

3.9 – Acid-base equilibria

Acid dissociation constant, K_a

When a weak acid dissociates an equilibrium is set up so it has an equilibrium constant.



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{ mol dm}^{-3}$$

The higher the K_a value, the stronger the acid.

$$\text{p}K_a = -\log K_a$$

The lower the $\text{p}K_a$, the stronger the acid.

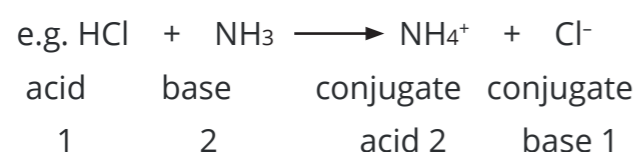
Lowry-Bronsted theory

Acids are proton (H^+) donors.

Bases are proton (H^+) acceptors.

Conjugate acids are formed by the addition of H^+ to a base.

Conjugate bases are formed by the loss of H^+ from an acid.



A **strong acid** is fully dissociated in water.

A **weak acid** is only partially dissociated in water.

Buffer solutions

Buffers are solutions whose pH stays relatively constant as a small amount of an acid or alkali is added.

Buffers are used where pH is very important, e.g. regulating the pH of blood and storing biological molecules such as enzymes.

Industrial examples are in fermentation and making dyes.

Ionic product of water, K_w

In pure water, a small fraction of molecules dissociates into H^+ and OH^- ions. An equilibrium is formed.



The amount of water that dissociates is tiny, so its concentration can be considered to be constant, and a new equilibrium constant, K_w , is defined.

$$K_w = [\text{H}^+][\text{OH}^-] \text{ mol}^2 \text{ dm}^{-6}$$

At 25°C, $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$.

In pure water: $[\text{H}^+] = [\text{OH}^-]$ and $K_w = [\text{H}^+][\text{OH}^-]$

$$K_w = [\text{H}^+]^2 = 1.00 \times 10^{-14} \text{ and } [\text{H}^+] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = 7$$

The ionic equation for all neutralisation reactions is the reverse of the equilibrium above, i.e. $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$

Acid buffers

These consist of a weak acid and a salt of the same acid, e.g. ethanoic acid and sodium ethanoate.



The solution contains lots of CH_3COO^- ions and CH_3COOH .

Adding an acid increases the amount of H^+ and the equilibrium shifts to the left, removing the H^+ ions by reaction with CH_3COO^- .

Adding an alkali increases the amount of OH^- ions, and this removes some of the H^+ ions. This causes the equilibrium to shift to the right, producing H^+ ions from CH_3COOH .

Calculating pH

Since **$\text{pH} = -\log[\text{H}^+]$** , to calculate the pH of any solution, the concentration of H^+ ions must be found.

For a strong acid, HX, $[\text{H}^+] = [\text{HX}]$.

e.g. $0.1 \text{ mol dm}^{-3} \text{ HCl}$,

$$\text{pH} = -\log 0.1 = 1$$

For a strong dibasic acid, H_2A , that fully dissociates, $[\text{H}^+] = [2\text{HA}]$.

To calculate hydrogen ion concentration from pH use

$$[\text{H}^+] = 10^{-\text{pH}}$$

e.g. for a sample with a pH of 3.6,

$$[\text{H}^+] = 10^{-3.6} = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$$

For a strong base, MOH, since $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

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

e.g. $0.1 \text{ mol dm}^{-3} \text{ NaOH}$,

$$[\text{H}^+] = 1.0 \times 10^{-14} / 0.1 = 1.0 \times 10^{-13} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log 1.0 \times 10^{-13} = 13$$

For a weak acid, HA,

$$\text{since } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{ and } [\text{H}^+] = [\text{A}^-]$$

$$[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$$

e.g. $0.1 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ ($K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$)

$$[\text{H}^+] = \sqrt{1.7 \times 10^{-5} \times 0.1} = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log 1.3 \times 10^{-3} = 2.9$$

To work out K_a given pH, use $[\text{H}^+] = 10^{-\text{pH}}$ to calculate $[\text{H}^+]$ and

$$\text{substitute it in } K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

e.g. For a 0.50 mol dm^{-3} solution of HClO with a pH of 3.92,

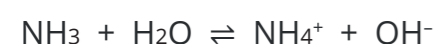
$$[\text{H}^+] = 10^{-3.92} = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_a = \frac{[1.2 \times 10^{-4}]^2}{0.5} = 2.9 \times 10^{-8} \text{ mol dm}^{-3}$$

3.9 – Acid-base equilibria

Basic buffers

These consist of a weak base and a salt of the same base, e.g. ammonia solution and ammonium chloride.



The solution contains lots of NH_4^+ ions and NH_3 .

Adding a base increases the amount of OH^- ions, and the equilibrium shifts to the left, removing the OH^- ions by reaction with NH_4^+ .

Adding an acid increases the amount of H^+ ions, and this removes some of the OH^- ions. This causes the equilibrium to shift to the right, producing more OH^- ions from NH_3 (and H_2O).

pH for buffers

Use the expression $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

$[\text{A}^-]$ = concentration of salt, $[\text{HA}]$ = concentration of acid

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

If $[\text{HA}] = [\text{A}^-]$ then $[\text{H}^+] = K_a$ and $\text{pH} = -\log K_a = \text{p}K_a$

e.g. for a solution containing $0.010 \text{ mol dm}^{-3}$ ethanoic acid and $0.020 \text{ mol dm}^{-3}$ sodium ethanoate,

(K_a for ethanoic acid = $1.78 \times 10^{-5} \text{ mol dm}^{-3}$)

$$[\text{H}^+] = 1.78 \times 10^{-5} \times \frac{0.010}{0.020} = 8.9 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log 8.9 \times 10^{-6} = 5.1$$

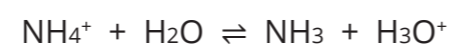
Salt hydrolysis

Salts of a strong acid/strong base, e.g. NaCl : $\text{pH} = 7$.

None of the ions present, Na^+ and Cl^- , react with water.

Salts of a strong acid/weak base, e.g. NH_4Cl : $\text{pH} < 7$.

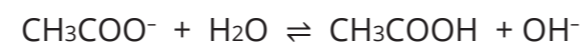
The NH_4^+ ions react with water to establish the equilibrium



Hydrogen ions are formed so pH is lower than 7.

Salts of a weak acid/strong base, e.g. CH_3COONa : $\text{pH} > 7$.

The CH_3COO^- ions react with water to establish the equilibrium



Hydroxide ions are formed so pH is greater than 7.

Indicators

Indicators are very weak acids that change colour as the pH changes. They change colour over a range of pH values, not at a specific pH . To make sure that an indicator is suitable for a titration, the pH range over which it changes colour must lie within the vertical part of the titration curve.

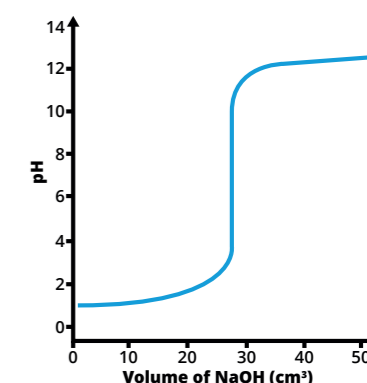
Titration curves

All solutions are 0.1 mol dm^{-3} , and the original volume is 25 cm^3 .

The vertical regions mark the equivalence point, i.e. the volume required for neutralisation.

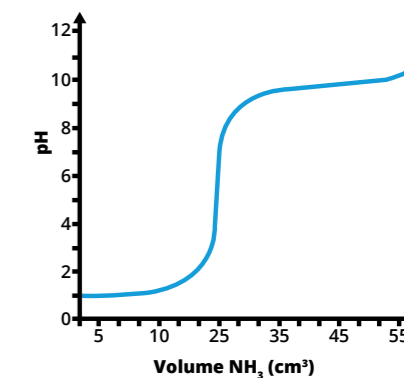
Strong acid – strong base

Graph starts at $\text{pH} 1$. Slow increase in pH as first 20 cm^3 is added. Sudden increase in pH from about 3 to 11 around 25 cm^3 (vertical line). Most indicators suitable. Slow increase to pH of around 13 as next 25 cm^3 added.



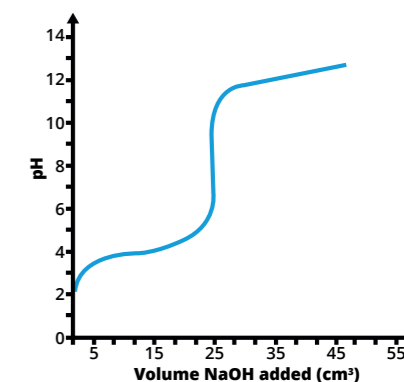
Strong acid – weak base

Graph starts at $\text{pH} 1$. Slow increase in pH as first 20 cm^3 is added. Sudden increase in pH from about 3 to 8 around 25 cm^3 . Suitable indicator – methyl orange. Increase in pH which levels off at around $35\text{-}40 \text{ cm}^3$ due to buffer effect, before increasing to $\text{pH} 11$.



Weak acid – strong base

Graph starts at around $\text{pH} 3$. Increases gradually, then levels off around $10\text{-}15 \text{ cm}^3$ due to buffer effect, before increasing again. Sudden increase in pH from about 6 to 11 around 25 cm^3 . Suitable indicator – phenolphthalein. Slow increase to pH of around 13 as next 25 cm^3 is added.



Weak acid – weak base

Graph has no vertical region so can't be studied using an indicator. A pH probe must be used.