

CAIE Chemistry A-level

25: Equilibria (A-level only)

Notes

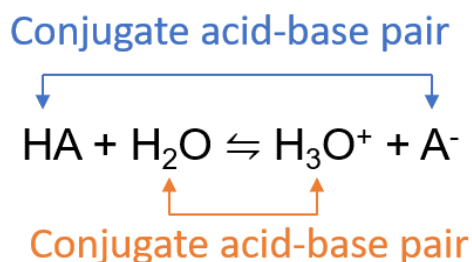
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Acids and Bases

Conjugate Acids and Bases

An acid and a base that are only different by one proton are called a **conjugate acid-base pair**. An example is that NH_3 is the conjugate base of NH_4^+ , and NH_4^+ is the conjugate acid of NH_3 . Another example is that HF is the conjugate acid of F^- , and F^- the conjugate base of HF .



For example, from the diagram:

- HA and A^- are a conjugate pair
- H_3O^+ and H_2O are a conjugate pair
- HA is acid-I
- A^- is base-I
- H_3O^+ is acid-II
- H_2O is base-II

Calculations

Calculating pH or H^+ concentration:

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

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

Calculations involving the acid dissociation constant, K_a :

For the equation $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

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

K_a is the **acid dissociation constant**. The lower the K_a value, the further left the equilibrium lies. For weak acids, the K_a is very small so K_a values can be converted into $\text{p}K_a$ values using the equation below. As $\text{p}K_a$ increases, the strength of the acid decreases.

$$\text{p}K_a = -\log_{10}(K_a)$$



Calculations involving the ionic product of water, K_w :

$$K_w = [H^+][OH^-]$$

K_w is the **ionic product of water**. The value of K_w varies with temperature. At room temperature, this is equal to $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$.

pH of Strong Bases

Follow these steps to work out the pH of a strong base:

1. Calculate the concentration of hydroxide ions.
2. Calculate the concentration of H^+ ions using K_w .
3. Convert $[H^+]$ into pH, $\text{pH} = -\log_{10}[H^+]$.

pH of Weak Acids

Follow these steps to work out the pH of a weak acid:

1. For the equation $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$:

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

- Assume that a very small number of hydrogen ions come from the dissociation of water, so $[H^+] = [A^-]$.
- Assume that the concentration of acid at equilibrium is the same as the original concentration because it is a weak acid so little dissociation has occurred.

2. Rewrite K_a :

$$K_a = \frac{[H^+]^2}{[HA]}$$

3. Rearrange K_a before entering the values to calculate $[H^+]$

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

4. Convert $[H^+]$ into pH:

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

pH of Strong Acids

Strong acids completely dissociate in solution so $[H^+] = [HA]$. This means pH can easily be calculated, $\text{pH} = -\log_{10}[H^+]$.



Buffers

A buffer **minimises the pH change** when a **small volume** of acid or alkali is added.

Acidic Buffer

An acidic buffer has a **pH less than 7** and contains a large amount of weak acid and its conjugate base (from a salt) and relatively few H^+ ions in equilibrium. An example of an acidic buffer is **ethanoic acid**: $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

- Adding acid to this buffer solution increases the **concentration of hydrogen ions**. The position of **equilibrium shifts left** as CH_3COO^- reacts with most of the added H^+ ions to form CH_3COOH in order to reduce the concentration of H^+ ions. This prevents a large **decrease in pH**.
- Adding alkali to this buffer solution increases the concentration of OH^- ions. The small concentration of H^+ ions reacts with the added OH^- ions to form water: $H^+ + OH^- \rightarrow H_2O$. The position of the **buffer equilibrium shifts to the right** in order to regenerate most of the H^+ ions.

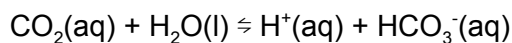
Alkaline Buffer

An alkaline buffer has a **pH greater than 7** and contains a weak base and its salt. An example of an alkaline buffer is **ammonia**: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

- Adding acid to this buffer solution increases the concentration of H^+ ions. Ammonia molecules react with H^+ ions to form ammonium ions and remove most of the added H^+ ions. Alternatively, the H^+ ions may react with OH^- ions which are present in the equilibrium to form water. This causes the position of equilibrium to shift to replace the reacted OH^- ions until most of the H^+ ions have reacted.
- Adding alkali to this buffer solution **increases the concentration of OH^- ions**. The position of **equilibrium shifts to the left** as NH_4^+ reacts with the added OH^- ions.

Buffers in the Blood

Blood pH must remain between **7.35 and 7.45**. One buffer in the blood is **HCO_3^- ions**:



If **pH increases** (hydrogen ion concentration decreases), the position of **equilibrium will shift to the right** to increase the concentration of hydrogen ions. If pH falls (hydrogen ion concentration increases), the position of equilibrium will shift to the left to remove the added H^+ ions.

Buffers can also be used to check and **adjust the readings on pH meters**. A pH probe would be inserted into a buffer solution with a known pH then the pH meter would be adjusted to match the known value.

Buffer Calculations

A buffer has the **general equation**: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$. This means K_a can be written like this:

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



For **weak acids**, two assumptions were made:

- 1) $[H^+] = [A^-]$ - this is no longer true as the buffer contains a much **larger concentration of A^-** . The concentration of A^- is assumed to be the same as the concentration of the salt as the number of A^- ions coming from HA is tiny (as it is a weak acid).
- 2) $[HA]$ at equilibrium = $[HA]$ at the start - this is assumed for the buffer because the added A^- ions from the salt push the equilibrium to the left meaning there is **little dissociation of the acid**.

Given the value of K_a , the $[H^+]$ can be calculated by rearranging the equation. This can then be used to work out the pH: $pH = -\log_{10}[H^+]$.

The **proportion of acid and conjugate base** (from the salt) present in the buffer can also be calculated when given K_a and pH:

- 1) Use pH to calculate the concentration of hydrogen ions, $[H^+] = 10^{-pH}$
- 2) Rearrange K_a and substitute in known values to find the proportion of weak acid and conjugate acid at equilibrium:

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

The same calculations can be completed for alkaline buffers such as ammonia. In this case, HA would be NH_4^+ and A^- would be NH_3 .

Solubility Product, K_{sp}

The solubility constant indicates **how much a compound dissociates in water**. It only applies to saturated compounds. The higher the value, the more soluble the compound.

When an ionic solid dissolves in water, an **equilibrium** is established between the ions and the compound. E.g. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

The equilibrium constant is called the **solubility product**:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$BaSO_4(s)$ isn't present in the equilibrium constant equation because it is a solid in a **heterogeneous equilibrium**. The number of molecules of each substance is used in the K_{sp} equation in the same way as in other equilibrium constant equations (e.g. if there were $2Ca^{2+}(aq)$ in the equilibrium equation, K_{sp} would contain $[Ca^{2+}]^2$).



The **units** for solubility products are worked out using the equation:

- For BaSO_4 :

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})$$

$$= \text{mol}^2 \text{ dm}^{-6}$$
- For $\text{Ca}_3(\text{PO}_4)_2$:

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

$$(\text{mol dm}^{-3})^3 \times (\text{mol dm}^{-3})^2$$

$$= \text{mol}^5 \text{ dm}^{-15}$$

The solubility product for a compound will always be **the same under the same conditions** provided that the solution is saturated. If two compounds are mixed together, a precipitate will only form if the ionic concentrations give a value greater than the solubility product (otherwise, the solution won't be saturated).

Example calculations:

- The solubility of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, at 298 K is $1.71 \times 10^{-4} \text{ mol dm}^{-3}$.

$$\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$$
 The concentration of $\text{Mg}(\text{OH})_2$ is $1.71 \times 10^{-4} \text{ mol dm}^{-3}$, so using the equation:
 - $[\text{Mg}^{2+}] = 1.71 \times 10^{-4} \text{ mol dm}^{-3}$
 - $[\text{OH}^{-}] = 2 \times (1.71 \times 10^{-4}) = 3.42 \times 10^{-4} \text{ mol dm}^{-3}$
$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$

$$= (1.71 \times 10^{-4}) \times (3.42 \times 10^{-4})^2$$

$$= 2.00 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$
- The solubility product of barium sulfate, BaSO_4 , at 298K is $1.10 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

$$\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$
 Using the equation (where y is the unknown solubility):
 - $[\text{Ba}^{2+}] = y$
 - $[\text{SO}_4^{2-}] = y$
$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$1.10 \times 10^{-10} = y \times y$$

$$1.10 \times 10^{-10} = y^2$$

$$y = \sqrt{(1.10 \times 10^{-10})} = 1.05 \times 10^{-5} \text{ mol dm}^{-3}$$

Common Ion Effect

The common ion effect occurs when you have a **sparingly soluble substance**. The substance will be **less soluble in a solution containing any ions it has in common**.

For example, if sodium chloride (NaCl) was added to a saturated solution of PbCl_2 , according to **Le Chatelier's principle**, the position of equilibrium ($\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$) would be affected. This is because the **concentration of Cl^{-} ions would increase** so to counteract the increased concentration of chloride ions so the position of equilibrium shifts to the left to form more $\text{PbCl}_2(\text{s})$. This also means that the **solubility of $\text{PbCl}_2(\text{s})$ will decrease** so the concentration of lead(II) ions will decrease.



Example calculation:

$\text{PbCl}_2(\text{s})$ is dissolved in a solution of $0.100 \text{ mol dm}^{-3}$ sodium chloride solution. The solubility product of PbCl_2 is $1.7 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$

$$[\text{Pb}^{2+}] = y \text{ mol dm}^{-3}$$

Assume the concentration of chloride ions is the same as the concentration of sodium chloride: $[\text{Cl}^-] = 0.100 \text{ mol dm}^{-3}$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$= y \times (0.100)^2$$

$$1.7 \times 10^{-5} = 0.0100 \times y$$

$$y = 1.7 \times 10^{-5} \div 0.0100 = 1.7 \times 10^{-3} \text{ mol dm}^{-3}$$

The $[\text{Pb}^{2+}]$ when $\text{PbCl}_2(\text{s})$ dissolves in water is $0.0162 \text{ mol dm}^{-3}$. This decreases by a scale factor of 10 to $0.0017 \text{ mol dm}^{-3}$ when $\text{PbCl}_2(\text{s})$ is dissolved in $0.100 \text{ mol dm}^{-3}$ NaCl solution.

Partition Coefficients, K_{pc}

Two **immiscible** liquids will form two separate layers in a separating funnel with the **less dense layer on top**. If substance X is dissolved in both of these liquids, it may be more soluble in one layer than another. A **dynamic equilibrium** will be set up at the boundary between the two liquids:

$X(\text{in more dense liquid}) \rightleftharpoons X(\text{in less dense liquid})$

$$K_{\text{pc}} = \frac{[\text{X in less dense liquid}]}{[\text{X in more dense liquid}]}$$

There are **no units** for the partition coefficient because any units cancel out.

Example calculation:

- 1.00g of X is in 100cm^3 of water and 5cm^3 of ether. $K_{\text{pc}} = 40$. m is mass of X dissolved in ether:

$$\text{Concentration of X in ether} = m/5 \text{ g cm}^{-3}$$

$$\text{Concentration of X in water} = (1.00 - m)/100 \text{ g cm}^{-3}$$

$$K_{\text{pc}} = \frac{[\text{X in less dense liquid}]}{[\text{X in more dense liquid}]}$$

$$40 = \frac{m/5}{(1.00 - m)/100}$$

$$\frac{40(1.00 - m)}{100} = \frac{m}{5}$$

$$200 - 200m = 100m$$

$$300m = 200$$

$$m = 0.67\text{g}$$

