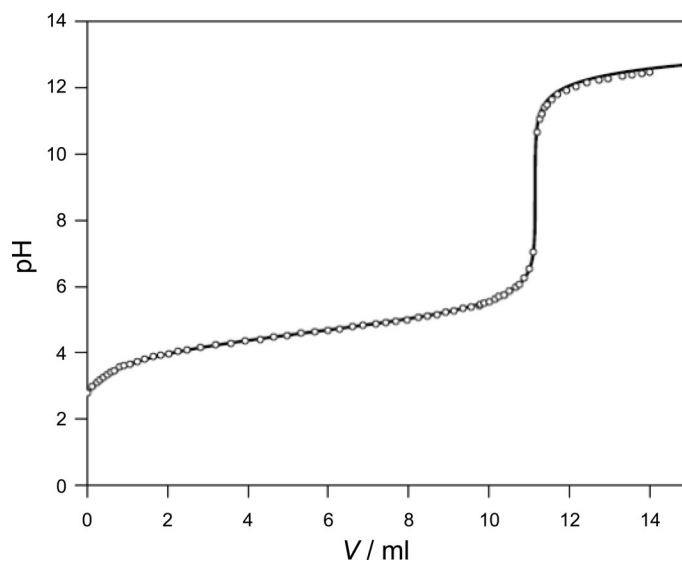
Fig. 6. *Titration of 0.1 l of a* $c_{CH_3COOH,total} = 0.1$M *aqueous CH₃COOH solution with a 1.0*M *solution of aqueous NaOH.* The pH value of the solution was measured (*open circles*) at 20 °C with a *Metrohm 691* pH meter equipped with a *Metrohm* pH glass electrode calibrated at pH 4.0 and pH 7.0. The *solid line* results from a simulation on the basis of the *Henderson–Hasselbalch* equation (*Eqn. 13*), and the self-ionization of water (*Eqn. 21*), with $pK_{a,CH_3COOH} = 4.63$ and $K_w = 6.8 \cdot 10^{-15}$ (at 20 °C). There is excellent agreement with the ideal model.

extrapolation of measured pK_a values obtained with different acetic acid concentrations to an infinitely diluted solution yields p$K_{a,CH_3COOH}(25\,°C) = 4.76$, which means that $K_{a,CH_3COOH}(25\,°C) = 10^{-4.76} = 1.74 \cdot 10^{-5}$, a value which was obtained in the 1920s and 1930s with a series of very careful experiments [69 – 71].

In all textbooks which tabulate the pK_a value for acetic acid in water, there is a rather good agreement about its numerical value; it varies between p$K_{a,CH_3COOH} = 4.76$ (*e.g.*, [8][72]) and p$K_{a,CH_3COOH} = 4.74$ (*e.g.*, [5][73]) at 25 °C.

As already mentioned above, the conventions used so far are thermodynamically meaningful and fully compatible not only with titration experiments, but also with tabulated thermodynamic data. To demonstrate this latter compatibility, K_{a,CH_3COOH} is calculated from the standard reaction *Gibbs* energy, $\Delta_r G°(T)$, for the reactions in *Eqn. 1* and *1'*, by using *Eqn. 14* [62 – 64].

$$K(T) = e^{\frac{-\Delta_r G°(T)}{RT}} \tag{14}$$

which is equivalent to *Eqn. 14'*:

$$\Delta_r G°(T) = -RT \ln K(T) \tag{14'}$$

R is the gas constant (8.3145 J K^{-1} mol^{-1}) and T the absolute temperature (in Kelvin, K).

The magnitude of $\Delta_r G°(25\,°C)$ can be calculated from tabulated values of the standard *Gibbs* energy of formation for each species A_i of the reaction, $\Delta_f G_i°(25\,°C)$, (see the *Table*), as shown in *Eqn. 15*:

$$\Delta_r G°(T) = \sum_{i=1}^{n} \nu_i \cdot \Delta_f G_i°(T) \tag{15}$$

For the reaction of *Eqn. 1*

$$\begin{aligned}
\Delta_r G°(25\,°C)_{Eqn.1} = &-\Delta_f G°_{CH_3COOH(aq)}(25\,°C) - \Delta_f G°_{H_2O(l)}(25\,°C) + \\
&\Delta_f G°_{CH_3COO^-(aq)}(25\,°C) + \Delta_f G°_{H_3O^+(aq)}(25\,°C) \\
= &-(-396.46\ \text{kJ/mol}) - (-237.13\ \text{kJ/mol}) + \\
&(-369.31\ \text{kJ/mol}) + (-237.13\ \text{kJ/mol}) = 27.15\ \text{kJ/mol}
\end{aligned} \tag{16}$$

Note, that the tabulated values for the solvated species and for the solvent again refer to their respective standard states, *i.e.*, $c = 1$M (solvated species) and $x = 1$ (solvent).

For the reaction of *Eqn. 1'*

$$\begin{aligned}
\Delta_r G°(25\,°C)_{Eqn.1'} = &-\Delta_f G°_{CH_3COOH(aq)}(25\,°C) + \Delta_f G°_{CH_3COO^-(aq)}(25\,°C) \\
&+ \Delta_f G°_{H^+(aq)}(25\,°C) = -(-396.46\ \text{kJ/mol}) + (-369.31\ \text{kJ/mol}) \\
&+ 0\ \text{kJ/mol} = 27.15\ \text{kJ/mol}
\end{aligned} \tag{16'}$$

Both calculations yield exactly the same value for $\Delta_r G^\circ(25\,^\circ C) = 27.15$ kJ/mol. This is reasonable since *Eqns. 1* and *1′* are stoichiometrically equivalent representations of one and the same reaction, as discussed above.

With this calculated value for $\Delta_r G^\circ(25\,^\circ C)$, the thermodynamic equilibrium constant $K(25\,^\circ C)$ for the reactions of *Eqns. 1* and *1′* can be calculated with *Eqn. 14:*
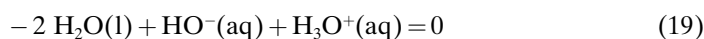
$$K(25\,^\circ C)_{Eqn.1} = K(25\,^\circ C)_{Eqn.1'} = e^{\frac{-\Delta_r G^\circ(25\,^\circ C)}{RT}}$$

$$= e^{\frac{-27150\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\cdot 298\ \text{K}}} = e^{-10.966} = 1.74 \cdot 10^{-5} = 10^{-4.76} \qquad (17)$$

Since $K(25\,^\circ C)_{Eqn.1} = K(25\,^\circ C)_{Eqn.1'} = K_{a,CH_3COOH}(25\,^\circ C)$, the acidity constant for acetic acid in water at $25\,^\circ C$, as calculated from the standard reaction *Gibbs* energy $\Delta_r G^\circ(25\,^\circ C)$, is $1.74 \cdot 10^{-5}$, and accordingly $pK_{a,CH_3COOH}(25\,^\circ C) = 4.76$. This value is in very good agreement with the value used for simulating experimental data (*Fig. 6*), confirming the statement made above that the conventions used in this *Sect.* and the definition of K are fully compatible with tabulated thermodynamic data. Any type of *Brønsted–Lowry* acid–base reaction can be treated in exactly the same way, including the particular case of the reaction of water as *Brønsted–Lowry* acid with water as *Brønsted–Lowry* base in water as solvent, as outlined in the following *Sect.*

4. The Thermodynamic Acidity Constant of Water. – Following exactly the same conventions as described in *Sect. 3* for the reaction of acetic acid with water, the thermodynamic equilibrium constant for the reaction of water as *Brønsted–Lowry* acid with water as *Brønsted–Lowry* base in water as solvent, as formulated in *Eqn. 18* can easily be obtained.

$$H_2O(l) + H_2O(l) \rightleftharpoons HO^-(aq) + H_3O^+(aq) \qquad (18)$$
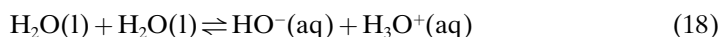
Eqn. 18 can also be expressed as in *Eqn. 19*

$$-2\ H_2O(l) + HO^-(aq) + H_3O^+(aq) = 0 \qquad (19)$$

For reasons discussed above, *Eqns. 18* and *19* can also be formulated as in *Eqns. 18′* and *19′*:

$$H_2O(l) \rightleftharpoons HO^-(aq) + H^+(aq) \qquad (18')$$

$$-H_2O(l) + HO^-(aq) + H^+(aq) = 0 \qquad (19')$$
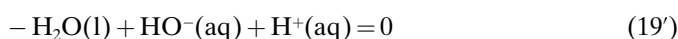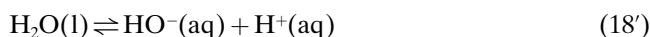
Eqns. 18, 18′, 19, and *19′* are 'equivalent' in the sense that they describe in a stoichiometrically equivalent way the same reaction, known as '*self-ionization of water*', '*autodissociation of water*', or '*autoprotolysis of water*'. The thermodynamic equilibrium constant for the reaction as formulated in *Eqns. 18* and *19* is given in *Eqn. 20:*

$$K_{Eqn.18} = a_{H_2O(l),x}^{-2} \cdot a_{HO^-(aq),c}^{+1} \cdot a_{H_3O^+(aq),c}^{+1} = \frac{a_{HO^-(aq),c} \cdot a_{H_3O^+(aq),c}}{a_{H_2O(l),x}^2} \tag{20}$$

With the conventions outlined above, in particular $a_{solvent,x} = a_{H_2O(l),x} = 1$, and assuming that all activity coefficients of the dissolved species are 1 ($\gamma_{i,c} = 1$), one obtains *Eqn. 21:*

$$K_{Eqn.18} = \frac{c_{HO^-(aq)}}{c^\circ} \cdot \frac{c_{H_3O^+(aq)}}{c^\circ} \tag{21}$$

Accordingly, the thermodynamic equilibrium constant for the reaction in *Eqns. 18′* and *19′* yields

$$K_{Eqn.18'} = a_{H_2O(l),x}^{-1} \cdot a_{HO^-(aq),c}^{+1} \cdot a_{H^+(aq),c}^{+1} = \frac{a_{HO^-(aq),c} \cdot a_{H^+(aq),c}}{a_{H_2O(l),x}} \tag{20′}$$

and by again taking into account that $a_{H_2O(l),x} = 1$ and assuming $\gamma_{i,c} = 1$, one obtains

$$K_{Eqn.18'} = \frac{c_{HO^-(aq)}}{c^\circ} \cdot \frac{c_{H^+(aq)}}{c^\circ} \tag{21′}$$

Since $c_{H_3O^+(aq)} = c_{H^+(aq)}$, K must have the same value for the reactions formulated in *Eqns. 18* and *19*, or *Eqns. 18′* and *19′*. This particular thermodynamic equilibrium constant is usually abbreviated as K_w.

Experimentally, it was found by electrochemical measurements that at 25 °C $c_{H_3O^+(aq)} = 10^{-7.0}$ M [74] (*Fig. 7*), *i.e.*, $c_{H_3O^+(aq)}/c^\circ = 10^{-7.0}$. This means that $c_{H^+(aq)}/c^\circ = 10^{-7.0}$, as well as $c_{HO^-(aq)}/c^\circ = 10^{-7.0}$. This latter relation is due to the fact that for each $H_3O^+(aq)$ formed from H_2O though the reaction shown in *Eqns. 18* or *18′*, one $HO^-(aq)$ is obtained. This is the actual meaning of *Eqns. 18* and *18′*. With these experimental data, one can easily calculate that $K_w(25 °C) = 10^{-7.0} \cdot 10^{-7.0} = 10^{-14.0}$ [75], as mentioned in basically all general-chemistry textbooks, although there is no general consensus on whether the 'water self-ionization constant' has dimensions or not. The constant may have dimensions only if the conventions used for defining the constant are *different* from the thermodynamic conventions outlined here (see below and *Appendix*).

$K_w(25 °C)$ can be calculated in the same way as outlined above for $K_{a,CH_3COOH}(25 °C)$ by taking into account tabulated values for $\Delta_f G_i^\circ(25 °C)$ for the relevant chemical species of the reaction, as given in the *Table* (see *Eqns. 22* and *22′* for the reactions of *Eqns. 18* and *18′*).

$$\begin{aligned}
\Delta_r G^\circ(25 °C)_{Eqn.18} &= -2\,\Delta_f G_{H_2O(l)}^\circ(25 °C) + \Delta_f G_{HO^-(aq)}^\circ(25 °C) + \Delta_f G_{H_3O^+(aq)}^\circ(25 °C) \\
&= -2\,(-237.13 \text{ kJ/mol}) + (-157.24 \text{ kJ/mol}) + (-237.13 \text{ kJ/mol}) \\
&= 79.89 \text{ kJ/mol}
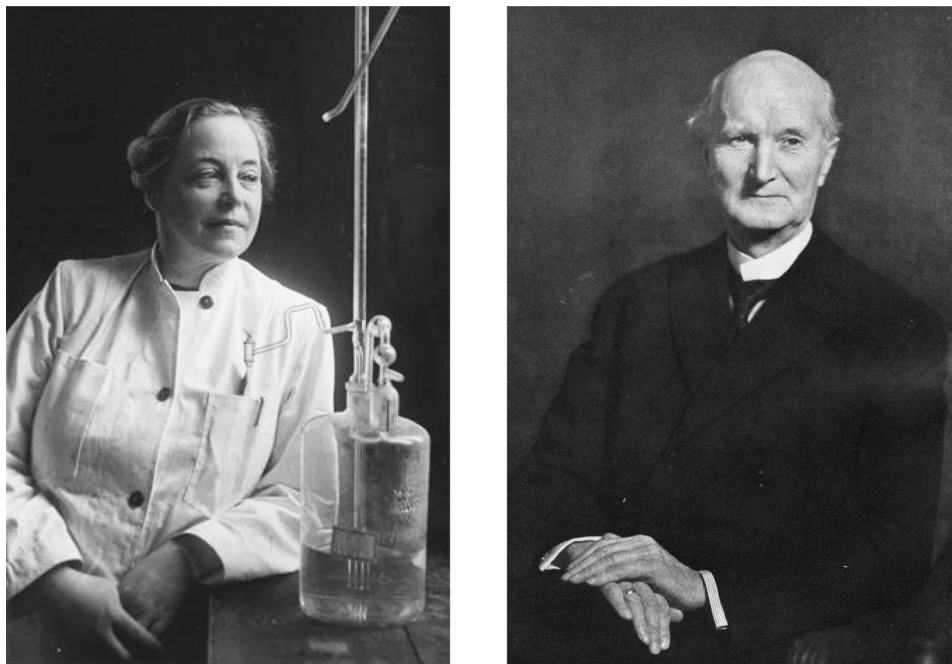\end{aligned} \tag{22}$$

Fig. 7. *Augusta Marie Unmack (1896 – 1990; left), assistant of Niels Janniksen Bjerrum (1879 – 1958; right) – one of the pioneers of physical chemistry –, analyzed aqueous solutions with a hydrogen electrode and determined from these measurements the ionization constant of water* [74]. See [76 – 78]. Photographs from the Royal Library, Copenhagen, Denmark (*Unmack*, © Royal Library Copenhagen, reprinted with permission); and N. Bohr, J. A. Christiansen, K. J. Pedersen, *et al.* (Eds.), 'Niels Bjerrum. Selected Papers, edited by friends and co-workers on the occasion of his 70th birthday the 11th of March, 1949', Einar Munksgaard, Copenhagen, 1949 (*Bjerrum*).

$$\Delta_r G^\circ (25\,^\circ C)_{Eqn.18'} = -\Delta_f G^\circ_{H_2O(l)}(25\,^\circ C) + \Delta_f G^\circ_{HO^-(aq)}(25\,^\circ C) + \Delta_f G^\circ_{H^+(aq)}(25\,^\circ C)$$
$$= -(-237.13 \text{ kJ/mol}) + (-157.24 \text{ kJ/mol}) + 0 \text{ kJ/mol}$$
$$= 79.89 \text{ kJ/mol} \qquad (22')$$

Independent of whether the autoprotolysis of water is formulated with *Eqns. 18, 18'*, or *Eqns. 19, 19'*, one obtains $\Delta_r G^\circ (25\,^\circ C) = 79.89$ kJ/mol. With this and applying *Eqn. 14*, one obtains $K_w(25\,^\circ C) = 10^{-14.0}$.

$$K_w(25\,^\circ C) = e^{\frac{-\Delta_r G^\circ (25\,^\circ C)}{RT}} = e^{\frac{-79890 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{mol}^{-1} \cdot 298 \text{ K}}} = e^{-32.243} = 9.93 \cdot 10^{-15} \approx 10^{-14.0} \quad (23)$$

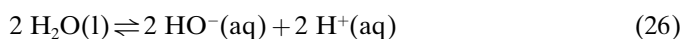Therefore, $pK_w(25\,^\circ C) = 14.0$.

Since *Eqns. 18, 19*, and *Eqns. 18', 19'* represent a chemical reaction in which water reacts as *Brønsted–Lowry* acid with water as *Brønsted–Lowry* base, K_w is also the acidity constant for water. Therefore, $K_w(25\,^\circ C) = 10^{-14.0}$ means that $K_{a,H_2O}(25\,^\circ C) =$

$10^{-14.0}$ and $pK_{a,H_2O}(25\,^{\circ}C) = -\log K_{a,H_2O}(25\,^{\circ}C) = 14.0 = pK_w(25\,^{\circ}C) = -\log K_w(25\,^{\circ}C)$. Therefore, *the thermodynamically correct pK_a value for the dissociation of water in the solvent water at a temperature $25\,^{\circ}C$ and an assumed pressure of $p = 1$ bar is 14.0.* This value can be found in a number of general-chemistry textbooks [4–11]. Often, however, pK_a tables in introductory-chemistry textbooks do not have an entry for H_2O (or H_3O^+), probably to avoid discussing the kind of question we address in this treatise. As will be also demonstrated in *Sect. 6*, the thermodynamically correct value for the $pK_{a,H_3O^+}(25\,^{\circ}C)$ is 0.

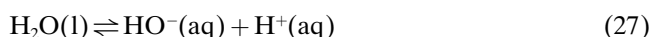Full compatibility of $pK_w(25\,^{\circ}C) = pK_{a,H_2O}(25\,^{\circ}C) = 14.0$ with tabulated thermodynamic data is further illustrated by considering the autodissociation of water as the sum of two redox half-cell reactions under standard conditions, the reduction of water to hydrogen gas and to two hydrated hydroxide ions, and the oxidation of hydrogen gas to two hydrated protons, as shown in *Eqns. 24* and *25*.

$$2\,H_2O(l) + 2\,e^- \rightleftharpoons H_2(g) + 2\,HO^-(aq) \tag{24}$$

$$H_2(g) \rightleftharpoons 2\,H^+(aq) + 2\,e^- \tag{25}$$

The sum of *Eqns. 24* and *25* yields

$$2\,H_2O(l) \rightleftharpoons 2\,HO^-(aq) + 2\,H^+(aq) \tag{26}$$

Divisions on both sides of *Eqn. 26* by 2 gives

$$H_2O(l) \rightleftharpoons HO^-(aq) + H^+(aq) \tag{27}$$

At $25\,^{\circ}C$ and standard pressure $p = 1$ bar, the tabulated standard reduction potential E°_{red} for the half-cell reaction of *Eqn. 24* is -0.8277 V [75]. The standard oxidation potential E°_{ox} for the half-cell reaction of *Eqn. 25* is 0.0000 V by definition [75], since all tabulated standard reduction potentials are related to this reaction, the standard hydrogen electrode. Therefore, the standard potential ΔE° for the reaction of *Eqn. 26* or *27* is $\Delta E^{\circ}_{Eqn.26} = \Delta E^{\circ}_{Eqn.27} = E^{\circ}_{red,Eqn.24} + E^{\circ}_{ox,Eqn.25} = -0.8277$ V $+ 0.0000$ V $= -0.8277$ V.

The relationship between ΔE° and $\Delta_r G^{\circ}$ is given as [62–64]:

$$\Delta_r G^{\circ} = -\,n_e \cdot F \cdot \Delta E^{\circ} \tag{28}$$

F being the *Faraday* constant (96485 C mol^{-1} $= 96485$ J V^{-1} mol^{-1}), and n_e the number of electrons involved in the redox half-cell reactions leading to the net reaction. For the reaction in *Eqn. 27*, $n_e = 1$.

For the reaction of *Eqn. 27*, one obtains *Eqn. 29*

$$\begin{aligned} \Delta_r G^{\circ}(25\,^{\circ}C)_{Eqn.27} &= -1 \cdot 96485 \text{ J V}^{-1} \text{ mol}^{-1} \cdot (-0.8277 \text{ V}) \\ &= 79860 \text{ J/mol} = 79.86 \text{ kJ/mol} \end{aligned} \tag{29}$$
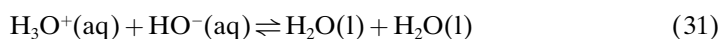
$\Delta_r G°(25°C)_{Eqn.27}$ is identical with the value $\Delta_r G°(25°C)_{Eqn.18'}$ calculated on the basis of the tabulated $\Delta_f G_i°(25°C)$ values for the individual chemical species. This yields $K_w(25°C) = K_{a,H_2O}(25°C) = 10^{-14.0}$ (see *Eqn. 23*), and $pK_w(25°C) = pK_{a,H_2O}(25°C) = 14.0$.)

As already mentioned repeatedly above, like all other thermodynamic equilibrium constants, K_w is a dimensionless constant. However, in several textbooks, this constant is given with units $(mol^2\,l^{-2} = M^2)$ [9][16][46][60][79–82] (see *Appendix*). Interestingly, somewhat strange appears the translation of an American general-chemistry textbook [83a] into German [83b] which resulted in a change of the units of K_w from dimensionless in the original edition to unit $mol^2\,l^{-2}$ in the German version (similar changes were made for other equilibrium constants, *e.g.*, for the solubility product, K_{sp}). This change was apparently done on purpose and not by mistake, 'in order to adapt to local customs', as quoted in the introduction to the German edition. Chemistry as scientific discipline should be language- and country-independent. Uncertainty about the proper dimensions is also evident if, in one particular case, various editions of one and the same textbook are compared: K_w was dimensionless in an early edition [84], while in a later edition [20], K_w is given in units $mol^2\,l^{-2}$.

5. Calculation of Equilibrium Constants for *Brønsted–Lowry* Acid–Base Reactions in Which the Base Is not Water. – Knowing the pK_a values for *Brønsted–Lowry* acids in water, *i.e.*, knowing the equilibrium constants for reactions between a *Brønsted–Lowry* acid and water as *Brønsted–Lowry* base, allows calculation of equilibrium constants for aqueous *Brønsted–Lowry* acid–base equilibria in which the base is *different* from water. The equilibrium constant for such reactions can be calculated from the individual acidity constants K_a of the two acids involved in the equilibrium. To illustrate this, let us consider the titration experiment discussed above and shown in *Fig. 6* (see *Eqn. 30*). Hydrated acetic acid, $CH_3COOH(aq)$, and hydrated hydroxide ions, $HO^-(aq)$, react to yield hydrated acetate ions, $CH_3COO^-(aq)$, and $H_2O(l)$. As indicated with '(aq)', the reaction takes place in $H_2O(l)$ as solvent.

$$CH_3COOH(aq) + HO^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l) \qquad (30)$$

The acid on the left hand side of *Eqn. 30* is $CH_3COOH(aq)$, its corresponding base on the right hand side is $CH_3COO^-(aq)$; the acid on the right hand side is $H_2O(l)$, its corresponding base on the left hand side $HO^-(aq)$. The chemical reaction represented with *Eqn. 30* can be considered as the *sum of two separate* Brønsted–Lowry *acid–base reactions*, both being reactions of *Brønsted–Lowry* acids with $H_2O(l)$ as *Brønsted–Lowry* base; the equilibrium constant, $K(25°C)_{Eqn.30}$ for the reaction of *Eqn. 30* can then be obtained as the *product* of the reaction constants of the two separate reactions. The two separate reactions are given in *Eqns. 1* and *31:*

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad (1)$$

$$H_3O^+(aq) + HO^-(aq) \rightleftharpoons H_2O(l) + H_2O(l) \qquad (31)$$

The *sum* of the two reactions yields *Eqn. 30*. Note that the reaction of *Eqn. 31* is the 'inverse' of the reaction of *Eqn. 18*.

In *Eqn. 1*, $CH_3COOH(aq)$ is the *Brønsted–Lowry* acid and $H_2O(l)$ the *Brønsted–Lowry* base, in *Eqn. 31* $H_3O^+(aq)$ is the *Brønsted–Lowry* acid and $HO^-(aq)$ the *Brønsted–Lowry* base. Since, at 25 °C, $K_{Eqn.1} = K_{a,CH_3COOH} = 10^{-4.76}$ and $K_{Eqn.31} = 1/K_{a,H_2O} = 1/K_w = 1/10^{-14.0} = 10^{14.0}$, one obtains $K_{Eqn.30} = K_{Eqn.1} \cdot K_{Eqn.31} = 10^{-4.76} \cdot 10^{14.0} = 10^{9.24}$.

The same value results from the tabulated thermodynamic data for the standard *Gibbs* energy of formation, $\Delta_f G_i^\circ(25\,°C)$, for the different species of *Eqn. 30* (see the *Table*):

$$\Delta_r G^\circ(25\,°C)_{Eqn.30} = -\Delta_f G^\circ_{CH_3COOH(aq)}(25\,°C) - \Delta_f G^\circ_{HO^-(aq)}(25\,°C) +$$
$$\Delta_f G^\circ_{CH_3COO^-(aq)}(25\,°C) + \Delta_f G^\circ_{H_2O(l)}(25\,°C)$$
$$= -(-396.46\ \text{kJ/mol}) - (-157.24\ \text{kJ/mol}) + (-369.31\ \text{kJ/mol}) + (-237.13\ \text{kJ/mol})$$
$$= -52.74\ \text{kJ/mol} \qquad (32)$$

$$K(25\,°C)_{Eqn.30} = e^{\frac{-\Delta_r G^\circ(25\,°C)_{Eqn.30}}{RT}} = e^{\frac{52740\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1} \cdot 298\ \text{K}}}$$
$$= e^{21.286} = 1.76 \cdot 10^9 = 10^{9.24} \qquad (33)$$

Note that the numerical value of the equilibrium constant of $1.76 \cdot 10^9$ is a large number, since a weak acid, $CH_3COOH(aq)$, reacts with a strong base, $HO^-(aq)$. This is the basis for any type of weak acid–strong base titration experiment.

6. The Thermodynamic Acidity Constant of the Oxonium Ion (H_3O^+) in Water. – To conclude the straightforward application of the thermodynamic conventions for the quantitative treatment of *Brønsted–Lowry* acid–base equilibria, let us ask the question: 'What is the thermodynamic pK_a value of H_3O^+ in water as solvent?' The answer must be clear: $pK_{a,H_3O^+} = 0$.

The reaction considered is

$$H_3O^+(aq) + H_2O(l) \rightleftharpoons H_2O(l) + H_3O^+(aq) \qquad (34)$$
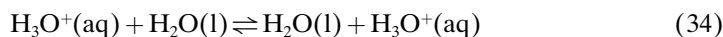
with

$$K_{a,H_3O^+} = \frac{a_{H_2O(l),x} \cdot a_{H_3O^+(aq),c}}{a_{H_3O^+(aq),c} \cdot a_{H_2O(l),x}} = 1 \qquad (35)$$

$K_{a,H_3O^+} = 1$ means $\Delta_r G^\circ = 0$ (see *Eqns. 14* and *14′*). Therefore, $pK_{a,H_3O^+} = -\log K_{a,H_3O^+} = -\log 1 = 0$, *independent of temperature*. This means that, whenever a H_2O molecule 'attacks' an oxonium ion, an oxonium ion and a molecule of H_2O result, irrespective of whether this process takes place at 25 °C, 50 °C, or any other temperature.

In summary, a description of *Brønsted–Lowry* acid–base reactions within the framework of the thermodynamic conventions yields $pK_{a,H_2O}(25\,°C) = 14.0 = pK_w(25\,°C)$ and $pK_{a,H_3O^+} = 0$.

7. Final Remarks and a Suggestion. – As outlined repeatedly above, apparent inconsistency in chemistry textbooks not only exists about the value of the pK_a of H_2O or H_3O^+ in water at $25\,°C$, but there is also an apparent inconsistency about the dimension of equilibrium constants, since comparison is made between constants that are defined differently. Therefore, a clear communication of the conventions applied is of outmost importance. A further observation that actually adds to the confusion in chemistry textbooks is the *change in conventions* on going from one chapter to the other, even if the topics of the two chapters may be directly related. This is particularly evident when moving from the treatment of reactions occurring in the gas phase between gaseous molecules to the treatment of reactions occurring in solution; either *i*) between dissolved species (the solvent being an 'inert' medium not directly taking part in the chemical reactions); or *ii*) between dissolved species and the solvent molecules (*e.g.*, the *Brønsted–Lowry* acid–base reactions discussed extensively in this treatise). Such a change in conventions is unnecessary, although it persists in chemistry textbooks since decades. It appears difficult to alter past customs to a uniform treatment of chemical reaction equilibria.

We are convinced that the concepts of activities and standard states – with all the consequences – could be introduced from the very beginning when teaching general chemistry. Certainly, changing the way the students get introduced into the quantitative treatment of chemical reaction equilibria – in particular *Brønsted–Lowry* acid–base reactions – would mean a considerable effort to modify certain chapters in general-chemistry textbooks. However, this can certainly be accomplished and should be accomplished. We feel that specific improvements in textbooks and in the teaching are indeed necessary. The fundamental concepts of chemistry should be independent of the textbook used, independent of the country in which chemistry is taught, and independent of the written and spoken language.

Improvements as we suggest here would be mainly for the benefit of chemistry students and for a better general reputation of chemistry as central, scientific discipline. The proposed changes are based on well-established physicochemical considerations, as outlined extensively in *Sect. 3–6*. There is no doubt that such changes can be made, but they clearly have to go beyond 'cosmetic modifications'.

The *thermodynamically correct* treatment of chemical reaction equilibria as outlined in *Sects. 3* to *6* is straightforward, useful, and transparent, and should be easy to understand. Even without a previous detailed education in chemical thermodynamics, a student should be able to follow the arguments presented. There are at the end only a few concepts and conventions to consider and apply. The main 'rules' are the following.

1) First, a chemically and stoichiometrically correct equation describing a particular chemical reaction in which one is interested in should be formulated. In this equation, the states of the chemical species involved have to be clearly indicated. The states are either gaseous (g), liquid (l), solid (s), or dissolved. If

the solvent is water, the dissolved species are indicated by adding (aq). The solvent used has to be clear from the equation.

2) Any chemical equilibrium can be represented with the generalized *Eqn. 3* in which the stoichiometric coefficients and the species involved are ν_i and A_i

$$\sum_{i=1}^{n} \nu_i A_i = 0 \tag{3}$$

Examples are *Eqns. 2* and *2′* in *Sect. 3*, and *Eqns. 19* and *19′* in *Sect. 4*.

3) The equilibrium constant K is then defined for the as formulated reaction according to *Eqn. 4*.

$$K = \prod_{i=1}^{n} a_i^{\nu_i} \tag{4}$$

whereby a_i is the activity of species A_i and ν_i is the stoichiometric coefficient of A_i. Examples are *Eqns. 5* and *5′* in *Sect. 3*, and *Eqn. 20* and *20′* in *Sect. 4*.

4) The activities of the different types of species involved in the equilibrium are *defined depending on their states*, as follows.

For *dissolved species* A_i as shown in *Eqn. 6*

$$a_{i,c} = \gamma_{i,c} \cdot \frac{c_i}{c^\circ} \tag{6}$$

$\gamma_{i,c}$ being the activity coefficient of the dissolved species A_i on the basis of molar concentration, c_i being the molar concentration of the dissolved species A_i, and c° being the standard concentration which is $1 \text{ mol } l^{-1} = 1\text{M}$.

For *liquid solvents* as in *Eqn. 7*

$$a_{\text{solvent},x} = \gamma_{\text{solvent},x} \cdot x_{\text{solvent}} \tag{7}$$

$\gamma_{\text{solvent},x}$ being the activity coefficient of the solvent on the basis of mole fraction, x_{solvent} being the mole fraction of the solvent ($x_{\text{solvent}} = n_{\text{solvent}}/n_{\text{total,solution}}$, n_{solvent} being the amount of solvent and $n_{\text{total,solution}}$ being the total amount of substances in the solution). In dilute solutions, $x_{\text{solvent}} = 1$.

For *gaseous species* A_i, as in *Eqn. 36*

$$a_{i,p} = \gamma_{i,p} \cdot \frac{p_i}{p^\circ} \tag{36}$$

$\gamma_{i,p}$ being the activity coefficient of gaseous species A_i on the basis of pressure in units of bar, p_i being the partial pressure of the gas A_i ($p_i = x_i \cdot p_{total}$, with x_i being the mole fraction of gas A_i), and p° being the standard pressure which is 1 bar. For *solids* as in *Eqn. 37*

$$a_{\text{solid},x} = \gamma_{\text{solid},x} \cdot x_{\text{solid}} \tag{37}$$

$\gamma_{\text{solid},x}$ being the activity coefficient of the solid on the basis of mole fraction $x_{\text{solid}} = n_{\text{solid}}/n_{\text{total,solid}}$. For a pure solid phase, $x_{\text{solid}} = 1$. Note that the standard state of the solid is its most stable polymorphic form at the temperature considered.

5) Since in introductory-chemistry textbooks, the discussion of chemical equilibria of any type usually is limited to ideal systems in which, for example, the concentrations of all dissolved species are low, all activity coefficients take a value of 1, *i.e.*, $\gamma_{i,c} = 1$, $\gamma_{\text{solvent},x} = 1$, $\gamma_{i,p} = 1$, $\gamma_{\text{solid},x} = 1$.

As a general summary of our rather detailed argumentations in this treatise, we propose to introduce straightforward thermodynamic conventions and the concept of activities at the very beginning when teaching reaction equilibria in a general-chemistry course. This is independent of whether reactions occurring in the gas phase are discussed, *i.e.*, reactions occurring without any solvent, or whether the reactions take place in a solvent with its participation in the reaction. When using tabulated 'pK_a values' for organic molecules taken from organic-chemistry textbooks, students should be made aware of the fact that the listed values often are based on conventions which are different from the thermodynamic ones. Differently defined constants should not be mixed-up.

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Appendix

Aim and Content. This *Appendix* contains two *Notes* which describe in detail how quantitative aspects of *Brønsted–Lowry* acid–base reaction equilibria often are treated in chemistry textbooks, and why these treatments frequently are confusing, and why they may lead to equilibrium constants which are not compatible with tabulated thermodynamic data. The main reason for the confusion is the apparent refusal of defining equilibrium constants on the basis of activities and the appropriate thermodynamic standard states. *We show that there are clear advantages of applying the concept of activities and thermodynamic standard states* when discussing quantitative aspects of chemical reaction equilibria (see the main text).

The first *Note* is on *molar-concentration-based reaction constants* (*Note A1*) and the second one on *the molar-concentration-based 'acidity constant' of water in water at 25 °C* (*Note A2*). In this second *Note*, we analyze the arguments which were brought up in literature for obtaining for the acidity constant of water in water at 25 °C a value of $10^{-15.7}$ (or $10^{-15.74}$) *vs.* the thermodynamically meaningful value of $10^{-14.0}$ (*Sect. 4* of the main text).

General Remarks. All equations in this *Appendix* which do not appear in the main text are labelled accordingly, *e.g.*, *Eqn. A1*.

As mentioned in *Sect. 3*, in the *strictly thermodynamic treatment* of *Brønsted–Lowry* acid–base reaction equilibria, there are clear conventions about the standard states which *vary depending on the nature of the species* involved in the equilibrium. They are $c^\circ = 1$ M for dissolved species, $p^\circ = 1$ bar for gaseous reactants, and for the solvent the standard state is the pure liquid solvent. With the assumption of strongly diluted solutions, *i.e.*, $\gamma_{i,c} = 1$ and $\gamma_{\text{solvent},x} = 1$, the activity of dissolved species A_i is $a_{i,c} = c_i/c^\circ$, and the activity of the solvent is always $a_{\text{solvent},x} = 1$.

In principle, there are *various ways to define an equilibrium constant* (*Notes 1* and *2*), although such arbitrarily defined constants may not necessarily be compatible with tabulated thermodynamic data, or they may not be useful for a quantitative, comparative treatment of the equilibrium state. In any case, it is important and absolutely neccessary that the rules used are clearly specified. If such specifications are not made, it is likely that unnecessary confusion arises. This may lead to the assumption that there is an inconsistency with other values of equilibrium constants for one and the same reaction, formulated with the same stoichiometric equation, although, in fact, there is only an *apparent inconsistency* due to the different rules and conventions used. All what follows originates from a disregard of the strictly thermodynamic conventions, although this is often not explicitly made clear.

We hope that our explanations here are useful for chemical educators and help understanding how *Brønsted–Lowry* acid–base reaction equilibria are actually treated *in most chemistry textbooks*.

Note A1. On the Molar-Concentration-Based Reaction Constants, K^c *and* K'^c. In this *Note*, we explain definitions of equilibrium constants of *Brønsted–Lowry* acid–base reactions for the following two cases:

Case i, in which the equilibrium constants are expressed in terms of molar concentrations of *all species* involved (including the solvent water) *without* relation to a standard state; and

Case ii, in which the equilibrium constants are expressed in terms of dimensionless molar concentrations of *all species* involved (including the solvent, *e.g.*, water).

These cases are actually applied in many general-chemistry textbooks, and in (virtually) all organic-chemistry textbooks we consulted. Furthermore, if the textbook authors consider activity coefficients at all, they are assumed to be 1, as we did in the strictly thermodynamic treatment outlined in *Sects. 3* to *6*. With this, one can say that for *Case ii*, the equilibrium constant is defined by taking into account the 'numerical value of molarity of *all* species' [A1]. Note, that this procedure does not rely on a true consideration of thermodynamic standard states but rather on the need to have 'dimensionless concentrations'.

Having clarified this point, we will first discuss *Case ii*. The equilibrium constant, $K^c_{\text{CH}_3\text{COOH}}$ for the reaction in *Eqn. 1* following the rules of *Case ii* can then be defined as in *Eqn. A1*:

$$K^c_{CH_3COOH} = \frac{\dfrac{c_{CH_3COO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{CH_3COOH(aq)}}{1M} \cdot \dfrac{c_{H_2O(l)}}{1M}} \qquad (A1)$$

In chemistry textbooks, *Eqn. A1* often appears with the different chemical species put within square brackets, as shown in *Eqn. A1′*:

$$K^c_{CH_3COOH} = \frac{[CH_3COO^-(aq)] \cdot [H_3O^+(aq)]}{[CH_3COOH(aq)] \cdot [H_2O(l)]} \qquad (A1')$$

whereby the 'bracket nomenclature' in this particular type of equation should mean 'dimensionless molar concentration', *i.e.*, the molar concentration divided by the concentration unit, $1M$, *i.e.*, $[CH_3COO^-(aq)]$ actually stands for $c_{CH_3COO^-(aq)}/1M$, $[H_3O^+(aq)]$ for $c_{H_3O^+(aq)}/1M$, $[CH_3COOH(aq)]$ for $c_{CH_3COOH(aq)}/1M$, and $[H_2O(l)]$ for $c_{H_2O(l)}/1M$. As already mentioned in *Sect. 3*, such change in nomenclature within the same book is confusing; the widely accepted nomenclature is that square brackets indicate molar concentrations only, *i.e.*, $[CH_3COO^-(aq)] = c_{CH_3COO^-(aq)}$, $[H_3O^+(aq)] = c_{H_3O^+(aq)}$, *etc.*

To avoid misunderstandings, it would be much better to use square brackets ([…]) for molar concentrations only. If one likes to stick on the use of brackets, then one could use, for example, square brackets with a dot as superscript ([…]$^•$) for molar concentrations divided by $1M$, to emphasize the difference. With this, *Eqn. A1* can then be written as

$$K^c_{CH_3COOH} = \frac{[CH_3COO^-(aq)]^• \cdot [H_3O^+(aq)]^•}{[CH_3COOH(aq)]^• \cdot [H_2O(l)]^•} \qquad (A1'')$$

Note that $K^c_{CH_3COOH}$ as defined in *Eqn. A1* or *A1″* is different from K_{a,CH_3COOH} defined in *Eqn. 8*, since $K^c_{CH_3COOH}$ contains in the denominator an additional $[H_2O(l)]^• = c_{H_2O(l)}/1M$.

With the certainly correct argument that, in this type of dilute aqueous solutions, the concentration of water as solvent is constant, *Eqn. A1* or *A1″* can be multiplied on both sides with $c_{H_2O(l)}/1M = [H_2O(l)]^•$, and one obtains

$$K^c_{CH_3COOH} \cdot \frac{c_{H_2O(l)}}{1M} = \frac{\dfrac{c_{CH_3COO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{CH_3COOH(aq)}}{1M}} = K'^c_{CH_3COOH} \qquad (A2)$$

$$K^c_{CH_3COOH} \cdot [H_2O(l)]^• = \frac{[CH_3COO^-(aq)]^• \cdot [H_3O^+(aq)]^•}{[CH_3COOH(aq)]^•} = K'^c_{CH_3COOH} \qquad (A2'')$$

$K'^c_{CH_3COOH}$ is here identical with the thermodynamic constant K_{a,CH_3COOH}, as elaborated for ideal solutions ($\gamma_i = 1$) (see *Eqn. 8* in *Sect. 3*). Therefore, for 25 °C, at which the concentration of water is $55.33M$, *i.e.*, $c_{H_2O(l)}/1M = [H_2O(l)]^• = 55.33$, one obtains *Eqns. A3* and *A3″*.

$$K^c_{CH_3COOH}(25\,°C) \cdot 55.33 = \frac{\dfrac{c_{CH_3COO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{CH_3COOH(aq)}}{1M}} = K'^c_{CH_3COOH}(25\,°C) = K_{a,CH_3COOH}(25\,°C) \qquad (A3)$$

$$K^c_{CH_3COOH}(25\,°C) \cdot 55.33 = \frac{[CH_3COO^-(aq)]^• \cdot [H_3O^+(aq)]^•}{[CH_3COOH(aq)]^•} = K'^c_{CH_3COOH}(25\,°C)$$
$$= K_{a,CH_3COOH}(25\,°C) \qquad (A3'')$$

Note that both constants, $K^c_{CH_3COOH}$ and $K'^c_{CH_3COOH}$, are dimensionless.

If as in *Case i*, no division of c_i by 1M would be considered at all, then the constant defined in analogy to $K^c_{CH_3COOH}$, *i.e.*, $(c_{CH_3COO^-(aq)}) \cdot (c_{H_3O^+(aq)}) \cdot (c_{CH_3COOH(aq)})^{-1} \cdot (c_{H_2O(l)})^{-1}$, would also be dimensionless, while the constant defined in analogy to $K'^c_{CH_3COOH}$, *i.e.*, $(c_{CH_3COO^-aq}) \cdot (c_{H_3O^+(aq)}) \cdot (c_{CH_3COOH(aq)})^{-1}$, would have the unit mol l^{-1} = M (and another numerical value). In some general-chemistry textbooks, equilibrium constants indeed are defined according to *Case i*, *i.e.*, the 'acidity constants' of *Brønsted–Lowry* acids have dimensions [A2 – A7].

The reason for defining equilibrium constants by using only molar concentrations for all chemical species involved, as in *Case i* is the early version of the 'mass action law', as originally proposed in 1864 by *Guldberg* and *Waage* (*Fig. A1* [A8 – A10]). This law was formulated before *Gibbs* published his famous work on chemical thermodynamics [A11], and well before *Lewis* introduced the concept of activities [A12][A13].
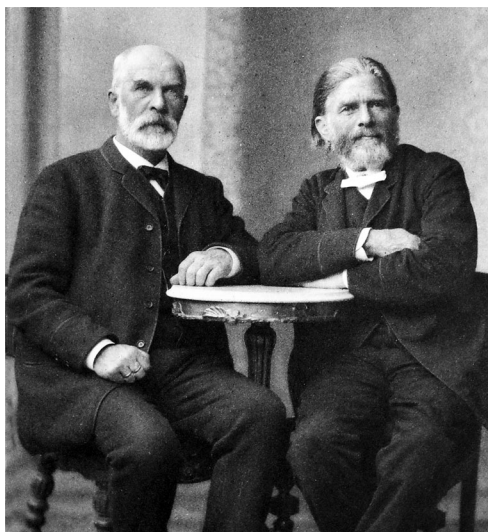

Fig. A1. Carlo Maximilian Guldberg (1836 – 1902; *left*) *and* Peter Waage (1833 – 1900; *right*). Photograph from http://de.wikipedia.org/wiki/Cato_Maximilian_Guldberg, accessed February 28, 2013.

It has to be pointed out that the equilibrium constant defined by the *Guldberg* and *Waage* version of the mass action law is not necessarily compatible with the thermodynamic equilibrium constant, since it does not make reference to the different standard states of solvated species and of the solvent (see the main text).

Let us return to the equilibrium of the reaction in *Eqn. 1*. If this equilibrium is considered but as formulated with *Eqn. 1′*, the same treatment corresponding to *Case ii* yields a reaction constant, abbreviated as $K''^c_{CH_3COOH}$, which is *different* from $K^c_{CH_3COOH}$, as shown in *Eqn. A4*, although *Eqns. 1* and *1′* represent one and the same reaction with one and the same stoichiometry.

$$K''^c_{CH_3COOH} = \frac{\dfrac{c_{CH_3COO^-(aq)}}{1M} \cdot \dfrac{c_{H^+(aq)}}{1M}}{\dfrac{c_{CH_3COOH(aq)}}{1M}} \tag{A4}$$

In this expression, the molar concentration of the solvent water is not considered at all, since it does not appear explicitly in *Eqn. 1'*. Since $c_{H^+(aq)}/1M = c_{H_3O^+(aq)}/1M$, one obtains *Eqn. A5*, which indicates that $K''^c_{CH_3COOH} = K'^c_{CH_3COOH} = K_{a,CH_3COOH}$.

$$K''^c_{CH_3COOH} = \frac{\dfrac{c_{CH_3COO^-(aq)}}{1M} \cdot \dfrac{c_{H^+(aq)}}{1M}}{\dfrac{c_{CH_3COOH(aq)}}{1M}} = \frac{\dfrac{c_{CH_3COO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{CH_3COOH(aq)}}{1M}} = K'^c_{CH_3COOH} = K_{a,CH_3COOH} \qquad (A5)$$

The equilibrium constants $K'^c_{CH_3COOH}$ and $K''^c_{CH_3COOH}$ obtained as outlined in this *Note* have the same numerical values as the thermodynamical equilibrium constant K_{a,CH_3COOH} elaborated in *Sect. 3*, and all constants are dimensionless. Therefore, one may argue that it does not matter whether chemical reaction equilibria are treated in the strictly thermodynamic way outlined in *Sect. 3*, or in the way illustrated here, *Case ii*. The situation changes, however, if water is a *Brønsted–Lowry* acid and reacts with water as a *Brønsted–Lowry* base in water as solvent, *i.e.*, if the 'self-ionization of water' is considered. The arguments then become a bit 'dubious', as outlined in *Note A2*.

Note A2. On the Molar-Concentration-Based 'Acidity Constant' of Water in Water, $K'^{c*}_{H_2O}(25\,°C)$ and Its Negative Logarithm, $pK'^{c*}_{H_2O}(25\,°C)$. Considering the reaction in *Eqn. 18* and taking for all species, *i.e.*, the dissolved ions $HO^-(aq)$ and $H_3O^+(aq)$ and the solvent $H_2O(l)$, molar dimensionless concentrations, *Case ii* mentioned in *Note A1*, one obtains – again by assuming that all activity coefficients are 1 – *Eqn. A6*

$$K^c_{H_2O} = \frac{\dfrac{c_{HO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{H_2O(l)}}{1M} \cdot \dfrac{c_{H_2O(l)}}{1M}} = \frac{\dfrac{c_{HO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\left(\dfrac{c_{H_2O(l)}}{1M}\right)^2} \qquad (A6)$$

Multiplying both sides of *Eqn. A6* with the constant term $(c_{H_2O(l)}/1M)^2$ gives

$$K^c_{H_2O} \cdot \left(\frac{c_{H_2O(l)}}{1M}\right)^2 = \frac{c_{HO^-(aq)}}{1M} \cdot \frac{c_{H_3O^+(aq)}}{1M} = K'^c_{H_2O} = K_w \qquad (A7)$$

At $25\,°C$, $c_{HO^-(aq)}/1M = c_{H_3O^+(aq)}/1M = 10^{-7.0}$ [A14]. Therefore, one obtains $K^c_{H_2O}(25\,°C) = 3.27 \cdot 10^{-18}$ and $K'^c_{H_2O} = 10^{-14.0}$ (see *Eqns. A8* and *A9*.)

$$K^c_{H_2O}(25\,°C) = \frac{K_w(25\,°C)}{\left(\dfrac{c_{H_2O(l)}}{1M}\right)^2} = \frac{10^{-14.0}}{\left(\dfrac{55.33\,mol\,l^{-1}}{1M}\right)^2} = \frac{10^{-14.0}}{3061.4} = 3.27 \cdot 10^{-18} \qquad (A8)$$

$$K'^c_{H_2O}(25\,°C) = K_w(25\,°C) = \frac{c_{HO^-(aq)}}{1M} \cdot \frac{c_{H_3O^+(aq)}}{1M} = \frac{10^{-7.0}\,M}{1M} \cdot \frac{10^{-7.0}\,M}{1M} = 10^{-14.0} \qquad (A9)$$

Again, all constants $K^c_{H_2O}$ and $K'^c_{H_2O} = K_w$ are dimensionless.

The constant $K^c_{H_2O}(25\,°C) = 3.27 \cdot 10^{-18}$ and its negative logarithm $pK^c_{H_2O}(25\,°C) = 17.5$ are not of any great direct use, since they are *not* compatible with tabulated thermodynamic data, and, therefore can, for example, not be used for a comparison of acid strengths. On the other hand, $K'^c_{H_2O}(25\,°C) = K_w(25\,°C) = 10^{-14.0}$ [A15] and its negative logarithm, $pK_w(25\,°C) = 14.0$, are fully compatible with thermodynamic data (see *Sect. 4*). $K'^c_{H_2O}(25\,°C) = K_w(25\,°C) = 10^{-14.0}$ is the self-ionization constant for water at $25\,°C$, which is identical with the thermodynamic acidity constant of water in water at $25\,°C$, $K_{a,H_2O}(25\,°C)$, *i.e.*, $pK_{a,H_2O}(25\,°C) = 14.0$ (see *Sect. 4*).

The question we address now is how a 'pK_a value' for water at $25\,°C$ of 15.7 was attained, as mentioned in essentially all organic-chemistry textbooks. Obviously, $pK_a = 15.7$ means $K_a = 10^{-15.7}$, a value which is obtained if $K_w(25\,°C) = 10^{-14.0}$ is divided by $55.33 = c_{H_2O}/1M$. This simple mathematical

operation is hard to rationalize from a chemical point of view if one takes into account the *Brønsted–Lowry* acid–base reactivity of water as formulated the way it is done with *Eqn. 18*, unless one argues on the basis of rather 'dubious' considerations; to make it clear, *Eqn. 18* is not really compatible with an equilibrium constant of $10^{-15.7}$, as outlined in the following.

The forward reaction of the chemical equilibrium in *Eqn. 18* is the description of the reaction of water as *Brønsted–Lowry* acid with water as *Brønsted–Lowry* base in water as solvent, whereby H_2O simultaneously plays three roles, as *Brønsted–Lowry* acid, as *Brønsted–Lowry* base, and as solvent. If comparison is made with the forward reaction of *Eqn. 1*, one realizes one fundamental difference. In the forward reaction of *Eqn. 1*, water plays only two roles, as *Brønsted–Lowry* base and as solvent, while $CH_3COOH(aq)$ is the *Brønsted–Lowry* acid. One may consider a kind of 'unified view' of the two reactions shown in *Eqns. 18* and *1* by replacing *Eqn. 2* with *Eqn. A10*:

$$H_2O(aq) + H_2O(l) \rightleftharpoons HO^-(aq) + H_3O^+(aq) \tag{A10}$$
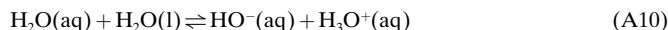
Eqn. A10 certainly is strange since it implies something which is more hairsplitting than reasonable. In any case, for *Eqn. A10* one obtains – with all the assumptions and conventions mentioned above in this chapter – for the 'acidity constant' of H_2O first *Eqn. A11*

$$K_{H_2O}^{c*} = \frac{\dfrac{c_{HO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{H_2O(aq)}}{1M} \cdot \dfrac{c_{H_2O(l)}}{1M}} \tag{A11}$$

Multiplying on both sides of *Eqn. A11* with $c_{H_2O(l)}/1M$ yields *Eqn. A12*

$$K_{H_2O}^{c*} \cdot \left(\frac{c_{H_2O(l)}}{1M}\right) = \frac{\dfrac{c_{HO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{H_2O(aq)}}{1M} \cdot \dfrac{c_{H_2O(l)}}{1M}} \cdot \frac{c_{H_2O(l)}}{1M} = \frac{\dfrac{c_{HO^-(aq)}}{1M} \cdot \dfrac{c_{H_3O^+(aq)}}{1M}}{\dfrac{c_{H_2O(aq)}}{1M}} = K'^{c*}_{H_2O} \tag{A12}$$

For $25\,°C$, $c_{HO^-(aq)} = c_{H_3O^+(aq)} = 10^{-7.0}$ M, and if one uses for $c_{H_2O(aq)}/1M$ a value of 55.33, the numerical value of $10^{-15.7}$ is obtained for $K'^{c*}_{H_2O}$, *i.e.*, as negative logarithm of this constant, $pK'^{c*}_{H_2O}(25\,°C)$, a value of 15.7. Obviously, however, it cannot be that $c_{H_2O(aq)} = c_{H_2O(l)} = 55.33M$ in one and the same solution, if $H_2O(aq)$ and $H_2O(l)$ are considered to be different species as it appears from *Eqn. A10*. At $25\,°C$, the *total* amount of water in 1 l is 55.33 mol, not 110.66 mol (see *Sect. 3*). Therefore, all the above arguments are 'dubious' and should not be used at all since they are wrong. In contrary, the considerations made here are useful to explain the students in a hopefully convincing way why the $pK_a(25\,°C)$ value of water in water *cannot* be 15.7, if $pK_w(25\,°C) = 14.0$.

Two questions remain. *Question 1:* 'Why should a division of $K_w(25\,°C)$ by 55.33 be appropriate for expressing the acidity of water?' *Question 2:* 'Who was, or who were, the first to define the equilibrium constant for the reaction of water as *Brønsted–Lowry* acid with water as *Brønsted–Lowry* base such that a value of $10^{-15.7}$ at $25\,°C$ is obtained?'

The answer to *Question 1* can be given by considering instead of *Eqn. 18* *Eqn. 18′*, or even – to be somehow consistent with *Eqn. 1′* – the following equation:

$$H_2O(aq) \rightleftharpoons HO^-(aq) + H^+(aq) \tag{A10′}$$
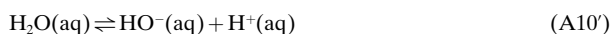
Eqn. A10′ certainly is unusual but it is written here to emphasize the lines of thinking and the ideas of having a similar formalism as in *Eqn. 1′*. $H_2O(aq)$ is the same as $H_2O(l)$, *i.e.*, liquid water.

If one considers the concentration of $H_2O(aq)$ at $25\,°C$ as the same as the concentration of $H_2O(l)$ at $25\,°C$, although with *Eqn. A10* it is assumed that they represent two different species, one obtains *Eqn. A13*

$$K_{H_2O}^{c*}(25\,°C) = \frac{K_w(25\,°C)}{\dfrac{c_{H_2O(aq)}}{1M}} = \frac{10^{-14}}{\dfrac{55.33M}{1M}} = \frac{10^{-14}}{55.33} = 1.81 \cdot 10^{-16} = 10^{-15.7} \tag{A13}$$

and with this value, one obtains *Eqn. A14*

$$\mathrm{p}K_{\mathrm{H_2O}}^{c*}(25\,^{\circ}\mathrm{C}) = -\log\left(K_{\mathrm{H_2O}}^{c*}(25\,^{\circ}\mathrm{C})\right) = -\log(1.81 \cdot 10^{-16}) = 15.7 \qquad (A14)$$

Note that for the sake of distinguishing the water acidity constant, as obtained with the conventions just outlined, from the thermodynamic constant $K_{\mathrm{a,H_2O}} = K_{\mathrm{w}}$ (see *Sect. 4*), we use a different abbreviation that is $K_{\mathrm{H_2O}}^{*}$ (see *Eqn. A13*).

The true significance of the *thermodynamically incorrect equilibrium constant*, $K_{\mathrm{H_2O}}^{c*}$, and its negative logarithm, $\mathrm{p}K_{\mathrm{H_2O}}^{c*}$, is questionable. It is very doubtful whether $\mathrm{p}K_{\mathrm{H_2O}}^{c*}$ is meaningful for a comparison with the acidity of organic acids which are almost insoluble in water [A16]. In this latter case, the '$\mathrm{p}K_{\mathrm{a}}$ values' reported for organic acids in organic-chemistry textbooks, *e.g.*, the '$\mathrm{p}K_{\mathrm{a}}$ values' of CH_4 or benzene are relative values and *cannot* be compared with the thermodynamic values determined for 'conventional acids' that are soluble in aqueous solution. Therefore, these '$\mathrm{p}K_{\mathrm{a}}$ values' should *not* be included in tables together with thermodynamic $\mathrm{p}K_{\mathrm{a}}$ values. Alternatively, corrections of listed '$\mathrm{p}K_{\mathrm{a}}$ values' for organic acids should be made, as already mentioned previously [A17]. In any case, the estimated acidity of very weakly acidic organic molecules are approximate values anyway, although these approximate, relative acidity values are extremely useful when discussing the reactivity of organic molecules [A18][A19].

If two differently defined '$\mathrm{p}K_{\mathrm{a}}$ values' of two acids are compared, then one may draw wrong conclusions. This is what seems to be the case if the acidity of water is compared with the acidity of methanol [A20–A23]. Using for both *Brønsted–Lowry* acids the same thermodynamic definitions, then – at $25\,^{\circ}\mathrm{C}$ – water in water ($\mathrm{p}K_{\mathrm{a,H_2O}}(25\,^{\circ}\mathrm{C}) = 14.0$) is more acidic than methanol in water ($\mathrm{p}K_{\mathrm{a,CH_3OH}}(25\,^{\circ}\mathrm{C}) = 15.6$).

In any case, to avoid confusion, it would be better to use different abbreviations for differently defined reaction constants, for example $K_{\mathrm{a,H_2O}}$ and $K_{\mathrm{a,H_2O}}^{*}$, as proposed here.

An answer to *Question 2* – who was, or who were, the first stating that $\mathrm{p}K_{\mathrm{a,H_2O}}(25\,^{\circ}\mathrm{C}) = 15.7$ – cannot be given with full certainty. They were the ones who did the pioneering work on the quantitative determination of the *relative acidity* of weakly acidic organic molecules by '*non-aqueous competition experiments*' [A24–A27]. They thought – without any experimental data – that the '$\mathrm{p}K_{\mathrm{a}}$ value of water' at $25\,^{\circ}\mathrm{C}$ has to be 15.7 and the '$\mathrm{p}K_{\mathrm{a}}$ value of H_3O^{+}' -1.8, although the arguments put forward at that time [A24] were not very convincing. For example, for the reaction of $H_3O^{+}(\mathrm{aq})$ with water, the equilibrium considered was formulated as in *Eqn. A15* [A24]:

$$H_3O^{+} + H_2O(\text{solvent}) \rightleftharpoons H_3O^{+} + H_2O \qquad (A15)$$

and the argument was that '$H_2O(\text{solvent})$' is not included in the equilibrium constant, while the concentration of 'H_2O' is taken as $55.33\mathrm{M}$ (or $55.5\mathrm{M}$ as in the original report [A24]). Therefore, an equilibrium constant K is obtained with a value of $55.33\mathrm{M}$ (or $55.5\mathrm{M}$, [A24]). The following text is taken from an organic textbook [A28]: '*Note that the K_a for water is obtained by dividing K_w by the concentration of water, 55.5 moles L^{-1}. This change is necessary to put all of the ionizations on the same scale and in the same units. Recall that the ion product of water, K_w, has units of moles^2 L^{-2} or M^2, whereas K_a values are given in units of moles L^{-1} or M.*' Obviously, these arguments of the necessity of having equilibrium constants with uniform units are not compatible at all with the thermodynamic conventions outlined in *Sect. 3–6*. As repeatedly emphasized in the main text, thermodynamic equilibrium constants are dimensionless, including K_{w}; they all have no units.

Final Remarks. There are convincing arguments for introducing and using activities and appropriate thermodynamic standard states when teaching quantitative aspects of chemical equilibria (main text). If properly and systematically performed, existing confusions in chemistry textbooks can be eliminated, and with this, full compatibility of thermodynamic equilibrium constants and tabulated thermodynamic data can be attained. This is the case not only for the *Brønsted–Lowry* acid–base equilibria discussed in this review, but also for other chemical equilibria, including the water solubility of sparingly soluble salts with their characteristic solubility products $K_{\mathrm{sp}}(T)$.

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