

$$\begin{aligned} C_{\text{H}^+} C_{\text{OH}^-} &= 1.8 \times 10^{-16} \times 55.5 = 1.01 \times 10^{-14} \\ &= K_w = 1.01 \times 10^{-14} \end{aligned} \quad (1.5)$$

at 25°C.

This new constant K_w , termed the **ion product of water**, expresses the relation between the concentration of H^+ and OH^- ions in dilute aqueous solutions; for example, this relation may be used to calculate the concentration of H^+ in pure water. To do this, let x equal the concentration of H^+ . Since in pure water, one OH^- is produced for every H^+ formed on dissociation of a molecule of H_2O , x must also equal the concentration of OH^- . Substituting in Equation 1.5, we have

$$\begin{aligned} \text{Therefore,} \quad (x)(x) &= 1.01 \times 10^{-14} = x^2 \\ x &= 1 \times 10^{-7} \\ &= C_{\text{H}^+} = C_{\text{OH}^-} = 1.0 \times 10^{-7} \text{ mole/l} \end{aligned}$$

1.7 pH

In 1909, Sorensen introduced the term **pH** as a convenient manner of expressing the concentration of H^+ ion by means of a base 10 logarithmic function; pH may be defined as

$$\text{pH} = \log \frac{1}{a_{\text{H}^+}} = -\log a_{\text{H}^+} \quad (1.6)$$

where a_{H^+} is defined as the activity of H^+ . If the activity coefficient is assumed to be 1, then

$$\text{pH} = \log \frac{1}{[\text{H}^+]} = -\log [\text{H}^+] \quad (1.7)$$

In this equation, to indicate that we are dealing with concentrations, we use brackets. Thus, the concentration of H^+ , (C_{H^+}), is represented as $[\text{H}^+]$.

The hydrogen ion is one of the few substances for which estimates of both the concentration and the activity routinely are obtained in the biochemical laboratory. The pH meter is an electrochemical instrument that is connected to two electrodes. These electrodes are in contact with a solution, one directly and one through a special glass membrane that is far more permeable to protons than it is to most other cations. The potential difference between the two electrodes, which is measured by the pH meter, is related logarithmically to the hydrogen ion activity and hence to the pH as defined by Equation 1.6. (Note that in some modern pH meter systems, the two electrodes are combined into one "concentric" electrode.)

The distinction between activity and concentration is indicated by the following example. The pH of 0.1M HCl when measured with a pH meter is 1.09. This value can be substituted in Equation 1.6, as the pH meter measures activities.

$$\begin{aligned} 1.09 &= \log \frac{1}{a_{\text{H}^+}} \\ a_{\text{H}^+} &= 10^{-1.09} \\ &= 8.1 \times 10^{-2} \text{ moles/liter} \end{aligned}$$

The concentration of hydrogen ion is expected to be 0.1 moles/liter in 0.1M HCl since HCl is a strong, fully dissociated acid. The activity coefficient may be calculated as

$$\begin{aligned}\gamma &= a_{H^+}/[H^+] \\ &= 0.081/0.1 \\ &= 0.81\end{aligned}$$

Thus, even at a concentration of 0.1M, the activity coefficient for hydrogen ions in an HCl solution is only slightly less than 1. It approaches 1 more closely at the lesser hydrogen ion concentrations that are characteristic of most biochemical reactions.

It is important to stress that the pH is a logarithmic function; thus, when the pH of a solution is decreased one unit from 5 to 4, the H^+ concentration has increased tenfold from $10^{-5}M$ to $10^{-4}M$. When the pH has increased three-tenths of a unit from 6 to 6.3, the H^+ concentration has decreased, by a factor of about 2, from $10^{-6}M$ to $5 \times 10^{-7}M$.

If we now apply the term of pH to the ion product expression for pure water, we obtain another useful expression

$$[H^+] \times [OH^-] = 1.0 \times 10^{-14}$$

We take the logarithms of this equation

$$\begin{aligned}\log [H^+] + \log [OH^-] &= \log (1.0 \times 10^{-14}) \\ &= -14\end{aligned}$$

and multiply by -1

$$-\log [H^+] - \log [OH^-] = 14$$

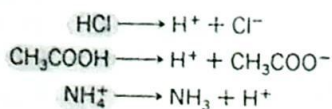
If we now define $-\log [OH^-]$ as pOH, a definition similar to that of pH, we have an expression relating the pH and pOH in any aqueous solution

$$pH + pOH = 14 \quad (1.8)$$

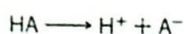
1.8 BRÖNSTED ACIDS

A most useful definition of acids and bases in biochemistry is that proposed by Brönsted. He defined *an acid as any substance that can donate a proton*, and *a base as a substance that can accept a proton*. Although other definitions of acids, notably one proposed by Lewis, are even more general, the Brönsted concept should be thoroughly understood by students of biochemistry.

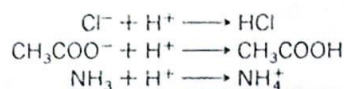
The following substances shown in orange are examples of Brönsted acids:



and the generalized expression would be

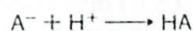


The corresponding bases are now shown reacting with a proton:



Note that the first of these three reactions does not occur to an appreciable extent in aqueous solution because HCl is a strong acid.

The corresponding base for the generalized weak acid HA is



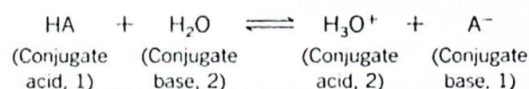
It is customary to refer to the acid-base pair as follows: HA (or HA^+ in the case of protonated amines) is the **Brønsted acid** because it can furnish a proton; the anion A^- (or neutral A in the case of amines) is called the **conjugate base** because it can accept the proton to form the acid HA.

1.9 IONIZATION OF WEAK ACIDS

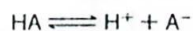
Hydrochloric acid (HCl), a familiar mineral acid, is completely dissociated in H_2O .



Note that the dissociation is represented as an irreversible reaction. The same is true of strong bases, such as NaOH, and the salts of strong bases and strong acids, such as NaCl. A weak acid, in contrast to a strong acid, is only partially ionized in aqueous solution. This is represented by a reversible ionization of the generalized weak acid, HA.



or the simpler



The proton donated by HA is accepted by H_2O to form the hydronium ion, H_3O^+ . Although it is strictly correct to recognize that the proton is hydrated in solution, other ions are as well, and the formulas for ions generally are written in the simple, unhydrated form. Hence, we can write the equilibrium constant as

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad (1.11)$$

where K_a is the dissociation constant for the weak acid.

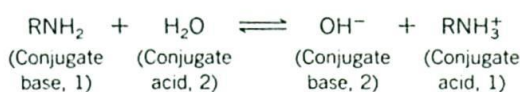
1.10 IONIZATION OF WEAK BASES

One way to consider the ionization of a weak base is by direct analogy with the ionization of a strong base, writing the equation as reversible rather than the irreversible $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$. That is, both a strong base and a weak base may be defined as a substance that furnishes OH^- ions on dissociation.

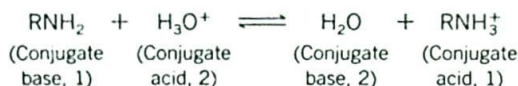


For ammonium hydroxide (NH_4OH), for example, the K_b is given in chemical handbooks as 1.8×10^{-5} . Therefore, the extent of dissociation of NH_4OH is identical with that of acetic acid (CH_3COOH ; $K_a = 1.8 \times 10^{-5}$). The important difference, of course, is that NH_4OH dissociates to form hydroxyl ions (OH^-), whereas CH_3COOH dissociates to form protons (H^+), and that the pH of 0.1M solutions of these two substances is by no means similar, the former being above pH 7 and the latter, acetic acid, below pH 7.

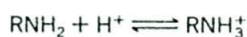
One of the most common types of weak base encountered in biochemistry is the group called organic amines (e.g., the amino groups of amino acids). Such compounds, when represented with the general formula $\text{R}-\text{NH}_2$, do not contain hydroxyl groups that can dissociate as in Reaction 1.12. Note that even ammonium hydroxide itself can be written in this form, as HNH_2 , or more simply, NH_3 . Such compounds can ionize in H_2O to produce hydroxyl ions, according to an equation that has a form similar to that of Equation 1.10.



or, alternatively, (1.13)



which simplifies to



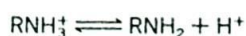
In the first representation of this reaction, H_2O serves as an acid to contribute a proton to the base RNH_2 . The corresponding ionization constant is

$$K_{\text{ion}} = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2][\text{H}_2\text{O}]} \quad (1.14)$$

that by analogy with Equation 1.12 can be rewritten as

$$K_b = [\text{H}_2\text{O}]K_{\text{ion}} = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} \quad (1.15)$$

The simplified version of Equation 1.13 can be written in reverse, as we have done for NH_4^+ in Section 1.8. This is the dissociation of a Brønsted weak acid.



The corresponding dissociation equilibrium constant is defined by

$$K_a = \frac{[\text{RNH}_2][\text{H}^+]}{[\text{RNH}_3^+]} \quad (1.16)$$

Thus, it is possible, and convenient, to treat both weak acids and weak bases as Brønsted acids by simply writing the dissociation of the protonated form of the