

CAIE Chemistry A-level

7: Equilibria Notes

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Chemical Equilibria

- **Reversible reaction:** a reaction which can go forwards or backwards depending on the conditions.
- **Dynamic equilibrium:** for a reversible reaction in a **closed system**, dynamic equilibrium occurs when the rate of the forward and backward reactions is equal. The concentrations of products and reactants remain constant despite the fact particles are continually reacting.
- **Le Chatelier's principle:** if a dynamic equilibrium is subject to changing conditions, the position of equilibrium will shift to counteract this change.

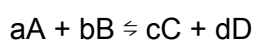
Le Chatelier's Principle

Le Chatelier's principle states that if a reaction at equilibrium is subjected to a change in concentration, temperature or pressure, the position of equilibrium will move to counteract the change. Therefore, altering conditions can impact the position of equilibrium:

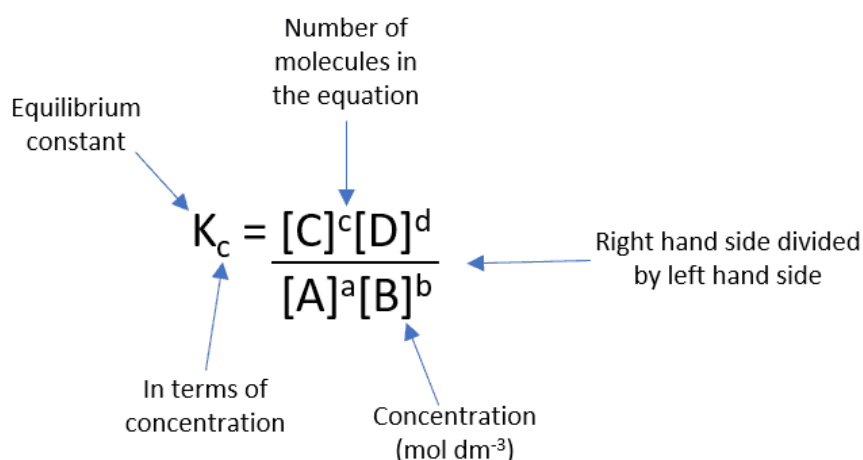
- **Concentration:** increasing the concentration of reactants causes the position of equilibrium to shift right in order to reduce the concentration of reactants and form more products. The reverse occurs if concentration is decreased.
- **Pressure:** increasing the pressure will cause the position of equilibrium to shift towards the side with the fewest gaseous molecules in order to decrease the pressure. The opposite occurs if pressure is decreased. If there is an equal number of gaseous molecules on both sides of the equation, changing pressure will have no effect on the position of equilibrium.
- **Temperature:** for an equilibrium where the forward reaction is exothermic, increasing the temperature will cause the position of equilibrium to shift to the left (so more endothermic reactions occur) to take in more heat energy and reduce the temperature. For the same reaction, decreasing the temperature will cause the position of equilibrium to shift to the right (so more exothermic reactions occur) to release more heat energy and increase the temperature. The opposite is true if the forward reaction is endothermic.
- **Catalyst:** a catalyst has no effect on the position of equilibrium because it speeds up the rate of the forward and backward reactions equally, increasing the rate at which dynamic equilibrium is reached.

Equilibrium Constant (K)

Homogeneous equilibria have all substances in the **same phase**. In **heterogeneous** equilibria, substances are in **different phases**. For this general equilibrium equation, all substances are (g), (l) or (aq):



This equation is used below to show how to calculate K_c :



In heterogeneous equilibria, **solids are not included** in the K_c equation.

To work out K_p , more calculations are required:

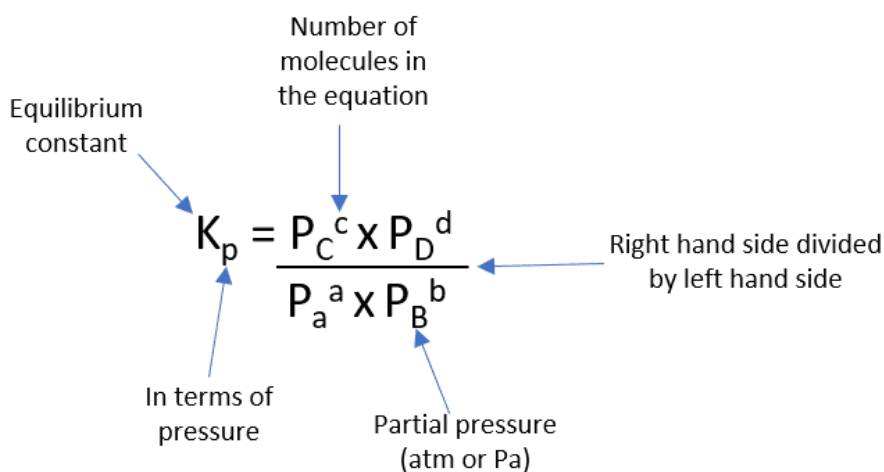
- **Mole fractions** - in a mixture of gases, the mole fraction of gas A (X_A) is:

$$X_A = \frac{\text{number of moles of gas A}}{\text{total number of moles of gas}}$$

- **Partial pressures** - in a mixture of gases, the partial pressure is the pressure that one gas would exert if it occupied the whole container:

$$P_A = \text{mole fraction of gas A} \times \text{total pressure}$$

K_p can then be calculated using partial pressures:



Only include substances that are **gaseous** in the K_p expression.



The value of the equilibrium constant is **only changed by temperature**. It stays the same when concentration or pressure change or when a catalyst is added. For an equilibrium where the forward reaction is **exothermic**, increasing the temperature will cause the position of equilibrium to shift to the left (so more endothermic reactions occur) to take in more heat energy and reduce the temperature. This means the equilibrium constant (K) will decrease because more reactants will be produced. If the forward reaction is **endothermic**, the reverse is true and K would increase. If temperature is decreased, the opposite rule occurs.

Equilibrium Quantities

Below is an example of how the amounts of substances at equilibrium can be calculated:

1 mol of $\text{CH}_3\text{COOH}(\text{l})$ reacts with 1 mole of $\text{C}_2\text{H}_5\text{OH}(\text{l})$ to form $\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$ and $\text{H}_2\text{O}(\text{l})$. An equilibrium is established and at 298K, K_c is equal to 4.0. This data can be added to a table:

	$\text{CH}_3\text{COOH}(\text{l})$ +	$\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons$	$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$ +	$\text{H}_2\text{O}(\text{l})$
Ratio	1	1	1	1
Initial moles	1.0	1.0	0.0	0.0
Equilibrium moles	$1.0 - x$	$1.0 - x$	x	x
Concentration (when volume is 1 dm^3)	$(1.0 - x) / 1$ $= 1.0 - x$	$(1.0 - x) / 1$ $= 1.0 - x$	$x / 1$ $= x$	$x / 1$ $= x$

Haber Process

The Haber process produces **ammonia** from nitrogen and hydrogen: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. Nitrogen is obtained from the **air** and hydrogen from **natural gas**. Once the equilibrium is established, gases leaving the reactor are cooled in order to liquify the ammonia and separate it from the unreacted nitrogen and hydrogen. The unreacted nitrogen and hydrogen is **recycled** back into the reactor.

The forward reaction in the Haber process is **exothermic** ($\Delta H = -92 \text{ kJ mol}^{-1}$). Using Le Chatelier's principle, a low temperature would be favoured in order to shift the position of equilibrium to the right. However, a relatively higher temperature (**400 - 450°C**) is used to **increase the rate of reaction**. This temperature is a **compromise**.

There are more molecules on the left side of the equation, suggesting a **high pressure** should be used (according to Le Chatelier's principle) in order to shift the position of equilibrium to the right. However, high pressures are **expensive** to maintain and they have **safety risks**, so a lower pressure of **200 atm** is used.

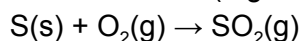
The **iron catalyst** used in the Haber process has **no effect on the position of equilibrium**. Instead, it **increases the rate** at which the equilibrium is established.



Contact Process

The Contact process involves several stages to **produce sulfuric acid**.

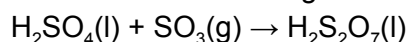
1. How sulfur dioxide is made: Sulfur or sulfur ores (e.g. FeS_2) are heated in excess air.



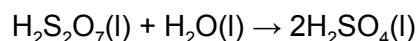
2. Sulfur dioxide to sulfur trioxide:



3. Sulfur trioxide to concentrated sulfuric acid: Sulfur trioxide is dissolved in concentrated sulfuric acid (as adding it to water would create a fog of sulfuric acid).



4. The product is then dissolved in water:



The formation of sulfur trioxide, Step 2, is a **reversible reaction** so changing the conditions will affect the position of equilibrium.

The forward reaction in the Contact process is **exothermic** ($\Delta H = -196 \text{ kJ mol}^{-1}$). Using Le Chatelier's principle, a low temperature would be favoured in order to shift the position of equilibrium to the right. However, a higher temperature (**400 - 450°C**) is used to **increase the rate of reaction**.

There are more molecules on the left side of the equation, suggesting a high pressure should be used (according to Le Chatelier's principle) in order to shift the position of equilibrium to the right. However, the conversion of sulfur dioxide to sulfur trioxide at lower pressures (**1-2 atm**) is 99.5% so the **expense and safety risk** of using high pressures isn't worth the slight increase in percentage conversion.

The **V_2O_5 catalyst** used in the Contact process has **no effect on the position of equilibrium**. Instead, it **increases the rate** at which the equilibrium is established.

Brønsted-Lowry Theory of Acids and Bases

Brønsted-Lowry Acids and Bases

- An acid is a **proton (H^+ ion) donor**
- A base is a **proton (H^+ ion) acceptor**

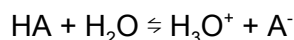
Common acids are - hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), ethanoic acid (CH_3COOH).

Common alkalis are - sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonia (NH_3).

A **neutralisation reaction** is when equal moles of an acid and a base react to make **water and a salt** that involves the combination of H^+ ions and OH^- ions to generate the water.



When an acid dissolves in water, it can be considered as a **reversible reaction**:



- *Forward reaction*: HA donates a proton to water so HA is an acid. Water accepts a proton from HA so water is a base.
- *Backwards reaction*: H_3O^+ donates a proton to A^- so H_3O^+ is an acid. A^- accepts a proton from H_3O^+ so A^- is a base.

Strength of Acids and Bases

The strength of an acid or base refers to the **degree of dissociation** (sometimes known as **ionisation**). This is different to concentration which refers to the amount of a substance in a given volume of solution.

Strong acids **completely dissociate** in solution meaning there is a large number of H^+ ions in solution. They typically have a pH ranging from 0 - 1.

Weak acids **partially dissociate** in solution and they typically have a pH ranging from 2 - 6. This is typically shown as a reversible reaction using \rightleftharpoons .

Strong bases **completely dissociate** in solution meaning there is a large number of OH^- ions in solution. They typically have a pH close to 14.

Weak bases **partially dissociate** in solution and have a lower pH than strong bases (always above pH 7).

Titration Curves

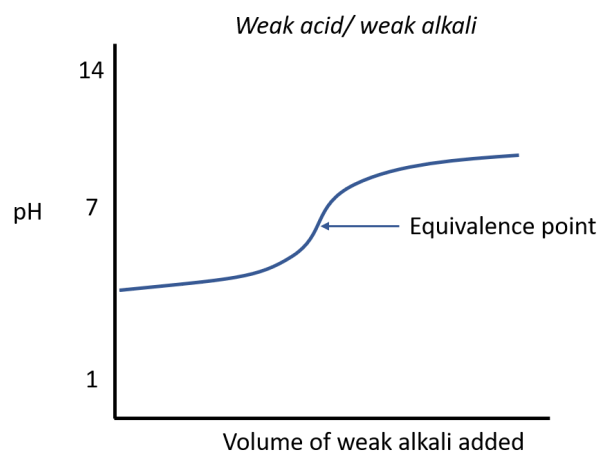
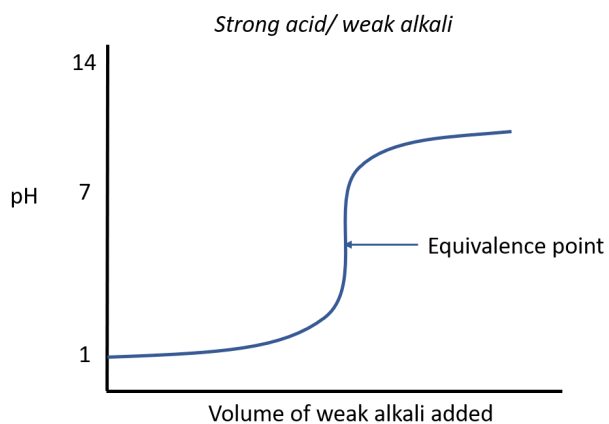
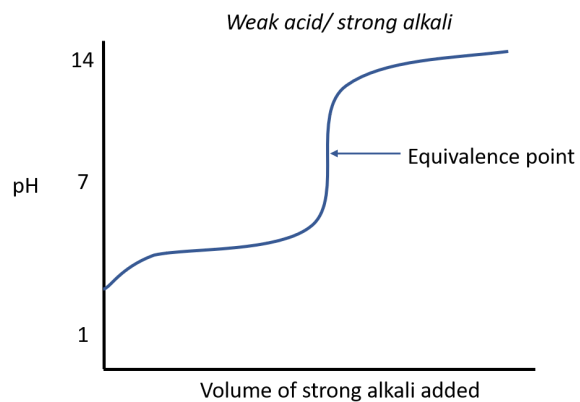
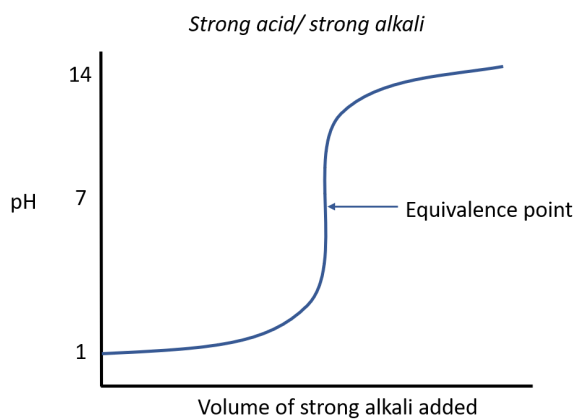
During an **acid-base titration**, an indicator is used to show when exactly the right volumes of acid and base have been added together to neutralise each other. The **end point** of a titration is the point when the indicator first permanently changes colour. The **equivalence point** is when the exact volumes of acid and base have been added to just neutralise one another.

*Key points when **drawing titration curves**:*

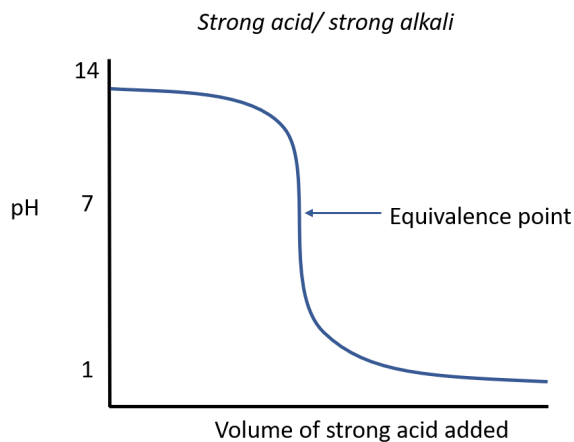
- If acid is added from the burette into the alkali, the pH will decrease. If alkali is added from the burette into acid, pH will increase.
- The pH of strong bases is usually 13 - 14.
- The pH will be 11 or 12 for weak bases.
- The pH of water is 7.
- The pH of strong acids is typically 1 - 2.
- Weak acids normally have a pH of around 4.

Titration curves show how pH changes during an acid-base titration. Below are some examples of titration curves where alkali is added from a burette into the acid:



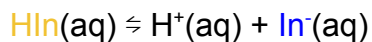


If the acid was added from the burette instead, the curve would look like this:



Indicators

An indicator is a **weak acid** that **changes colour** when it donates a proton. Below is an equation which shows the equilibrium that is established when the indicator dissolves in water (In^- represents the indicator after it has lost a proton):



The table below shows the colours of two common indicators:

Indicator	Colour in acid	Colour in alkali
Methyl orange	Red	Yellow
Phenolphthalein	Colourless	Pink

Titration curves are used to select appropriate indicators for acid-base titrations. The indicator must change colour on the **vertical section** of the graph. Usually, the end point of the indicator is different to the equivalence point, however, as the vertical section of the graph is so steep, there is very little difference between the volume of acid (or alkali) added.

Methyl orange or phenolphthalein can be used for a titration between a strong acid and strong base. For a weak base-strong acid titration, methyl orange can be used. For a strong base-weak acid titration, phenolphthalein is typically used. **No indicators give an accurate end point for weak acid-weak base titrations** because there is no vertical section on the graph.

