Water dissociation and pH

The ionic product, K_w

Water dissociation (autoionization) occurs endothermically[d] due to electric field fluctuations between neighboring molecules. Dipole librations [191], resulting from thermal effects and favorable localized hydrogen bonding [567] that, together with nuclear quantum effects [2025], cause these fluctuations. The process may be facilitated by exciting the O-H stretch overtone vibration [393]. Once formed (at an average concentration of about 0.9 M $H_2O\text{-}H^+\cdots OH^-$ [1984]), the ions may separate by means of the Grotthuss mechanism but normally (>99.9%) rapidly recombine. Rarely (about once every eleven hours per molecule at 25 °C, or less than once a week at 0 °C) the localized hydrogen bonding arrangement breaks before allowing the separated ions to return [191]. The pair of ions (H^+, OH^-)[g] hydrate independently and continue their separate existence[a] for about 70 µs (this lifetime also dependent on the extent of hydrogen bonding, being shorter at lower temperatures). They tend to recombine when separated by only one or two water molecules.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$K_w = [H^+][OH^-]$$

Although the extent of dissociation is tiny ($[H^+]/[H_2O] = 2.8 \times 10^{-9}$ at 37 °C), the dissociation and consequential changes in the tiny concentrations of hydrogen ions have absolute importance to living processes. Hydrogen ions are produced already hydrated (that is, as oxonium ions, H_3O^+; also called oxonium or hydroxonium ions) and have negligible existence as naked protons in liquid or solid water, where they interact extremely strongly with electron clouds. All three hydrogen atoms in the oxonium ion are held by strong covalent bonds and are equivalent (that is, C_{3v} symmetry). The thermodynamic properties of the dissociation at 25 °C and 100,000 Pa are $\Delta U = 59.5$ kJ mol^{-1}, $\Delta V = 21.4$ cm^3 mol^{-1}, $\Delta H =$ kJ mol^{-1}, $\Delta G = 79.9$ kJ mol^{-1}, $\Delta S = -77.2$ J K^{-1} mol^{-1} [1938].

The above equations are better written as:

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$K_w = [H_3O^+][OH^-]$$

Both ions are ionic kosmotropes, creating order in forming stronger hydrogen bonds with surrounding water molecules and creating short chains of hydrogen bonded water molecules [2025]. The concentrations of H_3O^+ and OH^- are normally taken as the total concentrations of all the small clusters including these species. As other water molecules are required to promote the hydrolysis, the equation below includes the most important.

$$4\ H_2O \rightleftharpoons H_5O_2^+ + H_3O_2^-$$

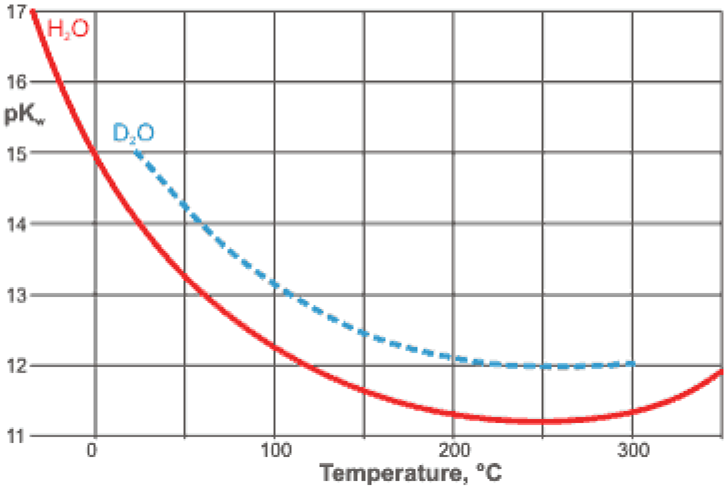
The concentration of oxonium and hydroxide ions produced is therefore equal to the square root of the dissociation constant (K_w).

Aqueous OH^- does not ionize further as ($O^{2-} + H_2O \longrightarrow 2OH^-$, $K > 10^{22}$). [**Back to Top** ▲]

pH

The oxonium ion concentration (commonly called 'hydrogen ion concentration') is often given in terms of the pH, where pH = $Log_{10}(1/[H_3O^+])$ = $-Log_{10}([H_3O^+])$ (that is, $[H_3O^+] = 10^{-pH})^f$ with the concentration of H_3O^+ in mol l^{-1}. More precisely pH = $-Log_{10}(a_H)$ = $-Log_{10}(m_H\lambda_H/m°)$ where $a_{H,}$ $m_{H,}$ λ_H and m° are the relative (molality based) activity, molality, molal activity coefficient and standard molality (1 mol kg^{-1}) of the hydrogen ions. At the low concentrations normally found, the hydrogen ion concentration is close enough to the relative (molality based) activity for its use for most purposes. The presence of salts and other solutes will generally reduce this activity. The molal activity of hydrogen ions cannot be determined directly but may be determined using a glass electrode relative to the response of standard buffer solutions of suitable ionic strength. Glass electrode-determined pH values are error-prone and calculated hydrogen ion concentrations should be treated with caution, particularly at the extremes of pH [1890]. For more information and a list of primary pH standards see [813]. Proof that the use of the equation pH = $-Log_{10}(H^+)$ may give misleading results (and pH = $-Log_{10}(a_H)$ is preferred) is easily shown as the pH of 0.1 M HCl decreases when it is diluted with 5% M LiCl [1107]. The pH scale was first introduced by Sørensen (as $p_{H\cdot}$) in 1909 [1036] using colorimetric measurements and the hydrogen electrode, which gives an electrode potential proportional to pH. The pH scale extends to negative numbers (for example, concentrated HCl has a pH of about -1.1) and to greater than 14 (for example, saturated NaOH has a pH of about 15.0) [1187]. There is a recent review of the pH of natural water [1712]. [Back]

In a similar manner pK_w is defined by $pK_w = Log_{10}(1/K_w) = -Log_{10}(K_w)$, utilizing concentrations in mol l^{-1}.^{e} [**Back to Top** ▲]



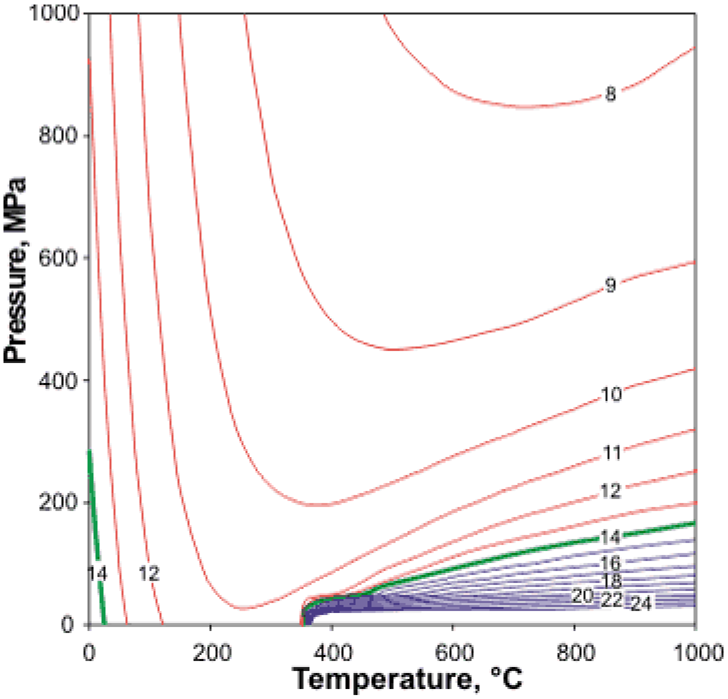
$pK_w = -log_{10}(K_w)$ [IAPWS]

Variation in K_w with T and P

K_w is very temperature dependent, increasing with temperature (that is, from 0.001 x 10^{-14} mol^2 l^{-2} at -35 °C (pH 8.5) [112], 0.112 x 10^{-14} mol^2 l^{-2} at 0 °C (pH 7.5), to 0.991 x 10^{-14} mol^2 l^{-2} at 25 °C (pH 7.0), to 9.311 x $10^{-14}$$mol^2$ l^{-2} at 60 °C (pH 6.5) [87]), to 10^{-12} mol^2 l^{-2} at 300 °C (pH 6.0, ~50 MPa) [456] in agreement with the high positive standard free energy.^{b} There is a minimum at about 249 °C along the saturated pressure line for H_2O and at about 257 °C for D_2O (see right [1865]).

The pK_w H_2O minimum is about 0.74 lower than that for D_2O [1865]. (see also conductivity maximum).

A theoretical treatment of this temperature dependence is available [763].



Temperature and density dependence of dissociation has been examined [1321]. Dissociation depends on the pressure, with K_w doubling at about 100 MPa; unsurprising in view of the negative ΔV associated with the dissociation, -18.1 cm^3 mol^{-1}.

Dissociation also varies with solute concentration and ionic strength; for example, K_w goes through a maximum of about 2 x 10^{-14} mol^2 l^{-2} at about 0.25 M ionic strength (using tetramethylammonium chloride, where possibly the change in hydrogen bonding caused by clathrate formation encourages dissociation) before dropping to a value of about 1 x $10^{-16}$$mol^2$ l^{-2}at 5 M (with higher concentrations disrupting the hydrogen bonding). Dissociation will also be different at interfaces; for example, it is greater at lipid membrane surfaces [1964].

In ice, where the local hydrogen bonding rarely breaks to separate the constantly forming and re-associating ions, the dissociation constant is much lower (for example at -4 °C, K_w= 2 x 10^{-20} mol^2 l^{-2}). [**Back to Top** ▲]

Footnotes

[a] This low occurrence means that at neutrality (pH 7 at 25 °C)[c], similarly charged ions are, on average, separated by vast distances (~0.255 μm) in molecular terms and (for example) bacteria contain only a few tens of free hydrogen ions. Contributing to this effect are the high dielectric constant (encouraging charge separation) and high concentration of H_2O (~55.5 M; increasing the absolute amount dissociated). The mean lifetime of a oxonium ion (1 ps; about the same as that of a hydrogen bond) is such that the charge could be associated with over 10^7 molecules of water before neutralization.

Also, pure water droplets containing less than about 10^8 water molecules (~100 nm radius) would usually contain no ions in the absence of surface effects. [Back]

[b] A bulk energy diagram for the dissociation in bulk water has been described [604]. [Back]

[c] Note that acid-base neutrality only occurs when the concentration of hydrogen ions equals the concentration of hydroxyl ions (whatever the pH). This only occurs at pH 7 in pure water when at 25 °C. A solution is acidic when the hydrogen ion concentration is greater than the hydroxide ion concentration, whatever the pH. The pH of a neutral solution is numerically equal to half the pK_w of the solution. Therefore a pH of 7 at 0 °C indicates a slightly acid solution (neutrality is pH 7.5) whereas a pH of 7 at 50 °C indicates a slightly alkaline solution (neutrality is pH 6.6). [Back]

[d] In a vacuum the reaction $H_2O \longrightarrow H^+ + OH^-$ requires over three times more energy (1.66 MJ mol^{-1}) than dissociation $H_2O \longrightarrow H^{\bullet} + {}^{\bullet}OH$ (531 kJ mol^{-1}). In water the hydration of the ions (H^+ ΔG° hydration -1112.5 kJ mol^{-1}, this includes H_3O^+ ΔG° hydration -461.1 kJ mol^{-1}; OH^- ΔG° hydration -437.6 kJ mol^{-1} [1067]) reduces the ΔG° of the reaction $2\ H_2O \rightleftharpoons H_3O^+ + OH^-$ to +99.78 kJ mol^{-1} (These calculations assumes that the standard state of the solvent water is taken as 1.0 M. If the standard state of the solvent water is its mole fraction (= 1.0), the ΔG° is +79.907 kJ mol^{-1}). The dissociated radicals ($H^{\bullet}$, ${}^{\bullet}OH$) are also somewhat stabilized in liquid water, as shown by the occasional dissociation of water [1066, seeequations]. [Back]

[e] The acidity constant (K_a) of acid HA and the basicity constant of its conjugate base A^- are defined by the equations:

$$\begin{array}{lll} HA + H_2O \rightleftharpoons A^- + H_3O^+ & \Delta G_a^\circ & = -RT\,Ln(K_a) \\ A^- + H_2O \rightleftharpoons HA + OH^- & \Delta G_b^\circ & = -RT\,Ln(K_b) \\ \hline H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- & \Delta G_w^\circ & = -RT\,Ln(K_w) \end{array}$$

Where the ΔG° values are the standard Gibbs free energies for the equilibria.
Therefore, as $\Delta G_w^\circ = \Delta G_a^\circ + \Delta G_b^\circ$, $Ln(K_w) = Ln(K_a) + Ln(K_b)$ and

$$\mathbf{pK_a + pK_b = pK_w} \quad \text{and} \quad \mathbf{K_w = K_a \times K_b}$$

The acidity constant (K_a) of H_2O is defined (as other acids) by the equation $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$. Therefore, $K_a = [H_3O^+][OH^-]/[H_2O] = K_w/[H_2O] = K_w/55.345$ (at 25 °C) and $pK_a = pK_w + 1.743$ (= 15.738 at 25 °C; a very weak acid, compare pK_as of H_2Te, H_2Se and H_2S are 2.6, 3.89 and 7.04 respectively). The pK_b (= $pK_w - pK_a$ = -1.743) related to this K_a is for the conjugate base (OH^-) not H_2O as commonly mistakenly cited. OH^- is a strong base whereas H_2O is a very weak base. The pK_b of H_2O is derived exactly as pK_a (above, as the equation generates both an acid and a base) and gives the same value (= 15.738 at 25 °C). Its associated pK_a (= -1.743) relates to H_3O^+, a strong acid. There is a difficulty that has been ignored in these definitions as K_a and K_b would normally be expressed in terms of activities rather than concentrations [1188] and the activity of pure H_2O is defined as unity whereas that of solutes is defined relative to their standard state (1 mol kg^{-1}) rather than the concentration of water here (~55.345 mol L^{-1}). The principal reason why the values chosen (e.g. pK_a = 15.738 for H_2O) are preferred is that these values fit in with the known acidity and basicity of water compared with other materials (e.g. the alcohols; pK_a C_2H_5OH = 16, pK_a $C_2H_5OH_2^+$ = -3.6, pK_b C_2H_5OH = 17.6, pK_b $C_2H_5O^-$ = -2) with the pK_a of H_2O (15.738) lying between that of methanol (15.54) and ethanol (16.0), methoxide being a slightly weaker base than hydroxide [2107] whilst ethoxide being a stronger base. [Back]

[f] As Logarithms may only be taken of dimensionless numbers, all the concentrations (activities, partial pressures, etc.) in any Logarithmic expression are actually divided by unit values in the same units of that concentration (activity, partial pressure, etc.); thus, for example here [H_3O^+] (concentration of of H_3O^+ in mol l^{-1}) is actually [H_3O^+]/(1.0 mol l^{-1}).

The p in pH originated as the arbitrary choice for the naming of the electrode solutions 'p' and 'q' by Sørensen [1036,1891], but is now taken to mean the 'logarithm to the base 10 of the reciprocal of' (cologarithm) as in the function described above. [Back]

[g] Strictly speaking these equations should be expressed in terms of activities rather than concentrations; thus K_w = [a_H+][a_{OH}-]. The derivations are easier to follow as given and usually the concentrations are so small that the difference is inconsequential. [Back]

Source:http://www1.lsbu.ac.uk/water/ionis.html