CIE Chemistry A Level

7 : Equilibria

Notes

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.
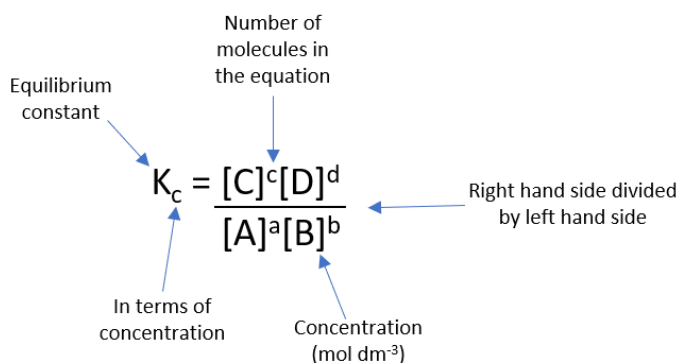
Le Chatelier's principle
Altering conditions can impact the position of equilibrium according to the Le Chatelier principle:
- **Concentration**: increasing the concentration of reactants causes the position of equilibrium to shift right in order to reduce the concentration of reactants and form more 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): $aA + bB \rightleftharpoons cC + dD$
This equation is used below to show how to calculate K_c:

Equilibrium constant

Number of molecules in the equation

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Right hand side divided by left hand side

In terms of concentration

Concentration (mol dm^{-3})

In heterogeneous equilibria, **don't include solids** 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:

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

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 $CH_3COOH(l)$ reacts with 1 mole of $C_2H_5OH(l)$ to form $CH_3COOC_2H_5(l)$ and $H_2O(l)$. An equilibrium is established and at 298K, K_c is equal to 4.0. This data can be added to a table:

	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ ⇌	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
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 dm³)	(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: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. 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** ($\Delta H = -92$ 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**.
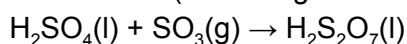
There are more molecules on the left side of the equation, suggesting a **high pressure** should be used (according to Le Chatelier's principle) in order to shift the position of equilibrium to the right. However, high pressures are **expensive** to maintain and they have **safety risks**, so a lower 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
   $S(s) + O_2(g) \rightarrow SO_2(g)$
2. Sulfur dioxide to sulfur trioxide: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\qquad \Delta H = -196$ kJ mol^{-1}
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).
   $H_2SO_4(l) + SO_3(g) \rightarrow H_2S_2O_7(l)$
   The product (oleum) is then dissolved in water: $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$

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** ($\Delta H = -196$ 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.
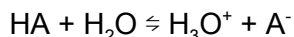
Ionic equilibria

Brønstead-Lowry Acids and Bases
- An acid is a **proton (H^+ ion) donor**
- A base is a **proton (H^+ ion) acceptor**

When an acid dissolves in water, it can be considered as a **reversible reaction**:
$HA + H_2O \leftrightharpoons H_3O^+ + A^-$
- *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.

A **conjugate acid-base pair** is two species that differ from each other by a H^+ ion.

Conjugate acid-base pair

$$HA + H_2O \leftrightharpoons H_3O^+ + A^-$$

Conjugate acid-base pair
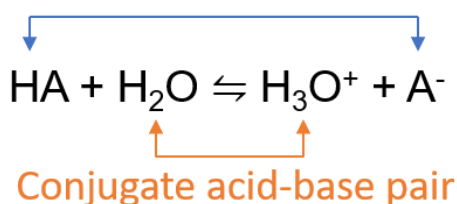
For example, from the diagram:
- HA and A^- are a conjugate pair
- H_3O^+ and H_2O are a conjugate pair
- HA is acid-I
- A^- is base-I
- H_3O^+ is acid-II
- H_2O is base-II

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 $\leftrightharpoons$.

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).

Calculations **(A Level only)**
Calculating pH or H^+ concentration:
$$\textbf{pH} = -\log_{10}[H^+]$$
$$\textbf{[H}^+\textbf{]} = 10^{-pH}$$

Calculations involving the acid dissociation constant, K_a:
For the equation $HA \leftrightharpoons H^+ + A^-$
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log_{10}(K_a)$$

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 pK_a values using the equation above. As pK_a increases, the strength of the acid decreases.

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 **1.00×10^{-14} mol^2 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, $pH = -\log_{10}[H^+]$.

pH of weak acids
Follow these steps to work out the pH of a weak acid:
1. For the equation $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$:

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

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

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

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 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:
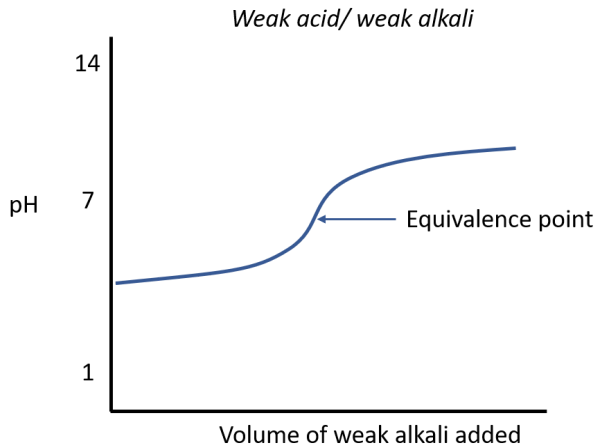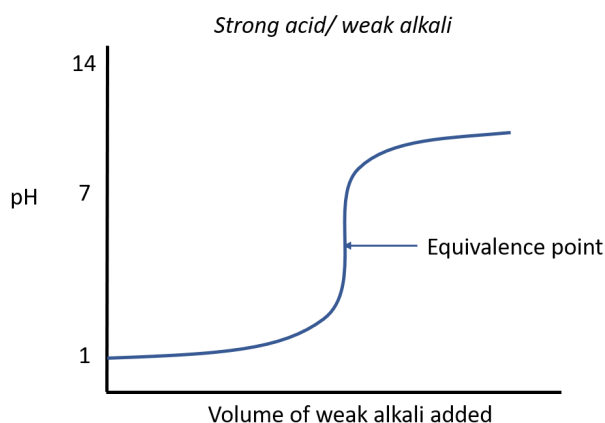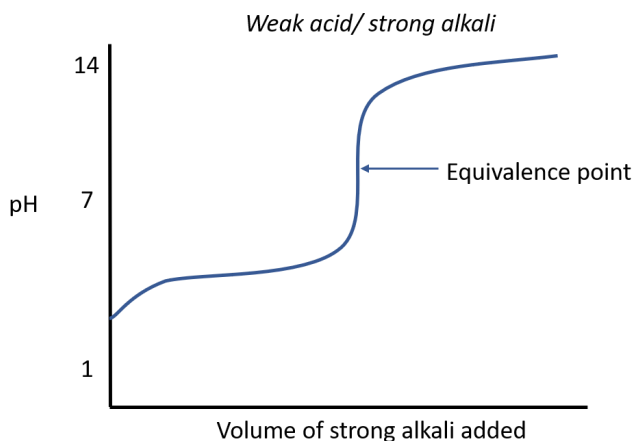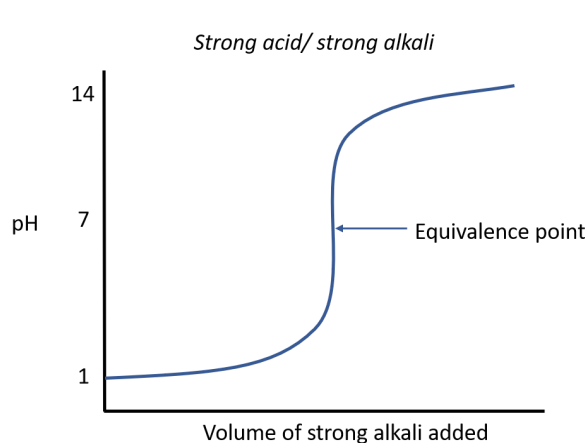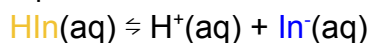

If the acid was added from the burette instead, the curve would look like this:
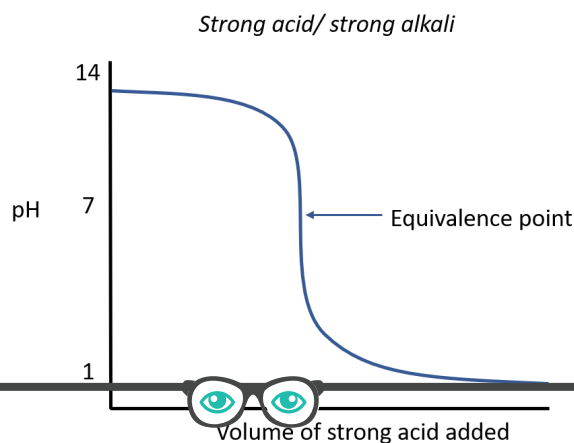
Indicators

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):

$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

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.

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**:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
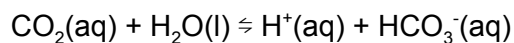
If **pH increases** (hydrogen ion concentration decreases), the position of **equilibrium will shift to the right** to increase the concentration of hydrogen ions. If pH falls (hydrogen ion concentration increases), the position of equilibrium will shift to the left to remove the added H^+ ions.

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 $BaSO_4$:
  $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
  $(mol\ dm^{-3})$ x $(mol\ dm^{-3})$
  $= mol^2\ dm^{-6}$
- For $Ca_3(PO_4)_2$:
  $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$
  $(mol\ dm^{-3})^3$ x $(mol\ dm^{-3})^2$
  $= mol^5\ dm^{-15}$

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, $Mg(OH)_2$, at 298 K is 1.71 x $10^{-4}\ mol\ dm^{-3}$.
  $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$
  The concentration of $Mg(OH)_2$ is 1.71 x $10^{-4}\ mol\ dm^{-3}$, so using the equation:
  - $[Mg^{2+}] = 1.71$ x $10^{-4}\ mol\ dm^{-3}$
  - $[OH^-] = 2$ x $(1.71$ x $10^{-4}) = 3.42$ x $10^{-4}\ mol\ dm^{-3}$
  $K_{sp} = [Mg^{2+}][OH^-]^2$
  $\quad = (1.71$ x $10^{-4})$ x $(3.42$ x $10^{-4})^2$
  $\quad = 2.00$ x $10^{-11}\ mol^3\ dm^{-9}$
- The solubility product of barium sulfate, $BaSO_4$, at 298K is 1.10 x $10^{-10}\ mol^2\ dm^{-6}$.
  $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$
  Using the equation (where y is the unknown solubility):
  - $[Ba^{2+}] = y$
  - $[SO_4^{2-}] = y$
  $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
  1.10 x $10^{-10} = y$ x y
  1.10 x $10^{-10} = y^2$
  $y = \sqrt{(1.10 \times 10^{-10})} = 1.05$ x $10^{-5}\ mol\ dm^{-3}$

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 ($PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$) 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 $PbCl_2(s)$. This also means that the **solubility of $PbCl_2(s)$ will decrease** so the concentration of lead(II) ions will decrease.

Example calculation:

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

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

Assume the concentration of chloride ions is the same as the concentration of sodium chloride:

$[Cl^-]$ = 0.100 mol dm^{-3}

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

= y x $(0.100)^2$

1.7 x 10^{-5} = 0.0100 x y

y = 1.7 x 10^{-5} ÷ 0.0100 = 1.7 x 10^{-3} mol dm^{-3}

The $[Pb^{2+}]$ when $PbCl_2(s)$ dissolves in water is 0.0162 mol dm^{-3}. This decreases by a scale factor of 10 to 0.0017 mol dm^{-3} when $PbCl_2(s)$ is dissolved in 0.100 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(in more dense liquid) $\rightleftharpoons$ X(in less dense liquid)

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

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_{pc} = 40. m is mass of X dissolved in ether:

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

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

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

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

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

$$200 - 200m = 100m$$

$$300m = 200$$

$$m = 0.67g$$