

pK_w Is Almost Never 14.0

Contribution from the Task Force on the General Chemistry Curriculum

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The presentation of autoprotolysis calculations in our introductory texts is divorced from reality. pK_w is usually defined as $-\log [H^+][OH^-]$ and is said to be 14.00 at 25 °C. This is true in absolutely pure water, but the ionization of pure water is rarely important. Our texts regularly apply this definition and the value 14.00 to solutions where it is certainly not 14.00. In standard seawater, for example, it is 13.76.

The presence of ionic solutes or organic matter changes the ionization of water and also changes its activity from the tacitly assumed value of 1.00. Yet our texts regularly incorporate the 14.00 into calculations on buffer solutions, industrial waste, blood, seawater, and other solutions to which it does not apply, and report the answers to as many as three significant figures or the second decimal of pH. It is arguable that students might be told that the answer is approximate and instructed to round it to one significant figure or to the first decimal of pH, but our texts never do that.

We do not need to teach introductory students to calculate activity coefficients to remedy the problem. We need to change ourselves and our thinking, which is more difficult for us but easier for our students.

A Larger Agenda

The teaching of ionic equilibria in introductory chemistry consists largely of recipes for calculating the wrong answer. Because values of the autoprotolysis constant have been compiled exhaustively in a wider variety of conditions than any other equilibrium constant, they can be used effectively to illustrate the errors that are endemic in the ionic equilibrium chapters of introductory texts. In addition, the presentation of the simultaneous effect of pressure and temperature on autoprotolysis in this paper is more succinct than that found elsewhere.

The Definition of K_w

Several definitions of K_w are possible, and we must choose the one that is most useful to our students in their later lives and work, while keeping the subject within the intellectual capacity of a beginner. For example, the definition

$$K_w (\text{conditional}) = [H^+][OH^-]$$

is the commonest, but is seldom useful in real-world calculations because $[H^+]$ is not known. A pH meter yields a good approximation to a_{H^+} , the activity of H^+ , but does not give the concentration (1–3). Moreover, the value of this product is strongly dependent on the ionic strength

$$\mu = 0.5 \sum (\text{ion molarity})(\text{ion charge})^2$$

of the solution and on the concentration of other substances in the solution.

The product of molalities,

$$K_w (\text{molal}) = m_{H^+}m_{OH^-}$$

is a form that is widely used because it is independent of the expansion or contraction of the solution. It is the form used in the IUPAC collection of K_w values (4), so in compiling Tables 1–3, I found it necessary to convert them. Until the educational world is ready to abandon volumetric calculation in favor of gravimetric, this form will not find favor among educators, although it is used to advantage by chemists, chemical engineers, and oceanographers.

Thermodynamic Definition

The thermodynamic definition

$$K_w (\text{thermodynamic}) = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}}$$

has theoretical value but is of little value in real-world calculation. Although the activity of H^+ is easily measured by a pH meter, those of OH^- and H_2O are seldom available, and teachers will not wish to teach beginning students how to calculate them. In very dilute solutions, the activity of H_2O is 1.00, so in this rare case the thermodynamic definition reduces to

$$K_w (\text{thermodynamic}) = a_{H^+}a_{OH^-}$$

Real-world solutions are seldom dilute enough to warrant this approximation.

Bronsted Definition

The useful definition is the practical or Bronsted definition,

$$K_w (\text{practical}) = a_{H^+}[OH^-] = 10^{-pH}[OH^-]$$

This is directly useful when calculating the pH of a solution with known concentration of hydroxide. More importantly, it allows $[OH^-]$ to be substituted in any other calculation by

$$\frac{K_w (\text{practical})}{a_{H^+}}$$

or

$$\frac{K_w (\text{practical})}{10^{-pH}}$$

This will produce correct answers to the accuracy with which K_w is known, and to the extent that junction poten-

tials in the measurement of pH can be minimized or allowed for (2). For example, the pH of a pure acetate solution can be obtained by the usual textbook approach with only the trivial modification

$$[\text{CH}_3\text{CO}_2\text{H}] = [\text{OH}^-] = \frac{K_w (\text{practical})}{a_{\text{H}^+}} = \frac{K_w (\text{practical})}{10^{-\text{pH}}}$$

and is then given by

$$2\text{pH} = \text{p}K_a (\text{practical}) + \text{p}K_w (\text{practical}) + 2\log [\text{CH}_3\text{CO}_2^-]$$

The use of $\text{p}K_a$ (practical) is discussed elsewhere (3, 5), and a short table of values is given in ref 3. It is defined in this case as

$$\frac{a_{\text{H}^+}[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{10^{-\text{pH}}[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

For pure water the ionic strength is negligible, except at temperatures and pressures that even engineers are unlikely to meet, so the conditional, the practical, and the thermodynamic definitions are identical. The ionization of pure water, however, is rarely of more than academic interest.

Temperature and Pressure

The variation of $\text{p}K_w$ for pure water as temperature and pressure vary is shown in Figure 1. The figure includes the regular curve for liquid water under the pressure of its own vapor up to the critical point. Curves for higher pressures run unbroken through the critical temperature from liquid water to supercritical fluid.

Most introductory texts nowadays mention the effect of temperature. The effect of pressure is too small to be important to most workers, but it is important to engineers and oceanographers. It is easy to bring these variations to students' attention without cognitive overload by setting exercises that use values of $\text{p}K_w$ at nonstandard temperatures and pressures. Tables 1 and 2 give such values.

A recent article (6) in *National Geographic* describes water issuing from a volcanic vent at the ocean floor at about 250 bar and 400 °C with a salt content one twelfth of that of regular seawater, suggesting ionic strength substantially less than 0.1. It was highly acidic, but it is evident from Figure 1 that the acidity was not the result of dissociation of the water.

However, at even more extreme conditions, water can become a strong acid. The IUPAC collection (7, 8) shows that the $\text{p}K_w$ is

- 1.05 at 133 kbar and 804 °C
- 3.05 at 93 kbar and 527 °C
- 5.70 at 71 kbar and 373 °C

giving $\text{pH} = 0.5, 1.5,$ and 2.8 for pure water. An interesting graph of $\log K_w$ against density that extends to these extremes is shown

in ref 9. Such extremes may perhaps occur in some geologic situations, so the acidity of the water would be a factor in the solution and recrystallization of rocks.

Ionic Strength

The erroneous assumption that K_w does not vary with the medium is almost universal in introductory texts. They regularly give examples of acid-base calculations in seawater, based on the assumption that $\log [\text{H}^+][\text{OH}^-]$ is -14.00 at 25°C . Actually it is -13.76 in standard seawater. If K_w were defined as

$$\frac{a_{\text{H}^+}a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}$$

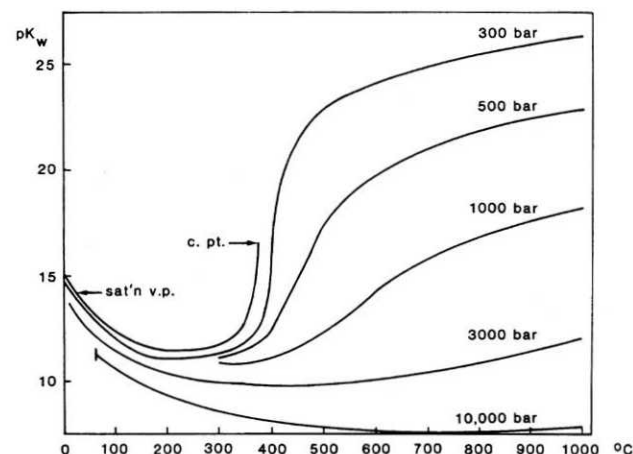


Figure 1. Variation of $\text{p}K_w$ with pressure and temperature.

Table 1. $\text{p}K_w$ in Pure Liquid Water

Under the pressure of its own vapor. Recalculated from the molal values in ref 4, by subtracting $2 \log$ (density) from them using densities from ref 14

T (°C)	0	5	10	15	20	25
$\text{p}K_w$	14.983	14.727	14.528	14.341	14.165	13.998
T (°C)	30	35	40	45	50	55
$\text{p}K_w$	13.840	13.690	13.549	13.414	13.285	13.165
T (°C)	60	65	70	75	80	85
$\text{p}K_w$	13.049	12.938	12.834	12.733	12.638	12.548
T (°C)	90	95	100	125	150	175
$\text{p}K_w$	12.462	12.379	12.301	11.966	11.712	11.530
T (°C)	200	225	250	275	300	325
$\text{p}K_w$	11.414	11.365	11.387	11.490	11.701	12.073
T (°C)	350	374				
$\text{p}K_w$	12.663	16.625				

Table 2. $\text{p}K_w$ for Pure Water at Various Pressures[†]

bar	0 °C	25 °C	50 °C	100 °C	150 °C	200 °C
300	14.79	13.88	13.17	12.19	11.58	11.24
1000	14.50	13.66	12.96	11.96	11.32	10.92
3000	13.91	13.18	12.53	11.46	10.79	10.33
10000	*	*		10.49	9.78	9.25

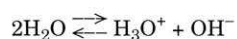
*Solid under these conditions (15).

[†]Calculated from molal K_w values in ref 4 using densities in ref 14.

its log would of course be -13.998, but that is not the definition that our texts use. Most teachers of introductory chemistry do not use it, nor is it used by most researchers.

Few teachers introduce first-year students to the calculation of activity coefficients. The problem is not that the plug-in formulas are difficult, but that they add another layer of complexity to an already difficult subject. Moreover, they require that the students be taught how to decide when the formula relating activity coefficient to ionic strength is reliable.

Qualitatively, however, the subject is easy to grasp. In the equilibrium



the reverse action is hindered by the electric fields of other ions, so the degree of ionization increases.

To allow for ionic strength, it is easiest to specify its value in tables of equilibrium constants. These are then conditional constants, in which the condition is the specified ionic strength. They are used in exactly the manner now explained in introductory texts and thrust the inconstancy of the equilibrium constant on the students' attention without introducing the calculation of activity. The values of pK_w in this paper are therefore tabulated against ionic strength μ . This must also be done for other constants such as the values of K_a tabulated in ref 3.

With students for whom the calculation of ionic strength is considered inappropriate, the concept can still be brought to their attention with problems that use wording like " pK_w is 13.89 when the solution contains this concentration of ions". Students are then notified that the presence of ions affects the equilibrium and that they should consult a chemist who can make allowance for them in any real situation where the calculated value must be better than approximate in the first decimal.

Values of pK_w in seawater can be found from Table 3 by interpolating the ionic strength $\mu = 0.71$ for standard seawater. They should be used regularly in problem sets given to students to show them that solution properties affect equilibrium constants.

Effect of Temperature on pK_w when Ions are Present

The shift of pK_w with ionic strength at 25 °C in Table 3 will provide the illustration and examples of the effect of ionic interference that teachers will need in order to construct examples and test questions. However, data at other temperatures are given in the IUPAC collection (7) and Christensen et al. (10). Values at several temperatures and ionic strengths in KCl solution are given in Table 4.

Other Media

River water and tap water usually have ionic strength less than 0.01 (often much less), which would decrease the practical pK_w at 25 °C by 0.05 or less (or $-\log ([\text{H}^+][\text{OH}^-])$ by 0.09 or less). Rain water has negligible ionic strength, so values of K_w at $\mu = 0.0$ are appropriate. Standard seawater

Table 3. Values of Conditional and Practical pK_w at Various Ionic Strengths and 25 °C

The pure water value 13.998 is from Table 1. Other data is from ref 13.

Ionic strength, μ	0.0	0.1	0.5	1.0	2.0	3.0
pK_w (conditional) = $-\log ([\text{H}^+][\text{OH}^-])$	13.998	13.78	13.74	13.75	13.9 [#]	14.0 [#]
pK_w (practical) = $-\log (10^{-\text{pH}}[\text{OH}^-])$	13.998	13.89	13.89	13.89	14.0 [#]	14.1 [#]

[#] The second decimal is too dependent on the nature of the electrolyte to be generally useful.

Table 4. Variation of Conditional and Practical pK_w of KCl Solutions with Temperature and Ionic Strength (16)

	μ	0 °C	25 °C	50 °C	75 °C	100 °C
pK_w (conditional) = $-\log ([\text{H}^+][\text{OH}^-])$	0.1	14.74	13.78	13.05	12.47	12.00
pK_w (practical) [#] = $-\log (10^{-\text{pH}}[\text{OH}^-])$		14.85	13.89	13.16	12.59	12.14
pK_w (conditional) = $-\log ([\text{H}^+][\text{OH}^-])$	0.5	14.68	13.72	12.97	12.38	11.90
pK_w (practical) [#] = $-\log (10^{-\text{pH}}[\text{OH}^-])$		14.84	13.88	13.14	12.56	12.09
pK_w (conditional) = $-\log ([\text{H}^+][\text{OH}^-])$	1.0	14.72	13.75	13.00	12.40	11.92
pK_w (practical) [#] = $-\log (10^{-\text{pH}}[\text{OH}^-])$		14.87	13.91	13.16	12.57	12.10

Notice that pK_w (practical) varies less with ionic strength μ than does pK_w (conditional).

[#] obtained by calculating $-\log$ (activity coefficient of H^+) from the Davies equation (17), using coefficients tabulated in (2,18) and adding it to the conditional pK_w .

ter has $\mu = 0.71$, so values of K_w can be interpolated between $\mu = 0.5$ and 1.0.

Blood has presumably the same ionic strength as normal saline (9 g/L NaCl) or $\mu = 0.15$, but it is unlikely that the pK_w is the same as in normal saline because blood serum also contains 8% of organic matter. This will change the structure, the concentration, and therefore the activity of the water in the serum. It also will change the dielectric constant and therefore the rate of reassociation of the ions. I have not found any data on the value of K_w or $\alpha_{\text{H}_2\text{O}}$ or the dielectric constant of blood. Assuming $\alpha_{\text{H}_2\text{O}} = 0.92$, I get 13.93 as the calculated value for pK_w (practical) and 13.83 for $-\log ([\text{H}^+][\text{OH}^-])$ at 25 °C. It would seem reasonable to rely on these values in the first decimal but to be suspicious of the second.

Thermodynamic Quantities

There is little occasion to use $\ln K_w = -\Delta G^\circ/RT$ when so many reliable values of K_w are available. This is fortunate because the thermodynamic constants are not constant (10). ΔH° varies almost linearly from 14.95 kcal/mol at 0 °C to 10.0 kcal/mol at 100 °C. ΔS° varies from about -14 cal/mol·K at 0 °C to -29 cal/mol·K at 100 °C. This kind of variation seems typical of protonation but not of other kinds of association, as shown in later papers in this series.

Pedagogy

Plugging into $K_w = [\text{H}^+][\text{OH}^-]$ or $\alpha_{\text{H}}[\text{OH}^-]$ is easy. How can we ensure that the equation is understood? We can challenge students with thought-provoking questions and request explanations for what is seen in the calculations.

- Why is the product a constant (over a reasonable range of concentrations)?
- Give the chemical (not algebraic) reason that $[\text{H}^+]$ increases as $[\text{OH}^-]$ decreases.
- K_w is the equilibrium constant of what reaction?
- Why is $[\text{H}_2\text{O}]$ omitted?

- What two reactions must have equal rates when the product equals K_w ?
- Why does increasing $[\text{OH}^-]$ not increase K_w , as the algebra suggests?

Honors students could be asked,

- Explain why K_w varies with temperature or pressure.

(Pressure closes the open structure of liquid water, forcing the molecules closer together, changing the rate of the forward autoprotolysis reaction.)

Another approach is to ask them to apply the same logic to another solvent. Nonaqueous solvent chemistry is not sufficiently important to be taught in introductory chemistry for its own sake, but the logic of K_w can be tested by asking the above questions in respect of the self-ionization constant K_i for CH_3OH , or asking what is $[\text{H}_3\text{SO}_4^+]$ in pure H_2SO_4 or $[\text{NH}_2^-]$ in pure NH_3 . Questions involving solutions in such solvents (as opposed to ionization of the solvent itself) are not usually realistic because salts and acids tend not to ionize substantially in nonaqueous solvents (HClO_4 has $\text{p}K_a = 4.7$ in acetic acid). However, such questions are realistic in the few cases where the dielectric constant is similar to that of water (78.5) or greater. Complete ionization of alkali metal salts is probably a good approximation in H_2SO_4 (dielectric constant = 101 at 25 °C), HF (about 85) (11), and water, but not the others. It is therefore fair to ask

- What is $[\text{H}_3\text{SO}_4^+]$ in 0.1 M NaHSO_4 in H_2SO_4 ?
- What is $[\text{F}^-]$ in 0.1 M HClO_4 in HF ?

These are exactly analogous to solutions of NaOH or HCl in water, and they emphasize the logic underlying the use of K_w .

Finding values of self-ionization constants involves a literature search that is longer than most teachers will wish to undertake, so they are compiled in Table 5. The values are reviewed by the authors of the references. I have omitted data that they consider doubtful or that appear doubtful from the later collection by Izutsu (12).

Why Calculate?

Calculations that we have taught for over half a century give the wrong answers, and this should make us wonder whether they are of any value. If students went on to apply them on the job, they would realize that they had been misled. By now the several generations that have learned them would have amended the texts when they became teachers. That this has not happened is evidence that we are wasting students' time on manipulations that they will never use.

Accuracy

Even the values of the practical constants vary in the second decimal with the nature of the electrolyte, and this becomes increasingly important at higher ionic strengths. This illustrates the limited reliability of calculations even when the data is obtained for real solutions. A pH calculated from the practical constants in Tables 3 and 4 are reliable in the first decimal. At lower ionic strengths they are at least approximate in the second decimal. The value at ionic strength 0.5 varies with the nature of the electro-

Table 5. Self-Ionization Constants at 25 °C

Solvent	$\text{p}K_i$	Ref
H_2O	14.00	5
D_2O	14.71	19
H_2SO_4	3.6	11
NH_3	29.8	11
HF	11	11
CH_3OH	16.7	11
$\text{C}_2\text{H}_5\text{OH}$	19	11
$\text{CH}_3(\text{CHOH})\text{CH}_3$	20.8	20
$\text{CH}_3\text{CO}_2\text{H}$	14.45	20

lyte over a range of 0.05; the tabulated value 13.74 in Table 3 is a mean with uncertainty of 0.03. At ionic strengths less than 0.5 the second decimal will have even lower uncertainty. More exact methods that allow for the nature of the electrolyte are given in advanced texts such as ref 2. Precise values for specific electrolytes are given in refs 5 and 13. However, the values given here will suffice for test questions in introductory courses.

When we teach students to use 14.00, the pH that they calculate may differ from reality by 0.3 log units or a factor of 2 in $[\text{H}^+]$ even at normal pressures in solutions containing no organic matter. This is not a reasonable approximation.

If introductory students are taught to do these calculations, they should be taught that pH calculations based on K_w are reliable only in the first decimal even when using practical constants. They may, if a teacher thinks it appropriate for the group being taught, be told that the second decimal is meaningful but not accurate except in dilute solutions or when using calculation methods that are not appropriate for an introductory course. When texts use 14.00 and give answers to two decimals they are guilty of professional malpractice.

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