The dissociation constant specifies the tendency of a substance $M_xN_y$ to reversibly dissociate (separate) in a solution (often aqueous) into smaller components $M$ and $N$:

$$[ M_xN_y(aq) + H_2O_{(l)} \rightleftharpoons xM_{(aq)} + yN_{(aq)} ] \tag{1}$$

The dissociation constant is denoted $K_d$ and is calculated by

$$K_d = \dfrac{a_M^x \cdot a_N^y}{a_{M_xN_y} \cdot a_{H_2O}} \approx \dfrac{[M]^x[\text{N}]^{y}}{[M_xN_y](1)} \tag{2}$$

where $A$ represents the activity of a species, and $[M]$, $[N]$, and $[M_xN_y]$ are the molar concentrations of the entities $M$, $N$, and $M_xN_y$. Because water is the solvent, and the solution is assumed to be dilute, the water is assumed to be pure, and the activity of pure water is defined as 1. The activities of the solutes are approximated with molarities. The dissociation constant is an immediate consequence of the law of mass action which describes equilibria in a more general way. The dissociation constant is also sometimes called ionization constant when applied to salts. The inverse of the dissociation constant is called association constant.

Dissociation constant of water

Formally, the dissociation (autoprotolysis) of water follows the following equation:

$$[H_2O_{(l)} \rightleftharpoons H_{(aq)}^+ + OH_{(aq)}^-] \tag{3}$$

or

$$[H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O_{(aq)}^+ + OH_{(aq)}^-] \tag{4}$$

These two reaction equations are thermodynamically equivalent, thus the law of mass action for the two equations must be equivalent. Their equivalency is shown by

$$[K_d = \dfrac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} = \dfrac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O}^2} \approx \dfrac{[H^+] \cdot [\text{OH}^-]}{1} = \dfrac{[H_3O^+] \cdot [\text{OH}^-]}{[1]^2} = [H^+] \cdot [\text{OH}^-] = [H_3O^+] \cdot [\text{OH}^-] = 1.00 \times 10^{-14} = K_w] \tag{5}$$

In these reactions (and equations), the activity of water, as the solvent in a dilute solution, is approximated as the activity of pure water, which has a defined value of 1. The activity of the ions, as solutes, can be approximated as the molarity of the ions. Thus, equation 3 and the equation 4 both have the same law of mass action and the same $\langle K_d \rangle$, which is commonly written as $\langle K_w \rangle$.

The value of $K_w$ changes considerably with temperature. Consequently this variation must be taken into account when making precise measurements (i.e. when determining the pH).

<table>
<thead>
<tr>
<th>Water Temperature [°C]</th>
<th>$K_w$ [10^{-14}]</th>
<th>p$K_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>14.92</td>
</tr>
</tbody>
</table>
Acid base reactions

The dissociation constant can also be applied to the reaction of acids with water, sometimes called the deprotonation of acids. These reactions can be written in two, equivalent forms, depending on whether water is shown as the solvent, or not:

\[
\text{HA}^{\text{(aq)}} + \text{H}_2\text{O}^{\text{(l)}} \rightleftharpoons \text{H}_3\text{O}^+^{\text{(aq)}} + \text{A}^-^{\text{(aq)}} \tag{6}
\]

or

\[
\text{HA}^{\text{(aq)}} \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{A}^-^{\text{(aq)}} \tag{7}
\]

In either case, the dissociation constant is denoted as $K_a$, and because the activity of water has a value of 1, there is no net difference in whether water is formally included in the reaction or the law of mass action equation. The greater the dissociation constant of an acid the stronger the acid. Polyprotic acids (e.g. carbonic acid or phosphoric acid) show several dissociation constants, because more than one proton can be separated (one after the other):

\[
\text{H}_3\text{A}^{\text{(aq)}} \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{H}_2\text{A}^-^{\text{(aq)}} \quad K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]} 
\]

\[
pK_{a1} = -\log(K_{a1})
\]

\[
\text{H}_2\text{A}^-^{\text{(aq)}} \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{HA}^{2-}^{\text{(aq)}} \quad K_{a2} = \frac{[\text{H}^+][\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]} 
\]

\[
pK_{a2} = -\log(K_{a2})
\]

\[
\text{HA}^{2-}^{\text{(aq)}} \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{A}^{3-}^{\text{(aq)}} \quad K_{a3} = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]} 
\]

\[
pK_{a3} = -\log(K_{a3})
\]

A list of acid dissociation constants can be found here.
Other applications

The concept of the dissociation constant is applied in various fields of chemistry and pharmacology. In protein-ligand binding the dissociation constant describes the affinity between a protein and a ligand. A small dissociation constant indicates a more tightly bound the ligand. In the case of antibody-antigen binding the inverted dissociation constant is used and is called affinity constant.

Contributors

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