Acidobasic equilibria

Dissociation of acids or bases can be described by these equations:

$$\mathrm{HA + H_2O \rightleftharpoons A^- + H_3O^+}$$
$$\mathrm{B + H_2O \rightleftharpoons BH^+ + OH^-}$$

The equilibrium of these reactions depends on a particular acid or base and it is described by constant, which can be calculated from equilibria concentrations (in $\mathrm{mol \cdot dm^{-3}}$) of particles in equations above.

$$K_\mathrm{a} = \frac{[\mathrm{A^-}] \cdot [\mathrm{H_3O^+}]}{[\mathrm{HA}] \cdot [\mathrm{H_2O}]} \qquad \text{or} \qquad K_\mathrm{b} = \frac{[\mathrm{BH^+}] \cdot [\mathrm{OH^-}]}{[\mathrm{B}] \cdot [\mathrm{H_2O}]} \tag{1}$$

The water concentration is considered as a constant. One liter of water is 55.51 mol and this is also its concentration in $\mathrm{mol \cdot dm^{-3}}$. Changes of the water concentration during dissociation are insignificant.

$$K_\mathrm{a} = \frac{[\mathrm{A^-}] \cdot [\mathrm{H_3O^+}]}{[\mathrm{HA}]} \qquad \text{or} \qquad K_\mathrm{b} = \frac{[\mathrm{BH^+}] \cdot [\mathrm{OH^-}]}{[\mathrm{B}]} \tag{2}$$

The constants are temperature-dependent and they are typical for a particular acids or a bases. In tables we can see them as $\mathrm{p}K_\mathrm{a}$ and $\mathrm{p}K_\mathrm{b}$, which is a negative common logarithm of the K_a and K_b respectively. For example if the $K_\mathrm{a} = 2.69 \times 10^{-5}$, then $\mathrm{p}K_\mathrm{a} = -\log(2.69 \times 10^{-5}) = 4.57$.

Only a few acids and bases are fully dissociated.

Calculation of pH

pH of a solution is defined as the negative common logarithm of concentration of $\mathrm{H_3O^+}$. In case of strong acids and bases, can be assumed the 100% dissociation in solutions with concentrations of 10^{-3} $\mathrm{mol \cdot dm^{-3}}$ or less.

Water undergoes auto- or self-ionization as shown in the following equation.

$$\mathrm{2\,H_2O \rightleftharpoons H_3O^+ + OH^-}$$

An equilibrium is established between the ions produced and the unionised water. An equilibrium expression can be written for this system.

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{3}$$

K_w is used to represent the equilibrium constant for the autoionization of water. It is a special notation of the general representation K_c.

The value of K_w when measured at 25 °C has been determined to be 1×10^{-14}.

Mathematically, if one takes the logarithm of both sides of the equation, remembering that when numbers are multiplied their logarithms are added, we arrive at the following equation.

$$\log(1 \times 10^{-14}) = \log[H_3O^+] + \log[OH^-]$$
$$-14 = \log[H_3O^+] + \log[OH^-]$$

The $-\log[H_3O^+]$ is defined as the pH, and the $-\log[OH^-]$ is defined as the pOH. Substituting into the equation yields the relationship between pH and pOH of a solution.

$$14 = \mathrm{pH} + \mathrm{pOH}$$

Strong acids and bases

Example 1. Calculate pH of a solution of hydrochloric and sulfuric acid and assume 100% dissociation of the acids at these conditions. The concentration is 5.2×10^{-4} mol · dm^{-3}.

Hydrochloric acid dissociates according the equation $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$. It means, that concentration of H_3O^+ is the same as the concentration of HCl.

$$\mathrm{pH} = -\log(5.2 \times 10^{-4}) = 3.28$$

Dissociation of sulfuric acid can be described as $H_2SO_4 + 2\,H_2O \longrightarrow 2\,H_3O^+ + SO_4{}^{2-}$. It means, that the concentration of H_3O^+ is two times higher, than the concentration of the sulphuric acid.

$$\mathrm{pH} = -\log(1.04 \times 10^{-3}) = 2.98$$

Example 2. Calculate pH of a solution of potassium hydroxide and assume 100% dissociation of the hydroxide at these conditions. The concentration is 2.5×10^{-4} mol · dm^{-3}.

Dissociation of potassium hydroxide can be described as $NaOH \longrightarrow Na^+ + OH^-$. It means, that the concentration of the OH^- is the same as the concentration of the potassium hydroxide.

$$\mathrm{pOH} = -\log(2.5 \times 10^{-4}) = 3.60$$

$$\mathrm{pH} = 14 - 3.60 = 10.4$$

Weak acids and bases

Most of the molecules of weak acids or bases remain undissociated in their aqueous solutions. It means, that concentration of the H_3O^+ or OH^- ions doesn't correspond to concentration of particular acid or base.

$$\begin{aligned} HA + H_2O &\rightleftharpoons A^- + H_3O^+ \\ B + H_2O &\rightleftharpoons BH^+ + OH^- \end{aligned}$$

Based on the original acid or base concentration $c_\circ$ and the equilibrium concentration of the corresponding ion c_d is possible to calculate **degree of ionization** α.

$$\alpha = \frac{c_d}{c_\circ} = \frac{n_d}{n_\circ} \tag{4}$$

In case of an acid.

$$\begin{aligned} [H_3O^+] = [A^-] &= \alpha \cdot c_\circ \\ [HA] &= c_\circ \cdot (1 - \alpha) \end{aligned} \tag{5}$$

By combination of the formulas (5) and (2) we will get the formula for calculation of the dissociation constant (6). If the value of $(1 - \alpha) \approx 1$ there is possible to use simplified formula (7).

$$K_a = \frac{c_\circ \cdot \alpha^2}{1 - \alpha} \tag{6}$$

$$K_a = c_\circ \cdot \alpha^2 \tag{7}$$

For the calculation of α, based of the equation (6) we get the formula (8). In case of very weak acids is possible to use the simplified formula (7) and we get the formula (9).

$$\alpha = \frac{-K_\mathrm{a} + \sqrt{K_\mathrm{a}^2 + 4c_\circ K_\mathrm{a}}}{2c_\circ} \tag{8}$$

$$\alpha = \sqrt{\frac{K_\mathrm{a}}{c_\circ}} \tag{9}$$

If we combine the equation (5) and (7), we obtain the formula (10) for the equilibrium concentration of H_3O^+. Because $\mathrm{pH} = -\log[H_3O^+]$, it's possible to obtain the formula (11) for calculation of pH from pK_a and $c_\circ$.

$$c_{[H_3O^+]} = \sqrt{K_\mathrm{a} \cdot c_\circ} \tag{10}$$

$$\mathrm{pH} = \tfrac{1}{2}(pK_\mathrm{a} - \log c_\circ) \tag{11}$$

Salts hydrolysis

Solutions of salts of weak acids and strong bases are basic. Generally, the conjugated bases (anions) weak acids are relatively strong. As the example potassium cyanide is used.

$$\begin{aligned} \mathrm{KCN} &\longrightarrow \mathrm{K^+ + CN^-} \\ \mathrm{CN^- + H_2O} &\rightleftharpoons \mathrm{HCN + OH^-} \end{aligned}$$

Analogical situation is in case of salts of strong acids and weak bases. Conjugated acids of weak bases are relatively strong acids – the solutions are acidic. As the example ammonium chloride is used.

$$\begin{aligned} \mathrm{NH_4Cl} &\longrightarrow \mathrm{NH_4^+ + Cl^-} \\ \mathrm{NH_4^+ + H_2O} &\rightleftharpoons \mathrm{NH_3 + H_3O^+} \end{aligned}$$

Using $\mathrm{p}K_\mathrm{a}$ or $\mathrm{p}K_\mathrm{b}$ and concentration of the salt c_s can be calculated pH of solutions of these salts – the formula (13) in case of a salt of a weak base and formula (12) in case of a salt of a weak acid.

$$\mathrm{pH} = 7 + \tfrac{1}{2}(\mathrm{p}K_\mathrm{a} + \log c_s) \tag{12}$$

$$\mathrm{pH} = 7 - \tfrac{1}{2}(\mathrm{p}K_\mathrm{b} + \log c_s) \tag{13}$$

Buffers

Buffers are used for stabilisation of pH. For this purpose are usually used mixtures of a week acid and its salt with a strong base, or a week base with its salt with a strong acid.

$$\begin{aligned} \mathrm{CH_3COOH + H_2O} &\rightleftharpoons \mathrm{CH_3COO^- + H_3O^+} \\ \mathrm{CH_3COONa} &\longrightarrow \mathrm{CH_3COO^- + Na^+} \end{aligned}$$

Mechanism of buffers action can be described by these reactions.

$$\begin{aligned} \mathrm{CH_3COONa + HCl} &\longrightarrow \mathrm{CH_3COOH + NaCl} \\ \mathrm{CH_3COOH + NaOH} &\longrightarrow \mathrm{CH_3COONa + H_2O} \end{aligned}$$

For calculations of pH of the buffer solutions is used the **Henderson–Hasselbalch equation** (14).

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{c_s}{c_A} \quad \text{or} \quad \mathrm{pH} = 14 - (\mathrm{p}K_\mathrm{b} + \log \frac{c_s}{c_B}) \tag{14}$$