Cambridge (CIE) A Level Chemistry

Acids & Bases

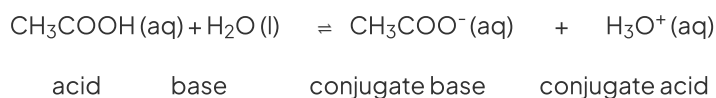### Contents

Conjugate Acids & Bases

- A **Brønsted–Lowry acid** is a species that can donate a proton

- A **Brønsted–Lowry base** is a species that can accept a proton

- In an equilibrium reaction, the products are formed at the same rate as the reactants are used

$$CH_3COOH\,(aq) + H_2O\,(l) \quad \rightleftharpoons \quad CH_3COO^-\,(aq) \quad + \quad H_3O^+\,(aq)$$

$$\text{acid} \qquad \text{base} \qquad \text{conjugate base} \qquad \text{conjugate acid}$$

- The reactant CH_3COOH is linked to the product CH_3COO^- by the transfer of a **proton** from the acid to the base

  - Similarly, the H_2O molecule is linked to H_3O^+ ion by the transfer of a proton

- These pairs are therefore called **conjugate acid–base pairs**

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

    - **Conjugate** here means related

    - In other words, the acid and base are related to each other by one proton difference

Worked Example

Identifying conjugate acid–base pairs

Identify the conjugate acid–base pairs in the following equilibrium reaction:

$$NH_3\,(g) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$
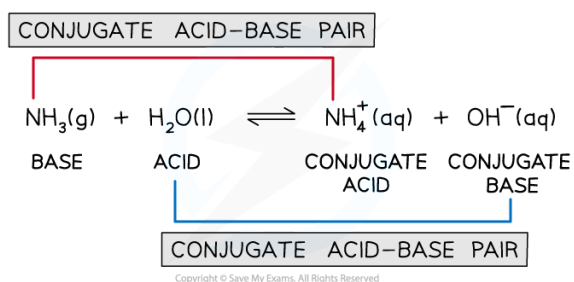
Answer:

- In the forward reaction:

  - NH_4^+ is the conjugate acid of the base NH_3
  - OH^- is the conjugate base of the acid H_2O
- In the reverse reaction

  - NH_3 is the conjugate base of the acid NH_4^+
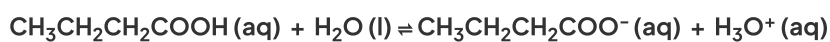 - H_2O is the conjugate acid of the base OH^-

Worked Example

In the equilibrium reaction shown below, which species are a conjugate acid-base pair?

$$CH_3CH_2CH_2COOH \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons CH_3CH_2CH_2COO^- \text{ (aq)} + H_3O^+ \text{ (aq)}$$

A. $CH_3CH_2CH_2COOH$ and H_2O

B. H_2O and H_3O^+

C. H_2O and $CH_3CH_2CH_2COO^-$

D. $CH_3CH_2CH_2COO^-$ and H_3O^+

Answer:

- The correct option in **B**
    - A conjugate acid-base pair differ only by an H^+ ion

Calculating pH, Ka, pKA & Kw

pH

- The **pH** indicates the **acidity** or **basicity** of an acid or alkali

- The pH scale goes from 0.0 to 14.0

  - Acids have a pH below 7.0

  - Pure water is **neutral** with a pH of 7.0

  - Bases and alkalis have a pH above 7.0

- pH can be calculated using:

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

- where $[H^+]$ = concentration of H^+ ions (mol dm^{-3})

- The pH can also be used to calculate the concentration of H^+ ions in solution by rearranging the equation to:

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

Worked Example

Calculating the pH of acids

Calculate the pH of ethanoic acid, at 298K, when the hydrogen ion concentration is 1.32×10^{-3} mol dm^{-3}.
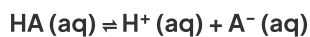
Answer

$$pH = -\log[H^+]$$

$$pH = -\log 1.32 \times 10^{-3}$$

$$pH = 2.9$$

K$_a$ & pK$_a$

- The K_a is the **acidic dissociation constant**

  - It is the **equilibrium constant** for the dissociation of a **weak acid** at 298 K

- For the **partial ionisation** of a weak acid HA, the equilibrium expression to find K_a is:

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$

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

- When writing the equilibrium expression for weak acids, the following assumptions are made:

    - The concentration of hydrogen ions due to the ionisation of water is negligible

    - The dissociation of the weak acid is so small that the concentration of HA can be approximated by its initial value

        - This is calculated from the number of moles divided by the volume of solvent

- The value of K_a indicates the extent of dissociation

    - A high value of K_a means that:

        - The equilibrium position lies to the right

        - The acid is **almost completely ionised**

        - The acid is **strongly acidic**

    - A low value of K_a means that:

        - The equilibrium position lies to the left

        - The acid is **only slightly ionised** (there are mainly HA and only a few H⁺ and A⁻ ions)

        - The acid is **weakly acidic**

- Since K_a values of many weak acids are **very low**, pK_a values are used instead to compare the strengths of weak acids with each other

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

- The **less positive** the pK_a value the **more acidic** the acid is

Worked Example

Calculating the K_a & pK_a of weak acids

Calculate the K_a and pK_a values of 0.100 mol dm⁻³ ethanoic acid at 298K which forms 1.32 x 10⁻³ of H⁺ ions in solution.

Answer

- **Step 1:** Write down the equation for the partial dissociation of ethanoic acid:
    $$\text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$$

- **Step 2:** Write down the equilibrium expression to find K_a:
    $$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

- **Step 3:** Simplify the expression:

  The ratio of H^+ to CH_3COO^- is 1:1

  The concentration of H^+ and CH_3COO^- is, therefore, the same

  The equilibrium expression can be simplified to:

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

- **Step 4:** Substitute the values into the expression to find K_a:

$$K_a = \frac{[1.32 \times 10^{-3}]^2}{[0.100]}$$

$$K_a = 1.74 \times 10^{-5}$$

- **Step 5:** Determine the units of K_a:

$$K_a = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]} = mol\ dm^{-3}$$

  Therefore, K_a is 1.74×10^{-5} mol dm^{-3}

- **Step 6:** Find pK_a:

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

$$pK_a = -\log_{10}(1.74 \times 10^{-5})$$

$$pK_a = 4.76$$

K_w

- The K_w is the **ionic product of water**

  - It is the **equilibrium constant** for the dissociation of **water** at 298 K

  - Its value is 1.00×10^{-14} mol^2 dm^{-6}

- For the **ionisation** of water, the equilibrium expression to find K_w is:

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

$$K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

- As the **extent of ionisation** is very low, only small amounts of H^+ and OH^- ions are formed

- The concentration of H_2O can therefore be regarded as constant and removed from the K_w expression

- The equilibrium expression therefore becomes:

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

- As the $[H^+] = [OH^+]$ in pure water, the equilibrium expression can be further simplified to:

$$K_w = [H^+]^2$$

✏️ Worked Example

Calculating the concentration of H⁺ of pure water

Calculate the concentration of H^+ in pure water, using the ionic product of water

Answer

- **Step 1:** Write down the equation for the partial dissociation of water:
    - In pure water, the following equilibrium exists:
    $$H_2O \ (l) \rightleftharpoons H^+ \ (aq) + OH^- \ (aq)$$

- **Step 2:** Write down the equilibrium expression to find K_w:
    $$K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

- **Step 3:** Simplify the expression:
    - Since the concentration of H_2O is constant, this expression can be simplified to:
    $$K_w = [H^+][OH^-]$$

- **Step 4:** Further simplify the expression:
    - The ratio of H^+ to OH^- is 1:1
    - The concentration of H^+ and OH^- is, therefore, the same and the equilibrium expression can be further simplified to:
    $$K_w = [H^+]^2$$

- **Step 5:** Rearrange the equation to find $[H^+]$:
    $$[H^+] = \sqrt{K_w}$$

- **Step 6:** Substitute the values into the expression to find K_w:
    $$[H^+] = \sqrt{1.00 \times 10^{-14}}$$

    $$[H^+] = 1.00 \times 10^{-7} \ mol \ dm^{-3}$$

💡 Examiner Tips and Tricks

- The greater the K_a value, the **more strongly acidic** the acid is
- The greater the pK_a value, the **less strongly acidic** the acid is.
- Also, you should be able to rearrange the following expressions:
    $$pH = -\log_{10}[H^+] \iff [H^+] = 10^{-pH}$$

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

$$pK_a = -\log_{10} K_a \quad \leftrightarrow \quad K_a = 10^{-pK_a}$$

[H+] & pH Calculations

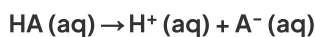- If the concentration of H^+ of an acid or alkali is known, the **pH** can be calculated using the equation:

$$pH = -\log [H^+]$$

- Similarly, the **concentration of H^+** of a solution can be calculated if the pH is known by rearranging the above equation to:

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

Strong acids

- **Strong acids** are completely **ionised** in solution

$$HA\ (aq) \rightarrow H^+\ (aq) + A^-\ (aq)$$

- Therefore, the concentration of hydrogen ions ($[H^+]$) is **equal** to the concentration of acid ($[HA]$)

- The number of hydrogen ions ($[H^+]$) formed from the ionisation of water is **very small** relative to the $[H^+]$ due to the ionisation of the strong acid and can therefore be **neglected**

- The **total** $[H^+]$ is therefore the same as the $[HA]$
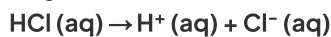
Worked Example

pH calculations of a strong acid

For a solution of hydrochloric acid, calculate the following:

1. The pH when the hydrogen ion concentration is 1.6×10^{-4} mol dm^{-3}.
2. The hydrogen ion concentration when the pH is 3.1.

Answer

- Hydrochloric acid is a strong monobasic acid

$$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$$

Answer 1

- The pH of the solution is:

$$pH = -\log [H^+]$$

$$pH = -\log 1.6 \times 10^{-4}$$

$$pH = 3.80$$

Answer 2

- The hydrogen concentration can be calculated by rearranging the equation for pH:

$$pH = -\log [H^+]$$

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

$$[H^+] = 10^{-3.1}$$
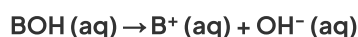
$$[H^+] = 7.9 \times 10^{-4} \text{ mol dm}^{-3}$$

Strong alkalis

- **Strong alkalis** are completely **ionised** in solution

$$BOH \text{ (aq)} \rightarrow B^+ \text{ (aq)} + OH^- \text{ (aq)}$$

- Therefore, the concentration of hydroxide ions ($[OH^-]$) is **equal** to the concentration of base ($[BOH]$)

  - Even strong alkalis have small amounts of H^+ in solution which is due to the ionisation of water

- The concentration of OH^- in solution can be used to calculate the pH using the **ionic product of water**

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

$$[H^+] = \frac{K_w}{[OH^-]}$$

- Since K_w is $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

$$[H^+] = \frac{1.00 \times 10^{-14}}{[OH^-]}$$

- Once the $[H^+]$ has been determined, the pH of the strong alkali can be found using $pH = -\log[H^+]$

- Similarly, the ionic product of water can be used to find the concentration of OH^- ions in solution if $[H^+]$ is known

$$[OH^-] = \frac{1.00 \times 10^{-14}}{[H^+]}$$

Worked Example

pH calculations of a strong alkali

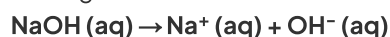For a solution of sodium hydroxide, calculate the following:

1. The pH when the hydrogen ion concentration is $3.5 \times 10^{-11} \text{ mol dm}^{-3}$.
2. The hydroxide ion concentration when the pH is 12.3.

Answer

- Sodium hydroxide is a strong base which ionises as follows:

$$NaOH\,(aq) \rightarrow Na^+\,(aq) + OH^-\,(aq)$$

Answer 1

- The pH of the solution is:

$$pH = -\log[H^+]$$

$$pH = -\log 3.5 \times 10^{-11}$$

$$pH = 10.5$$

Answer 2

- **Step 1:** Calculate the hydrogen concentration by rearranging the equation for pH:

$$pH = -\log[H^+]$$

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

$$[H^+] = 10^{-12.3}$$

$$[H^+] = 5.01 \times 10^{-13}\,mol\,dm^{-3}$$

- **Step 2:** Rearrange the **ionic product of water** to find the concentration of hydroxide ions:

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

$$[OH^-] = \frac{K_w}{[H^+]}$$

- **Step 3:** Substitute the values into the expression to find the concentration of hydroxide ions:

  - Since K_w is $1.00 \times 10^{-14}\,mol^2\,dm^{-6}$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{5.01 \times 10^{-13}}$$

$$[OH^-] = 0.0199\,mol\,dm^{-3}$$

Weak acids

- The pH of **weak acids** can be calculated when the following is known:

  - The **concentration** of the acid

  - The K_a value of the acid
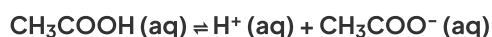
Worked Example

pH calculations of weak acids

Calculate the pH of 0.100 mol dm^{-3} ethanoic acid at 298K with a K_a value of 1.74 x 10^{-5} mol dm^{-3}.

Answer

- Ethanoic acid is a weak acid which ionises as follows:

$$CH_3COOH \ (aq) \rightleftharpoons H^+ \ (aq) + CH_3COO^- \ (aq)$$

- **Step 1:** Write down the equilibrium expression to find K_a:

$$K_a = \frac{[H+]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]}$$

- **Step 2:** Simplify the expression:
  - The ratio of H^+ to CH_3COO^- ions is 1:1
  - Therefore the concentration of H^+ and CH_3COO^- ions are the same
  - So, the expression can be simplified to:

$$K_a = \frac{[H+]^2}{\left[CH_3COOH\right]}$$

- **Step 3:** Rearrange the expression to find $[H^+]$:

$$[H^+] = \sqrt{K_a \times \left[CH_3COOH\right]}$$

- **Step 4:** Substitute the values into the expression to find $[H^+]$:

$$[H^+] = \sqrt{\left(1.74 \times 10^{-5}\right) \times 0.100}$$

$$[H^+] = 1.32 \times 10^{-3} \ mol \ dm^{-3}$$

- **Step 5:** Find the pH:

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

$$pH = -\log_{10} 1.32 \times 10^{-3}$$

$$pH = 2.88$$

Buffers

- A **buffer solution** is a solution in which the pH does not change a lot when small amounts of acids or alkalis are added
    - A buffer solution is used to keep the pH almost constant
    - A buffer can consist of a **weak acid – conjugate base** or a **weak base – conjugate acid**

Ethanoic acid & sodium ethanoate as a buffer

- A common buffer solution is an **aqueous mixture of ethanoic acid** and **sodium ethanoate**
- Ethanoic acid, CH_3COOH, is a **weak acid** and partially ionises in solution to form a relatively **low** concentration of **ethanoate ions**, CH_3COO^-

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$
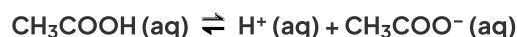
- Sodium ethanoate, CH_3COONa, is a **salt** which fully ionises in solution to form a relatively **high** concentration of **ethanoate ions**, CH_3COO^-

$$CH_3COONa\ (a) + aq \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

- There are **reserve supplies** of the acid (CH_3COOH) and its conjugate base (CH_3COO^-)
    - The buffer solution contains relatively high concentrations of CH_3COOH (due to the ionisation of **ethanoic acid**) and CH_3COO^- (due to the ionisation of **sodium ethanoate**)
- In the **buffer solution**, the ethanoic acid is **in equilibrium** with hydrogen and ethanoate ions

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$
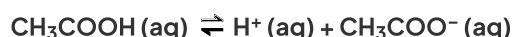
When H+ ions are added:

- The equilibrium position shifts to the **left** as H^+ ions react with CH_3COO^- ions to form more CH_3COOH until equilibrium is **re-established**
- As there is a large reserve supply of CH_3COO^-, the concentration of CH_3COO^- in solution doesn't change much as it reacts with the added H^+ ions
- As there is a large reserve supply of CH_3COOH, the concentration of CH_3COOH in solution doesn't change much as CH_3COOH is formed from the reaction of CH_3COO^- with H^+
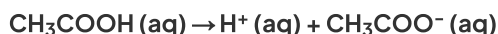- As a result, the pH remains reasonably constant

When OH- ions are added:

- The OH^- reacts with H^+ to form water

$$OH^- \text{ (aq)} + H^+ \text{ (aq)} \rightarrow H_2O \text{ (l)}$$
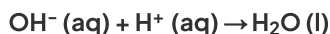
- The H^+ concentration **decreases**

- The equilibrium position shifts to the right and more CH_3COOH molecules ionise to form more H^+ and CH_3COO^- until equilibrium is re-established

$$CH_3COOH \text{ (aq)} \rightarrow H^+ \text{ (aq)} + CH_3COO^- \text{ (aq)}$$

- As there is a large reserve supply of CH_3COOH the concentration of CH_3COOH in solution doesn't change much when CH_3COOH dissociates to form more H^+ ions

- As there is a large reserve supply of CH_3COO^- the concentration of CH_3COO^- in solution doesn't change much

- As a result, the pH remains reasonably constant

# Uses of buffer solutions in controlling the pH of blood

- In humans, HCO_3^- ions act as a buffer to keep the blood pH between 7.35 and 7.45

- Body cells produce CO_2 during **aerobic respiration**

- This CO_2 will combine with water in the blood to form a solution containing H^+ ions

$$CO_2 \text{ (g)} + H_2O \text{ (l)} \rightleftharpoons H^+ \text{ (aq)} + HCO_3^- \text{ (aq)}$$
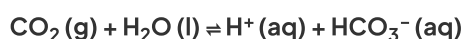
- This equilibrium between CO_2 and HCO_3^- is extremely important

- If the concentration of H^+ ions is not regulated, the blood pH would drop and cause '**acidosis**'

  - **Acidosis** refers to a condition in which there is too much acid in the body fluids such as blood

    - This could cause body malfunctioning and eventually lead to coma

- **If there is an increase in H^+ ions**

- The equilibrium position shifts to the **left** until equilibrium is restored

$$CO_2 \text{ (g)} + H_2O \text{ (l)} \rightarrow H^+ \text{ (aq)} + HCO_3^- \text{ (aq)}$$

- This reduces the concentration of H^+ and keeps the pH of the blood **constant**

- **If there is a decrease in H^+ ions**

  - The equilibrium position shifts to the **right** until equilibrium is restored

$$CO_2 \text{ (g)} + H_2O \text{ (l)} \rightarrow H^+ \text{ (aq)} + HCO_3^- \text{ (aq)}$$
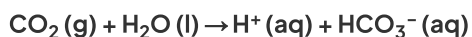
- This increases the concentration of H^+ and keeps the pH of the blood **constant**

Examiner Tips and Tricks

- Remember that buffer solutions cannot cope with **excessive addition** of acids or alkalis as their pH will change significantly
- The pH will only remain relatively constant if **small amounts** of acids or alkalis are added.

Buffer Solution pH Calculations

- The pH of a **buffer solution** can be calculated using:

  - The K_a of the **weak acid**

  - The **equilibrium concentration** of the **weak acid** and its **conjugate base** (salt)

- To determine the pH, the concentration of **hydrogen ions** is needed which can be found using the equilibrium expression:

$$K_a = \frac{[\text{ salt }][\text{H}^+]}{[\text{ acid }]}$$

- This can be rearranged to determine the concentration of hydrogen ions:

$$[\text{H}^+] = K_a \times \frac{[\text{ acid }]}{[\text{ salt }]}$$

- To simplify the calculations, **logarithms** are used such that the expression becomes:

$$-\log_{10}[\text{H}^+] = -\log_{10} K_a \times -\log_{10} \frac{[\text{ acid }]}{[\text{ salt }]}$$

- Since $-\log_{10}[\text{H}^+]$ = pH and $-\log_{10}[K_a]$ = pK_a, the expression can also be rewritten as:

$$\text{pH} = \text{p}K_a a + \log_{10} \frac{[\text{ salt }]}{[\text{ acid }]}$$

Worked Example

Calculating the pH of a buffer solution

Calculate the pH of a buffer solution containing 0.305 mol dm^{-3} ethanoic acid and 0.520 mol dm^{-3} sodium ethanoate.

The K_a of ethanoic acid = 1.43 x 10^{-5} mol dm^{-3}.

Answer

- Ethanoic acid is a weak acid that ionises as follows:
  $$\text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$$

- **Step 1:** Write down the equilibrium expression to find K_a:

$$K_a = \frac{\left[\text{CH}_3\text{COO}^-\right]\left[\text{H}^+\right]}{\left[\text{CH}_3\text{COOH}\right]}$$

- **Step 2:** Rearrange the equation to find [H$^+$]:

$$[H^+] = K_a \times \frac{\left[CH_3COOH\right]}{\left[CH_3COO^-\right]}$$

■ **Step 3:** Substitute the values into the expression:

$$[H^+] = 1.43 \times 10^{-5} \times \frac{[0.305]}{[0.520]}$$

$$[H^+] = 8.39 \times 10^{-6} \text{ mol dm}^{-3}$$

■ **Step 4:** Calculate the pH:

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

$$pH = -\log 8.39 \times 10^{-6}$$

$$pH = 5.08$$

The Solubility Product, Ksp

- **Solubility** is defined as the **number of grams** or **moles** of compound needed to **saturate** 100 g of **water**, or it can also be defined in terms of 1 kg of water, at a given temperature

  - For example, sodium chloride (NaCl) is considered to be a **soluble** salt as a saturated solution contains 36 g of NaCl per 100 g of water

  - Lead chloride ($PbCl_2$) on the other hand is an **insoluble** salt as a saturated solution only contains 0.99 g of $PbCl_2$ per 100 g of water
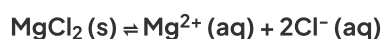
Solubility product

- The **solubility product** (K_{sp}) is:

  - The product of the concentrations of each ion in a saturated solution of a relatively soluble salt

  - At 298 K

 - Raised to the power of their relative concentrations

$$C \text{ (s)} \rightleftharpoons aA^{x+} \text{ (aq)} + bB^{y-} \text{ (aq)}$$

$$K_{sp} = [A^{x+} \text{ (aq)}]^a [B^{y-} \text{ (aq)}]^b$$

- When an **undissolved ionic compound** is in contact with a **saturated solution of its ions**, an equilibrium is established

- The ions move from the solid to the saturated solution at the same rate as they move from the solution to the solid

  - For example, the undissolved magnesium chloride ($MgCl_2$) is in equilibrium with a saturated solution of its ions

$$MgCl_2 \text{ (s)} \rightleftharpoons Mg^{2+} \text{ (aq)} + 2Cl^- \text{ (aq)}$$

Ions in a saturated solution
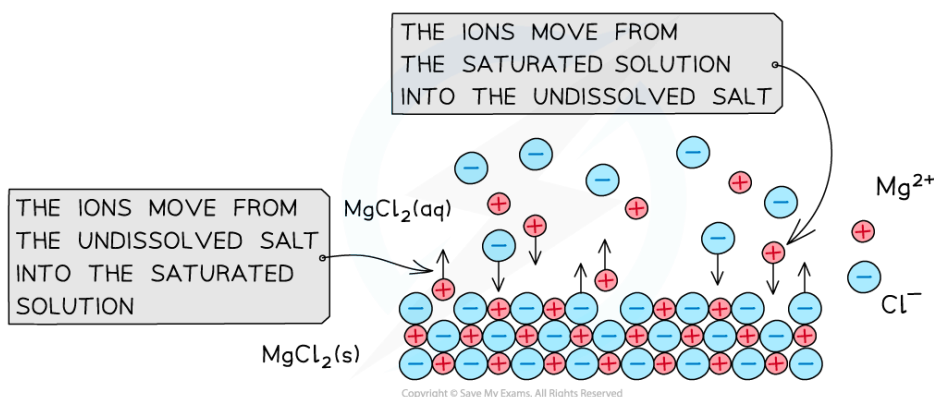
When the undissolved magnesium chloride salt comes in contact with its ions in a saturated solution, an equilibrium between the salt and ions is established

Your notes

- The **solubility product** for this equilibrium is:

$$K_{sp} = [Mg^{2+} (aq)] [Cl^- (aq)]^2$$

- The K_{sp} is only useful for **sparingly soluble salts**

- The smaller the value of K_{sp}, the lower the solubility of the salt

Ksp Expressions

- The general equilibrium expression for the **solubility product** (K_{sp}) is:

$$C (s) \rightleftharpoons aA^{x+} (aq) + bB^{y-} (aq)$$

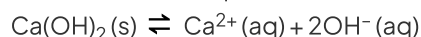$$K_{sp} = [A^{x+} (aq)]^a [B^{y-} (aq)]^b$$

Worked Example

Expressing K_{sp} of ionic compounds

- Give the equilibrium expressions, including units, for the solubility products of the following ionic compounds:

  1. $Ca(OH)_2$
  2. Fe_2O_3
  3. $SnCO_3$

Answer 1 – $Ca(OH)_2$:

- **Step 1** - Write the balanced chemical equation:
$$Ca(OH)_2 (s) \rightleftharpoons Ca^{2+} (aq) + 2OH^- (aq)$$

- **Step 2** - Write the K_{sp} expression:
$$K_{sp} = [Ca^{2+} (aq)] [OH^- (aq)]^2$$

- **Step 3** - Deduce the units:
$$K_{sp} = [mol\ dm^{-3}] \times [mol\ dm^{-3}]^2$$

$$K_{sp} = [mol\ dm^{-3}]^3$$

$$K_{sp} = mol^3\ dm^{-9}$$

Answer 2 – Fe_2O_3:

- **Step 1** - Write the balanced chemical equation:
$$Fe_2O_3 (s) \rightleftharpoons 2Fe^{3+} (aq) + 3O^{2-} (aq)$$

- **Step 2** - Write the K_{sp} expression:
$$K_{sp} = [Fe^{3+} (aq)]^2 [O^{2-} (aq)]^3$$

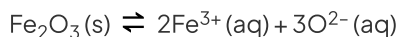1. **Step 3** - Deduce the units:

$$K_{sp} = [\text{mol dm}^{-3}]^2 \times [\text{mol dm}^{-3}]^3$$
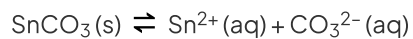
$$K_{sp} = [\text{mol dm}^{-3}]^5$$

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

Answer 3 – SnCO₃:

- **Step 1** – Write the balanced chemical equation:
$$\text{SnCO}_3\,(s) \rightleftharpoons \text{Sn}^{2+}\,(aq) + \text{CO}_3^{2-}\,(aq)$$

- **Step 2** – Write the K_{sp} expression:
$$K_{sp} = [\text{Sn}^{2+}\,(aq)]\,[\text{CO}_3^{2-}\,(aq)]$$

- **Step 3** – Deduce the units:
$$K_{sp} = [\text{mol dm}^{-3}] \times [\text{mol dm}^{-3}]$$

$$K_{sp} = [\text{mol dm}^{-3}]^2$$

$$K_{sp} = \text{mol}^2 \text{dm}^{-6}$$

Solubility Product Calculations

- Calculations involving the **solubility product** (K_{sp}) may include::
  - Calculating the solubility product of a compound from its **solubility**
  - Calculating the solubility of a compound from the **solubility product**
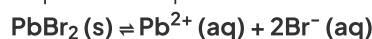
Worked Example

Calculating the solubility product of a compound from its solubility

Calculate the solubility product of a saturated solution of lead(II) bromide, $PbBr_2$, with a solubility of 1.39×10^{-3} mol dm^{-3}.

Answer

- **Step 1:** Write down the equilibrium equation:
$$PbBr_2 \text{ (s)} \rightleftharpoons Pb^{2+} \text{ (aq)} + 2Br^- \text{ (aq)}$$

- **Step 2:** Write down the equilibrium expression:
$$K_{sp} = [Pb^{2+}(aq)] \, [Br^- (aq)]^2$$

- **Step 3:** Calculate the ion concentrations in the solution:
  - $[PbBr_2(s)] = 1.39 \times 10^{-3}$ mol dm^{-3}
  - The ratio of $PbBr_2$ to Pb^{2+} is 1:1
$$[Pb^{2+}(aq)] = [PbBr_2(s)] = 1.39 \times 10^{-3} \text{ mol dm}^{-3}$$

- The ratio of $PbBr_2$ to Br^- is 1:2
$$[Br^-(aq)] = 2 \times [PbBr_2(s)] = 2 \times 1.39 \times 10^{-3} \text{ mol dm}^{-3} = 2.78 \times 10^{-3} \text{ mol dm}^{-3}$$

- **Step 4:** Substitute the values into the expression to find the solubility product:
$$K_{sp} = (1.39 \times 10^{-3}) \times (2.78 \times 10^{-3})^2$$

$$K_{sp} = 1.07 \times 10^{-8}$$

- **Step 6:** Determine the correct units of K_{sp}:
$$K_{sp} = (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^2$$

$$K_{sp} = \text{mol}^3 \text{ dm}^{-9}$$

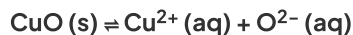- Therefore, the solubility product is 1.07×10^{-8} mol^3 dm^{-9}

Worked Example

Calculating the solubility of a compound from its solubility product

Calculate the solubility of a saturated solution of copper(II) oxide, CuO, with a solubility product of 5.9×10^{-36} mol^2 dm^{-6}.

Answer

- **Step 1:** Write down the equilibrium equation:
$$CuO \text{ (s)} \rightleftharpoons Cu^{2+} \text{ (aq)} + O^{2-} \text{ (aq)}$$

- **Step 2:** Write down the equilibrium expression:
$$K_{sp} = [Cu^{2+} \text{ (aq)}][O^{2-} \text{ (aq)}]$$

- **Step 3:** Simplify the equilibrium expression:

  - The ratio of Cu^{2+} to O^{2-} is 1:1
  - $[Cu^{2+}\text{(aq)}] = [O^{2-}\text{(aq)}]$ so the expression can be simplified to:
$$K_{sp} = [Cu^{2+} \text{ (aq)}]^2$$

- **Step 4:** Substitute the value of K_{sp} into the expression to find the concentration:
$$5.9 \times 10^{-36} = [Cu^{2+} \text{ (aq)}]^2$$

$$[Cu^{2+} \text{ (aq)}] = \sqrt{5.9 \times 10^{-36}}$$

$$[Cu^{2+} \text{ (aq)}] = 2.4 \times 10^{-18} \text{ mol dm}^{-3}$$

- Since $[CuO \text{ (s)}] = [Cu^{2+} \text{ (aq)}]$, the solubility of copper oxide is 2.4×10^{-18} mol dm^{-3}

💡

Examiner Tips and Tricks

Remember that the solubility product is only applicable to very slightly soluble salts and cannot be used for soluble salts such as:

- Group 1 element salts
- All nitrate salts
- All ammonium salts
- Many sulfate salts
- Many halide salts (except for lead(II) halides and silver halides)

The Solubility Product & the Common Ion Effect

- A **saturated solution** is a solution that contains the **maximum** amount of dissolved salt

- If a second compound, which has an ion **in common** with the dissolved salt, is added to the saturated solution, the solubility of the salt reduces, and a solid **precipitate** will be formed

- This is also known as the **common ion effect**

- For example, if a solution of **potassium chloride** (KCl) is added to a **saturated solution of silver chloride** (AgCl) a precipitate of silver chloride will be formed

  - The chloride ion is the common ion

- The **solubility product** can be used to predict whether a precipitate will form or not

  - A precipitate will form if the product of the ion concentrations is **greater than** the solubility product (K_{sp})

Common ion effect in silver chloride

- When a **KCl** solution is added to a saturated solution of **AgCl**, an AgCl precipitate forms

- In a **saturated** AgCl solution, the silver chloride is in equilibrium with its ions
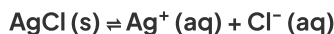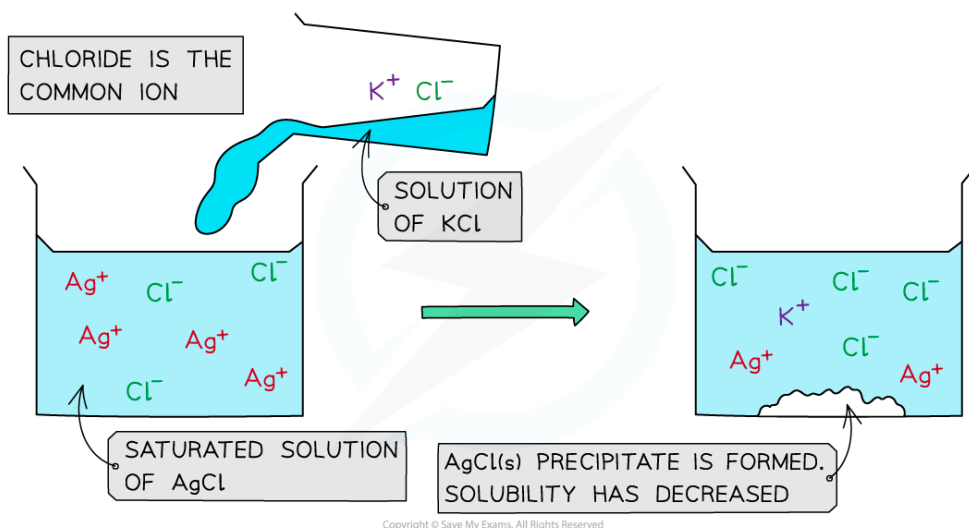
$$AgCl (s) \rightleftharpoons Ag^+ (aq) + Cl^- (aq)$$

- When a solution of potassium chloride is added:

  - Both KCl and AgCl have the common Cl^- ion

  - There is an increased Cl^- concentration so the equilibrium position shifts to the left

  - The increase in Cl^- concentration also means that $[Ag^+ (aq)]$ $[Cl^-(aq)]$ is **greater** than the K_{sp} for AgCl

  - As a result, the AgCl is **precipitated**

The common ion effect with KCl (aq) and AgCl (aq)

The addition of potassium chloride to a saturated solution of silver chloride results in the precipitate of silver chloride
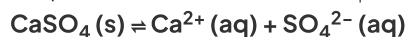
Worked Example

Calculations using the K_{sp} values and the concentration of the common ion

Predict whether a precipitate of $CaSO_4$ will form if a saturated solution of 1.0×10^{-3} mol dm^{-3} $CaSO_4$ is mixed with an equal volume of 1.0×10^{-3} mol dm^{-3} Na_2SO_4.

K_{sp} $CaSO_4$ = 2.0×10^{-5} mol^2 dm^{-6}.

Answer

- **Step 1:** Determine the equilibrium reaction of $CaSO_4$:
$$CaSO_4 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)}$$

- **Step 2:** Write down the equilibrium expression for K_{sp}:
$$K_{sp} = [Ca^{2+} \text{ (aq)}] [SO_4^{2-} \text{ (aq)}]$$

- **Step 3:** Determine the concentrations of the ions:

  - There are equal volumes of each solution
  - This means that the total solution was diluted by a factor of 2
  - The new concentration of the Ca^{2+} ion is **halved**:

    - $[Ca^{2+}] = \dfrac{1.0 \times 10^{-3}}{2}$
    - $[Ca^{2+}] = 5.0 \times 10^{-4}$ mol dm^{-3}
  - The sulfate ion concentration remains the same as it is a common ion and its concentration is the same in both solutions
- **Step 4:** Substitute the values into the expression:

  - Product of the ion concentrations = $[Ca^{2+} \text{ (aq)}] \times [SO_4^{2-} \text{ (aq)}]$
  - Product of the ion concentrations = $(5.0 \times 10^{-4}) \times (1.0 \times 10^{-3})$

- Product of the ion concentrations = 5.0×10^{-7} mol^2 dm^{-6}
- **Step 5:** Determine if a precipitate will form:

  - As the product of the ion concentration (5.0×10^{-7} mol dm^{-3}) is smaller than the K_{sp} value (2.0×10^{-5} mol^2 dm^{-6}), the CaSO$_4$ precipitate will **not** be formed