



# Cambridge (CIE) A Level Chemistry



## Acids & Bases

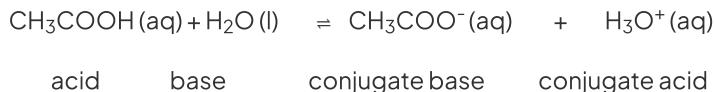
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# Conjugate Acids & Bases

- 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<sub>3</sub>COOH is linked to the product CH<sub>3</sub>COO<sup>-</sup> by the transfer of a **proton** from the acid to the base
  - Similarly, the H<sub>2</sub>O molecule is linked to H<sub>3</sub>O<sup>+</sup> 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<sup>+</sup> 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:

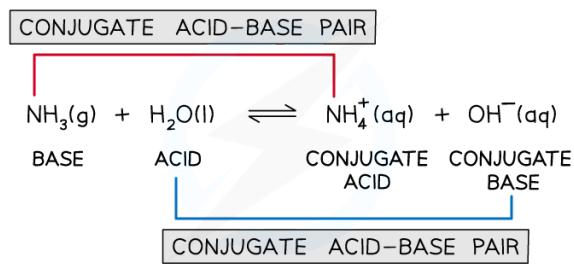


**Answer:**

- In the forward reaction:
  - NH<sub>4</sub><sup>+</sup> is the conjugate acid of the base NH<sub>3</sub>
  - OH<sup>-</sup> is the conjugate base of the acid H<sub>2</sub>O
- In the reverse reaction:
  - NH<sub>3</sub> is the conjugate base of the acid NH<sub>4</sub><sup>+</sup>
  - H<sub>2</sub>O is the conjugate acid of the base OH<sup>-</sup>



Your notes

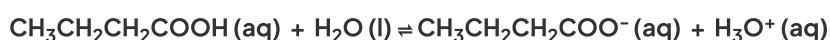


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### Worked Example

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  $\text{H}_2\text{O}$
- B.  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$
- C.  $\text{H}_2\text{O}$  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  $\text{H}_3\text{O}^+$

**Answer:**

- The correct option in B
  - A conjugate acid-base pair differ only by an  $\text{H}^+$  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  $\text{H}^+$  ions ( $\text{mol dm}^{-3}$ )
- The pH can also be used to calculate the concentration of  $\text{H}^+$  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

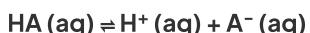
$$\text{pH} = -\log [\text{H}^+]$$

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

$$\text{pH} = 2.9$$

## K<sub>a</sub> & pK<sub>a</sub>

- 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:





Your notes

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

- 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

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

- 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  $298\text{K}$  which forms  $1.32 \times 10^{-3}$  of  $H^+$  ions in solution.

### Answer

- **Step 1:** Write down the equation for the partial dissociation of ethanoic acid:  
 $\text{CH}_3\text{COOH} \text{ (aq)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$
- **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<sup>+</sup> to CH<sub>3</sub>COO<sup>-</sup> is 1:1

The concentration of H<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup> 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<sub>a</sub>:

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

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

- **Step 5:** Determine the units of K<sub>a</sub>:

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

Therefore, K<sub>a</sub> is 1.74 × 10<sup>-5</sup> mol dm<sup>-3</sup>

- **Step 6:** Find pK<sub>a</sub>:

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

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

$$pK_a = 4.76$$

## K<sub>w</sub>

- The K<sub>w</sub> 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<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>

- For the **ionisation** of water, the equilibrium expression to find K<sub>w</sub> is:



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

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

- The concentration of H<sub>2</sub>O can therefore be regarded as constant and removed from the K<sub>w</sub> expression

- The equilibrium expression therefore becomes:

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

- As the [H<sup>+</sup>] = [OH<sup>-</sup>] in pure water, the equilibrium expression can be further simplified to:

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



Your notes

## Worked Example

### Calculating the concentration of H<sup>+</sup> of pure water

Calculate the concentration of H<sup>+</sup> 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<sub>w</sub>:

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

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

- Since the concentration of H<sub>2</sub>O is constant, this expression can be simplified to:

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

- **Step 4:** Further simplify the expression:

- The ratio of H<sup>+</sup> to OH<sup>-</sup> is 1:1
- The concentration of H<sup>+</sup> and OH<sup>-</sup> is, therefore, the same and the equilibrium expression can be further simplified to:

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

- **Step 5:** Rearrange the equation to find [H<sup>+</sup>]:

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

- **Step 6:** Substitute the values into the expression to find K<sub>w</sub>:

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

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



## Examiner Tips and Tricks

- The greater the K<sub>a</sub> value, the **more strongly acidic** the acid is
- The greater the pK<sub>a</sub> value, the **less strongly acidic** the acid is.
- Also, you should be able to rearrange the following expressions:

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

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

L

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



Your notes



# [H<sup>+</sup>] & pH Calculations

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

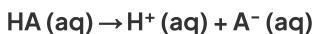
$$\text{pH} = -\log [\text{H}^+]$$

- Similarly, the concentration of H<sup>+</sup> 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<sup>+</sup>]) is equal to the concentration of acid ([HA])
- The number of hydrogen ions ([H<sup>+</sup>]) formed from the ionisation of water is very small relative to the [H<sup>+</sup>] due to the ionisation of the strong acid and can therefore be neglected
- The total [H<sup>+</sup>] is therefore the same as the [HA]



### Worked Example

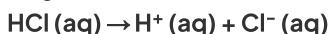
#### pH calculations of a strong acid

For a solution of hydrochloric acid, calculate the following:

- The pH when the hydrogen ion concentration is  $1.6 \times 10^{-4}$  mol dm<sup>-3</sup>.
- 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



Your notes

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

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

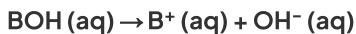
$$[\text{H}^+] = 10^{-\text{pH}}$$

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

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

## 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  $\text{H}^+$  in solution which is due to the ionisation of water
- The concentration of  $\text{OH}^-$  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  $\text{OH}^-$  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:



Your notes

### 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  $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

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

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

## 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:  
 $\text{CH}_3\text{COOH} \text{ (aq)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$

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

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

- Step 2:** Simplify the expression:

- The ratio of  $\text{H}^+$  to  $\text{CH}_3\text{COO}^-$  ions is 1:1
- Therefore the concentration of  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  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:

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

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

$$\text{pH} = 2.88$$

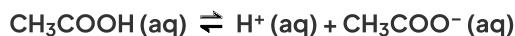


# Buffers

- 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

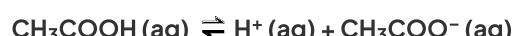
- A common buffer solution is an **aqueous mixture of ethanoic acid and sodium ethanoate**
- Ethanoic acid,  $\text{CH}_3\text{COOH}$ , is a **weak acid** and partially ionises in solution to form a relatively **low** concentration of **ethanoate ions**,  $\text{CH}_3\text{COO}^-$



- Sodium ethanoate,  $\text{CH}_3\text{COONa}$ , is a **salt** which fully ionises in solution to form a relatively **high** concentration of **ethanoate ions**,  $\text{CH}_3\text{COO}^-$



- There are **reserve supplies** of the acid ( $\text{CH}_3\text{COOH}$ ) and its conjugate base ( $\text{CH}_3\text{COO}^-$ )
  - The buffer solution contains relatively high concentrations of  $\text{CH}_3\text{COOH}$  (due to the ionisation of **ethanoic acid**) and  $\text{CH}_3\text{COO}^-$  (due to the ionisation of **sodium ethanoate**)
- In the **buffer solution**, the ethanoic acid is **in equilibrium** with hydrogen and ethanoate ions



### When $\text{H}^+$ ions are added:

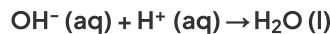
- The equilibrium position shifts to the **left** as  $\text{H}^+$  ions react with  $\text{CH}_3\text{COO}^-$  ions to form more  $\text{CH}_3\text{COOH}$  until equilibrium is **re-established**
- As there is a large reserve supply of  $\text{CH}_3\text{COO}^-$ , the concentration of  $\text{CH}_3\text{COO}^-$  in solution doesn't change much as it reacts with the added  $\text{H}^+$  ions
- As there is a large reserve supply of  $\text{CH}_3\text{COOH}$ , the concentration of  $\text{CH}_3\text{COOH}$  in solution doesn't change much as  $\text{CH}_3\text{COOH}$  is formed from the reaction of  $\text{CH}_3\text{COO}^-$  with  $\text{H}^+$
- As a result, the pH remains reasonably constant

### When $\text{OH}^-$ ions are added:

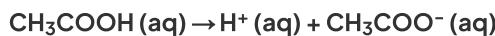
- The  $\text{OH}^-$  reacts with  $\text{H}^+$  to form water



Your notes



- The  $\text{H}^+$  concentration **decreases**
- The equilibrium position shifts to the right and more  $\text{CH}_3\text{COOH}$  molecules ionise to form more  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  until equilibrium is re-established



- As there is a large reserve supply of  $\text{CH}_3\text{COOH}$  the concentration of  $\text{CH}_3\text{COOH}$  in solution doesn't change much when  $\text{CH}_3\text{COOH}$  dissociates to form more  $\text{H}^+$  ions
- As there is a large reserve supply of  $\text{CH}_3\text{COO}^-$  the concentration of  $\text{CH}_3\text{COO}^-$  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,  $\text{HCO}_3^-$  ions act as a buffer to keep the blood pH between 7.35 and 7.45
- Body cells produce  $\text{CO}_2$  during **aerobic respiration**
- This  $\text{CO}_2$  will combine with water in the blood to form a solution containing  $\text{H}^+$  ions



- This equilibrium between  $\text{CO}_2$  and  $\text{HCO}_3^-$  is extremely important
- If the concentration of  $\text{H}^+$  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  $\text{H}^+$  ions**
- The equilibrium position shifts to the **left** until equilibrium is restored



- This reduces the concentration of  $\text{H}^+$  and keeps the pH of the blood **constant**
- **If there is a decrease in  $\text{H}^+$  ions**
  - The equilibrium position shifts to the **right** until equilibrium is restored



- This increases the concentration of  $\text{H}^+$  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:

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

- 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:
$$\text{CH}_3\text{COOH} \text{ (aq)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$$
- 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  $[\text{H}^+]$ :



Your notes

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

- **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:

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

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

$$\text{pH} = 5.08$$



# 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

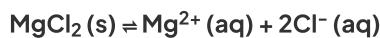
## Solubility product

- 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

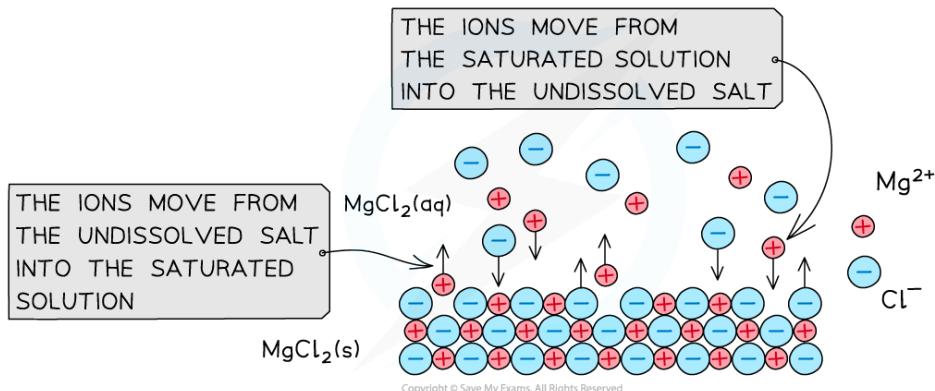


$$K_{sp} = [A^{x+}(aq)]^a [B^{y-}(aq)]^b$$

- 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



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- 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<sub>sp</sub> 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

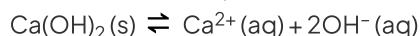
#### Expressing $K_{sp}$ of ionic compounds

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

1.  $\text{Ca(OH)}_2$
2.  $\text{Fe}_2\text{O}_3$
3.  $\text{SnCO}_3$

#### Answer 1 - $\text{Ca(OH)}_2$ :

- 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:

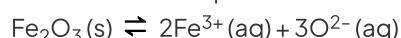
$$K_{sp} = [\text{mol dm}^{-3}] \times [\text{mol dm}^{-3}]^2$$

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

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

#### Answer 2 - $\text{Fe}_2\text{O}_3$ :

- 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:



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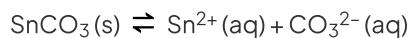
$$K_{sp} = [\text{mol dm}^{-3}]^2 \times [\text{mol dm}^{-3}]^3$$

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

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

### Answer 3 - $\text{SnCO}_3$ :

- **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**



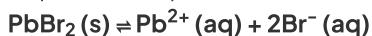
## Worked Example

### Calculating the solubility product of a compound from its solubility

Calculate the solubility product of a saturated solution of lead(II) bromide,  $\text{PbBr}_2$ , 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  $\text{PbBr}_2$  to  $\text{Pb}^{2+}$  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  $\text{PbBr}_2$  to  $\text{Br}^-$  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

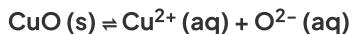
Calculate the solubility of a saturated solution of copper(II) oxide, CuO, with a solubility product of  $5.9 \times 10^{-36}$  mol<sup>2</sup> dm<sup>-6</sup>.



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### 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<sup>2+</sup> to O<sup>2-</sup> is 1:1

- [Cu<sup>2+</sup>(aq)] = [O<sup>2-</sup>(aq)] so the expression can be simplified to:

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

- **Step 4:** Substitute the value of K<sub>sp</sub> 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 [CuO (s)] = [Cu<sup>2+</sup> (aq)], the solubility of copper oxide is  $2.4 \times 10^{-18}$  mol dm<sup>-3</sup>



### 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)

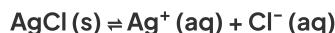


# The Solubility Product & the Common Ion Effect

- 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

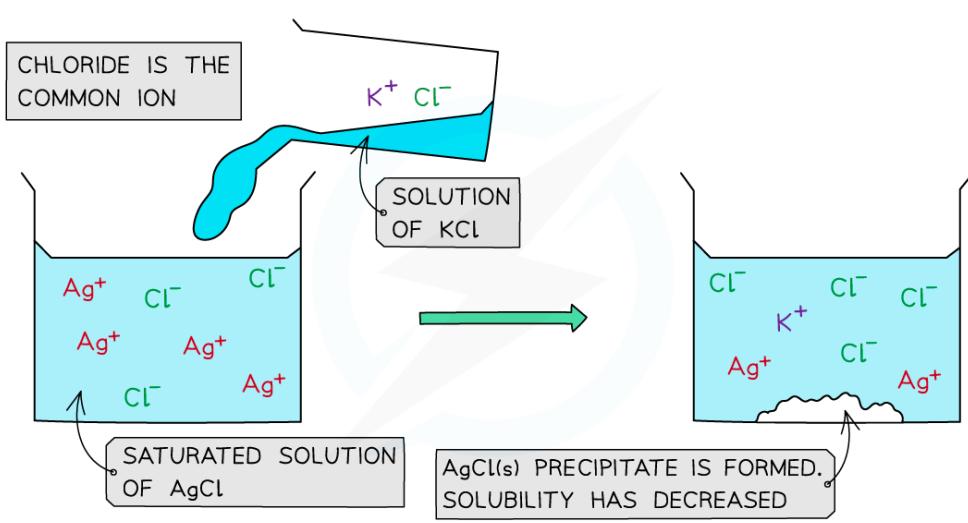


- When a solution of potassium chloride is added:
  - Both KCl and AgCl have the common Cl<sup>-</sup> ion
  - There is an increased Cl<sup>-</sup> concentration so the equilibrium position shifts to the left
  - The increase in Cl<sup>-</sup> concentration also means that [Ag<sup>+</sup>(aq)][Cl<sup>-</sup>(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



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

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

### Answer

- **Step 1:** Determine the equilibrium reaction of  $\text{CaSO}_4$ :  

$$\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$
- **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  $\text{Ca}^{2+}$  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:

- Product of the ion concentrations =  $[\text{Ca}^{2+}(\text{aq})] \times [\text{SO}_4^{2-}(\text{aq})]$
- Product of the ion concentrations =  $(5.0 \times 10^{-4}) \times (1.0 \times 10^{-3})$

- Product of the ion concentrations =  $5.0 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$
- **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  $\text{CaSO}_4$  precipitate will **not** be formed



Your notes