

Cambridge (CIE) A Level Chemistry



Your notes

Acids & Bases

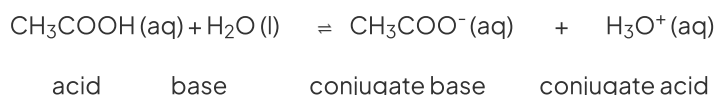
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Conjugate Acids & Bases

- 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



- 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:

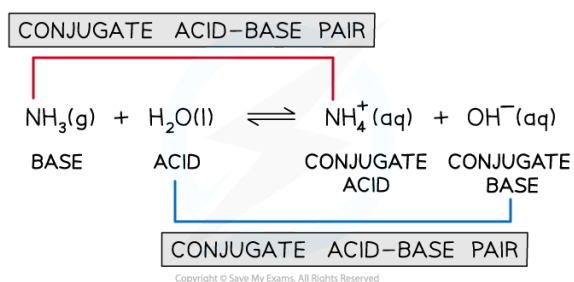


Answer:

- 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^-

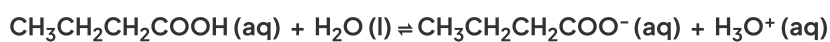


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Worked Example

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



- A. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ and H_2O
- B. H_2O and H_3O^+
- C. H_2O and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$
- D. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$ 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:

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

- where $[\text{H}^+]$ = 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:

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



Worked Example

Calculating the pH of acids

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

Answer

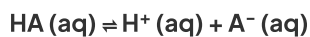
$$\text{pH} = -\log [\text{H}^+]$$

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

$$\text{pH} = 2.9$$

K_a & $\text{p}K_a$

- 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:



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



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- 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

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

- 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 $0.100 \text{ mol dm}^{-3}$ ethanoic acid at 298K which forms 1.32×10^{-3} of H^+ ions in solution.

Answer

- Step 1:** Write down the equation for the partial dissociation of ethanoic acid:

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

- Step 2:** Write down the equilibrium expression to find K_a :

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



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- **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:

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

- **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 :

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

Therefore, K_a is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$

- **Step 6:** Find $\text{p}K_a$:

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

$$\text{p}K_a = -\log_{10} (1.74 \times 10^{-5})$$

$$\text{p}K_a = 4.76$$

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 $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
- For the **ionisation** of water, the equilibrium expression to find K_w is:



$$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

- 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:

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

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

$$K_w = [\text{H}^+]^2$$



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:



- **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 :

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

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



Your notes



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:

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

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



$$\text{p}K_{\text{a}} = -\log_{10} K_{\text{a}} \Leftrightarrow K_{\text{a}} = 10^{-\text{p}K_{\text{a}}}$$



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[H⁺] & pH Calculations

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

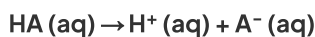
$$\text{pH} = -\log [\text{H}^+]$$

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

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

Strong acids

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



- 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

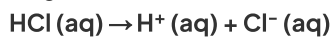
pH calculations of a strong acid

For a solution of hydrochloric acid, calculate the following:

- The pH when the hydrogen ion concentration is $1.6 \times 10^{-4} \text{ mol dm}^{-3}$.
- The hydrogen ion concentration when the pH is 3.1.

Answer

- Hydrochloric acid is a strong monobasic acid



Answer 1

- The pH of the solution is:

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

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

$$\text{pH} = 3.80$$

Answer 2

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

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

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

$$[\text{H}^+] = 10^{-3.1}$$

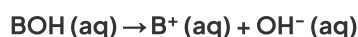
$$[\text{H}^+] = 7.9 \times 10^{-4} \text{ mol dm}^{-3}$$



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Strong alkalis

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



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

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

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

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

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

- Once the $[\text{H}^+]$ has been determined, the pH of the strong alkali can be found using $\text{pH} = -\log[\text{H}^+]$
- Similarly, the ionic product of water can be used to find the concentration of OH^- ions in solution if $[\text{H}^+]$ is known

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



Worked Example

pH calculations of a strong alkali

For a solution of sodium hydroxide, calculate the following:

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

Answer

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



Answer 1

- The pH of the solution is:

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

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

$$\text{pH} = 10.5$$

Answer 2

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

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

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

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

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

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

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

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

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

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

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

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



Your notes

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

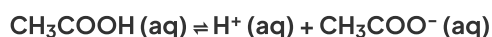
Calculate the pH of $0.100 \text{ mol dm}^{-3}$ ethanoic acid at 298K with a K_a value of $1.74 \times 10^{-5} \text{ mol dm}^{-3}$.

Answer



Your notes

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



- Step 1:** 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 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:

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

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

$$[\text{H}^+] = \sqrt{K_a \times [\text{CH}_3\text{COOH}]}$$

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

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

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

- Step 5:** Find the pH:

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

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

$$\text{pH} = 2.88$$

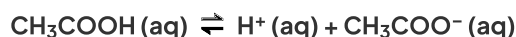


Buffers

- 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

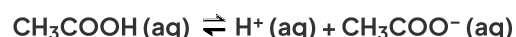
- A common buffer solution is an **aqueous mixture of ethanoic acid** and **sodium ethanoate**
- Ethanoic acid, CH_3COOH , is a **weak acid** and partially ionises in solution to form a relatively **low** concentration of **ethanoate ions**, CH_3COO^-



- Sodium ethanoate, CH_3COONa , is a **salt** which fully ionises in solution to form a relatively **high** concentration of **ethanoate ions**, CH_3COO^-



- 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

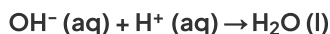


When H^+ ions are added:

- 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

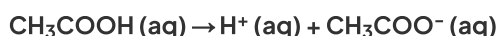
When OH^- ions are added:

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



Your notes

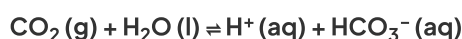
- The H^+ concentration **decreases**
- The equilibrium position shifts to the right and more CH_3COOH molecules ionise to form more H^+ and CH_3COO^- until equilibrium is re-established



- 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

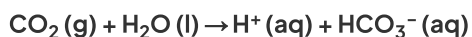
- In humans, HCO_3^- ions act as a buffer to keep the blood pH between 7.35 and 7.45
- Body cells produce CO_2 during **aerobic respiration**
- This CO_2 will combine with water in the blood to form a solution containing H^+ ions



- 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



- 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



- 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.



Your notes



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

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



Worked Example

Calculating the pH of a buffer solution

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

The K_a of ethanoic acid = $1.43 \times 10^{-5} \text{ mol dm}^{-3}$.

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 :

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

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

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

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

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

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

- **Step 4:** Calculate the pH:

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

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

$$\text{pH} = 5.08$$



Your notes



The Solubility Product, K_{sp}

- **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

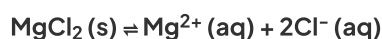
Solubility product

- 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

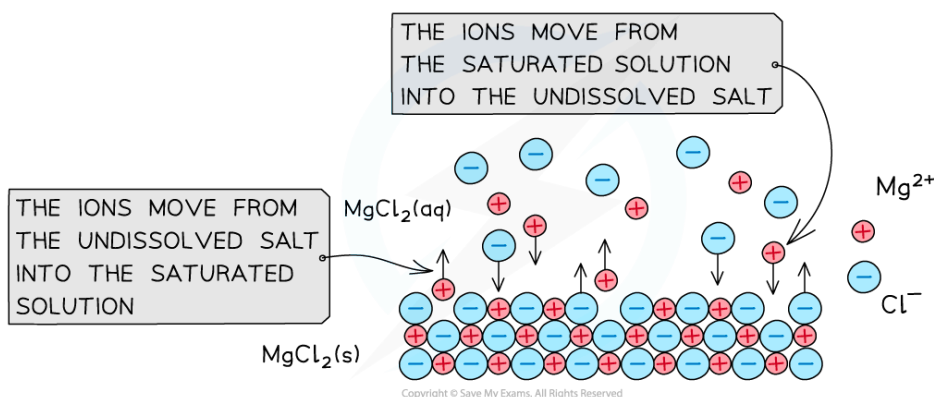


$$K_{sp} = [A^{x+}(aq)]^a [B^{y-}(aq)]^b$$

- 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



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:

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

- The K_{sp} is only useful for **sparingly soluble salts**
- The smaller the value of K_{sp} , the lower the solubility of the salt

K_{sp} Expressions

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



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



Worked Example

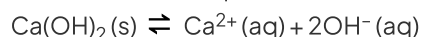
Expressing K_{sp} of ionic compounds

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

1. $\text{Ca}(\text{OH})_2$
2. Fe_2O_3
3. SnCO_3

Answer 1 – $\text{Ca}(\text{OH})_2$:

- **Step 1** – Write the balanced chemical equation:



- **Step 2** – Write the K_{sp} expression:

$$K_{sp} = [\text{Ca}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2$$

- **Step 3** – Deduce the units:

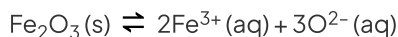
$$K_{sp} = [\text{mol dm}^{-3}] \times [\text{mol dm}^{-3}]^2$$

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

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

Answer 2 – Fe_2O_3 :

- **Step 1** – Write the balanced chemical equation:



- **Step 2** – Write the K_{sp} expression:

$$K_{sp} = [\text{Fe}^{3+}(\text{aq})]^2 [\text{O}^{2-}(\text{aq})]^3$$

1. **Step 3** – Deduce the units:

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

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

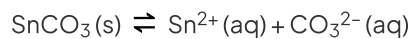
$$K_{sp} = \text{mol}^5 \text{ dm}^{-15}$$



Your notes

Answer 3 – SnCO₃:

- **Step 1** – Write the balanced chemical equation:



- **Step 2** – Write the K_{sp} expression:

$$K_{sp} = [\text{Sn}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})]$$

- **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**



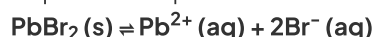
Worked Example

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 $1.39 \times 10^{-3} \text{ mol dm}^{-3}$.

Answer

- Step 1:** Write down the equilibrium equation:



- Step 2:** Write down the equilibrium expression:

$$K_{sp} = [\text{Pb}^{2+}(\text{aq})][\text{Br}^{-}(\text{aq})]^2$$

- Step 3:** Calculate the ion concentrations in the solution:

- $[\text{PbBr}_2(\text{s})] = 1.39 \times 10^{-3} \text{ mol dm}^{-3}$

- The ratio of PbBr_2 to Pb^{2+} is 1:1

$$[\text{Pb}^{2+}(\text{aq})] = [\text{PbBr}_2(\text{s})] = 1.39 \times 10^{-3} \text{ mol dm}^{-3}$$

- The ratio of PbBr_2 to Br^{-} is 1:2

$$[\text{Br}^{-}(\text{aq})] = 2 \times [\text{PbBr}_2(\text{s})] = 2 \times 1.39 \times 10^{-3} \text{ mol dm}^{-3} = 2.78 \times 10^{-3} \text{ mol dm}^{-3}$$

- 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 $1.07 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$



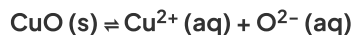
Worked Example

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 $5.9 \times 10^{-36} \text{ mol}^2 \text{ dm}^{-6}$.

Answer

- **Step 1:** Write down the equilibrium equation:



- **Step 2:** Write down the equilibrium expression:

$$K_{sp} = [\text{Cu}^{2+} \text{ (aq)}] [\text{O}^{2-} \text{ (aq)}]$$

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

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

$$K_{sp} = [\text{Cu}^{2+} \text{ (aq)}]^2$$

- **Step 4:** Substitute the value of K_{sp} into the expression to find the concentration:

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

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

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

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



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)



Your notes

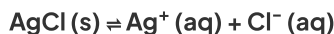


The Solubility Product & the Common Ion Effect

- 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

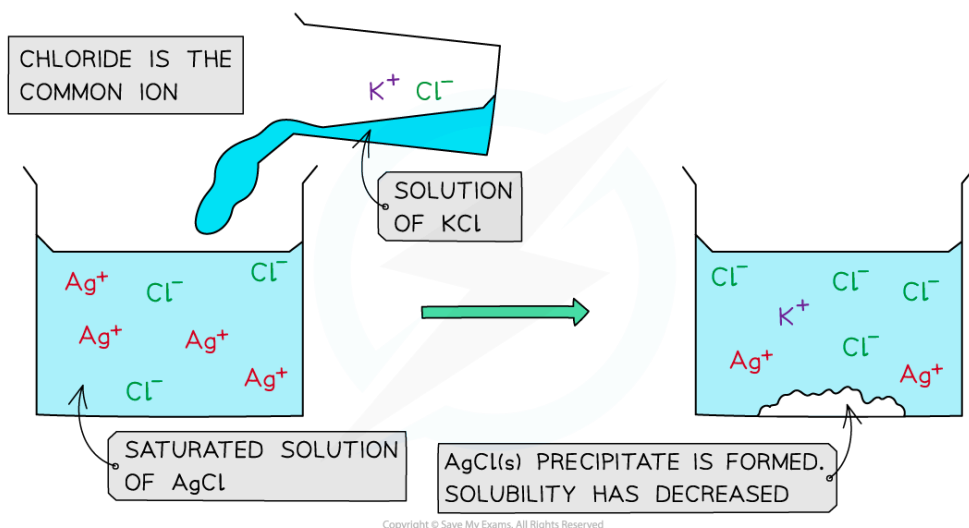


- When a solution of potassium chloride is added:
 - Both KCl and AgCl have the common Cl^- ion
 - There is an increased Cl^- concentration so the equilibrium position shifts to the left
 - The increase in Cl^- concentration also means that $[\text{Ag}^+ \text{ (aq)}][\text{Cl}^- \text{ (aq)}]$ is **greater than** the K_{sp} for AgCl
 - As a result, the AgCl is **precipitated**

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



Your notes



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



Worked Example

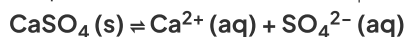
Calculations using the K_{sp} values and the concentration of the common ion

Predict whether a precipitate of CaSO_4 will form if a saturated solution of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ CaSO}_4$ is mixed with an equal volume of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$.

$$K_{sp} \text{ CaSO}_4 = 2.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}.$$

Answer

- Step 1: Determine the equilibrium reaction of CaSO_4 :



- Step 2: Write down the equilibrium expression for K_{sp} :

$$K_{sp} = [\text{Ca}^{2+} (\text{aq})] [\text{SO}_4^{2-} (\text{aq})]$$

- 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**:

$$[\text{Ca}^{2+}] = \frac{1.0 \times 10^{-3}}{2}$$

$$[\text{Ca}^{2+}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$$

- 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:

$$\text{Product of the ion concentrations} = [\text{Ca}^{2+} (\text{aq})] \times [\text{SO}_4^{2-} (\text{aq})]$$

$$\text{Product of the ion concentrations} = (5.0 \times 10^{-4}) \times (1.0 \times 10^{-3})$$

- Product of the ion concentrations = $5.0 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$
- **Step 5:** Determine if a precipitate will form:
 - As the product of the ion concentration ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) is smaller than the K_{sp} value ($2.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$), the CaSO_4 precipitate will **not** be formed



Your notes