A Level Chemistry OCR

5. Physical Chemistry & Transition Elements (A Level Only)

CONTENTS

5.1 Rates, Orders & Arrhenius

5.1.1 Rates & Orders

Rates Equations & Rates Terms

- The **rate of reaction** can be found by:
  - Measuring the decrease in the concentration of a reactant over time
  - Measuring the increase in the concentration of a product over time
  - The units for rate of reaction are mol dm^{-3} s^{-1}

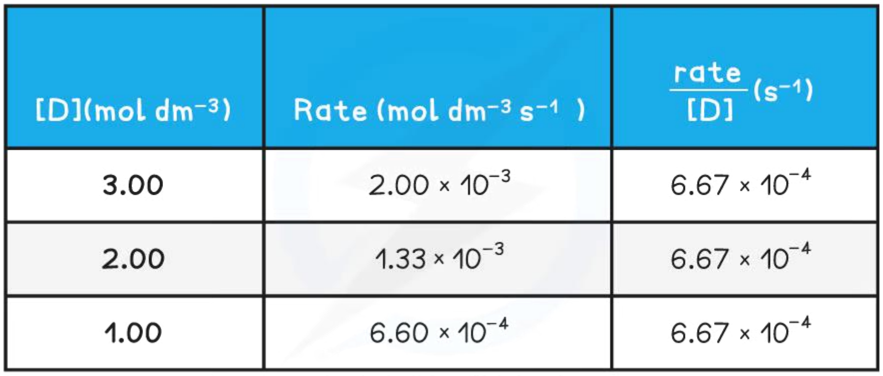
Rate of Reaction

- The following general reaction will be used as an example to study the rate of reaction

$$D\ (aq) \rightarrow E\ (aq) + F\ (g)$$

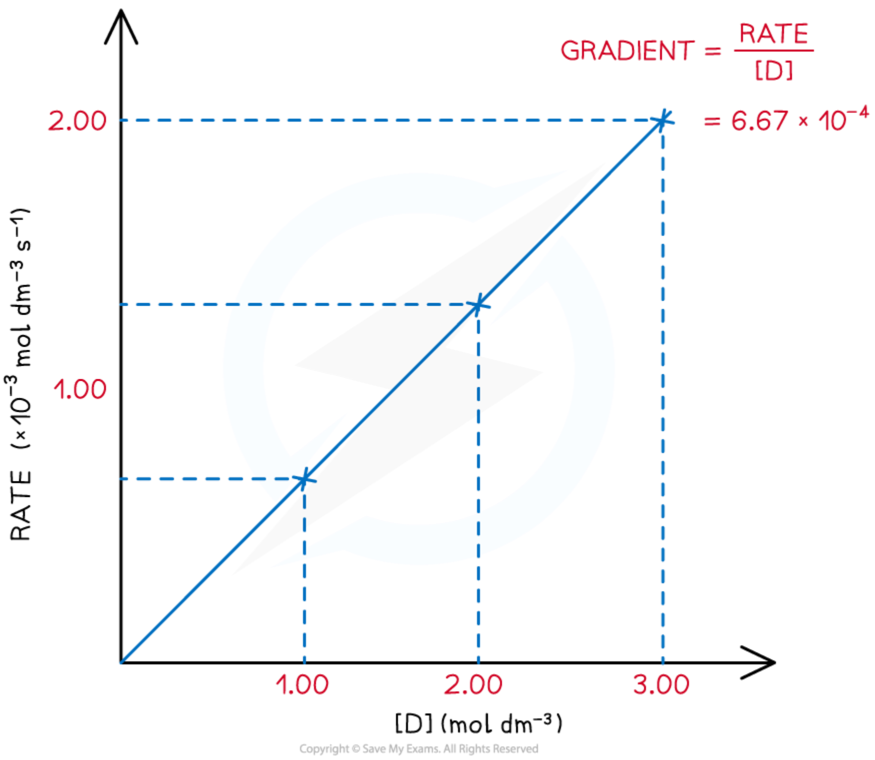
- The rate of reaction at different concentrations of D is measured and tabulated

Rate of reactions table



[D](mol dm^{-3})	Rate (mol dm^{-3} s^{-1})	$\frac{rate}{[D]}$ (s^{-1})
3.00	2.00×10^{-3}	6.67×10^{-4}
2.00	1.33×10^{-3}	6.67×10^{-4}
1.00	6.60×10^{-4}	6.67×10^{-4}

- A **directly proportional** relationship between the **rate** of reaction and **concentration of D** is observed when the results are plotted on a graph:



Rate of reaction over various concentrations of D

- This leads to a very common rate expression:

Rate ∝ [D] or Rate = *k*[D]

- This rate expression means that if the concentration of D is doubled, then the rate doubles
- Equally, if the concentration of D halves, then the rate halves

Rate Equations

- The following reaction will be used to discuss rate equations:

A (aq) + B (aq) → C (aq) + D (g)

- The rate equation for this reaction is:

Rate of reaction = $k\,[A]^m\,[B]^n$

- Rate equations can only be determined experimentally and cannot be found from the stoichiometric equations
- In the above rate equation:
  - [A] and [B] are the concentrations of the reactants
  - m and n are orders with respect to each reactant involved in the reaction
- Products and catalysts may feature in rate equations
- Intermediates do not feature in rate equations

Order of reaction

- The **order** of a reactant shows how the concentration of a chemical, typically a reactant, affects the rate of reaction
- It is the power to which the concentration of that reactant is raised in the rate equation
- The order can be a positive, negative or fractional value
  - Orders that are a fraction suggest that the reaction involves multiple steps
- When the order of reaction with respect to a chemical is 0
  - Changing the concentration of the chemical has no effect on the rate of the reaction
  - Therefore, it is not included in the rate equation
- When the order of reaction with respect to a chemical is 1
  - The concentration of the chemical is directly proportional to the rate of reaction, e.g. doubling the concentration of the chemical doubles the rate of reaction
  - The chemical is included in the rate equation
- When the order of reaction with respect to a chemical is 2
  - The rate is directly proportional to the square of the concentration of that chemical, e.g. doubling the concentration of the chemical increases the rate of reaction by a factor of four
  - The chemical is included in the rate equation (appearing as a squared term)
- The **overall order of reaction** is the sum of the powers of the reactants in a rate equation

Worked Example

The chemical equation for the thermal decomposition of dinitrogen pentoxide is:

$$2N_2O_5\ (g) \rightarrow 4NO_2\ (g) + O_2\ (g)$$

The rate equation for this reaction is:

$$\text{Rate} = k[N_2O_5\ (g)]$$

1. State the order of the reaction with respect to dinitrogen pentoxide
2. Deduce the effect on the rate of reaction if the concentration of dinitrogen pentoxide is tripled

Answers

Answer 1:

- Dinitrogen pentoxide features in the rate equation, therefore, it cannot be order zero / 0
- The dinitrogen pentoxide is not raised to a power, which means that it cannot be order 2 / second order

- Therefore, the order with respect to dinitrogen pentoxide must be **order 1 / first order**

Answer 2:

- Since the reaction is first order, the concentration of dinitrogen pentoxide is directly proportional to the rate
- This means that if the concentration of the dinitrogen pentoxide is tripled, then the rate of reaction will also **triple**

Worked Example

The following equation represents the oxidation of bromide ions in acidic solution

$$BrO_3^- (aq) + 5Br^- (aq) + 6H^+ (aq) \rightarrow 3Br_2 (l) + 3H_2O (l)$$

The rate equation for this reaction is:

$$\text{Rate} = k[BrO_3^- (aq)][Br^- (aq)][H^+ (aq)]$$

1. State the overall order of the reaction
2. Deduce the effect on the rate of reaction if the concentration of bromate ions is doubled and the concentration of bromide ions is halved

Answers

Answer 1:

- All three reactants feature in the rate equation but they are not raised to a power, this means that the order with respect to each reactant is order 1 / first order.
- The overall order of the reaction is 1 + 1 + 1 = **3** or **third order**.

Answer 2:

- Since each reactant is first order, the concentration of each reactant is directly proportional to the effect that it has on rate
- If the concentration of the bromate ion is doubled, then the rate of reaction will also double
- If the concentration of the bromide ion is halved then the rate will also halve
- Therefore, there is **no overall effect** on the rate of reaction – one change doubles the rate and the other change halves it

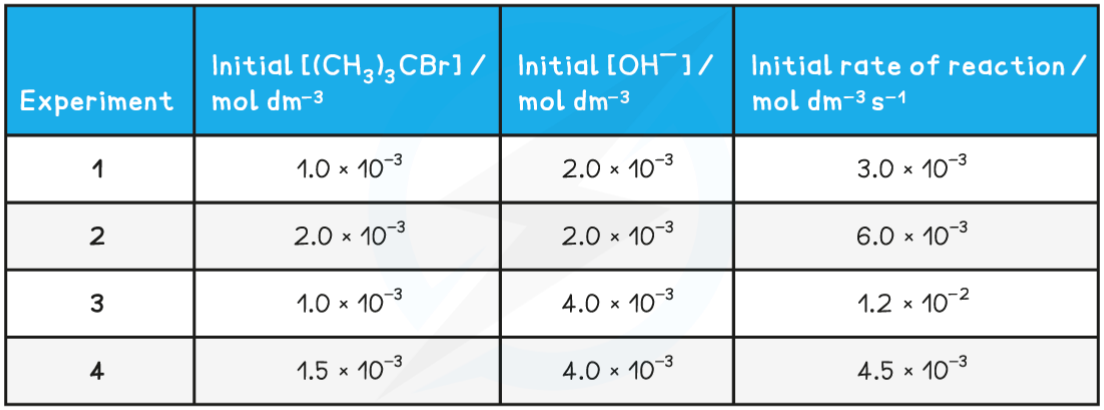
Deducing Orders

Deriving Rate Equations from data

- Let's take the following reaction and derive the rate equation from experimental data

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

Table to show the experimental data of the above reaction



Experiment	Initial [$(CH_3)_3CBr$] / mol dm^{-3}	Initial [OH^-] / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
2	2.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}
3	1.0×10^{-3}	4.0×10^{-3}	1.2×10^{-2}
4	1.5×10^{-3}	4.0×10^{-3}	4.5×10^{-3}

- To derive the rate equation for a reaction, you must first determine all of the orders with respect to each of the reactants
- This can be done using a graph, but it doesn't have to be - you can use tabulated data provided
- Take the reactants one at a time and find the order with respect to each reactant individually

- Identify two experiments where the concentration of the reactant you are looking at first changes, but the concentrations of all other reactants remain constant
- Repeat this for all of the reactants, one at a time, until you have determined the order with respect to all reactants

Order with respect to [$(CH_3)_3CBr$]

- From the above table, that is experiments 1 and 2
  - The [$(CH_3)_3CBr$] has doubled, but the [OH^-] has remained the same
  - The rate of the reaction has also doubled
  - Therefore, the order with respect to [$(CH_3)_3CBr$] is 1 (first order)

Order with respect to [OH^-]

- From the above table, that is experiments 1 and 3
  - The [OH^-] has doubled, but the [$(CH_3)_3CBr$] has remained the same
  - The rate of reaction has increased by a factor of 4 (i.e. increased by 2^2)
  - Therefore, the order with respect to [OH^-] is 2 (second order)

Putting the rate equation together

- Once you know the order with respect to all of the reactants, you put them together to form the rate equation

- If a reactant has an order of 0, then you do not include it in the rate equation
- If a reactant has an order of 1, then you do not need to include the number 1 as a power
- If a reactant has an order of 2, then you raise that reactant concentration to the power of 2
- For this reaction, the rate equation will be:

$$\textbf{Rate} = k\,[(CH_3)_3CBr]\,[OH^-]^2$$

Exam Tip

Be careful when reading the values in standard form! It is easy to make a mistake.

Rate Calculations

- The **rate constant** (*k*) of a reaction can be calculated using the initial rates and the rate equation

Calculating the rate constant from the initial rate

- The reaction of sodium carbonate with chloride ions (from hydrochloric acid) to form sodium chloride will be used as an example to calculate the rate constant from the **initial rate and initial concentrations**
- The reaction and rate equation are as follows:

$$Na_2CO_3\ (s) + 2Cl^-\ (aq) + 2H^+\ (aq) \rightarrow 2NaCl\ (aq) + CO_2\ (g) + H_2O\ (l)$$

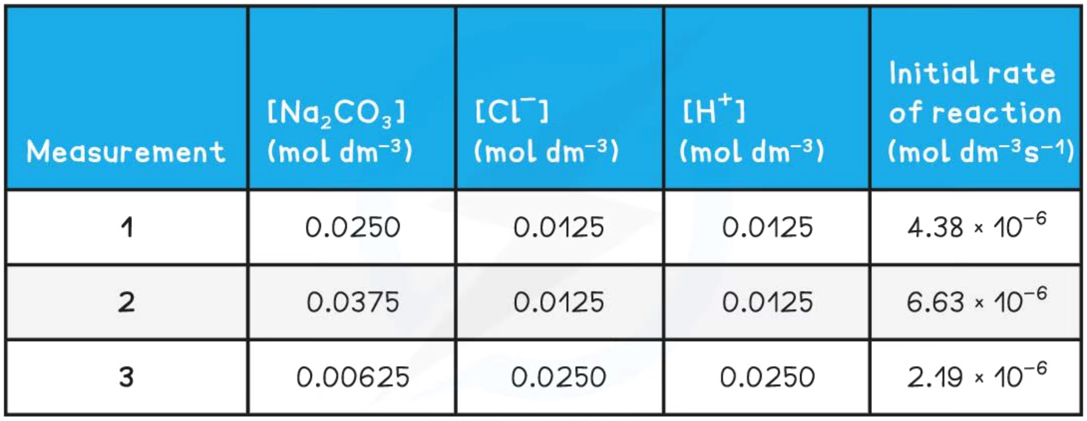
$$\text{RATE} = k[Na_2CO_3][Cl^-]$$

THIS REARRANGES TO GIVE:

$$k = \frac{\text{RATE}}{[Na_2CO_3][Cl^-]}$$

- The **progress** of the reaction can be followed by measuring the **initial rates** of the reaction using various **initial concentrations** of each reactant

Experimental results of concentrations & initial rates table



Measurement	$[Na_2CO_3]$ (mol dm^{-3})	$[Cl^-]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	Initial rate of reaction (mol dm^{-3}s^{-1})
1	0.0250	0.0125	0.0125	4.38×10^{-6}
2	0.0375	0.0125	0.0125	6.63×10^{-6}
3	0.00625	0.0250	0.0250	2.19×10^{-6}

- To find the rate constant (*k*):
- Substitute the values of one of the experiments to find *k* (for example **measurement 1**)

$$k = \frac{4.38 \times 10^{-6}}{(0.0250) \times (0.0125)}$$

$$k = 1.40 \times 10^{-2}$$

- The values of **measurement 2** or **3** could also have been used to find *k*
  - They all give the same result of 1.40×10^{-2}

Calculating Units

- When you are asked to calculate the rate constant, k, for a reaction you must also be able to deduce the units
- This is done by replacing the values in the rearranged rate equation with the units of that value
- The units can then be combined or cancelled as required
- For example, to calculate the units for the above reaction:

$$\text{UNITS OF } k = \frac{(\cancel{\text{mol dm}^{-3}}\,\text{s}^{-1})}{(\cancel{\text{mol dm}^{-3}})\,(\text{mol dm}^{-3})}$$

$$= \frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

$$= \text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}$$

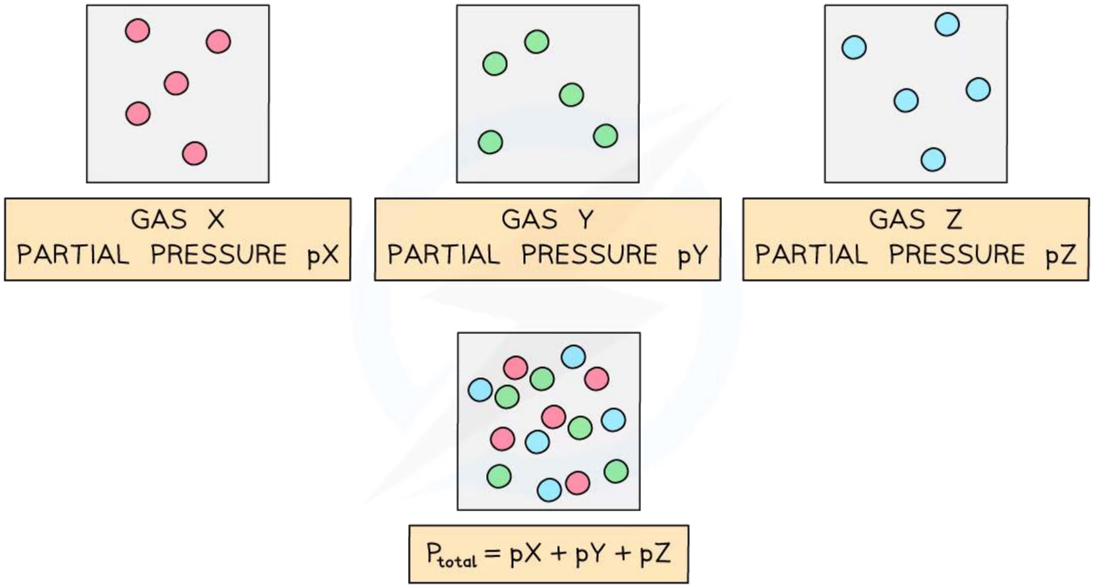
YOUR NOTES

5.2 Equilibria

5.2.1 Equilibrium Terms

Mole Fractions & Partial Pressure

- Mole fractions and partial pressures are a feature of K_p calculations
    - Put simply, the mole fraction is the fraction of the total number of moles that each chemical in a reaction is responsible for
    - Partial pressure is the part of the total pressure that each chemical in a reaction is responsible for
- The partial pressure of a gas is the pressure it exerts in a mixture of gases if it occupied the container on its own
- Partial pressure is given the symbol p, so for a gas X, it is written as pX
- The total pressure is the sum of the partial pressures (this is known as **Daltons' Law**)



The relationship between partial pressures in a mixture of gases and the total pressure

- To find the partial pressure of a gas, you need two pieces of information
    - The total pressure in the container
    - The mole fraction
- The mathematical relationships are as follows

$$\text{PARTIAL PRESSURE OF GAS A} = \text{TOTAL PRESSURE} \times \text{MOLE FRACTION}$$

$$\text{MOLE FRACTION OF A} = \frac{\text{NUMBER OF MOLES OF GAS A}}{\text{TOTAL NUMBER OF MOLES OF GAS}}$$

Partial pressure and mole fraction expressions

YOUR NOTES

Equilibrium Quantities

- When dealing with equilibrium calculations there are certain calculations that you will be expected to be able to perform
    - Calculating concentrations
        - Concentration (mol dm^{-3}) $= \frac{\text{number of moles}}{\text{volume } (dm^3)}$
    - Calculating equilibrium quantities
    - Calculating mole fractions and partial pressures

Worked Example

Calculating concentrations

Ethanoic acid and ethanol react according to the following equation:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

At equilibrium, 500 cm^3 of the reaction mixture contained 0.235 mol of ethanoic acid and 0.035 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water.

Calculate the concentration of each chemical at equilibrium.

Answer

- $[CH_3COOH] = \frac{0.235}{0.500} = 0.470$ mol dm^{-3}
- $[C_2H_5OH] = \frac{0.035}{0.500} = 0.070$ mol dm^{-3}
- $[CH_3COOC_2H_5] = \frac{0.182}{0.500} = 0.364$ mol dm^{-3}
- $[H_2O] = \frac{0.182}{0.500} = 0.364$ mol dm^{-3}

Calculating equilibrium quantities

- Some questions give the **initial and equilibrium concentrations** of the reactants but not the products
- An initial, change and equilibrium table should be used to determine the equilibrium concentration of the products **using the molar ratio of reactants and products in the stoichiometric equation**

Worked Example

Ethyl ethanoate is hydrolysed by water:

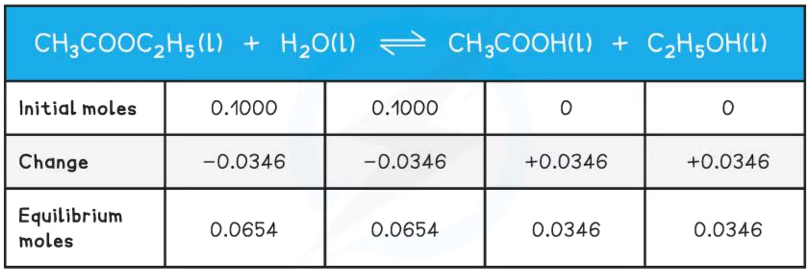
$$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$$

0.1000 mol of ethyl ethanoate are added to 0.1000 mol of water. A little acid catalyst is added and the mixture made up to 1dm^3. At equilibrium 0.0654 mol of water are present.

Use this data to calculate the equilibrium concentrations of each chemical.

Answer

Step 1: Write out the balanced chemical equation with the concentrations of beneath each substance using an initial, change and equilibrium table



	$CH_3COOC_2H_5(l)$	$H_2O(l)$	$CH_3COOH(l)$	$C_2H_5OH(l)$
Initial moles	0.1000	0.1000	0	0
Change	−0.0346	−0.0346	+0.0346	+0.0346
Equilibrium moles	0.0654	0.0654	0.0346	0.0346

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Step 2: Calculate the concentrations of the reactants and products

- $[CH_3COOC_2H_5] = \frac{0.0654}{1.00} = 0.0654 \text{ mol dm}^{-3}$
- $[H_2O] = \frac{0.0654}{1.00} = 0.0654 \text{ mol dm}^{-3}$
- $[CH_3COOH] = \frac{0.0346}{1.00} = 0.0346 \text{ mol dm}^{-3}$
- $[C_2H_5OH] = \frac{0.0346}{1.00} = 0.0346 \text{ mol dm}^{-3}$

Calculating mole fractions and partial pressures

- These are two of the fundamental calculations associated with K_p calculations

Worked Example

Working out mole fractions

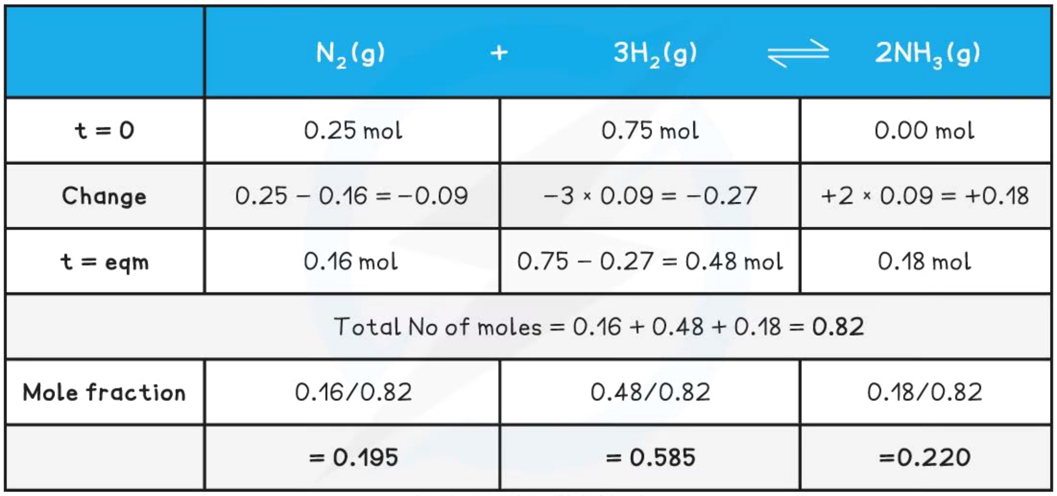
A sample of 0.25 mole of nitrogen and 0.75 mole of hydrogen were reacted together to form ammonia. The equilibrium amount of nitrogen was 0.16 mol.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

Calculate the mole fractions of nitrogen, hydrogen and ammonia.

Answer

Write out the equation and record the initial, the change and the equilibrium amounts:



	$N_2(g)$ +	$3H_2(g)$ ⇌	$2NH_3(g)$
t = 0	0.25 mol	0.75 mol	0.00 mol
Change	0.25 − 0.16 = −0.09	−3 × 0.09 = −0.27	+2 × 0.09 = +0.18
t = eqm	0.16 mol	0.75 − 0.27 = 0.48 mol	0.18 mol
Total No of moles = 0.16 + 0.48 + 0.18 = **0.82**			
Mole fraction	0.16/0.82	0.48/0.82	0.18/0.82
	= 0.195	**= 0.585**	**=0.220**

Exam Tip

You can check you have the mole fractions correct by adding them up and making sure they come to 1: 0.195 + 0.585 + 0.220 = 1

Worked Example

The total pressure for the reaction, described above, of nitrogen and hydrogen to form ammonia was 150 kPa.

Calculate the partial pressure of each gas.

Answer

- Partial pressure of N_2 (g) = 0.195 x 150 = 29.25 kPa
- Partial pressure of H_2 (g) = 0.585 x 150 = 87.75 kPa

- Partial pressure of NH_3 (g) = 0.220 x 150 = 33.0 kPa

Exam Tip

- You can check that your partial pressures are correct by adding them up:
  - 29.25 + 87.75 + 33.0 = 150
- They should add up to the total pressure - if they don't, then there is at least one calculation wrong somewhere!

5.2.2 Kc & Kp

Kc & Kp Expressions

- As previously discussed, the **equilibrium expression** links the **equilibrium constant**, K_c, to the **concentrations of reactants and products** at equilibrium taking the **stoichiometry** of the equation into account
- So, for the general reaction

aA + bB ⇌ cC + dD

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

Gaseous Equilibria

- This section covers how we manage gases in calculating the equilibrium constant and how an equilibrium yield is affected by the partial pressures of reactants and products
- Many industrial process involve reactions between gases so this application has important consequences for controlling reaction conditions
- In the generic example above, if all the substances are gases, we can show the equation with that state symbol

aA (g) + bB (g) ⇌ cC (g) + dD (g)

- We can write a different equilibrium expression in terms of the **partial pressure** of the gases
- This equilibrium constant is called K_p and is defined as follows

$$K_p = \frac{p^c\text{C(g)eqm}\ p^d\text{D(g)eqm}}{p^a\text{A(g) eqm}\ p^b\text{B(g) eqm}}$$

p^aA AND p^bB = EQUILIBRIUM REACTANT PARTIAL PRESSURES (kPa)

p^cC AND p^dD = EQUILIBRIUM PRODUCT PARTIAL PRESSURES (kPa)

a, b, c AND d = COEFFICIENTS IN THE BALANCED EQUATION

Equilibrium expression linking the partial pressures of reactants and products at equilibrium

- **Solids** and **liquids** are ignored in K_p equilibrium expressions
- The K_p of a reaction is constant and only changes if the **temperature** of the reaction changes

Exam Tip

There are a variety of ways to represent the partial pressure terms in a K_p expression

The only key point is do not use square brackets as these represent concentration and, therefore, imply a K_C expression

Worked Example

Write a K_p expression for the following equilibria and deduce the units of K_p :

1. N_2 (g) + $3H_2$ (g) ⇌ $2NH_3$ (g)
2. $2SO_2$ (g) + O_2 (g) ⇌ $2SO_3$ (g)

Answer 1

$$K_p = \frac{p^2NH_3(g)\,eqm}{pN_2(g)eqm\; p^3H_2(g)\,eqm} = \frac{kPa^2}{kPa \times kPa^3} = kPa^{-2}$$

Answer 2

$$K_p = \frac{p^2SO_3(g)\,eqm}{p^2SO_2(g)eqm\; pO_2(g)\,eqm} = \frac{kPa^2}{kPa^2 \times kPa} = kPa^{-1}$$

Kc & Kp Calculations

K_p calculations

- K_p calculations are a step-by-step process in which you need to find
  - the mole fractions of the gases present
  - their partial pressures
  - the K_p expression
  - the value of K_p

Worked Example

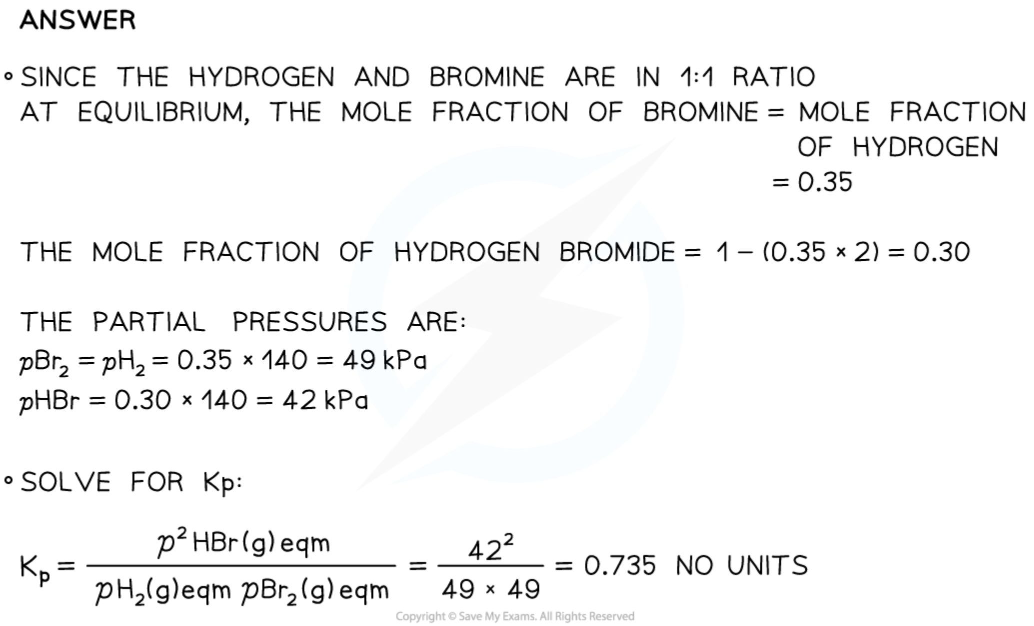
Finding K_p

Hydrogen and bromine were mixed in a flask in a 1: 1 ratio and allowed to reach equilibrium at 450 K. When equilibrium had been achieved the total pressure in the flask was 140 kPa and the mole fraction of bromine was 0.35.

The equation for the reaction is

$$H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g)$$

Determine the partial pressures for each gas at equilibrium and the value of K_p



ANSWER

- SINCE THE HYDROGEN AND BROMINE ARE IN 1:1 RATIO AT EQUILIBRIUM, THE MOLE FRACTION OF BROMINE = MOLE FRACTION OF HYDROGEN = 0.35

THE MOLE FRACTION OF HYDROGEN BROMIDE = 1 – (0.35 × 2) = 0.30

THE PARTIAL PRESSURES ARE:

$pBr_2 = pH_2 = 0.35 \times 140 = 49\ \text{kPa}$

$pHBr = 0.30 \times 140 = 42\ \text{kPa}$

- SOLVE FOR Kp:

$$K_p = \frac{p^2\,HBr(g)\,eqm}{pH_2(g)eqm\ pBr_2(g)\,eqm} = \frac{42^2}{49 \times 49} = 0.735 \text{ NO UNITS}$$

- Another style of K_p calculation involves being given the value of K_p and working backwards to deduce the partial pressure of one of the gases

Worked Example

Finding Partial Pressure

K_p for the dissociation equilibrium reaction of nitrogen monoxide is 0.0021.

$$2NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g)$$

If pure NO is introduced into a reaction flask at an initial pressure of 100 kPa, what is the equilibrium partial pressure of nitrogen?

ANSWER

- **STEP 1:** DEDUCE THE EQUILIBRIUM PARTIAL PRESSURE OF NITROGEN

LET x = THE EQUILIBRIUM PARTIAL PRESSURE OF NITROGEN

	$2NO(g)$	$\rightleftharpoons$	$N_2(g)$	+	$O_2(g)$
INITIALLY:	100 kPa		0 kPa		0 kPa
AT eqm:	(100 – 2x) kPa		x kPa		x kPa

- **STEP 2:** WRITE THE Kp EXPRESSION

$$K_p = \frac{pN_2(g)\,\text{eqm}\ pO_2(g)\,\text{eqm}}{p^2\,NO(g)\,\text{eqm}} = 0.0021$$

$$K_p = \frac{x^2}{(100-2x)^2} = 0.0021$$

TAKING THE SQUARE ROOTS:

$$\frac{x}{(100-2x)} = 0.04583$$

$$x = 0.04583 \times (100-2x)$$

$$x = 4.583 - 0.09166x$$

$$1.09166x = 4.583$$

$$x = \frac{4.582}{1.09166} = 4.198$$

THEREFORE, THE PARTIAL PRESSURE OF N_2 = 4.2 kPa (to 2 s.f.)

THE PARTIAL PRESSURE OF O_2 WOULD ALSO BE 4.2 kPa
AND THE PARTIAL PRESSURE OF NO WOULD BE 100 – (2 × 4.2) = 91.6 kPa

5.2.3 Equilibrium Constants & Changing Conditions

The Effect of Temperature on Equilibrium Constants

- We can apply Le Chatelier's Principle to gaseous equilibria in the same way it is applied to aqueous systems
- Here's a reminder of how the principle works

Le Chatelier’s principle

- **Le Chatelier’s principle** says that if a change is made to a system in dynamic equilibrium, the position of the equilibrium moves to counteract this change
- The principle is used to predict changes to the position of equilibrium when there are changes in temperature, pressure or concentration

Effects of temperature

- How the equilibrium shifts with temperature changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **ENDOTHERMIC** DIRECTION TO REVERSE THE CHANGE
DECREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **EXOTHERMIC** DIRECTION TO REVERSE THE CHANGE

Effect on the value of K_c

- For a reaction that is exothermic in the forward direction, increasing the temperature pushes the equilibrium from right to left
- Therefore, the value of K_c will decrease as the ratio of [products] to [reactants] decreases
- Conversely, if the temperature is raised in an endothermic reaction, the value of K_c will increase

Effect on the value of K_p

- For a reaction that is exothermic in the forward direction, increasing the temperature pushes the equilibrium from right to left
- Therefore, the value of K_p will decrease as the ratio of [products] to [reactants] decreases
- Conversely, if the temperature is raised in an endothermic reaction, the value of K_p will increase

Equilibria & Other Conditions

Effects of pressure

- Changes in pressure only affect reactions where the reactants or products are gases
- How the equilibrium shifts with pressure changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **SMALLER** NUMBER OF MOLECULES OF GAS TO DECREASE THE PRESSURE AGAIN
DECREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **LARGER** NUMBER OF MOLECULES OF GAS TO INCREASE THE PRESSURE AGAIN

Effect on the value of K_c

- The value of K_c is not affected by any changes in pressure as this does not involve gases.

Effect on the value of K_p

- The value of K_p is not affected by any changes in pressure.
- Changes in pressure cause a shift in the position of equilibrium to a new position which restores the value of K_p
- This is analogous to what happens to K_c when you change concentration in an aqueous equilibrium; a shift restores equilibrium to a new position maintaining K_c

Presence of a catalyst

- If all other conditions stay the same, the equilibrium constant K_p is **not affected** by the presence of a catalyst
- A catalyst speeds up both the forward and reverse reactions at the same rate so the ratio of [products] to [reactants] remains unchanged
- Catalysts only cause a reaction to reach equilibrium **faster**
- Catalysts therefore have **no effect** on the **position of the equilibrium** once this is reached

Worked Example

Factors affecting K_c

An equilibrium is established in the reaction

$$AB\ (aq) + CD\ (aq) \rightleftharpoons AC\ (aq) + BD\ (aq) \qquad \Delta H = +180\ kJ\ mol^{-1}$$

Which factors would affect the value of K_c in this equilibrium?

Answer

- Only a change in temperature will affect the value of K_c and any other changes in conditions would result in the position of the equilibrium moving in such way to oppose this change.
- Adding a catalyst will increase the rate of reaction meaning the state of equilibrium will be reached faster but will have no effect on the position of the equilibrium and therefore K_c is unchanged.

5.3 Acids, Bases & Buffers

5.3.1 Acids & Bases

Brønsted–Lowry Acids & Bases Theory

- A **Brønsted acid** is a species that can donate a proton
    - For example, hydrogen chloride (HCl) is a Brønsted acid as it can lose a proton to form a hydrogen (H^+) and chloride (Cl^-) ion

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

- A **Brønsted base** is a species that can accept a proton
    - For example, a hydroxide (OH^-) ion is a Brønsted base as it can accept a proton to form water

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

Weak acids dissociating

- In an equilibrium reaction, the products are formed at the same rate as the reactants are used
- This means that at equilibrium, both reactants and products are present in the solution
- For example, ethanoic acid (CH_3COOH) is a weak acid that partially dissociates in solution
- When equilibrium is established there are CH_3COOH, H_2O, CH_3COO^- and H_3O^+ ions present in the solution
- The species that can **donate** a proton are **acids** and the species that can **accept** a proton are **bases**

CH_3COOH (aq)	+	H_2O (l)	⇌	CH_3COO^- (aq)	+	H_3O^+ (aq)
		acid		**base**	**conjugate base**	**conjugate acid**

- The reactant CH_3COOH is linked to the product CH_3COO^- by the transfer of a **proton** from the acid (CH_3COOH) to the base (CH_3COO^-)
- 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 an H^+ ion
    - **Conjugate** here means related
    - In other words, the acid and base are related to each other by one proton difference

Monobasic, dibasic & tribasic acids

- Acids can be classified by the number of bases that they can donate protons to in a reaction, which depends on how many H^+ per molecule that they can give up in a reaction
- Acids such as HCl, HNO_3, and HCN that contain one ionisable hydrogen atom in each molecule are called **monobasic** (or **monoprotic) acids**

  - When HCl reacts with NaOH we can see that **one** hydrogen is replaced by a sodium atom

$$\mathbf{HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (aq)}$$

- **Dibasic** (or **diprotic**) **acids** contain two ionisable hydrogen atoms per molecule, for example H_2SO_4
  - Ionisation of such acids occurs in two steps
  - When H_2SO_4 reacts with NaOH we can see that **two** hydrogens are replaced by two sodium atoms

$$\mathbf{H_2SO_4\ (aq) + 2NaOH\ (aq) \rightarrow Na_2SO_4\ (aq) + 2H_2O\ (aq)}$$

- **Tribasic** (or **triprotic**) **acids** contain three ionisable hydrogen atoms per molecule, for example H_3PO_4
  - Ionisation of such acids occurs in three steps
  - When H_3PO_4 reacts with NaOH we can see that **three** hydrogens are replaced by three sodium atoms

$$\mathbf{H_3PO_4\ (aq) + 3NaOH\ (aq) \rightarrow Na_3PO_4\ (aq) + 3H_2O\ (aq)}$$

The Role of Hydrogen Ions in Equations

- As we have seen previously, metals, alkalis, metal oxides and metal carbonates react with acids to form salts
- We can represent the active species, $H^+\,(aq)$, by writing ionic equations
- Once we have written all the ions in the reaction, we can then cancel them out

Acids and metals

- The typical reaction of a metal and an acid can be summarised as

acid + metal → salt + hydrogen

- For example:

$$2HCl\,(aq) + Zn\,(s) \rightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Becomes

$$2H^+\,(aq) \cancel{+ 2Cl^-\,(aq)} + Zn\,(s) \rightarrow Zn^{2+}\,(aq) \cancel{+ 2Cl^-\,(aq)} + H_2\,(g)$$

$$2H^+\,(aq) + Zn\,(s) \rightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

Acids and metal oxides

- The reaction of an acid with a metal oxide forms two products:

acid + metal oxide → salt + water

- For example:

$$2HCl\,(aq) + CaO\,(s) \rightarrow CaCl_2\,(aq) + H_2O\,(l)$$

Becomes

$$2H^+\,(aq) \cancel{+ 2Cl^-\,(aq)} + CaO\,(s) \rightarrow Ca^{2+}\,(aq) \cancel{+ 2Cl^-\,(aq)} + H_2O\,(l)$$

$$2H^+\,(aq) + CaO(s) \rightarrow Ca^{2+}\,(aq) + H_2O\,(l)$$

Metals and carbonates

- The reaction between a metal carbonate and an acid produces three products:

acid + metal carbonate → salt + water + carbon dioxide

- For example:

$$2HNO_3\,(aq) + CuCO_3\,(s) \rightarrow Cu(NO_3)_2\,(aq) + H_2O\,(l) + CO_2\,(g)$$

Becomes

$$2H^+\,(aq) \cancel{+ 2NO_3^-\,(aq)} + CuCO_3\,(s) \rightarrow Cu^{2+}\,(aq) \cancel{+ 2NO_3^-\,(aq)} + H_2O\,(l) + CO_2\,(g)$$

$$2H^+\,(aq) + CuCO_3\,(s) \rightarrow Cu^{2+}\,(aq) + H_2O\,(l) + CO_2\,(g)$$

- If the carbonate is soluble, e.g. Na_2CO_3

$$2H^+\,(aq) \cancel{+ 2NO_3^-\,(aq) + 2Na^+\,(aq)} + CO_3^{2-}\,(aq) \rightarrow \cancel{2Na^+\,(aq) + 2NO_3^-\,(aq)} + H_2O\,(l) + CO_2\,(g)$$

$$2H^+ (aq) + CO_3^{2-} (aq) \rightarrow H_2O (l) + CO_2 (g)$$

Acids and alkalis

acid + alkali → salt + water

- For example:

$$HCl (aq) + NaOH (aq) \rightarrow NaCl (aq) + H_2O (l)$$

Becomes

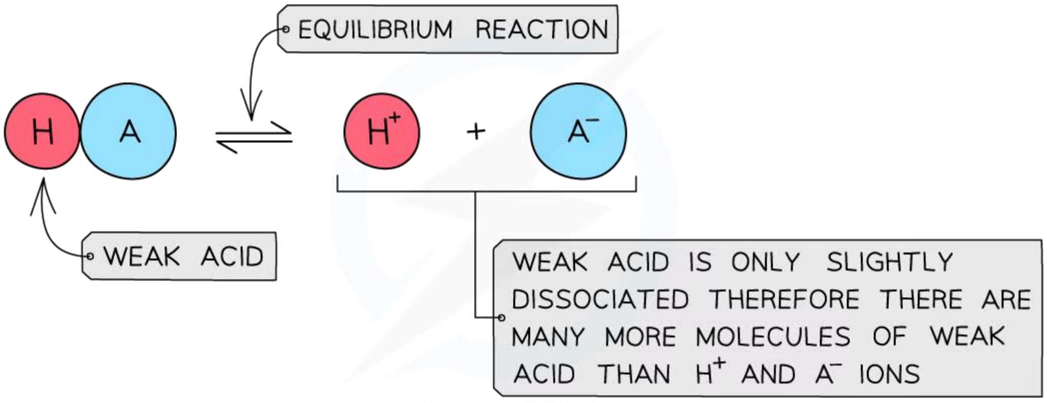
H^+ (aq) ~~+ Cl^- (aq) + Na^+ (aq)~~ + OH^- (aq) → ~~Na^+ (aq) + Cl^- (aq)~~ + H_2O (l)

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

The Acid Dissociation Constant, Ka

Weak acids

- A **weak acid** is an acid that **partially** (or incompletely) **dissociates** in aqueous solutions
  - Eg. most organic acids (ethanoic acid), HCN (hydrocyanic acid), H_2S (hydrogen sulfide) and H_2CO_3 (carbonic acid)
- The position of the equilibrium is more over to the **left** and an equilibrium is established



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The diagram shows the partial dissociation of a weak acid in aqueous solution

- As this is an equilibrium we can write an equilibrium constant expression for the reaction

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

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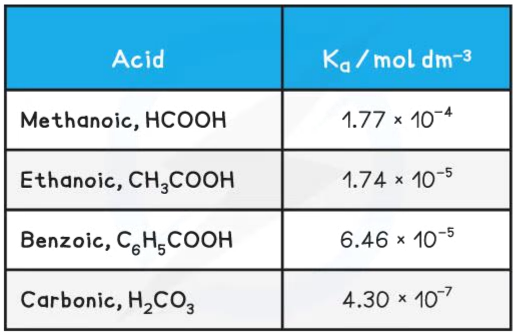
- This constant is called the **acid dissociation constant**, K_a, and has the units mol dm^{-3}
- Values of K_a are very small, for example for ethanoic acid $K_a = 1.74 \times 10^{-5}$ mol dm^{-3}
- When writing the equilibrium expression for weak acids, the following assumptions are made:
  - The concentration of hydrogen ions due to the ionisation of water is negligible
- The value of K_a indicates the extent of dissociation
  - The higher the value of K_a the more dissociated the acid and the stronger it is
  - The lower the value of K_a the weaker the acid

pK_a

- The range of values of K_a is very large and for weak acids, the values themselves are very small numbers

Table of K_a values



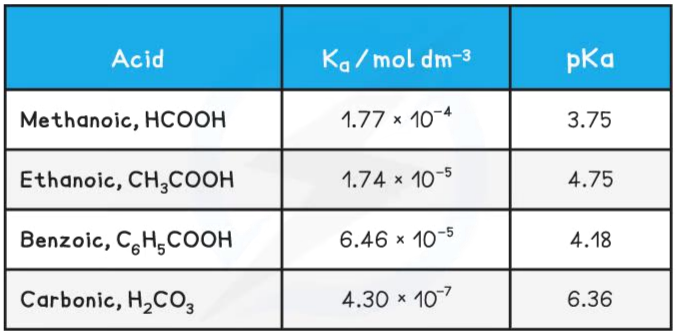
Acid	K_a / mol dm^{-3}
Methanoic, HCOOH	1.77×10^{-4}
Ethanoic, CH_3COOH	1.74×10^{-5}
Benzoic, C_6H_5COOH	6.46×10^{-5}
Carbonic, H_2CO_3	4.30×10^{-7}

- For this reason it is easier to work with another term called **pK_a**
- The **pK_a** is the negative log of the **K_a** value, so the concept is analogous to converting [H^+] into pH values

$$pK_a = -\log K_a$$

- Looking at the pK_a values for the same acids:

Table of pK_a values



Acid	K_a / mol dm^{-3}	pKa
Methanoic, HCOOH	1.77×10^{-4}	3.75
Ethanoic, CH_3COOH	1.74×10^{-5}	4.75
Benzoic, C_6H_5COOH	6.46×10^{-5}	4.18
Carbonic, H_2CO_3	4.30×10^{-7}	6.36

- The range of pK_a values for most weak acids lies between 3 and 7

pH & The Ionic Product of Water, Kw

pH

- The acidity of an aqueous solution depends on the number of **H^+** (**H_3O^+**) ions in solution
- The **pH** is defined as:

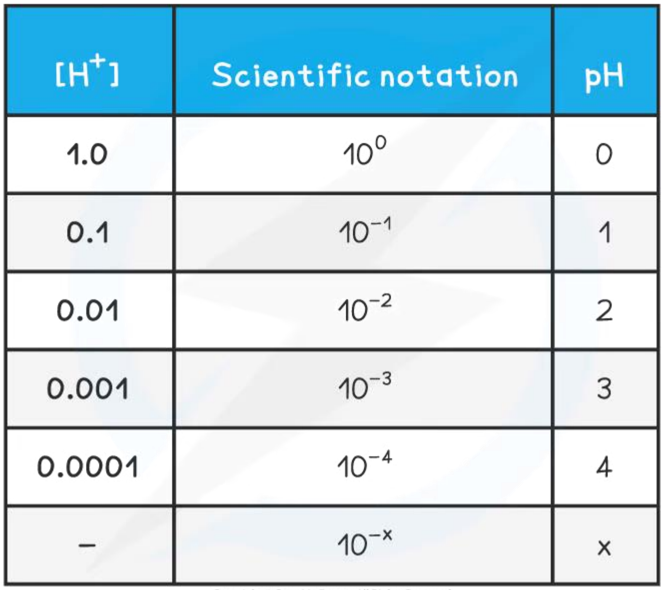
$$\mathbf{pH = -log[H^+]}$$

-
  - where $[H^+]$ is the concentration of hydrogen ions in mol dm^{-3}
- Similarly, the **concentration of H^+** of a solution can be calculated if the pH is known by rearranging the above equation to:

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

- The pH scale is a logarithmic scale with base 10
- This means that each value is 10 times the value below it. For example, pH 5 is 10 times more acidic than pH 6.
- pH values are usually given to 2 decimal places
- The relationship between concentration is easily seen on the following table

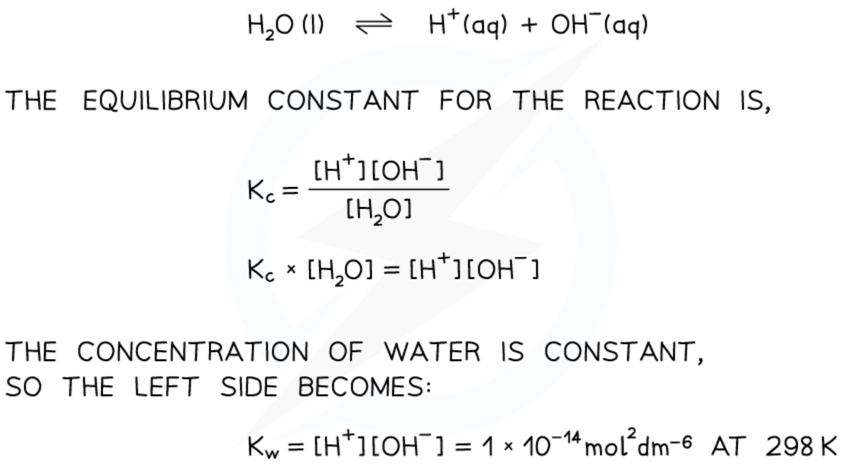
pH & [H+] Table



$[H^+]$	Scientific notation	pH
1.0	10^{0}	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
–	10^{-x}	x

The ionic product of water, K_w

- In all aqueous solutions, an equilibrium exists in water where a few water molecules dissociate into protons and hydroxide ions
- We can derive an equilibrium constant for the reaction:



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

THE EQUILIBRIUM CONSTANT FOR THE REACTION IS,

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

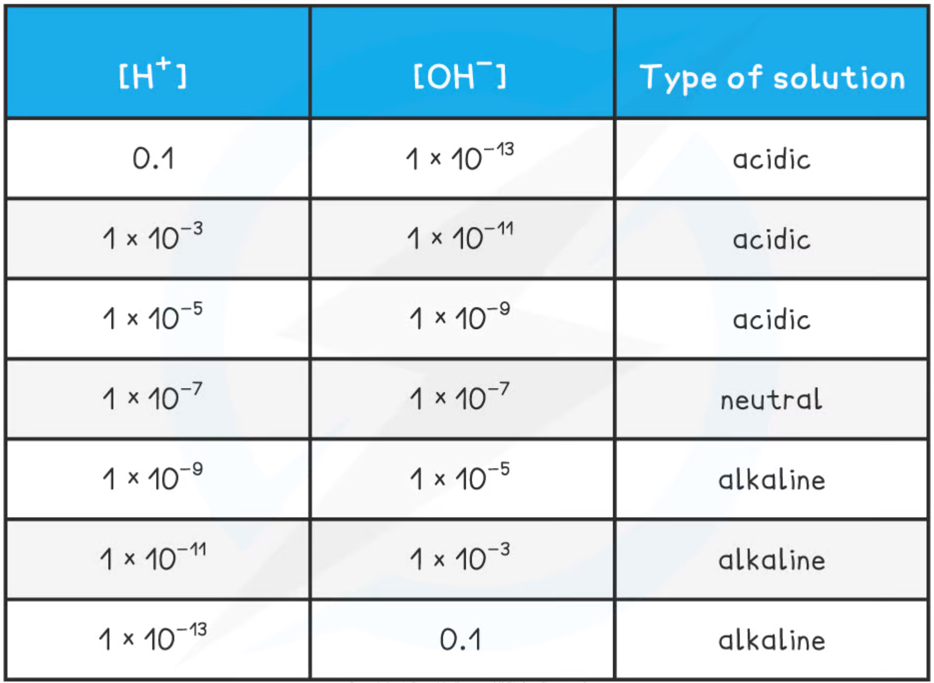
$$K_c \times [H_2O] = [H^+][OH^-]$$

THE CONCENTRATION OF WATER IS CONSTANT,
SO THE LEFT SIDE BECOMES:

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}\,mol^2dm^{-6} \text{ AT } 298\,K$$

- This is a specific equilibrium constant called the **ionic product for water**
- The product of the two ion concentrations is *always* **1×10^{-14} mol^2 dm^{-6}**
- This makes it straightforward to see the relationship between the two concentrations and the nature of the solution:

$[H^+]$ & $[OH^-]$ Table



$[H^+]$	$[OH^-]$	Type of solution
0.1	1×10^{-13}	acidic
1×10^{-3}	1×10^{-11}	acidic
1×10^{-5}	1×10^{-9}	acidic
1×10^{-7}	1×10^{-7}	neutral
1×10^{-9}	1×10^{-5}	alkaline
1×10^{-11}	1×10^{-3}	alkaline
1×10^{-13}	0.1	alkaline

pH Calculations for Strong Acids & Bases

Strong acids

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

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

- Therefore, the concentration of hydrogen ions, H^+, is **equal** to the concentration of acid, HA
- The number of hydrogen ions formed from the ionisation of water is **very small** relative to the $[H^+]$ due to ionisation of the strong acid and can therefore be **neglected**
- The **total** $[H^+]$ is therefore the same as the [HA]

Worked Example

What is the pH of 0.01 mol dm^{-3} hydrochloric acid?

Answer

$[HCl] = [H^+] = 0.01$ mol dm^{-3}

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

$pH = -\log[0.01] = 2.00$

Strong bases

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

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

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

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

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$pH = -\log[H^+] = -\log\left(\frac{1 \times 10^{-14}}{[OH^-]}\right)$$

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

Worked Example

Question 1: Calculate the pH of 0.15 mol dm^{-3} sodium hydroxide, NaOH

Question 2: Calculate the hydroxide concentration of a solution of sodium hydroxide when the pH is 10.50

Answer

Sodium hydroxide is a strong base which ionises as follows:

$$\mathbf{NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)}$$

Answer 1:

The pH of the solution is:

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

$[H^+] = (1 \times 10^{-14}) \div 0.15 = 6.66 \times 10^{-14}$

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

$= -\log 6.66 \times 10^{-14}$ **= 13.17**

Answer 2

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

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

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

$[H^+] = 10^{-10.50}$

$[H^+] = 3.16 \times 10^{-11}$ mol dm^{-3}

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

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

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

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

Since K_w is 1×10^{-14} $mol^2\ dm^{-6}$,

$[OH^-] = (1 \times 10^{-14}) \div (3.16 \times 10^{-11})$

$[OH^-] =$ **3.16×10^{-4} mol dm^{-3}**

Worked Example

What is the pH of a solution of hydroxide ions of concentration 1.0×10^{-3} mol dm^{-3} ?

$K_w = 1 \times 10^{-14}$ $mol^2\ dm^{-6}$

A. 3.00

B. 4.00

C. 10.00

D. 11.00

Answer

The correct option is **D**

Since $K_w = [H^+]\ [OH^-]$, rearranging gives $[H^+] = K_w \div [OH^-]$

The concentration of $[H^+]$ is $(1 \times 10^{-14}) \div (1.0 \times 10^{-3}) = 1.0 \times 10^{-11}$ mol dm^{-3}

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

So the **pH = 11.00**

pH Calculations for Weak Acids

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
- From the K_a expression we can see that there are three variables:

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

- However, the equilibrium concentration of $[H^+]$ and $[A^-]$ will be the same since one molecule of HA dissociates into one of each ion
- This means you can simplify and re-arrange the expression to

$$K_a \text{ x } [HA] = [H^+]^2$$

$$[H^+]^2 = K_a \text{ x } [HA]$$

- Taking the square roots of each side

$$[H^+] = \sqrt{(K_a \text{ x } [HA])}$$

- Then take the negative logs

$$pH = -\log[H^+] = -\log\sqrt{(K_a \text{ x } [HA])}$$

Worked Example

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

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

Step 2: Simplify the expression

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

The concentration of H^+ and CH_3COO^- ions are therefore the same

The expression can be simplified to:

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

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

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

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

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

$$= 1.32 \times 10^{-3} \text{ mol dm}^{-3}$$

Step 5: Find the pH

pH = –log$[H^+]$

= –log(1.32×10^{-3})

= 2.88

Limitations of Ka

We must make assumptions when calculating the pH of a **weak acid**

- $[H^+]$ at equilibrium is **equal** to the $[A^-]$ at equilibrium because they have dissociated according to a 1:1 ratio
  - This is because the amount of H^+ from the dissociation of water is insignificant
- The amount of dissociation is so small that we assume that the initial concentration of the undissociated acid has **remained constant**
  - So initial [HA] is equal to the [HA] at equilibrium

The strength of acid

- The stronger the acid the greater the concentration of hydrogen ions in the solution at equilibrium
  - This corresponds to a **larger value for K_a**
  - If the acid is stronger, the **dissociation will be greater**, therefore the difference in the values for initial [HA] and [HA] at equilibrium will be greater

5.3.4 Buffers

Buffer Solutions

- A **buffer solution** is a solution which resists changes in pH when small amounts of acids or alkalis are added
  - A buffer solution is used to keep the pH almost constant
  - A buffer can consists of **weak acid - conjugate base** or **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 is a **weak acid** and partially ionises in solution to form a relatively low concentration of **ethanoate ions**

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

Ethanoic acid (high conc.)

ethanoate ion (low conc.)

- Sodium ethanoate is a **salt** which fully ionises in solution

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

Sodium ethanoate (low conc.)

ethanoate ion (high conc.)

- 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 partial ionisation of **ethanoic acid**) and CH_3COO^- (due to full ionisation of **sodium ethanoate**)

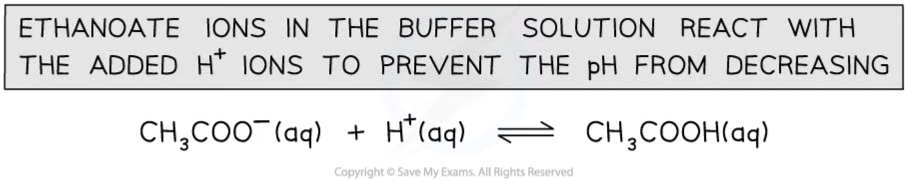
- In the **buffer solution**, the ethanoic acid is **in equilibrium** with hydrogen and ethanoate ions

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

(high conc.)

(high conc.)

- **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 hydrogen ions are added to the solution the pH of the solution would decrease; However, the ethanoate ions in the buffer solution react with the hydrogen ions to prevent this and keep the pH constant

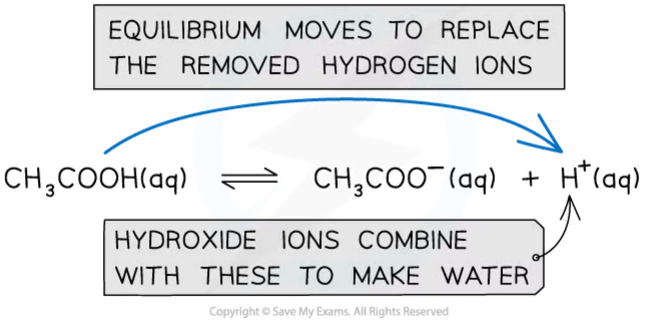
- **When OH^- ions are added:**
    - The OH^- reacts with H^+ to form water

$$\mathbf{OH^- (aq) + H^+ (aq) \rightarrow H_2O (l)}$$

-
    - 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

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

-
    - 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



When hydroxide ions are added to the solution, the hydrogen ions react with them to form water; The decrease in hydrogen ions would mean that the pH would increase however the equilibrium moves to the right to replace the removed hydrogen ions and keep the pH constant

Calculating the pH of a Buffer Solution

- 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

$$K_a = \frac{[salt]\,[H^+]}{[acid]} \text{ which can be rearranged to } [H^+] = K_a \times \frac{[acid]}{[salt]}$$

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

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

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

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

- This is known as the Hendersen-Hasselbalch equation

Worked Example

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

The K_a of ethanoic acid $= 1.74 \times 10^{-5}$ mol dm^{-3} at 298 K

Answer

Ethanoic acid is a weak acid that ionises as follows:

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

Step 1: Write down the equilibrium expression to find K_a

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

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

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

Step 3: Substitute the values into the expression

$$[H^+] = 1.74 \times 10^{-5} \times \frac{0.305}{0.520}$$

$$\mathbf{= 1.02 \times 10^{-5}\ mol\ dm^{-3}}$$

Step 4: Calculate the pH

pH = - log [H+]

= –log 1.02 x 10^{-5}

= 4.99

Uses of Buffers

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 blood to form a solution containing H^+ ions

$$CO_2 (g) + H_2O (l) \rightleftharpoons H^+ (aq) + HCO_3^- (aq)$$

- 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

$$H^+ (aq) + HCO_3^- (aq) \rightleftharpoons CO_2 (g) + H_2O (l)$$

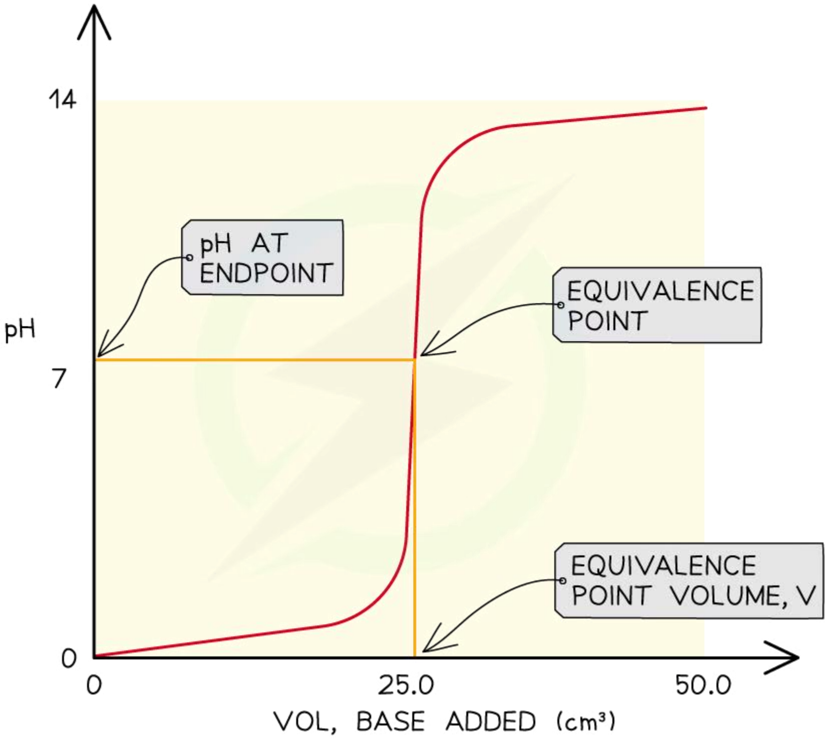
- This reduces the concentration of H^+ and keeps the pH of the blood **constant**
- **If there is a decrease in H^+ ions**
  - The equilibrium position shifts to the **right** until equilibrium is restored

$$CO_2 (g) + H_2O (l) \rightleftharpoons H^+ (aq) + HCO_3^- (aq)$$

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

pH Titration Curves

- During a titration a pH meter can be used and a pH curve plotted
- A pH curve is a graph showing how the pH of a solution changes as the acid (or base) is added
- The result is characteristically shaped graph which can yield useful information about how the particular acid and alkali react together with stoichiometric information



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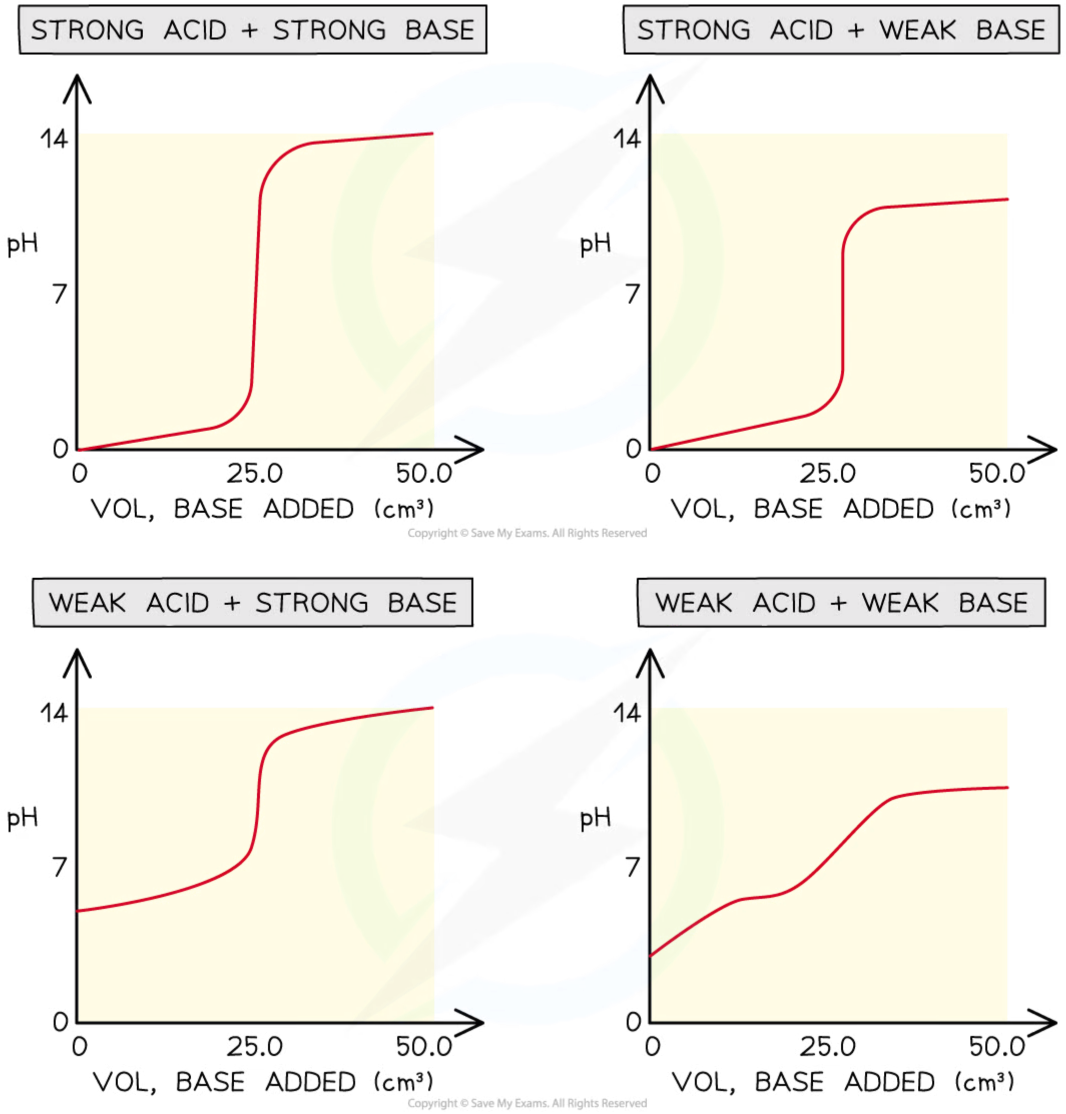
The features of a pH curve

- All pH curves show an s-shape curve and the midpoint of the inflection is called the **equivalence** or **stochiometric point**
- From the curves you can
  - Determine the pH of the acid by looking where the curve starts on the y-axis
  - Find the pH at the equivalence point
  - Find volume of base at the equivalence point
  - Obtain the range of pH at the vertical section of the curve

Four types of acid-base titrations

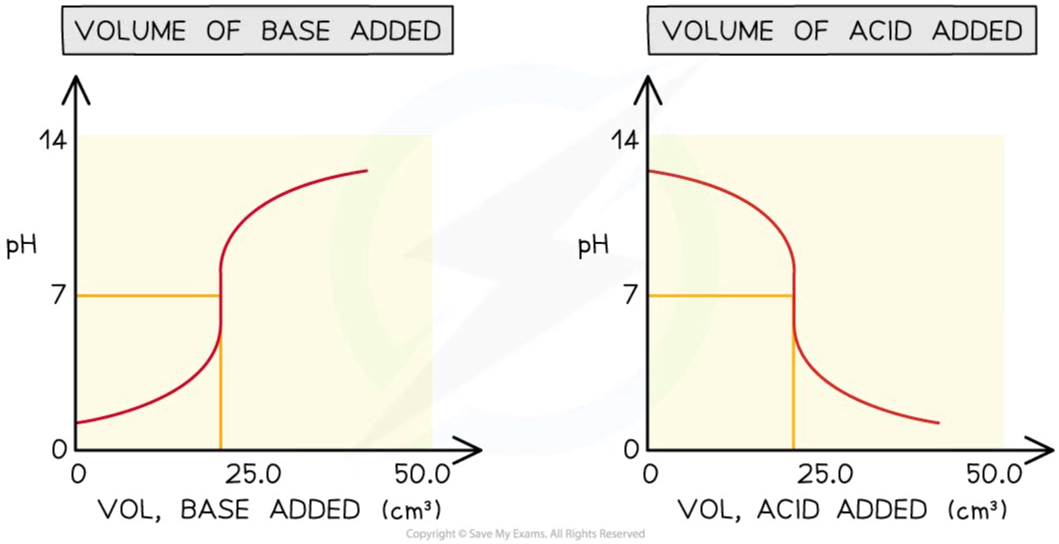
- There are four combinations of acids and alkalis that you should know about:
  - strong acid + strong base
  - weak acid + strong base
  - strong acid + weak base

  - weak acid + weak base



pH curves for the four types of acid–base titrations

- Without titles for the graph you can easily recognise which combination is shown by looking at the starting and ending pH and deducing whether the acid and alkali are strong or weak
- Sometimes you may see pH titration curves which show pH plotted against volume of acid added
- This produces the mirror image graph from which you can get all the same information



Comparing different versions of pH titration curves

Choosing an Indicator for a pH Titration

- An **acid-base indicator** is a weak acid which dissociates to give an anion of a different colour
- Consider a weak acid HIn:

$$\mathbf{HIn\ (aq)\ +\ H_2O\ (l)\ \rightleftharpoons\ H_3O^+\ (aq)\ +\ In^-\ (aq)}$$

colour 1 **colour 2**

- HIn and its **conjugate base** In^- are different colours
- The colour of the solution depends on the relative concentrations of the two species
- If the solution is **acidic**, the above equilibrium will be shifted to the left and more HIn will be present
  - **Colour 1** will thus dominate
- If the solution is **alkaline**, the above equilibrium will shift to the right and more In^- will be present
  - **Colour 2** will thus dominate
- The colour of the indicator thus depends on the pH of the solution
- The colour will not change suddenly at a certain pH, but will change gradually over a pH range
- The colour of the indicator depends on the ratio of [HIn] to $[In^-]$
- The pH at which these transitions will occur depends on the K_a of the indicator

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

- The endpoint of the reaction is where there is a balance between [HIn] and $[In^-]$. At this point these two concentrations are equal

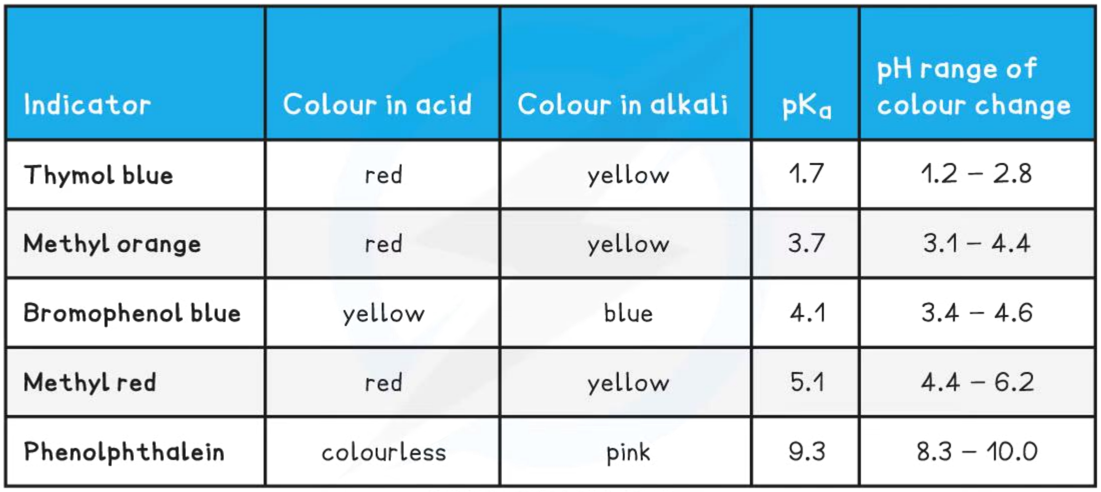
$$K_a = \frac{[H^+][\cancel{In^-}]}{[\cancel{HIn}]} = [H^+]$$

- Taking negative logs of both sides:

$$\mathbf{p}K_a = \mathbf{pH}$$

- This means the pK_a of an indicator is the same as the pH of its endpoint

Common Indicators and their colours table



Indicator	Colour in acid	Colour in alkali	pK_a	pH range of colour change
Thymol blue	red	yellow	1.7	1.2 – 2.8
Methyl orange	red	yellow	3.7	3.1 – 4.4
Bromophenol blue	yellow	blue	4.1	3.4 – 4.6
Methyl red	red	yellow	5.1	4.4 – 6.2
Phenolphthalein	colourless	pink	9.3	8.3 – 10.0

Choosing a suitable indicator

- Around the equivalence point of a titration, the pH changes very rapidly
- **Indicators** change colour over a narrow pH range approximately centred around the pK_a of the indicator
- An indicator will be appropriate for a titration if the pH range of the indicator falls within the rapid pH change for that titration

Strong acid-strong base

- In strong acid – strong base titrations, the pH changes from 4 to 10 at the end-point so a suitable indicator must change colour within this range
    - **Methyl red** and **phenolphthalein** are suitable indicators for these titrations
    - **Methyl orange** is not ideal but it shows a significant enough colour change at the end point so is widely used

Weak acid-strong base

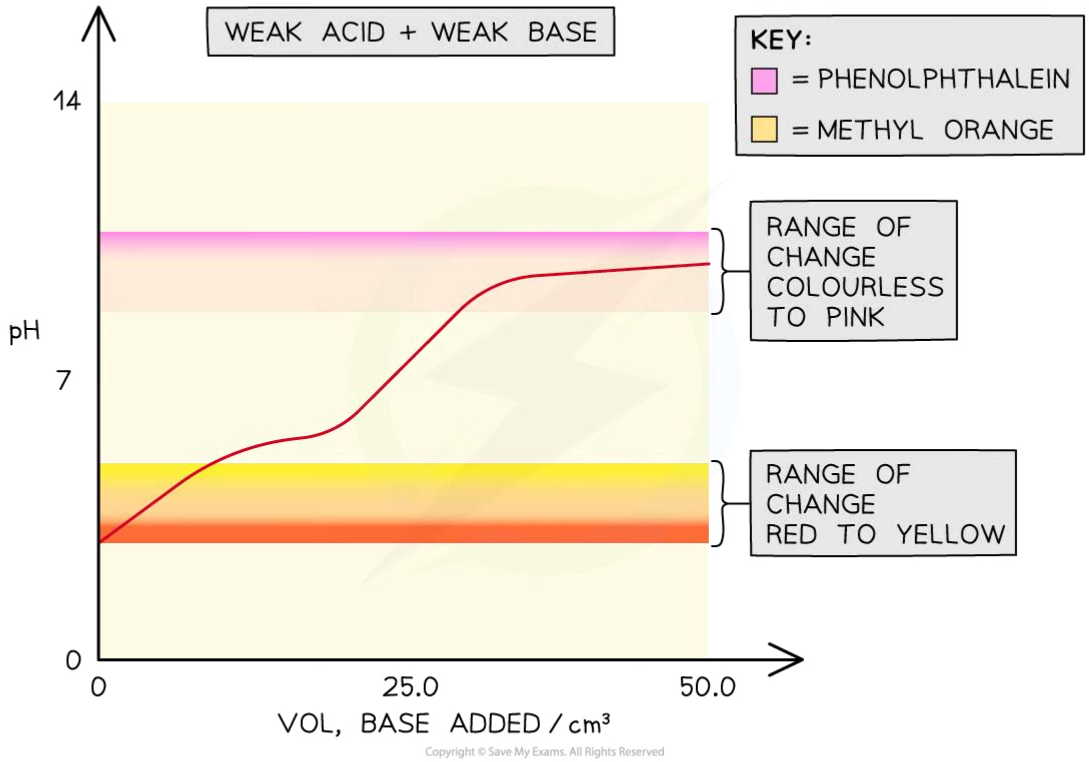
- In weak acid – strong base titrations, the pH changes from 7 to 10 at the end-point so a suitable indicator must change colour within this range
    - **Phenolphthalein** is the only suitable indicator for weak acid – strong base titrations that is widely available

Strong acid-weak base

- In strong acid – weak base titrations, the pH changes from 4 to 7 at the end-point so a suitable indicator must change colour within this range
    - **Methyl red** is the most suitable indicator for these titrations
    - However **methyl orange** is often used since it shows a significant enough colour change at the end-point and is more widely available than methyl red

Weak acid-weak base

- In weak acid –weak alkali titrations, there is **no sudden pH change** at the end-point and thus there are **no suitable indicators** for these titrations
- The end-points of these titrations cannot be easily determined



The overlay on the graph shows that both phenolphthalein and methyl orange would change colour outside the point of inflection in a weak acid–weak base titration so they would not be able to show the equivalence point of the titration

5.4 Thermodynamics

5.4.1 Lattice Enthalpy

Thermodynamic Terms

- **Thermodynamics** literally means *heat* and *movement* and is the branch of physical chemistry that deals with heat, energy, temperature and the physical properties of matter
- Energy cycles are special representations of enthalpy changes for ionic compounds using the principles of Hess's Law
- In order to understand how energy cycles work you need a good knowledge of some key **enthalpy change** definitions
- **Enthalpy change** (ΔH) refers to the amount of heat energy **transferred** during a chemical reaction, at a constant pressure
- The definitions you need to know are:
    - enthalpy of formation
    - ionisation enthalpy
    - enthalpy of atomisation
    - bond enthalpy
    - electron affinity

Enthalpy of formation

- The **enthalpy of formation** ($\Delta H_f^{\ominus}$) is the **enthalpy change** when **1 mole of a compound** is formed from its **elements** under standard conditions
    - Standard conditions in this syllabus are a temperature of 298 K and a pressure of 100 kPa
- The $\Delta H_f^{\ominus}$ can be **endothermic** or **exothermic** as the energy change is the sum of the bonds broken and formed, so the enthalpy change can have **positive** or **negative** values
- Equations can be written to show the standard enthalpy change of formation $(\Delta H^{\ominus})_f$ for compounds
- For example, the enthalpy of formation sodium chloride is shown as:

$$\text{Na (s)} + \tfrac{1}{2}\text{Cl}_2\text{ (g)} \rightarrow \text{NaCl (s)} \qquad \Delta H_f^{\ominus} = -411 \text{ kJ mol}^{-1}$$

- Notice that enthalpy of formation only refers to *compounds*
    - By definition the enthalpy of formation of elements is **zero**

Ionisation enthalpy

- The **ionisation enthalpy** ($\Delta H_{ie}^{\ominus}$) of an element is the amount of energy required to remove an electron from a gaseous atom of an element to form a gaseous ion under standard conditions
- **Ionisation enthalpy** is always endothermic as energy is need to overcome the attraction between an electron and the nucleus
- The **first ionisation energy** is the energy required to remove **one mole of electrons** from one mole of gaseous atoms of an element to form one mole of

gaseous 1+ ions

  - E.g. the first ionisation energy of gaseous sodium:

$$\mathbf{Na\,(g) \rightarrow Na^{+}\,(g) + e^{-} \qquad \Delta H_{ie}^{\ominus} = +500\ kJ\ mol^{-1}}$$

Enthalpy change of atomisation

- The **standard enthalpy change of atomisation** ($\Delta H_{at}^{\ominus}$) is the **enthalpy change** when **1 mole of gaseous atoms** is formed from its **element** under standard conditions
- The $\Delta H_{at}^{\ominus}$ is always **endothermic** as energy is always required to **break** any bonds between the atoms in the element, to break the element into its gaseous atoms
  - Since this is always an endothermic process, the enthalpy change will always have a **positive** value

- Equations can be written to show the standard enthalpy change of atomisation ($\Delta H_{at}^{\ominus}$) for elements
- For example, sodium in its elemental form is a **solid**
- The standard enthalpy change of atomisation for sodium is the energy required to form 1 mole of **gaseous** sodium atoms:

$$\mathbf{Na\,(s) \rightarrow Na\,(g) \qquad \Delta H_{at}^{\ominus} = +108\ kJ\ mol^{-1}}$$

Bond enthalpy

- The amount of energy required to break one mole of a **specific** covalent bond in the gas phase is called the bond dissociation energy
  - Bond dissociation energy (*E*) is usually just simplified to **bond energy** or **bond enthalpy**

- In symbols, the type of bond broken is written in brackets after *E*
  - Eg. *E* (H–H) is the bond energy of a mole of single bonds between two hydrogen atoms

- **Bond enthalpy** is usually treated as a bond breaking process, so it is quoted in data tables as an **endothermic** energy change with **positive** values
  - For bond forming processes simply put a negative sign in front of the value

- Equations can be written to show the bond enthalpy
- For example, chlorine in its elemental form is a gas
- The bond enthalpy of chlorine is shown as

$$\mathbf{Cl_2\,(g) \rightarrow 2Cl\,(g) \qquad E(Cl–Cl) = +242\ kJ\ mol^{-1}}$$

- Notice this looks very similar to atomisation enthalpy for chlorine
- However, atomisation enthalpy, by definition, produces **1 mole of atoms**, whereas bond enthalpy is expressed per **mole of bonds**
- So the atomisation enthalpy of chlorine would be half the bond enthalpy

$$\mathbf{½Cl_2\,(g) \rightarrow Cl\,(g) \qquad \Delta H_{at}^{\ominus} = +121\ kJ\ mol^{-1}}$$

- If the element was a liquid, instead of a gas, then atomisation enthalpy would also include vaporisation enthalpy – a change of state, before the bonds are broken

Lattice energy

- As with bond enthalpy, **lattice enthalpy** ($\Delta H_{latt}^{\square}$) can be expressed as a formation or dissociation process
- As a formation process, it is the enthalpy change when **1 mole** of an **ionic compound** is formed from its **gaseous ions** (under standard conditions)
- The $\Delta H_{latt}^{\square}$ is therefore **exothermic,** as when ions are **combined** to form an **ionic solid lattice** there is an extremely large release of energy
  - Since this is an exothermic process, the enthalpy change will have a **negative** value
  - Because of the huge release in energy when the gaseous ions combine, the value will be a very **large negative** value

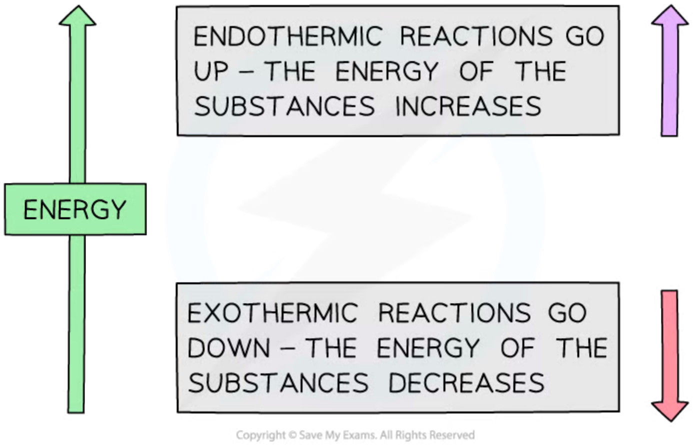
- The large negative value of $\Delta H_{latt}^{\square}$ suggests that the **ionic compound** is much more **stable** than its **gaseous ions**
  - This is due to the **strong electrostatic forces of attraction** between the oppositely charged ions in the solid lattice
  - Since there are no electrostatic forces of attraction between the ions in the gas phase, the gaseous ions are **less stable** than the ions in the **ionic lattice**
  - The **more exothermic** the value is, the **stronger the ionic bonds** within the lattice are

- The $\Delta H_{latt}^{\square}$ of an ionic compound **cannot** be determined **directly** by one single experiment
- Multiple experimental values and an **energy cycle** are used to find the $\Delta H_{latt}^{\square}$ of ionic compounds
- The lattice energy ($\Delta H_{latt}^{\square}$) of an ionic compound can be written as an equation
  - For example, sodium chloride is an ionic compound formed from sodium (Na^+) and chloride (Cl^-) ions
  - Since the lattice energy is the enthalpy change when 1 mole of sodium chloride is formed from gaseous sodium and chloride ions, the equation for this process is:

$$\mathbf{Na^+(g) + Cl^-(g) \rightarrow NaCl\ (s)\quad \Delta H_{latt}^{\square} = -776\ kJ\ mol^{-1}}$$

Born-Haber Cycles - Construction

- A **Born-Haber cycle** is a specific application of Hess's Law for ionic compounds and enable us to calculate lattice enthalpy which cannot be found by experiment
- The basic principle of drawing the cycle is to construct a diagram in which energy increases going up the diagram

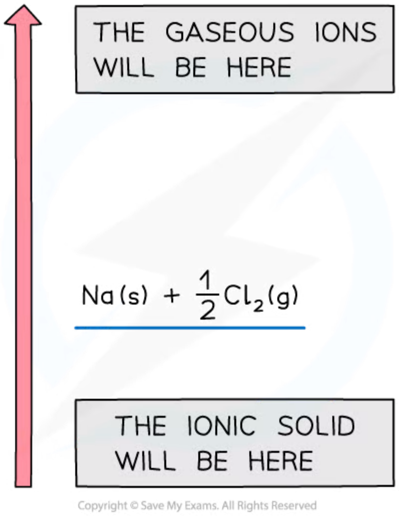


The basic principle of a Born-Haber cycle

- The cycle shows all the steps needed to turn atoms into gaseous ions and from gaseous ions into the ionic lattice
- The alternative route to the ionic lattice begins from the enthalpy of formation of the elements in their standard states

Drawing the cycle for sodium chloride

- A good starting point is to draw the elements with their state symbols about a third of the way up the diagram
- This is shown as the left hand side of the equation for the process indicated
- The location is marked by drawing a horizontal bar or line which represents the starting energy level



Drawing a Born–Haber cycle step 1

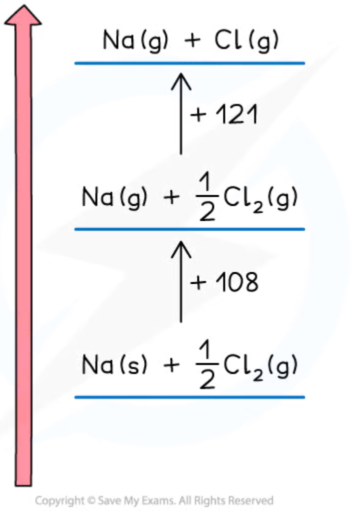
- Next, we need to create the gaseous ions
- This is a two step process of first creating the gaseous atoms and then turning them into ions
- Creating gaseous atoms is a bond breaking process, so arrows must be drawn upwards
- It doesn't matter whether you start with sodium or chlorine
- The enthalpy of atomisation of sodium is

$$\text{Na (s)} \rightarrow \text{Na (g)} \qquad \Delta H_{at}^{\circ} = +108 \text{ kJ mol}^{-1}$$

- The enthalpy of atomisation of chlorine is

$$\tfrac{1}{2}\text{Cl}_2\text{ (g)} \rightarrow \text{Cl (g)} \qquad \Delta H_{at}^{\circ} = +121 \text{ kJ mol}^{-1}$$

- We can show the products of the process on the horizontal lines and the energy value against a vertical arrow connecting the energy levels



Drawing a Born–Haber cycle step 2 - creating the gaseous atoms

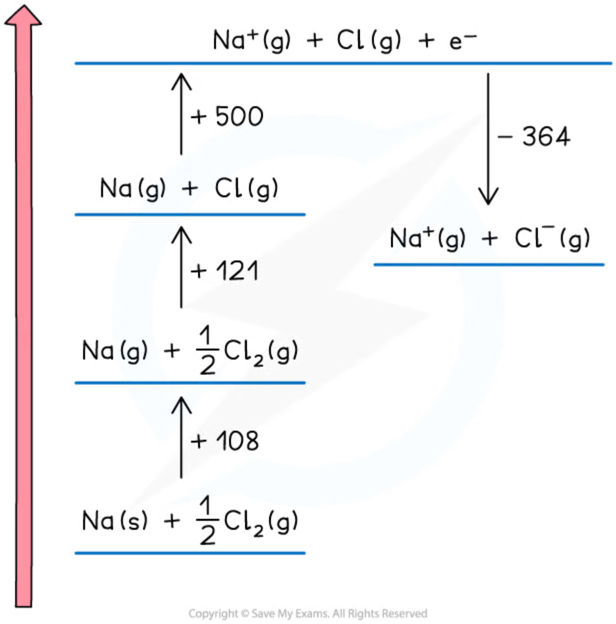
- Now the ions are created
- The sodium ion loses an electron, so this energy change is the first ionisation energy for sodium

$$\mathrm{Na\,(g)} \rightarrow \mathrm{Na^{+}\,(g)} + e^{-} \qquad \Delta H_{ie}^{\circ} = +500\ \mathrm{kJ\ mol^{-1}}$$

- The change is endothermic so the direction continues upwards
- The chlorine atom gains an electron, so this is electron affinity

$$\mathrm{Cl\,(g)} + e^{-} \rightarrow \mathrm{Cl^{-}\,(g)} \qquad \Delta H_{ea}^{\circ} = -364\ \mathrm{kJ\ mol^{-1}}$$

- The exothermic change means this is downwards
- The change is displaced to the right to make the diagram easier to read



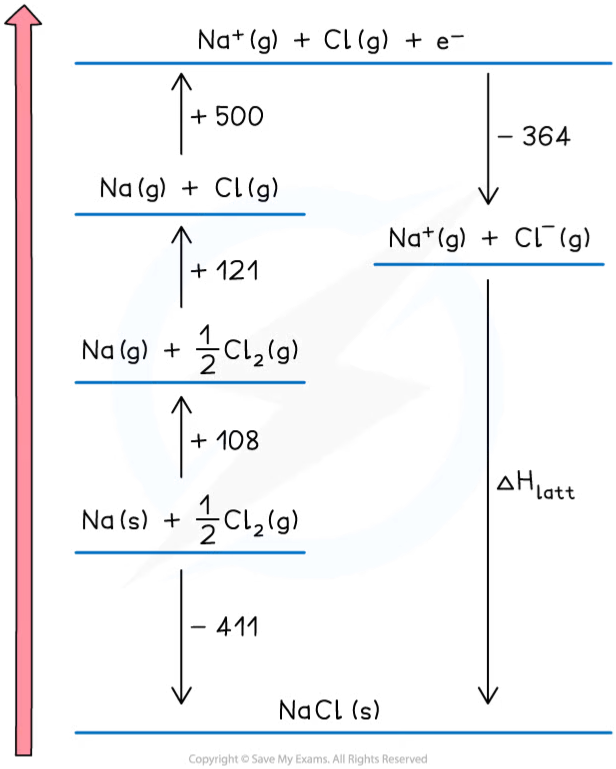
Drawing a Born–Haber cycle step 3 - creating the gaseous ions

- The two remaining parts of the cycle can now be completed
- The enthalpy of formation of sodium chloride is added at the bottom of the diagram

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{Cl_2\,(g)} \rightarrow \mathrm{NaCl\,(s)} \qquad \Delta H_{f}^{\circ} = -411\ \mathrm{kJ\ mol^{-1}}$$

- This is an exothermic change for sodium chloride so the arrow points downwards
- Enthalpy of formation can be exothermic or endothermic, so you may need to show it above the elements (and displaced to the right) for a endothermic change
- The final change is lattice enthalpy, which is usually shown a formation. For sodium chloride the equation is

$$\mathrm{Na^{+}(g)} + \mathrm{Cl^{-}(g)} \rightarrow \mathrm{NaCl\,(s)} \quad \Delta H_{latt}^{\circ}$$

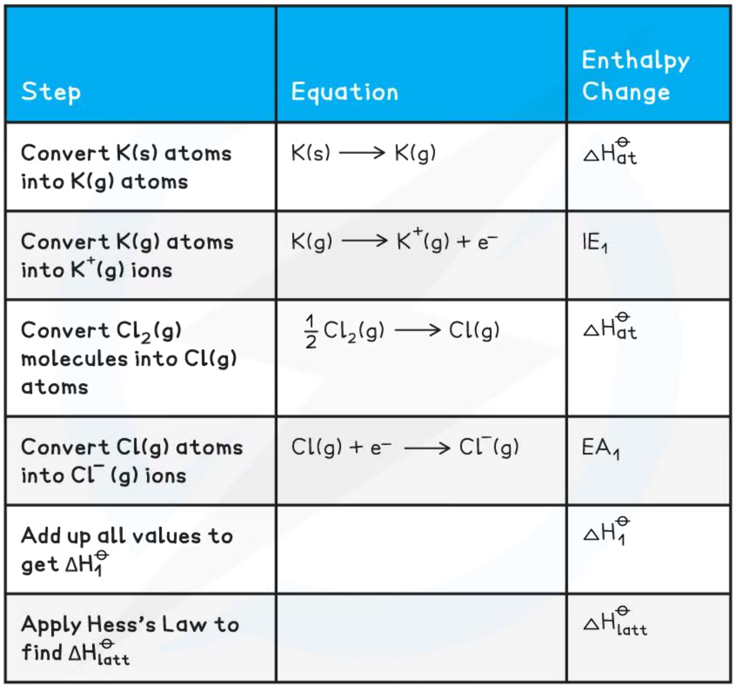


Drawing a Born–Haber cycle step 4 - completing the cycle

- The cycle is now complete
- The cycle is usually used to calculate the lattice enthalpy of an ionic solid, but can be used to find other enthalpy changes if you are given the lattice enthalpy

Worked Example

Construct a Born-Haber Cycle which can be used to calculate the lattice energy of potassium chloride.



Step	Equation	Enthalpy Change
Convert K(s) atoms into K(g) atoms	$K(s) \longrightarrow K(g)$	$\Delta H^\ominus_{at}$
Convert K(g) atoms into $K^+(g)$ ions	$K(g) \longrightarrow K^+(g) + e^-$	IE_1
Convert $Cl_2(g)$ molecules into Cl(g) atoms	$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	$\Delta H^\ominus_{at}$
Convert Cl(g) atoms into $Cl^-(g)$ ions	$Cl(g) + e^- \longrightarrow Cl^-(g)$	EA_1
Add up all values to get $\Delta H^\ominus_1$		$\Delta H^\ominus_1$
Apply Hess's Law to find $\Delta H^\ominus_{latt}$		$\Delta H^\ominus_{latt}$

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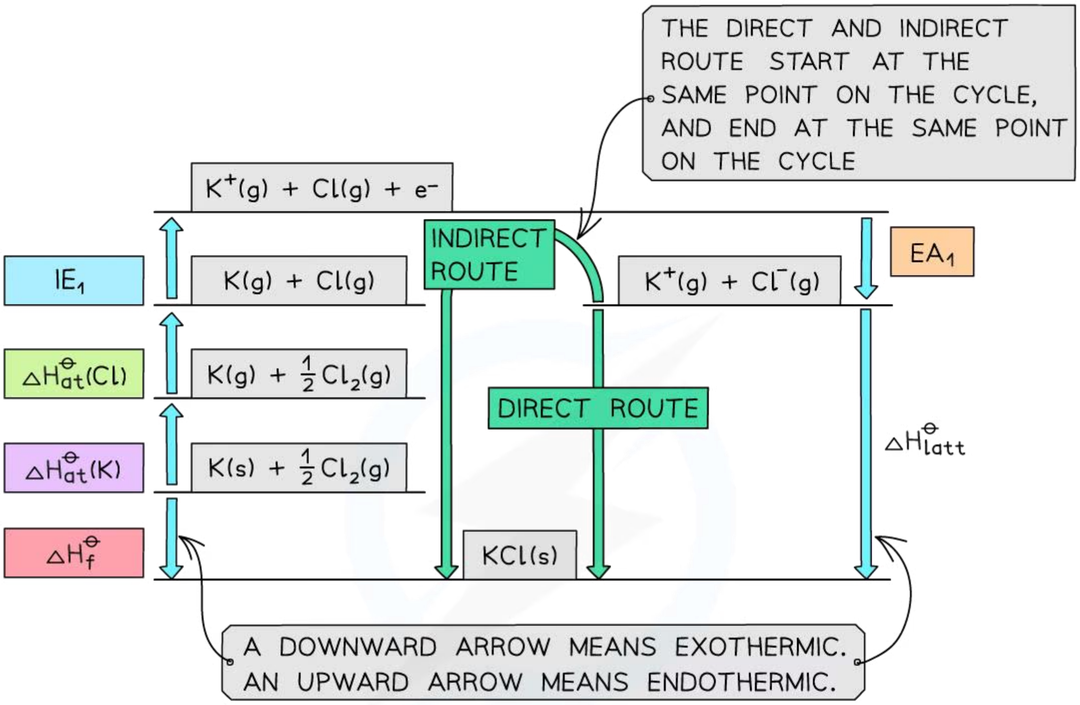
Answer

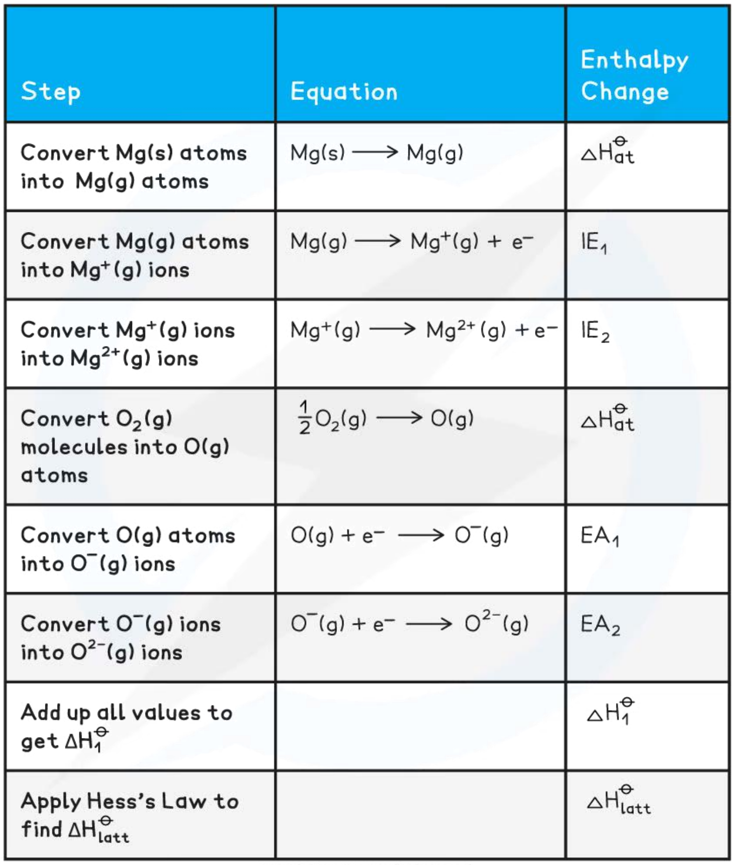


$$\Delta H_f^\ominus = \left(\Delta H_{at}^\ominus(K)\right) + \left(\Delta H_{at}^\ominus(Cl)\right) + \left(IE_1\right) + \left(EA_1\right) + \left(\Delta H_{latt}^\ominus\right)$$

$$\therefore \Delta H_{latt}^\ominus = \left(\Delta H_f^\ominus\right) \underbrace{- \left(EA_1\right) - \left(IE_1\right) - \left(\Delta H_{at}^\ominus(Cl)\right) - \left(\Delta H_{at}^\ominus(K)\right)}_{\Delta H_1^\ominus}$$

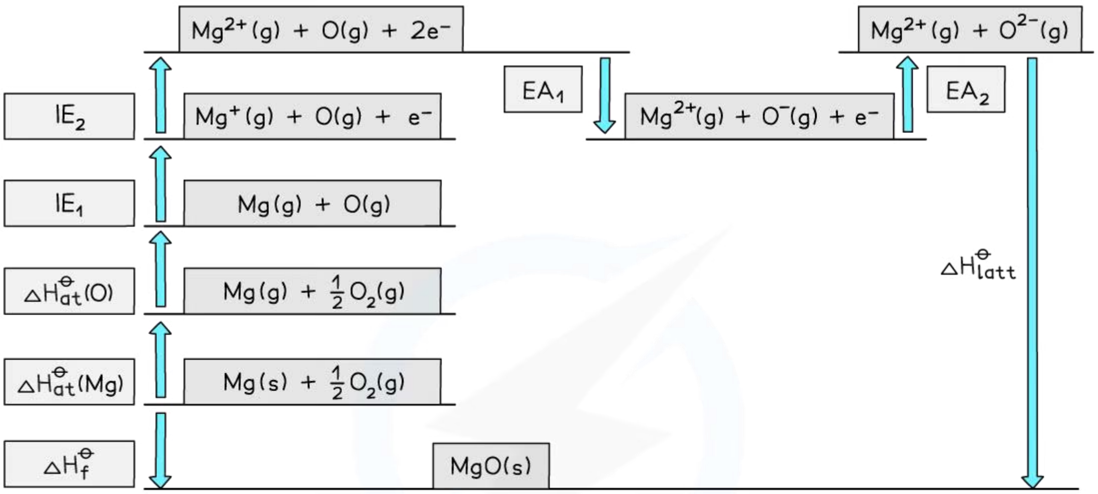
Worked Example

Construct a Born-Haber Cycle which can be used to calculate the lattice energy of magnesium oxide.



Step	Equation	Enthalpy Change
Convert Mg(s) atoms into Mg(g) atoms	$Mg(s) \longrightarrow Mg(g)$	$\Delta H^{\ominus}_{at}$
Convert Mg(g) atoms into $Mg^{+}(g)$ ions	$Mg(g) \longrightarrow Mg^{+}(g) + e^{-}$	IE_1
Convert $Mg^{+}(g)$ ions into $Mg^{2+}(g)$ ions	$Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e^{-}$	IE_2
Convert $O_2(g)$ molecules into O(g) atoms	$\frac{1}{2}O_2(g) \longrightarrow O(g)$	$\Delta H^{\ominus}_{at}$
Convert O(g) atoms into $O^{-}(g)$ ions	$O(g) + e^{-} \longrightarrow O^{-}(g)$	EA_1
Convert $O^{-}(g)$ ions into $O^{2-}(g)$ ions	$O^{-}(g) + e^{-} \longrightarrow O^{2-}(g)$	EA_2
Add up all values to get $\Delta H^{\ominus}_{1}$		$\Delta H^{\ominus}_{1}$
Apply Hess's Law to find $\Delta H^{\ominus}_{latt}$		$\Delta H^{\ominus}_{latt}$

Answer



$$\Delta H_f^\ominus = \left(\Delta H_{at}^\ominus(Mg)\right) + \left(\Delta H_{at}^\ominus(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right) + \left(\Delta H_{latt}^\ominus\right)$$

$$\therefore\ \Delta H_{latt}^\ominus = \left(\Delta H_f^\ominus\right) - \underbrace{\left(EA_1\right) - \left(EA_2\right) - \left(IE_1\right) - \left(IE_2\right) - \left(\Delta H_{at}^\ominus(Mg)\right) - \left(\Delta H_{at}^\ominus(O)\right)}_{\Delta H_1^\ominus}$$

5.4.3 Calculations Using Born-Haber Cycles

Born-Haber Cycles - Calculations

- Once a Born-Haber cycle has been constructed, it is possible to calculate the lattice energy ($\Delta H_{latt}^{\ominus}$) by applying Hess's law and rearranging:

$$\Delta H_f^{\ominus} = \Delta H_{at}^{\ominus} + \Delta H_{at}^{\ominus} + IE + EA + \Delta H_{latt}^{\ominus}$$

- If we simplify this into three terms, this makes the equation easier to see:
  - $\Delta H_{latt}^{\ominus}$
  - $\Delta H_f^{\ominus}$
  - $\Delta H_1^{\ominus}$ (the sum of all of the various enthalpy changes necessary to convert the elements in their standard states to gaseous ions)

- The simplified equation becomes

$$\Delta H_f^{\ominus} = \Delta H_1^{\ominus} + \Delta H_{latt}^{\ominus}$$

So, if we rearrange to calculate the lattice energy, the equation becomes

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - \Delta H_1^{\ominus}$$

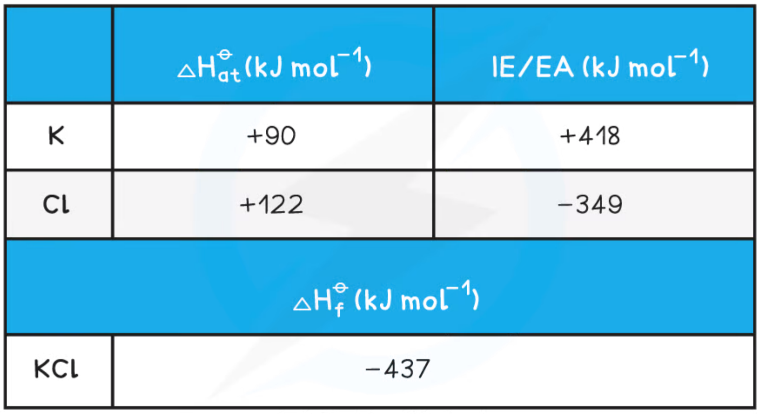
- When calculating the $\Delta H_{latt}^{\ominus}$, all other necessary values will be given in the question
- A Born-Haber cycle could be used to calculate any stage in the cycle
  - For example, you could be given the lattice energy and asked to calculate the enthalpy change of formation of the ionic compound
  - The principle would be exactly the same
  - Work out the **direct** and **indirect route** of the cycle (the stage that you are being asked to calculate will always be the direct route)
  - Write out the equation in terms of enthalpy changes and rearrange if necessary to calculate the required value

- **Remember:** sometimes a value may need to be doubled or halved, depending on the ionic solid involved
  - For example, with $MgCl_2$ the value for the first electron affinity of chlorine would need to be doubled in the calculation, because there are two moles of chlorine atoms
  - Therefore, you are adding **2 moles** of electrons to **2 moles** of chlorine atoms, to form **2 moles** of Cl^- ions

YOUR NOTES

Worked Example

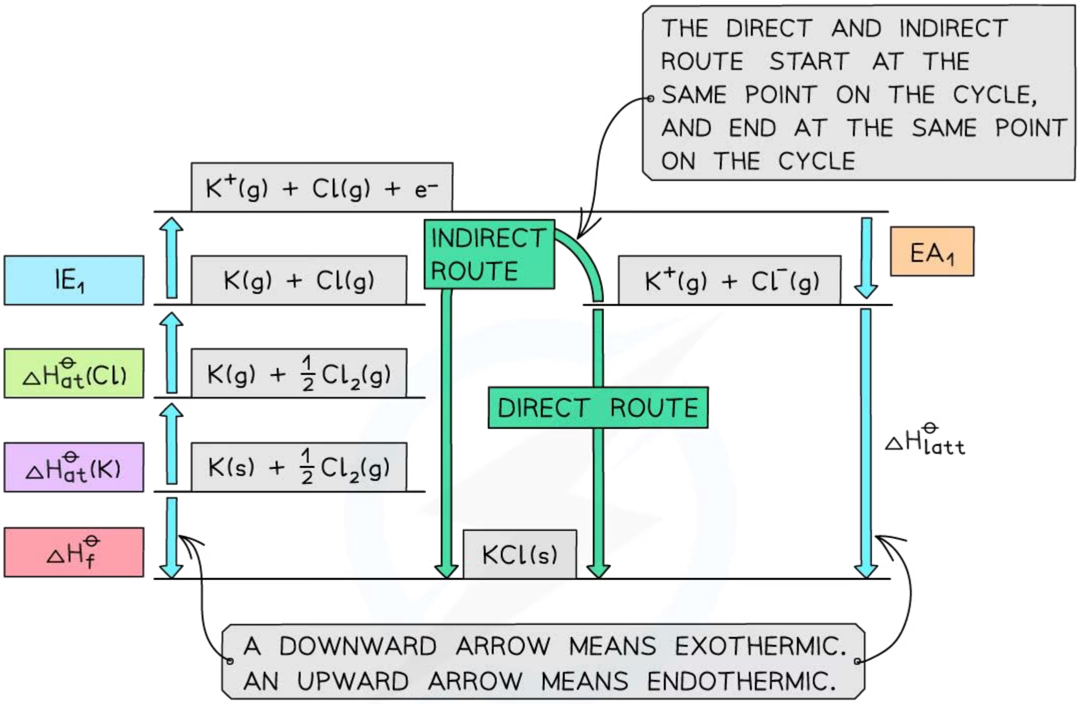
Given the data below, calculate the $\Delta H_{lat}^{\ominus}$ of potassium chloride (KCl)



	$\Delta H_{at}^{\ominus}$ (kJ mol^{-1})	IE/EA (kJ mol^{-1})
K	+90	+418
Cl	+122	−349
	$\Delta H_f^{\ominus}$ (kJ mol^{-1})	
KCl	−437	

Answer

Step 1: The corresponding Born-Haber cycle is:



THE DIRECT AND INDIRECT ROUTE START AT THE SAME POINT ON THE CYCLE, AND END AT THE SAME POINT ON THE CYCLE

A DOWNWARD ARROW MEANS EXOTHERMIC. AN UPWARD ARROW MEANS ENDOTHERMIC.

$$\Delta H^{\ominus}_f = \left(\Delta H^{\ominus}_{at}(K)\right) + \left(\Delta H^{\ominus}_{at}(Cl)\right) + \left(IE_1\right) + \left(EA_1\right) + \left(\Delta H^{\ominus}_{latt}\right)$$

$$\therefore \Delta H^{\ominus}_{latt} = \left(\Delta H^{\ominus}_f\right) - \underbrace{\left(EA_1\right) - \left(IE_1\right) - \left(\Delta H^{\ominus}_{at}(Cl)\right) - \left(\Delta H^{\ominus}_{at}(K)\right)}_{\Delta H^{\ominus}_1}$$

Step 2: Applying Hess' law, the lattice energy of KC*l* is:

$$\Delta H_{latt}^{\square} = \Delta H_f^{\square} - \Delta H_1^{\square}$$

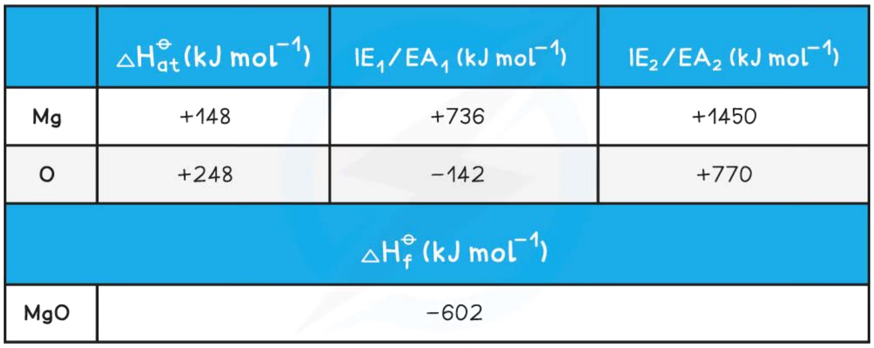
$$\Delta H_{latt}^{\square} = \Delta H_f^{\square} - [(\Delta H_{at}\ K) + (\Delta H_{at}\ Cl) + (IE_1\ K) + (EA_1\ Cl)]$$

Step 3: Substitute in the numbers:

$$\Delta H_{latt}^{\square} = (-437) - [(+90) + (+122) + (+418) + (-349)] = -718\ kJ\ mol^{-1}$$

Worked Example

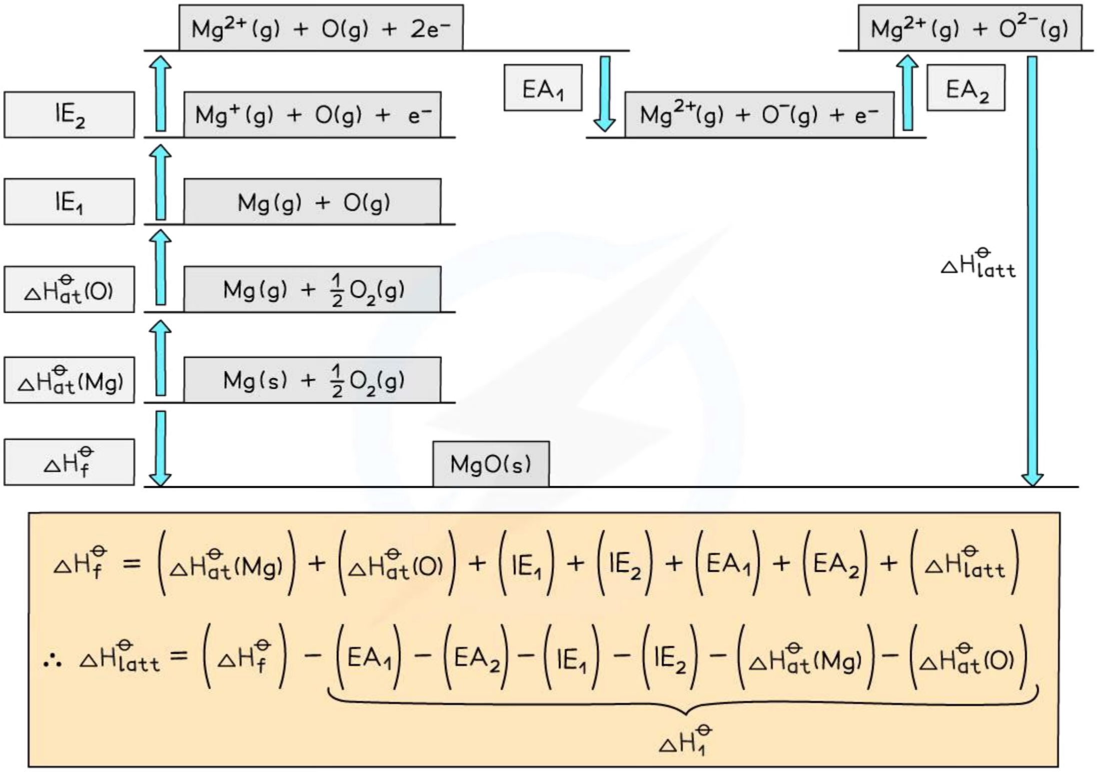
Given the data below, calculate the of $\Delta H_{latt}^{\ominus}$ magnesium oxide of magnesium oxide (MgO)



	$\Delta H_{at}^{\ominus}$ (kJ mol^{-1})	IE_1 / EA_1 (kJ mol^{-1})	IE_2 / EA_2 (kJ mol^{-1})
Mg	+148	+736	+1450
O	+248	−142	+770
	$\Delta H_f^{\ominus}$ (kJ mol^{-1})		
MgO	−602		

Answer

Step 1: The corresponding Born-Haber cycle is:



$$\Delta H_f^{\ominus} = \left(\Delta H_{at}^{\ominus}(Mg)\right) + \left(\Delta H_{at}^{\ominus}(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right) + \left(\Delta H_{latt}^{\ominus}\right)$$

$$\therefore \ \Delta H_{latt}^{\ominus} = \left(\Delta H_f^{\ominus}\right) \underbrace{- \left(EA_1\right) - \left(EA_2\right) - \left(IE_1\right) - \left(IE_2\right) - \left(\Delta H_{at}^{\ominus}(Mg)\right) - \left(\Delta H_{at}^{\ominus}(O)\right)}_{\Delta H_1^{\ominus}}$$

Step 2: Applying Hess' law, the lattice energy of MgO is:

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - \Delta H_1^{\ominus}$$

$$\Delta H_{latt}^{\circ} = \Delta H_f^{\circ} - [(\Delta H_{at}^{\circ}\ \text{Mg}) + (\Delta H_{at}^{\circ}\ \text{O}) + (IE_1\ \text{Mg}) + (IE_2\ \text{Mg}) + (EA_1\ \text{O}) + (EA_2\ \text{O})]$$

Step 3: Substitute in the numbers:

$$\Delta H_{latt}^{\circ} = (-602) - [(+148) + (+248) + (+736) + (+1450) + (-142) + (+770)]$$

$$= -3812\ \text{kJ mol}^{-1}$$

Enthalpy of Solution & Hydration

Enthalpy of solution

- The **standard enthalpy change of solution (ΔH_{sol})** is the enthalpy change when **1 mole** of an ionic substance **dissolves** in sufficient water to form an **infinitely dilute solution**
- The symbol **(aq)** is used to show that the solid is dissolved in **sufficient water**
  - For example, the enthalpy changes of solution for potassium chloride are described by the following equations:

$$\mathbf{KCl\ (s) + aq \rightarrow KCl\ (aq)}$$

OR

$$\mathbf{KCl\ (s) + aq \rightarrow K^{+}(aq) + Cl^{-}(aq)}$$

- ΔH_{sol}□ can be **exothermic** (negative) or **endothermic** (positive)

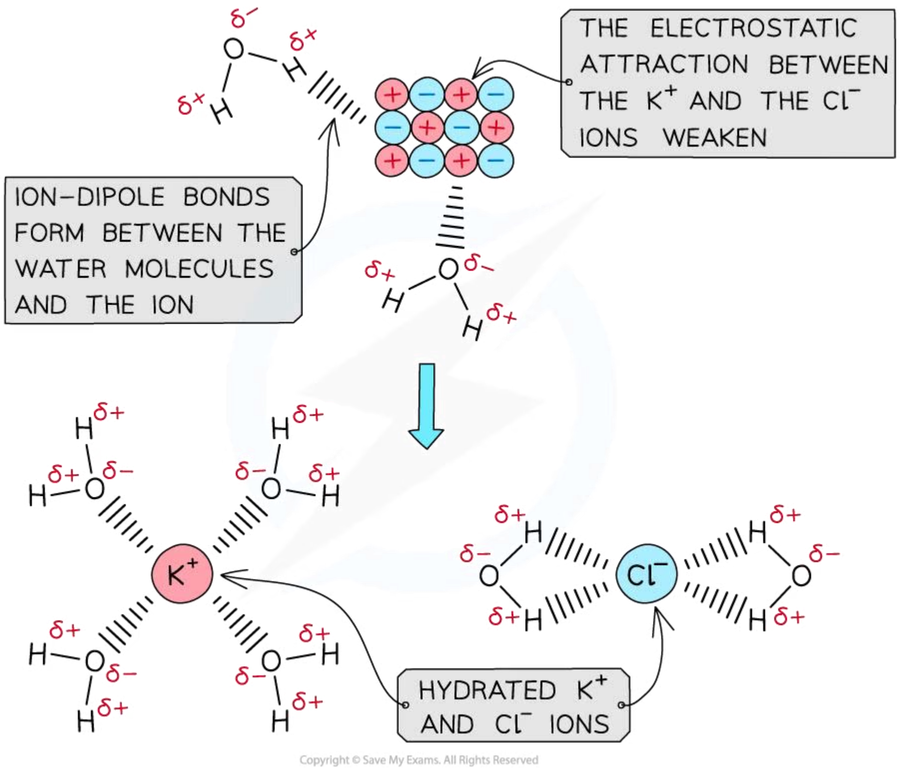
Enthalpy of hydration

- The **standard enthalpy change of hydration (ΔH_{hyd})** is the enthalpy change when **1 mole** of a specified **gaseous ion dissolves** in sufficient water to form an infinitely dilute **solution**
  - For example, the enthalpy change of hydration for magnesium ions is described by the following equation:

$$\mathbf{Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)}$$

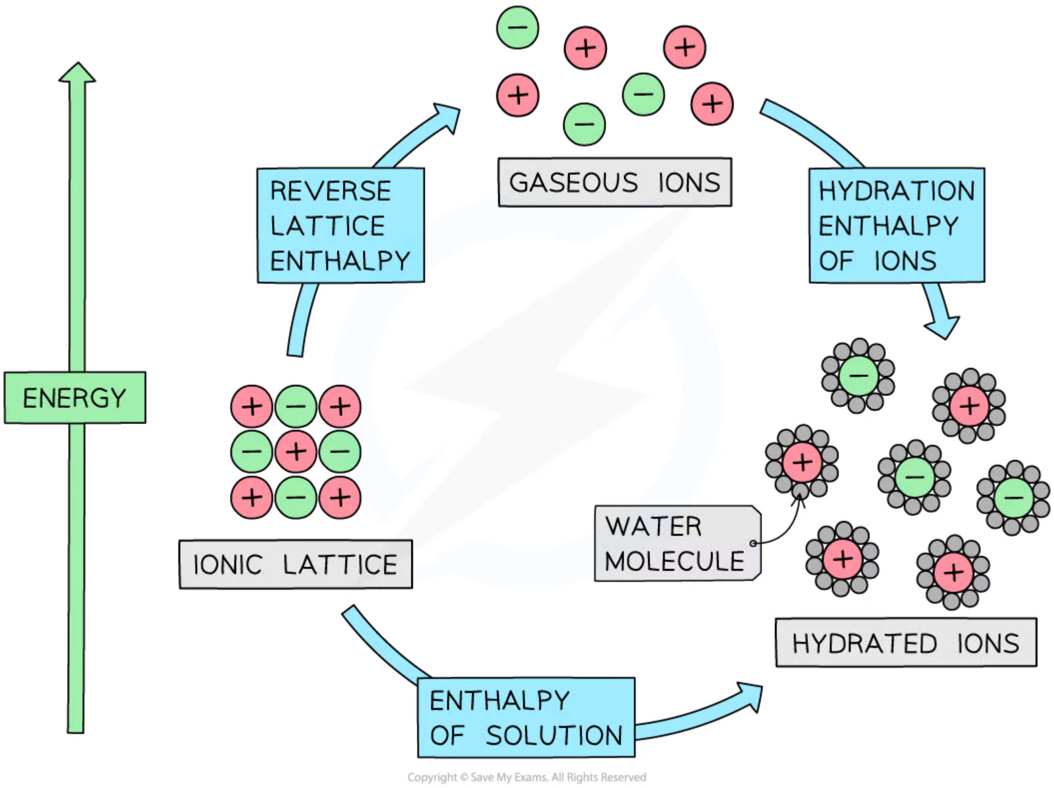
-
  - Hydration enthalpies are the measure of the energy that is released when there is an attraction formed between the ions and water molecules
  - Hydration enthalpies are **exothermic**

- When an **ionic solid** dissolves in water, positive and negative ions are formed
- Water is a **polar** molecule with a $\delta-$ oxygen (O) atom and $\delta+$ hydrogen (H) atoms which will form **ion-dipole attractions** with the ions present in the solution
- The oxygen atom in water will be attracted to the **positive ions** and the hydrogen atoms will be attracted to the **negative ions**



The polar water molecules will form ion-dipole bonds with the ions in solution causing the ions to become hydrated

How are enthalpy of solution and hydration enthalpies related?



The relationship between lattice enthalpy, hydration enthalpies and enthalpy of solution

- From the diagram we can see that the relationship is

Enthalpy of solution = reverse lattice enthalpy* + hydration enthalpy

- The hydration enthalpy is the **sum** of the hydration enthalpies of each ion
- If there is more than one cation or anion, such as in $MgCl_2$, then you must multiply by the appropriate coefficient for that ion

*To be consistent with lattice *formation* enthalpy

Enthalpy of Solution & Hydration Calculations

- Questions in this topic typically ask you to calculate the hydration enthalpy of one of the ions, given the lattice enthalpy, enthalpy of solution and hydration enthalpy of the other ion.
- This can be done by constructing an appropriate energy cycle and using Hess's Law to find the unknown energy value
- The energy cycle above shows that there are two routes to go from the gaseous ions to the ions in an aqueous solution:
    - **Route 1**: going from gaseous ions → ionic solid → ions in aqueous solution (this is the **indirect route**)
    - **Route 2**: going from gaseous ions → ions in aqueous solution (this is the **direct route**)
- According to **Hess's law,** the enthalpy change for both routes is the same, such that:

$$\Delta H_{hyd}^{\square} = \Delta H_{latt}^{\square} + \Delta H_{sol}^{\square}$$

- Each ion will have its own enthalpy change of hydration, $\Delta H_{hyd}^{\square}$, which will need to be taken into account during calculations
    - The total $\Delta H_{hyd}^{\square}$ is found by adding the $\Delta H_{hyd}^{\square}$ values of both anions and cations together

Worked Example

Calculate the enthalpy of hydration of the chloride ion given the following data:

$\Delta H_{latt}^{\square}$ [KCl] = −711 kJ mol^{-1}

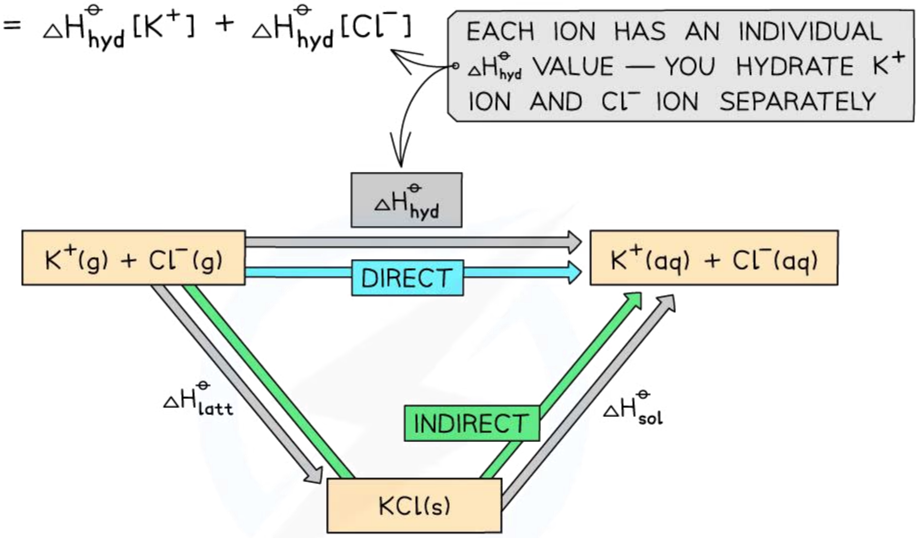
$\Delta H_{sol}^{\square}$ [KCl] = +26 kJ mol^{-1}

$\Delta H_{hyd}^{\square}$ [K^{+}] = −322 kJ mol^{-1}

Answer

Step 1: Draw the energy cycle and make $\Delta H_{hyd}^{\square}$ [Cl^{-}] the subject of the formula:

$$\Delta H^{\ominus}_{hyd} = \Delta H^{\ominus}_{hyd}[K^+] + \Delta H^{\ominus}_{hyd}[Cl^-]$$



$$\Delta H^{\ominus}_{hyd} = \Delta H^{\ominus}_{latt}[KCl] + \Delta H^{\ominus}_{sol}[KCl]$$

$$\Delta H^{\ominus}_{hyd}[K^+] + \Delta H^{\ominus}_{hyd}[Cl^-] = \Delta H^{\ominus}_{latt}[KCl] + \Delta H^{\ominus}_{sol}[KCl]$$

$$\therefore \Delta H^{\ominus}_{hyd}[Cl^-] = \Delta H^{\ominus}_{latt}[KCl] + \Delta H^{\ominus}_{sol}[KCl] - \Delta H^{\ominus}_{hyd}[K^+]$$

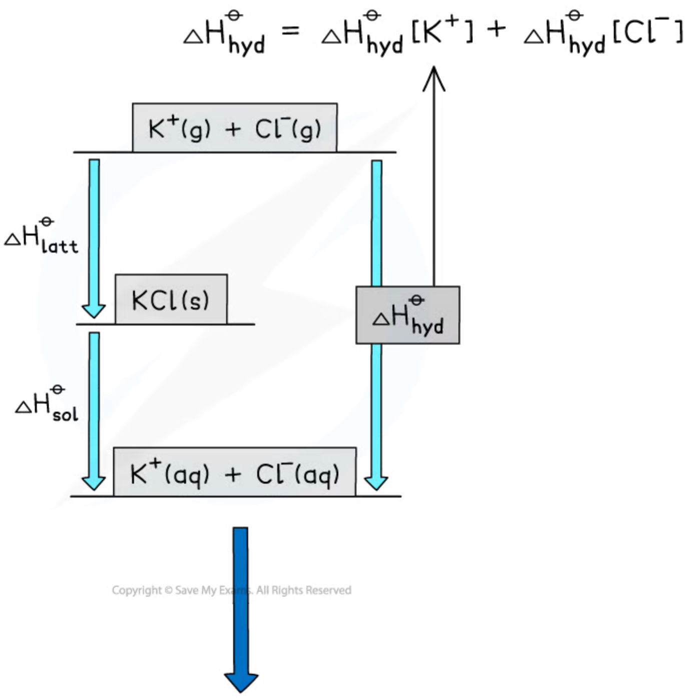
Step 2: Substitute the values to find ΔH_{hyd} $[Cl^-]$

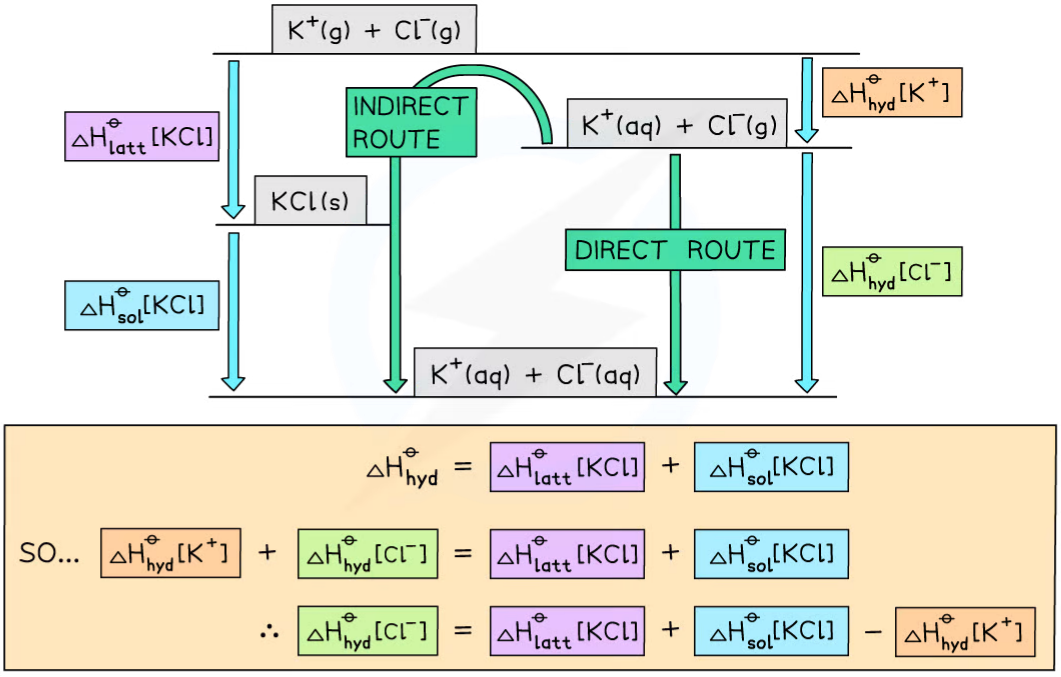
$$\Delta H_{hyd}{}^{\square}[Cl^-] = (-711) + (+26) - (-322) = -363 \text{ kJ mol}^{-1}$$

Alternative Diagram

- You can also draw a Born-Haber cycle as an alternative approach to the same problem

Energy level diagram:





$$\Delta H^\ominus_{hyd} = \Delta H^\ominus_{latt}[KCl] + \Delta H^\ominus_{sol}[KCl]$$

SO… $\Delta H^\ominus_{hyd}[K^+] + \Delta H^\ominus_{hyd}[Cl^-] = \Delta H^\ominus_{latt}[KCl] + \Delta H^\ominus_{sol}[KCl]$

$$\therefore \Delta H^\ominus_{hyd}[Cl^-] = \Delta H^\ominus_{latt}[KCl] + \Delta H^\ominus_{sol}[KCl] - \Delta H^\ominus_{hyd}[K^+]$$

Worked Example

Construct an energy cycle to calculate the $\Delta H_{hyd}^{\ominus}$ of magnesium ions in magnesium chloride, given the following data:

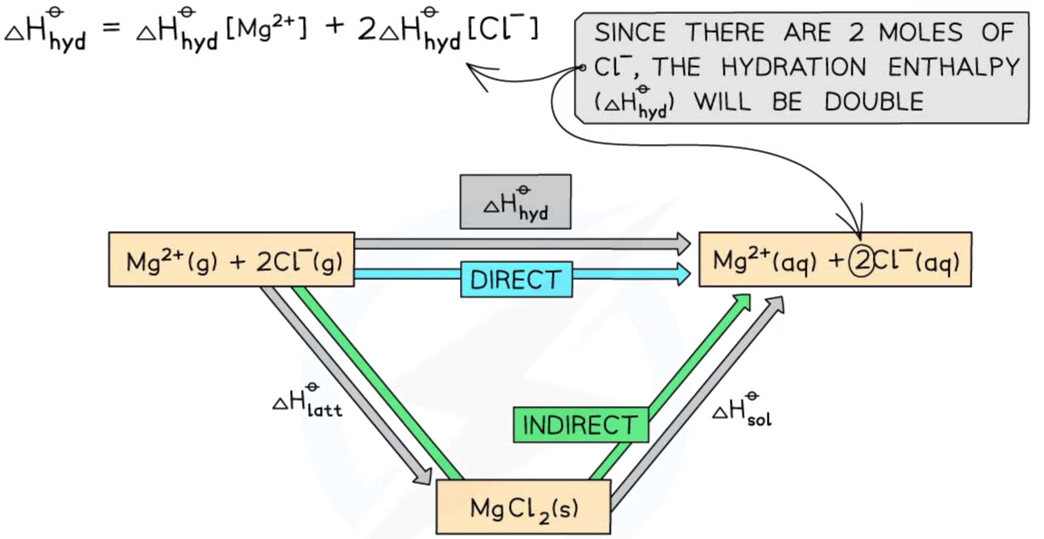
$\Delta H_{latt}^{\ominus}[MgCl_2]$ = –2592 kJ mol $^{-1}$

$\Delta H_{sol}^{\ominus}[MgCl_2]$ = –55 kJ mol $^{-1}$

$\Delta H_{hyd}^{\ominus}[Cl^-]$ = –363 kJ mol^{-1}

Answer

Step 1: Draw an energy cycle:



$$\Delta H_{hyd}^{\ominus} = \Delta H_{hyd}^{\ominus}[Mg^{2+}] + 2\Delta H_{hyd}^{\ominus}[Cl^-]$$

SINCE THERE ARE 2 MOLES OF Cl^-, THE HYDRATION ENTHALPY ($\Delta H_{hyd}^{\ominus}$) WILL BE DOUBLE

$$\Delta H_{hyd}^{\ominus} = \Delta H_{latt}^{\ominus}[MgCl_2] + \Delta H_{sol}^{\ominus}[MgCl_2]$$

$$\Delta H_{hyd}^{\ominus}[Mg^{2+}] + 2\Delta H_{hyd}^{\ominus}[Cl^-] = \Delta H_{latt}^{\ominus}[MgCl_2] + \Delta H_{sol}^{\ominus}[MgCl_2]$$

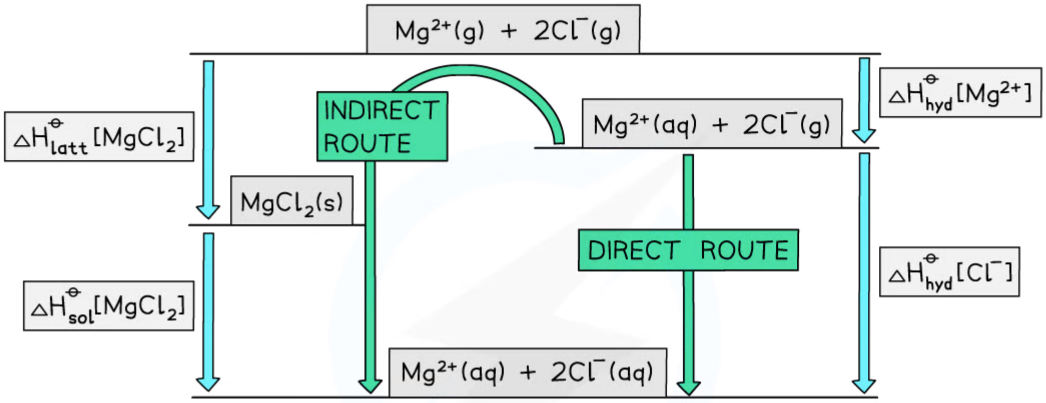
$$\therefore \Delta H_{hyd}^{\ominus}[Mg^{2+}] = \Delta H_{latt}^{\ominus}[MgCl_2] + \Delta H_{sol}^{\ominus}[MgCl_2] - 2\Delta H_{hyd}^{\ominus}[Cl^-]$$

Step 2: Substitute the values to find $\Delta H_{hyd}^{\ominus}$ $[Mg^{2+}]$

$$\mathbf{\Delta H_{hyd}^{\ominus}[Mg^{2+}] = (-2592) + (-55) - (2 \times -363) = -1921\ kJ\ mol^{-1}}$$

Alternative route to find $\Delta H_{hyd}^{\ominus}[Mg^{2+}]$

- Here is the same solution using a Born-Haber cycle



$$\Delta H^\ominus_{hyd} = \Delta H^\ominus_{latt}[MgCl_2] + \Delta H^\ominus_{sol}[MgCl_2]$$

$$\Delta H^\ominus_{hyd}[Mg^{2+}] + 2\Delta H^\ominus_{hyd}[Cl^-] = \Delta H^\ominus_{latt}[MgCl_2] + \Delta H^\ominus_{sol}[MgCl_2]$$

$$\Delta H^\ominus_{hyd}[Mg^{2+}] = \Delta H^\ominus_{latt}[MgCl_2] + \Delta H^\ominus_{sol}[MgCl_2] - 2\Delta H^\ominus_{hyd}[Cl^-]$$

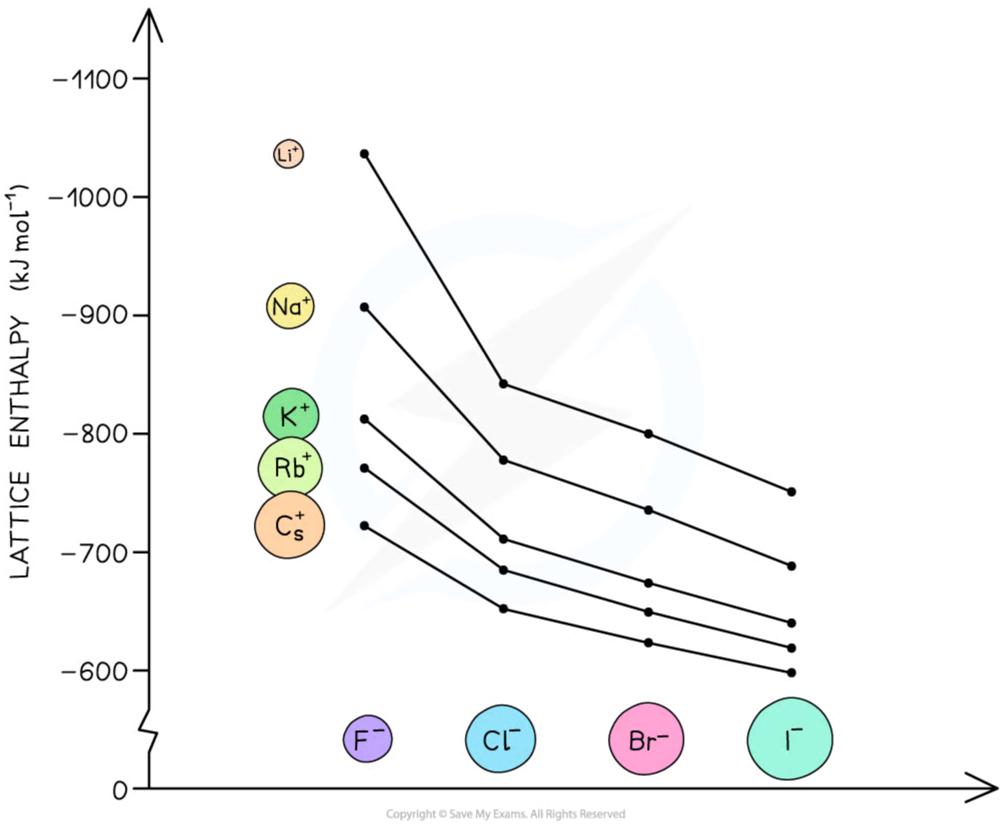
The Effect of Ionic Charge & Radius on Enthalpy

Factors affecting lattice enthalpy

- The two key factors which affect lattice energy, $\Delta H_{latt}^{\square}$, are the **charge** and **radius** of the ions that make up the **crystalline lattice**

Ionic radius

- The lattice energy becomes **less exothermic** as the **ionic radius** of the ions **increases**
- This is because the charge on the ions is more **spread out** over the ion when the ions are **larger**
- The ions are also **further apart** from each other in the lattice
  - The attraction between ions is between the centres of the ions involved, so the bigger the ions the bigger the distance between the centre of the ions
- Therefore, the **electrostatic forces of attraction** between the oppositely charged ions in the lattice are **weaker**
- For example, the lattice energy of caesium fluoride (CsF) is **less exothermic** than the lattice energy of potassium fluoride (KF)
  - Since both compounds contain a fluoride (F^-) ion, the difference in lattice energy must be due to the caesium (Cs^+) ion in CsF and potassium (K^+) ion in KF
  - Potassium is a Group 1 and Period 4 element
  - Caesium is a Group 1 and Period 6 element
  - This means that the Cs^+ ion is **larger** than the K^+ ion
  - There are **weaker** electrostatic forces of attraction between the Cs^+ and F^- ions compared to K^+ and F^- ions
  - As a result, the **lattice energy** of CsF is **less exothermic** than that of KF



The lattice energies get less exothermic as the ionic radius of the ions increases

Ionic charge

- The lattice energy gets **more exothermic** as the **ionic charge** of the ions **increases**
- The greater the ionic charge, the **higher the charge density**
- This results in **stronger electrostatic attraction** between the oppositely charged ions in the lattice
- As a result, the lattice energy is **more exothermic**
- For example, the lattice energy of calcium oxide (CaO) is **more exothermic** than the lattice energy of potassium chloride (KCl)
  - Calcium oxide is an ionic compound which consists of calcium (Ca^{2+}) and oxide (O^{2-}) ions
  - Potassium chloride is formed from potassium (K^+) and chloride (Cl^-) ions
  - The ions in calcium oxide have a **greater ionic charge** than the ions in potassium chloride
  - This means that the electrostatic forces of attraction are **stronger** between the Ca^{2+} and O^{2-}compared to the forces between K^+ and Cl^-
  - Therefore, the lattice energy of calcium oxide is **more exothermic,** as more energy is released upon its formation from its gaseous ions
  - Ca^{2+} and O^{2-} are also smaller ions than K^+ and Cl^-, so this also adds to the value for the lattice energy being more exothermic

Factors affecting enthalpy of hydration

- The standard enthalpy change of hydration ($\Delta H_{hyd}^{\ominus}$) is affected by the amount that the ions are attracted to the water molecules
- The factors which affect this attraction are the **ionic charge** and **radius**

Ionic radius

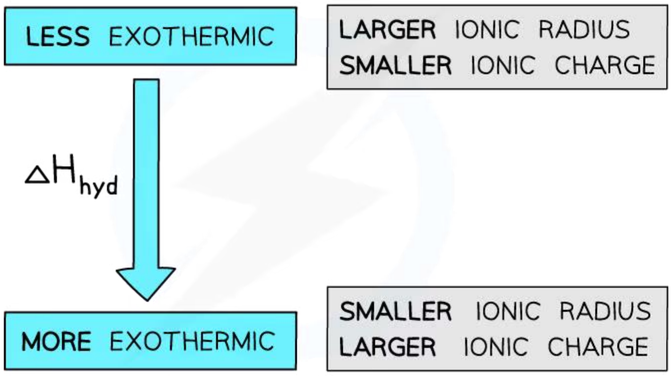
- $\Delta H_{hyd}^{\ominus}$ becomes **more exothermic** with **decreasing ionic radii**
  - Smaller ions have a greater **charge density** resulting in **stronger** ion-dipole attractions between the water molecules and the ions in the solution
  - Therefore, more energy is released when they become hydrated and $\Delta H_{hyd}^{\ominus}$ becomes **moreexothermic**

- For example, the $\Delta H_{hyd}^{\ominus}$ of magnesium sulfate ($MgSO_4$) is **more exothermic** than the $\Delta H_{hyd}^{\ominus}$ of barium sulfate ($BaSO_4$)
  - Since both compounds contain a sulfate (SO_4^{2-}) ion, the difference in $\Delta H_{hyd}^{\ominus}$ must be due to the magnesium (Mg^{2+}) ion in $MgSO_4$ and barium (Ba^{2+}) ion in $BaSO_4$
  - Magnesium is a Group 2 and Period 3 element
  - Barium is a Group 2 and Period 6 element
  - This means that the Mg^{2+} ion is **smaller** than the Ba^{2+} ion
  - The attraction is therefore much **stronger** for the Mg^{2+} ion
  - As a result, the standard enthalpy of hydration of $MgSO_4$ is **more exothermic** than that of $BaSO_4$

Ionic charge

- $\Delta H_{hyd}^{\ominus}$ is **more exothermic** for ions with **larger ionic charges**
  - Ions with **large ionic charges** have a greater **charge density** resulting in **stronger** ion-dipole attractions between the water molecules and the ions in the solution
  - Therefore, more energy is released when they become hydrated and $\Delta H_{hyd}^{\ominus}$becomes **more exothermic**

- For example, the $\Delta H_{hyd}^{\ominus}$ of calcium oxide (CaO) is **more exothermic** than the $\Delta H_{hyd}^{\ominus}$of potassium chloride (KCl)
  - Calcium oxide is an ionic compound that consists of calcium (Ca^{2+}) and oxide (O^{2-}) ions
  - Potassium chloride is formed from potassium (K^+) and chloride (Cl^-) ions
  - Both of the ions in calcium oxide have a **greater ionic charge** than the ions in potassium chloride
  - This means that the attractions are stronger between the water molecules and Ca^{2+} and O^{2-}ions upon hydration of CaO
  - The attractions are weaker between the water molecules and K^+ and Cl^- ions upon hydration of KCl
  - Therefore, the $\Delta H_{hyd}^{\ominus}$ of calcium oxide is **more exothermic** as more energy is released upon its hydration

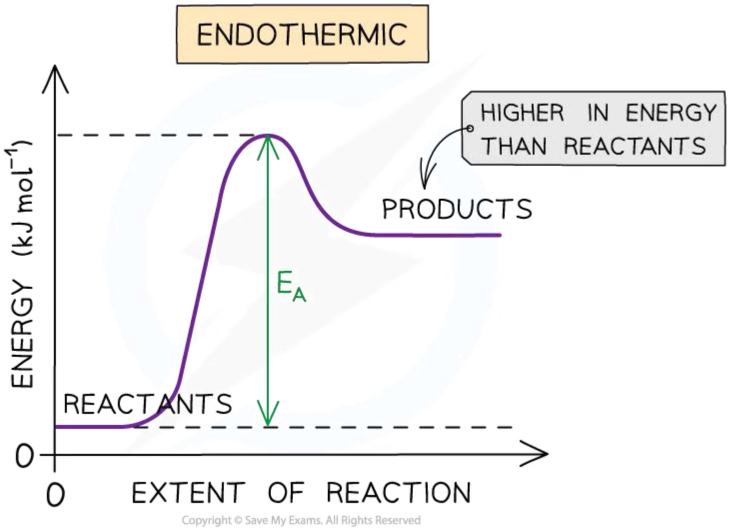


The enthalpy of hydration is more exothermic for smaller ions and for ions with a greater ionic charge

5.4.6 Entropy

Entropy & Disorder

- You may have wondered why it is that **endothermic** reactions occur at all, after all, what can be the driving force behind endothermic reactions if the products end up in a less stable, higher energy state?
- Although the majority of chemical reactions we experience everyday are **exothermic**, ΔH□ alone is not enough to explain why endothermic reactions occur



The driving force behind chemical reactions cannot be explained by enthalpy changes alone as it makes not sense for chemical to end up in a less stable higher energy state in endothermic reactions

- The answer is **entropy**

Chaos in the universe

- The **entropy (*S*)** of a given system is the number of possible arrangements of the particles and their energy in a given system
    - In other words, it is a measure of how **disordered** or **chaotic** a system is

- When a system becomes **more disordered**, its entropy will **increase**
- An increase in entropy means that the system becomes **energetically more stable**
- For example, during the thermal decomposition of calcium carbonate ($CaCO_3$) the entropy of the system increases:

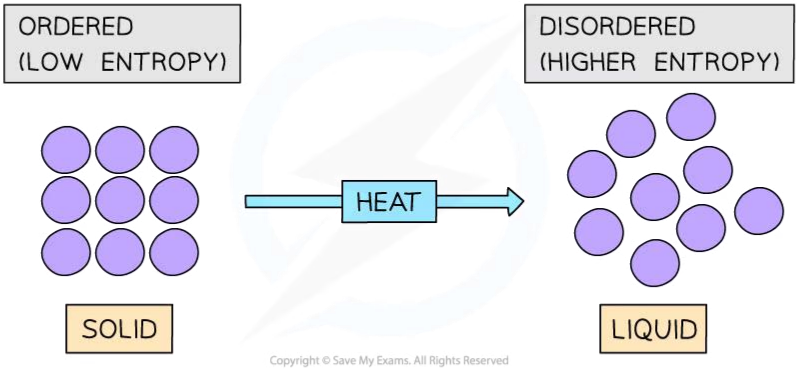
$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

- In this decomposition reaction, a gas molecule (CO_2) is formed
- The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$), as it is constantly moving around
- As a result, the system has become more **disordered** and there is an **increase** in **entropy**

- Another typical example of a system that becomes more disordered is when a solid is **melted**
- For example, melting ice to form liquid water:

$$H_2O(s) \rightarrow H_2O(l)$$

- The water molecules in ice are in fixed positions and can only vibrate about those positions
- In the liquid state, the particles are still quite close together but are arranged more randomly, in that they can move around each other
- Water molecules in the liquid state are therefore more **disordered**
- Thus, for a given substance, the **entropy increases** when its solid form melts into a liquid
- In both examples, the system with the **higher entropy** will be **energetically favourable** (as the energy of the system is more spread out when it is in a disordered state)



Melting a solid will cause the particles to become more disordered resulting in a higher entropy state

Feasible or spontaneous reactions

- Chemists talk about reactions being **feasible** or **spontaneous**
- What they mean is that reactions take place of their own accord, in other words, they are energetically favourable
- This is an outcome of the **second law of thermodynamics** which broadly states the the entropy of the universe is always increasing
- We can see examples of this all around us:
    - cups fall off tables and spontaneously break into many pieces, never the other way around
    - hot objects always cool and spread their heat into the surroundings, never the other way around
    - Earthquakes destroy buildings and create chaos and disorder
    - When living things die they decompose and change from complex ordered systems into disordered simple molecules
- However, **feasibility** takes no account of the **rate of reaction** and states only what is possible, not what actually happens. A feasible reaction might be incredibly slow, such as the rusting of iron.

Entropy Calculations

- Entropy changes are an order of magnitude smaller than enthalpy changes, so entropy is measured in joules rather than kilojoules. The full unit for entropy is **J K^{-1} mol^{-1}**
- The standard entropy change (ΔS) for a given reaction can be calculated using the standard entropies (S) of the reactants and products
- The equation to calculate the standard entropy change of a system is:

$$\Delta S^{\square} = \Sigma S_{products}^{\square} - \Sigma S_{reactants}^{\square}$$

(where Σ = sum of)

- For example, the standard entropy change for the formation of ammonia (NH_3) from nitrogen (N_2) and hydrogen (H_2) can be calculated using this equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\Delta S_{system}^{\square} = (2 \times \Delta S^{\square}(NH_3)) - (\Delta S^{\square}(N_2) + 3 \times \Delta S^{\square}(H_2))$$

- Notice that, unlike enthalpy of formation for elements, entropy for elements is **not** zero and you can find entropy values for elements and compounds in data books

Worked Example

Calculate the entropy change of the system for the following reaction:

$$2Mg\ (s) + O_2\ (g) \rightarrow 2MgO\ (s)$$

$S^{\square}[Mg(s)] = 32.60\ J\ K^{-1}\ mol^{-1}$

$S^{\square}[O_2(g)] = 205.0\ J\ K^{-1}\ mol^{-1}$

$S^{\square}[MgO(s)] = 38.20\ J\ K^{-1}\ mol^{-1}$

Answer

$\Delta S_{system}^{\square} = \Sigma\Delta S_{products}^{\square} - \Sigma\Delta S_{reactants}^{\square}$

$\Delta S_{system}^{\square} = (2 \times 38.20) - (2 \times 32.60 + 205.0)$

= **$-193.8\ J\ K^{-1}\ mol^{-1}$**

The Feasibility of a Reaction

- The Gibbs equation can be used to calculate whether a reaction is **feasible** or not

$$\Delta G^{\square} = \Delta H_{reaction}{}^{\square} - T\Delta S_{system}{}^{\square}$$

- When $\Delta G^{\square}$ is **negative**, the reaction is **feasible** and likely to occur
- When $\Delta G^{\square}$ is **positive**, the reaction is **not feasible** and unlikely to occur
- **Feasible** and **spontaneous** are fairly similar terms to describe reactions
  - Feasible tends to be used to describe reactions which are energetically favourable, so *reactions that should go*
  - Spontaneous tends to be used to describe *reactions that go of their own accord*

Worked Example

Calculate the Gibbs free energy change for the following reaction at 298 K and determine whether the reaction is feasible.

$2Ca (s) + O_2 (g) \rightarrow 2CaO (s)$ $\Delta H = -635.5$ kJ mol^{-1}

$S^{\square}[Ca(s)] = 41.00$ J K^{-1} mol^{-1}

$S^{\square}[O_2(g)] = 205.0$ J K^{-1} mol^{-1}

$S^{\square}[CaO(s)] = 40.00$ J K^{-1} mol^{-1}

Answer

Step 1: Calculate $\Delta S_{system}{}^{\square}$

$\Delta S_{system}{}^{\square} = \Sigma\Delta S_{products}{}^{\square} - \Sigma\Delta S_{reactants}{}^{\square}$

$\Delta S_{system}{}^{\square} = (2 \times \Delta S^{\square}\ [CaO(s)]) - (2 \times \Delta S^{\square}\ [Ca(s)] + \Delta S^{\square}\ [O_2(g)])$

$= (2 \times 40.00) - (2 \times 41.00 + 205.0)$

$= -207.0$ J K^{-1} mol^{-1}

Step 2: Convert $\Delta S^{\square}$ to kJ K^{-1} mol^{-1}

$= -207.0$ J K^{-1} mol^{-1} $\div$ 1000 $= -0.207$ kJ mol^{-1}

Step 3: Calculate $\Delta G^{\square}$

$\Delta G^{\square} = \Delta H_{reaction}{}^{\square} - T\Delta S_{system}{}^{\square}$

$= -635.5 - (298 \times -0.207)$

$=$ **-573.8 kJ mol^{-1}**

Step 4: Determine whether the reaction is feasible

Since the $\Delta G^{\square}$ is **negative** the reaction is **feasible**

Feasibility and Temperature

- The **feasibility** of a reaction can be affected by the **temperature**
- The Gibbs equation will be used to explain what will affect the feasibility of a reaction for exothermic and endothermic reactions

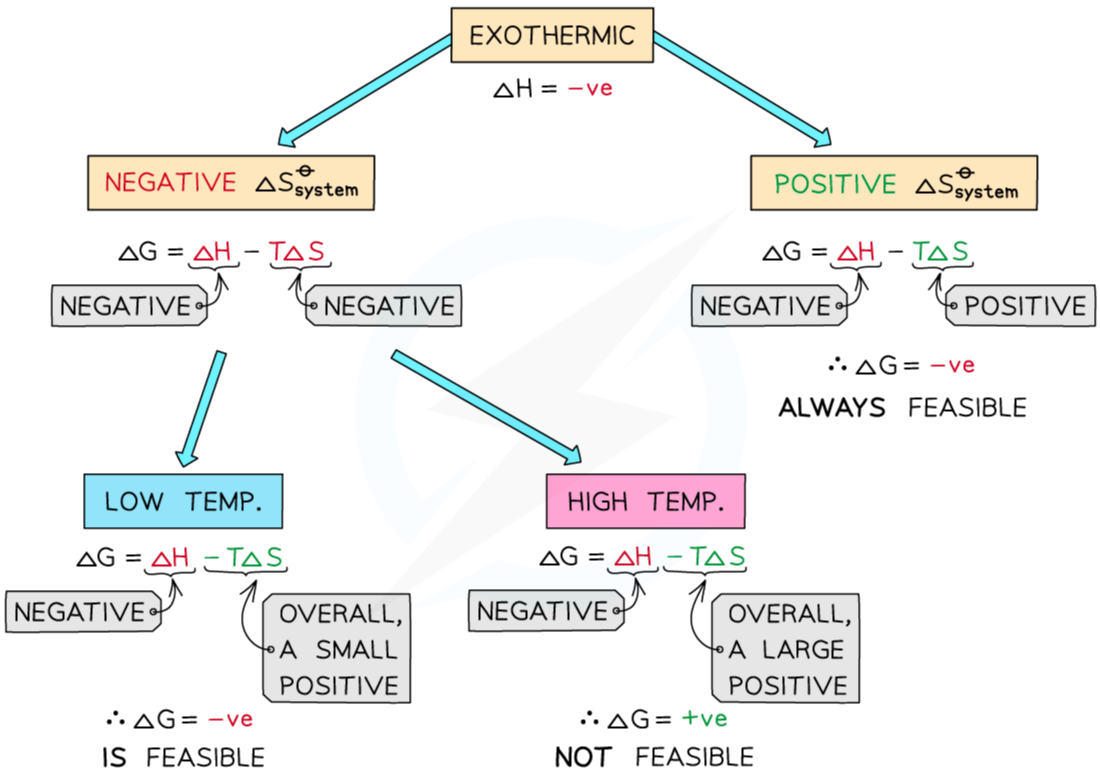
$$\Delta G = \underbrace{\Delta H_{reaction}}_{\boxed{\text{FIRST TERM}}} - \underbrace{T\Delta S_{system}}_{\boxed{\text{SECOND TERM}}}$$

Exothermic reactions

- In exothermic reactions, $\Delta H_{reaction}$□ is **negative**
- If the ΔS_{system}□ is **positive:**
    - Both the first and second term will be **negative**
    - Resulting in a **negative** ΔG□ so the reaction is **feasible**
    - Therefore, regardless of the temperature, an exothermic reaction with a positive ΔS_{system}□ will **always be feasible**

- If the ΔS_{system}□ is **negative:**
    - The first term is **negative** and the second term is **positive**
    - At very high temperatures, the $-T\Delta S_{system}$□ will be very **large** and **positive** and will overcome $\Delta H_{reaction}$□
    - Therefore, at high temperatures ΔG□ is **positive** and the reaction is **not feasible**

- Since the relative size of an entropy change is much smaller than an enthalpy change, it is unlikely that $T\Delta S > \Delta H$ as temperature increases
- These reactions are therefore usually spontaneous at normal conditions



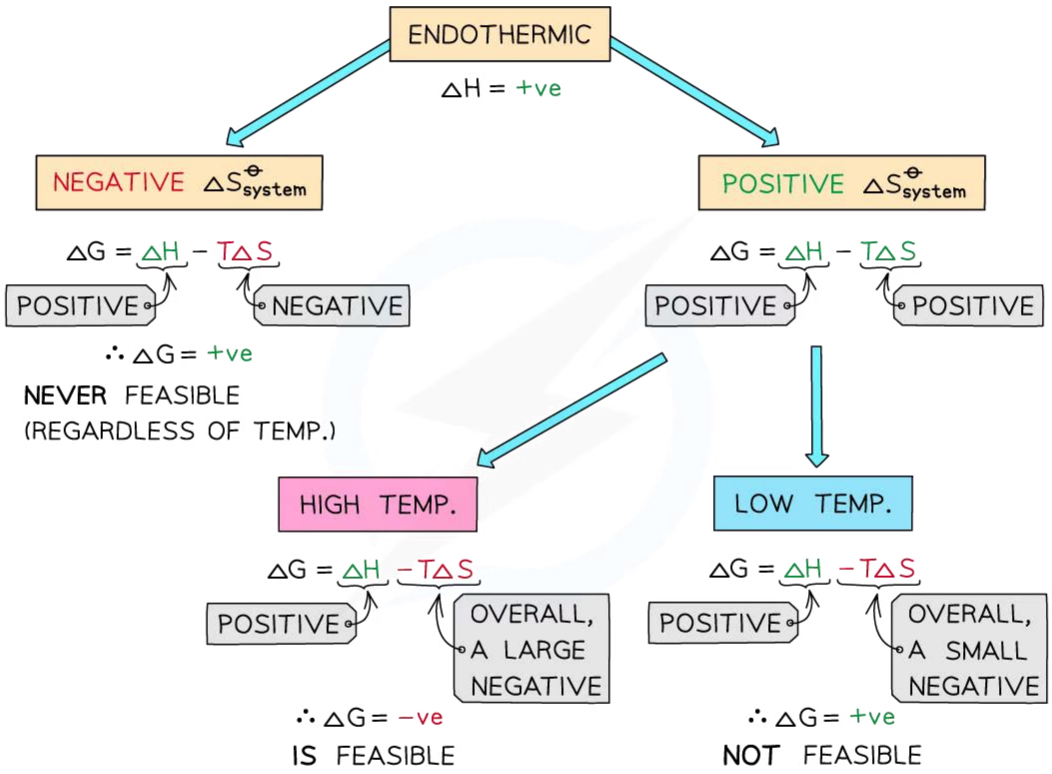
The diagram shows under which conditions exothermic reactions are feasible

Endothermic reactions

- In endothermic reactions, $\Delta H_{reaction}^{\ominus}$ is **positive**
- If the $\Delta S_{system}^{\ominus}$ is **negative:**
  - Both the first and second term will be **positive**
  - Resulting in a **positive** $\Delta G^{\ominus}$ so the reaction is **not feasible**
  - Therefore, regardless of the temperature, endothermic with a negative $\Delta S_{system}^{\ominus}$ will **never be feasible**

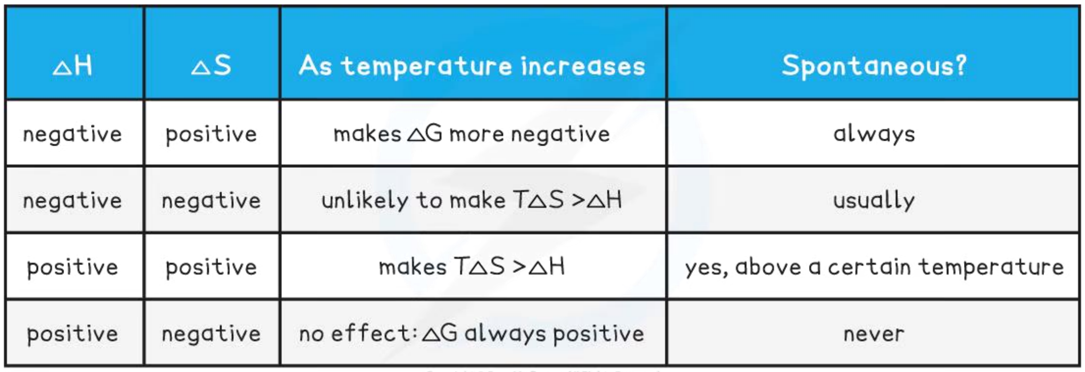
- If the $\Delta S_{system}^{\ominus}$ is **positive:**
  - The first term is **positive** and the second term is **negative**
  - At low temperatures, the $-T\Delta S_{system}^{\ominus}$ will be **small** and **negative** and will not overcome the larger $\Delta H_{reaction}^{\ominus}$
  - Therefore, at low temperatures $\Delta G^{\ominus}$ is **positive** and the reaction is not feasible
  - The reaction is **more feasible** at **high temperatures** as the second term will become negative enough to overcome the $\Delta H_{reaction}^{\ominus}$ resulting in a negative $\Delta G^{\ominus}$

- This tells us that for certain reactions which are not feasible at room temperature, they can become feasible at higher temperatures
  - An example of this is found in metal extractions, such as the extraction if iron in the blast furnace, which will be unsuccessful at low temperatures but can occur at higher temperatures (~1500 ^{o}C in the case of iron)



The diagram shows under which conditions endothermic reactions are feasible

A summary table of free energy conditions



ΔH	ΔS	As temperature increases	Spontaneous?
negative	positive	makes ΔG more negative	always
negative	negative	unlikely to make TΔS >ΔH	usually
positive	positive	makes TΔS >ΔH	yes, above a certain temperature
positive	negative	no effect: ΔG always positive	never

5.4.8 Gibbs Free Energy, ΔG

Gibbs Free Energy, ΔG

Gibbs free energy

- As we have seen in the previous sections, the feasibility of a reaction is determined by two factors, the **enthalpy change** and the **entropy change**
- The two factors come together in a fundamental thermodynamic concept called the **Gibbs free energy (G)**
- The Gibbs equation is:

$$\Delta G^{\ominus} = \Delta H_{reaction}{}^{\ominus} - T\Delta S_{system}{}^{\ominus}$$

- The units of $\Delta G^{\ominus}$ are in kJ mol^{-1}
- The units of $\Delta H_{reaction}{}^{\ominus}$ are in kJ mol^{-1}
- The units of T are in K
- The units of $\Delta S_{system}{}^{\ominus}$ are in J K^{-1} mol^{-1} (and must therefore be converted to kJ K^{-1} mol^{-1} by dividing by 1000)

Calculating $\Delta G^{\ominus}$

- There are two ways you can calculate the value of $\Delta G^{\ominus}$
  - From $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values
  - From $\Delta G^{\ominus}$ values of all the substances present

Worked Example

Calculate the free energy change for the following reaction:

$$2NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + H_2O\,(l) + CO_2\,(g)$$

$\Delta H^{\ominus} = +135$ kJ mol^{-1} $\Delta S = +344$ J K^{-1} mol^{-1}

Answer

Step 1: Convert the entropy value in kilojoules

$\Delta S^{\ominus} = +344$ J K^{-1} mol^{-1} $\div 1000 = +0.344$ kJ K^{-1} mol^{-1}

Step 2: Substitute the terms into the Gibbs Equation

$\Delta G^{\ominus} = \Delta H_{reaction}{}^{\ominus} - T\Delta S_{system}{}^{\ominus}$

$= +135 - (298 \times 0.344)$

$=$ **+32.49 kJ mol^{-1}**

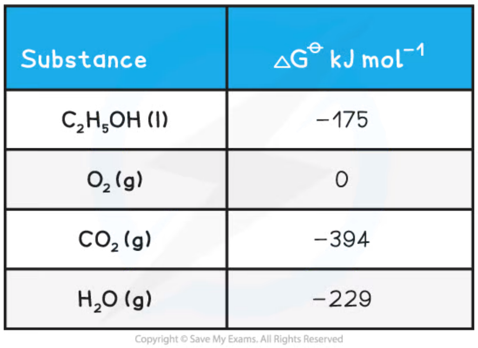
The temperature is 298 K since standard values are quoted in the question

YOUR NOTES

Worked Example

What is the standard free energy change, ΔG□, for the following reaction?

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$



Substance	$\Delta G^{\ominus}$ kJ mol^{-1}
C_2H_5OH (l)	−175
O_2 (g)	0
CO_2 (g)	−394
H_2O (g)	−229

Answer

ΔG□ = $\Sigma\Delta G_{products}$□ – $\Sigma\Delta G_{reactants}$□

ΔG□ = [(2 x CO_2) + (3 x H_2O)] – [(C_2H_5OH) + (3 x O_2)]

ΔG□ = [(2 x −394) + (3 x −229)] – [−175 + 0]

ΔG□ = **−1300 kJ mol^{-1}**

Free Energy & Equilibrium

YOUR NOTES

Limitations of using ΔG

- ΔG^o can only be used to predict the feasibility of a reaction under standard conditions
    - Under non-standard conditions, ΔG must be calculated
- It is important to note that just because a reaction is feasible does not mean that it will occur at an observable rate
- While ΔG can be used to determine the feasibility of a reaction, it does not take into account the kinetics of the reaction i.e. rate of reaction
- There might be a large energy barrier (E_a) which the reacting species have to overcome before a reaction can occur
- Some reactions are feasible since ΔG is negative, but kinetically not feasible since it just occurs too slowly
- Such reactions are feasible but very slow
- An example is the decomposition of hydrogen peroxide at 25 °C

$$H_2O_2\,(l) \rightarrow H_2O\,(l) + \tfrac{1}{2}O_2\,(g) \qquad \Delta G = -117\ kJ\ mol^{-1}$$

- This reaction has a very high E_a so must be catalysed using manganese dioxide, MnO_2
- If the reaction was left for long enough, the hydrogen peroxide would eventually decompose, however the addition of the MnO_2 allows the reaction to take place via an alternative route with a lower E_a
- Although the value for ΔG indicates the reaction is feasible, it does not take into account the kinetics of the reaction

5.5 Redox & Electrochemistry

5.5.1 Redox

Oxidising & Reducing Agents

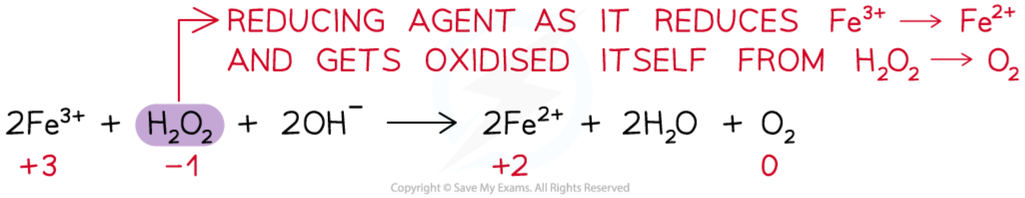
Oxidising agent

- **An oxidising agent** is a substance that **oxidises** another atom or ion by causing it to lose electrons
- An oxidising agent itself gets **reduced – gains electrons**
- Therefore, the **ox. no.** of the oxidising agent **decreases**

Example of an oxidising agent in a chemical reaction

Reducing agent

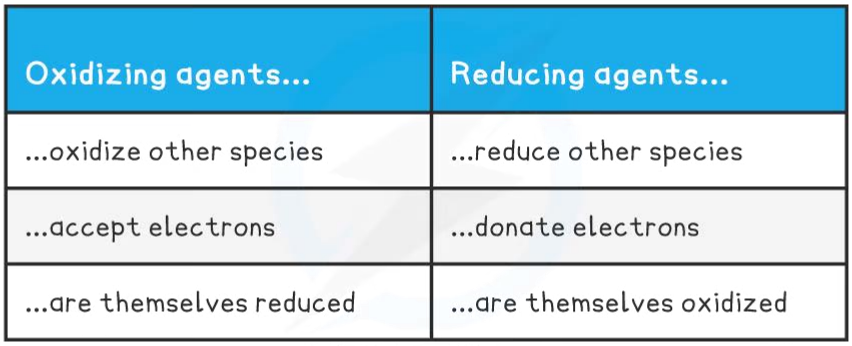
- **A reducing agent** is a substance that **reduces** another atom or ion by causing it to gain electrons
- A reducing agent itself gets **oxidised – loses/donates electrons**
- Therefore, the **ox. no.** of the reducing agent **increases**



Example of a reducing agent in a chemical reaction

- For a reaction to be recognised as a redox reaction, there must be both an oxidising and reducing agent
- Some substances can act both as oxidising and reducing agents
- Their nature is dependent upon what they are reacting with and the reaction conditions

Oxidising & Reducing Agents Table



Oxidizing agents...	Reducing agents...
...oxidize other species	...reduce other species
...accept electrons	...donate electrons
...are themselves reduced	...are themselves oxidized

Redox Equations

- Balancing equations using redox principles is a useful skill and is best illustrated by following an example
- It is important to follow a methodical step-by-step approach so that you don't get lost:

Worked Example

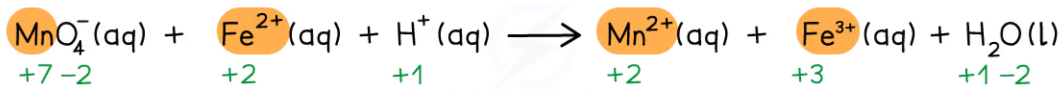
Writing overall redox reactions

Manganate(VII) ions (MnO_4^-) react with Fe^{2+} ions in the presence of acid (H^+) to form Mn^{2+} ions, Fe^{3+} ions and water

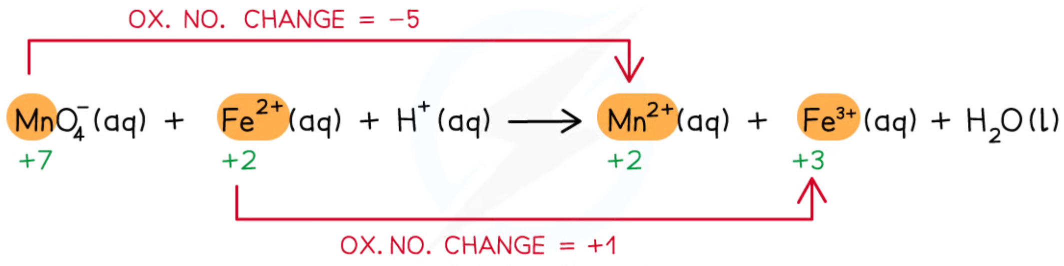
Write the overall redox equation for this reaction

Answer

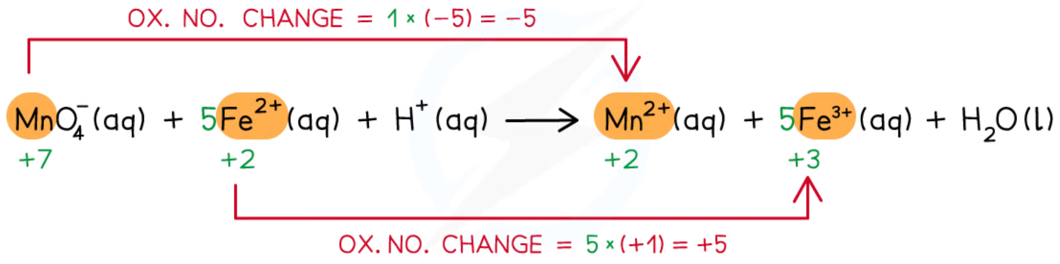
Step 1: Write the unbalanced equation and identify the atoms which change in oxidation state



Step 2: Deduce the oxidation state changes



Step 3: Balance the oxidation state changes



Step 4: Balance the charges

$$\underline{MnO_4^-}(aq) + \underline{5Fe^{2+}}(aq) + H^+(aq) \longrightarrow \underline{Mn^{2+}}(aq) + \underline{5Fe^{3+}}(aq) + H_2O(l)$$

IGNORING H^+

- TOTAL ⊕ CHARGE = (5 × 2+) = 10+
- TOTAL ⊖ CHARGE = 1−

TOTAL CHARGE REACTANTS = 9+

- TOTAL ⊕ CHARGE = 5 × (3+) + (2+)= 17+
- TOTAL ⊖ CHARGE = 0

TOTAL CHARGE PRODUCTS = 17+

$\boxed{\text{THUS } 8H^+ \text{ IONS ARE NEEDED TO BALANCE THE CHARGES ON BOTH SIDES}}$

Step 5: Finally, balance the atoms

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Interpreting & Predicting Redox Reactions

- All of the species involved in a chemical reaction might not be known
- You can be asked to interpret the information given to you and predict any other chemicals involved in the reaction
    - You can use the method shown in the Redox Equations section above
    - The worked example below is a method that works for balancing ionic half equations but can also be used to help predict redox equations

Worked Example

Write complete equations for the following reactions:

1. Hydrogen iodide reacting with sulfuric acid to form hydrogen sulfide, iodine and one other product
2. Lead(II) chloride, chlorine and one other product being formed from the reaction of concentrated hydrochloric acid with lead(IV) oxide

Answers

Answer 1:

Step 1: Start with what you know:

$$HI + H_2SO_4 \rightarrow H_2S + I_2$$

Step 2: Consider any unaccounted for elements

The only element that is not currently considered is oxygen

Step 3: Make a common and appropriate suggestion for the missing product

Most of these questions are in solution so there is always H_2O, H^+ and OH^- available

Missing product suggestion = $4H_2O$

$$HI + H_2SO_4 \rightarrow H_2S + I_2 + 4H_2O$$

Step 4: Balance the remaining chemicals

$$8HI + H_2SO_4 \rightarrow H_2S + 4I_2 + 4H_2O$$

Answer 2:

Step 1: Start with what you know:

$$PbO_2 + HCl \rightarrow PbCl_2 + Cl_2$$

Step 2: Consider any unaccounted elements

The only element that is not currently considered is oxygen

Step 3: Make a common and appropriate suggestion for the missing product

Missing product suggestion = $2H_2O$

$$PbO_2 + HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$

Step 4: Balance the remaining chemicals

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$

Exam Tip

A similar approach can be used to balance more complicated ionic half equations

In this situation, you will have H_2O, H^+, OH^- and electrons available

5.5.2 Redox Titrations

Redox Titrations

Redox Titrations

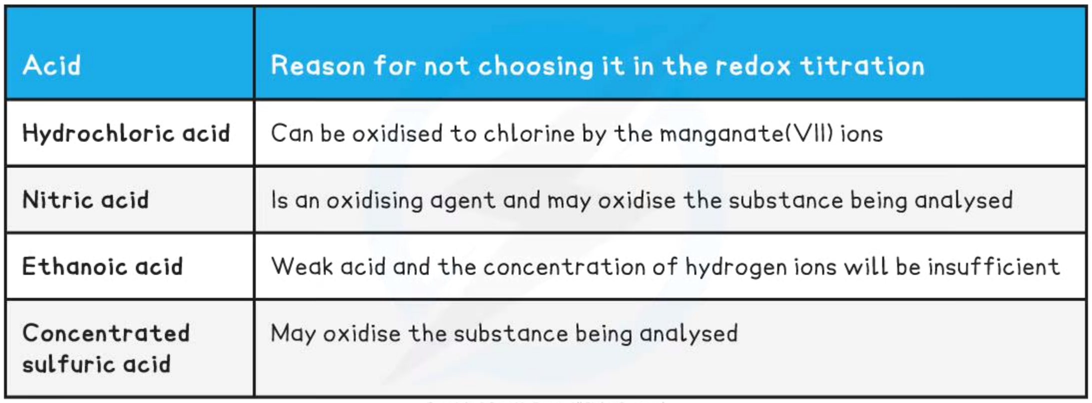
- In a **titration**, the concentration of a solution is determined by titrating with a solution of known concentration.
- In redox titrations, an **oxidizing agent** is titrated against a **reducing agent**
- Electrons are transferred from one species to the other
- **Indicators** are sometimes used to show the endpoint of the **titration**
- However, most **transition metal ions** naturally change colour when changing **oxidation state**
- There are two common **redox titrations** you should know about **manganate(VII) titrations** and **iodine-thiosulfate titrations**

Potassium manganate(VII) titrations

- In these redox titrations the manganate(VII) is the oxidising agent and is reduced to Mn^{2+}(aq)
- The iron is the reducing agent and is oxidised to Fe^{2+}(aq) and the reaction mixture must be acidified, to excess acid is added to the iron(II) ions before the reaction begins
- The choice of acid is important, as it must not react with the manganate(VII) ions, so the acid normally used is dilute sulfuric acid
    - As it does not oxidise under these conditions and does not react with the manganate(VII) ions

- You could be asked why other acids are not suitable for this redox titration in the exam so make sure you understand the suitability of dilute sulfuric acid

Table explaining why other acids are not suitable for the redox titration



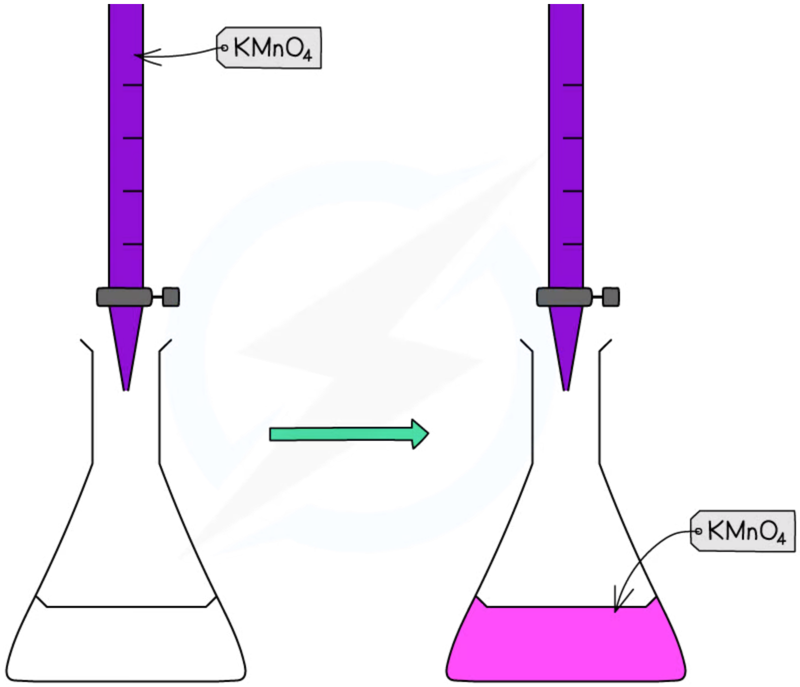
Acid	Reason for not choosing it in the redox titration
Hydrochloric acid	Can be oxidised to chlorine by the manganate(VII) ions
Nitric acid	Is an oxidising agent and may oxidise the substance being analysed
Ethanoic acid	Weak acid and the concentration of hydrogen ions will be insufficient
Concentrated sulfuric acid	May oxidise the substance being analysed

Indicator and end point

- Potassium permanganate acts as its own indicator, as the purple potassium permanganate solution is added to the titration flask from the burette and reacts rapidly with the Fe^{2+}(aq)

  - The burette used in this practical should be one with white numbering not black, as you would struggle to read the values for your titres against the purple colour of the potassium permanganate if black numbering was used

- The manganese(II) ions, $Mn^{2+}(aq)$, have a very pale pink colour but they are present in such a low concentration that the solution looks colourless
- As soon as all of the iron(II), $Fe^{2+}(aq)$, ions have reacted with the added manganate(VII) ions, $Mn^{7+}(aq)$, a pale pink tinge appears in the flask due to an excess of manganate(VII) ions, $Mn^{7+}(aq)$



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Redox titration colour change for potassium permanganate and iron(II) ions

Worked Example

Equations

Find the stoichiometry for the reaction and complete the two half equations:

$$MnO_4^- (aq) + 5e^- + 8H^+ (aq) \rightarrow Mn^{2+} (aq) + 4H_2O (l)$$

$$Fe^{2+} (aq) \rightarrow Fe^{3+} (aq) + e^-$$

Answers:

Balance the electrons:

$$MnO_4^- (aq) + 5e^- + 8H^+ (aq) \rightarrow Mn^{2+} (aq) + 4H_2O (l)$$

$$5Fe^{2+} (aq) \rightarrow 5Fe^{3+} (aq) + 5e^-$$

Add the two half equations:

$$MnO_4^- (aq) + 8H^+ (aq)\ 5Fe^{2+} (aq) \rightarrow Mn^{2+} (aq) + 4H_2O (l) + 5Fe^{3+} (aq)$$

Exam Tip

General sequence for redox titration calculations

1. Write down the half equations for the oxidant and reductant
2. Deduce the overall equation
3. Calculate the number of moles of manganate(VII) or dichromate(VI) used
4. Calculate the ratio of moles of oxidant to moles of reductant from the overall redox equation
5. Calculate the number of moles in the sample solution of the reductant
6. Calculate the number of moles in the original solution of reductant
7. Determine either the concentration of the original solution or the percentage of reductant in a known quantity of sample

Iodine–Thiosulfate Titrations

- A redox reaction occurs between iodine and thiosulfate ions:

$$2S_2O_3^{2-} (aq) + I_2 (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$$

- The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions
- When the solution is a straw colour, **starch** is added to clarify the end point
- The solution turns blue/black until all the iodine reacts, at which point the colour disappears.
- This titration can be used to determine the concentration of an **oxidizing agent**, which **oxidizes** iodide ions to iodine molecules
- The amount of iodine is determined from **titration** against a known quantity of sodium thiosulfate solution

Redox Titrations Calculations

- Common redox titration calculations can include:
  - Manganate(VII) titrations can be used to determine:
    - The percentage purity of iron supplements

$$\text{Percentage purity} = \frac{\text{mass of sample}}{\text{mass of impure sample}} \times 100$$

    - The formula of a sample of hydrated ethanedioic acid
  - Iodine / thiosulfate reactions can be used to determine:
    - The amount of chlorate(I), ClO^-, in bleach
    - The amount of copper(II) ions, Cu^{2+}, in copper(II) compounds
    - The copper content of alloys

Worked Example

Analysis of iron tablets

An iron tablet, weighing 0.960 g was dissolved in dilute sulfuric acid. An average titre of 28.50 cm^3 of 0.0180 mol dm^{-3} potassium manganate(VII) solution was needed to reach the endpoint.

What is the percentage by mass of iron in the tablet?

Answer:

- MnO_4^- (aq) + $8H^+$ (aq) + $5Fe^{2+} \rightarrow Mn^{2+}$ (aq) + $5Fe^{3+}$ (aq) + $4H_2O$ (l)
- 1 : 5 ratio of MnO_4^- : Fe^{2+}
- Number of moles of MnO_4^- (aq) = $\frac{0.0180 \times 28.5}{1000}$ = 5.13×10^{-4} moles
- Moles of iron(II) = 5 x 5.13×10^{-4} = 2.565×10^{-3} moles
- Mass of iron(II) = 56.0 x 2.565×10^{-3} = 0.14364 g
- Percentage by mass = = $\frac{0.14364}{0.960} \times 100 =$ 15.0%

Worked Example

Analysis of household bleach

Chlorate(I) ions, ClO^-, are the active ingredient in many household bleaches.

10.0 cm^3 of bleach was made up to 250.0 cm^3. 25.0 cm^3 of this solution had 10.0 cm^3 of 1.0 mol dm^{-3} potassium iodide and then acidified with 1.0 mol dm^{-3} hydrochloric acid.

$$ClO^- (aq) + 2I^- (aq) + 2H^+ (aq) \rightarrow Cl^- (aq) + I_2 (aq) + H_2O (l)$$

This was titrated with 0.05 mol dm^{-3} sodium thiosulfate solution giving an average titre of 25.20 cm^3.

$$2S_2O_3^{2-} (aq) + I_2 (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$$

What is the concentration of chlorate(I) ions in the bleach?

Answer:

- One mole of ClO^- (aq) produces one mole of I_2 (aq) which reacts with two moles of $2S_2O_3^{2-}$ (aq)
  - Therefore, 1 : 2 ratio of ClO^- (aq) : $S_2O_3^{2-}$ (aq)
- Number of moles of $S_2O_3^{2-}$ (aq) $= \dfrac{0.05 \times 25.20}{1000} = 1.26 \times 10^{-3}$ moles
- Number of moles of I_2 (aq) and ClO^- (aq) in 25.0 cm^3 $= \dfrac{1.26 \times 10^{-3}}{2} = 6.30 \times 10^{-4}$ moles
- Number of moles of ClO^- (aq) in 250.0 cm^3 $= 6.30 \times 10^{-4} \times 10 = 6.30 \times 10^{-3}$ moles
- The 250.0 cm^3 was prepared from 10.0 cm^3 bleach
  - 10 cm^3 bleach $= 6.30 \times 10^{-3}$ moles of ClO^- ions
  - 1.0 dm^3 bleach $= 0.630$ moles of ClO^- ions
  - Therefore, the concentration of ClO^- ions in the bleach is **0.630 mol dm^{-3}**

Exam Tip

- You are expected to be able to perform similar calculations on non-familiar redox titrations
- These could include:
  - Using other oxidising agents such as acidified potassium dichromate(VI) instead of potassium manganate(VII)
  - Completing titrations with potassium manganate(VII) where it is reduced

Standard Electrode Potential

Standard electrode potential

- The position of equilibrium and therefore the electrode potential depends on factors such as:
  - Temperature
  - Pressure of gases
  - Concentration of reagents
- So, to be able to compare the electrode potentials of different species, they all have to be measured against a common reference or standard
- **Standard conditions** also have to be used when comparing electrode potentials
- These standard conditions are:
  - Ion concentration of 1.00 mol dm^{-3}
  - A temperature of 298 K
  - A pressure of 100 kPa
- Standard measurements are made using a **high resistance voltmeter** so that no current flows and the maximum potential difference is achieved
- The electrode potentials are measured relative to a **standard hydrogen electrode**
- The standard hydrogen electrode is given a value of 0.00 V, and all other electrode potentials are compared to this standard
- This means that the electrode potentials are always referred to as a **standard electrode potential (E^{θ})**
- The **standard electrode potential (E^{θ})** is the potential difference (sometimes called voltage) produced when a **standard half-cell** is connected to a **standard hydrogen cell** under standard conditions
- For example, the standard electrode potential of bromine suggests that relative to the hydrogen half-cell it is more likely to get reduced, as it has a **more positive** E^{θ} value

$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \qquad E^{\theta} = +1.09\ V$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E^{\theta} = 0.00\ V$$

- The standard electrode potential of sodium, on the other hand, suggests that relative to the hydrogen half-cell it is less likely to get reduced as it has a **more negative** E^{θ} value

$$Na^+(aq) + e^- \rightleftharpoons Na(s) \qquad E^{\theta} = -2.71\ V$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E^{\theta} = 0.00\ V$$

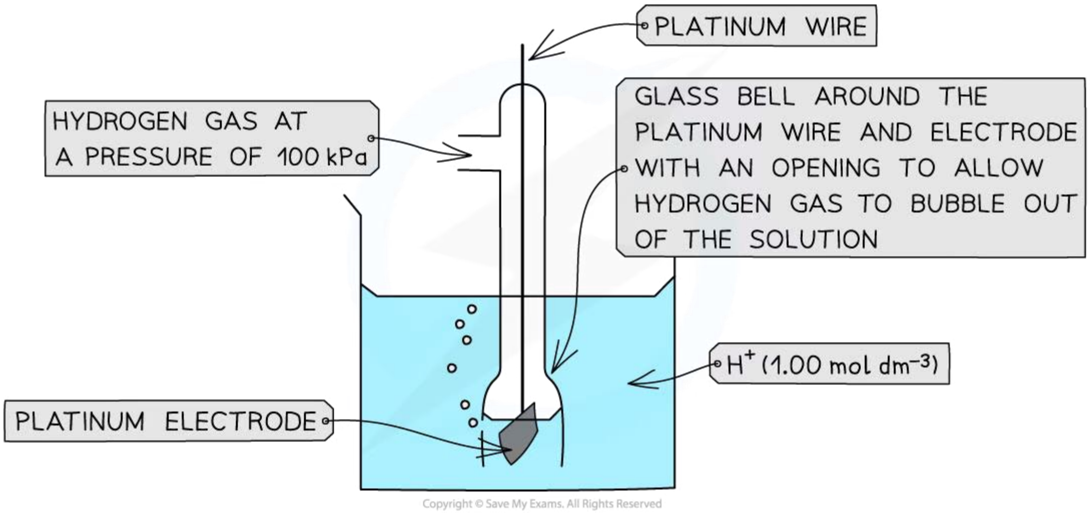
Electrochemical Cells

- The **standard hydrogen electrode** is a half-cell used as a **reference electrode** and consists of:
  - Hydrogen gas in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3} (at 100 kPa)

$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$$

  - An **inert platinum** electrode that is in contact with the hydrogen gas and H^+ ions

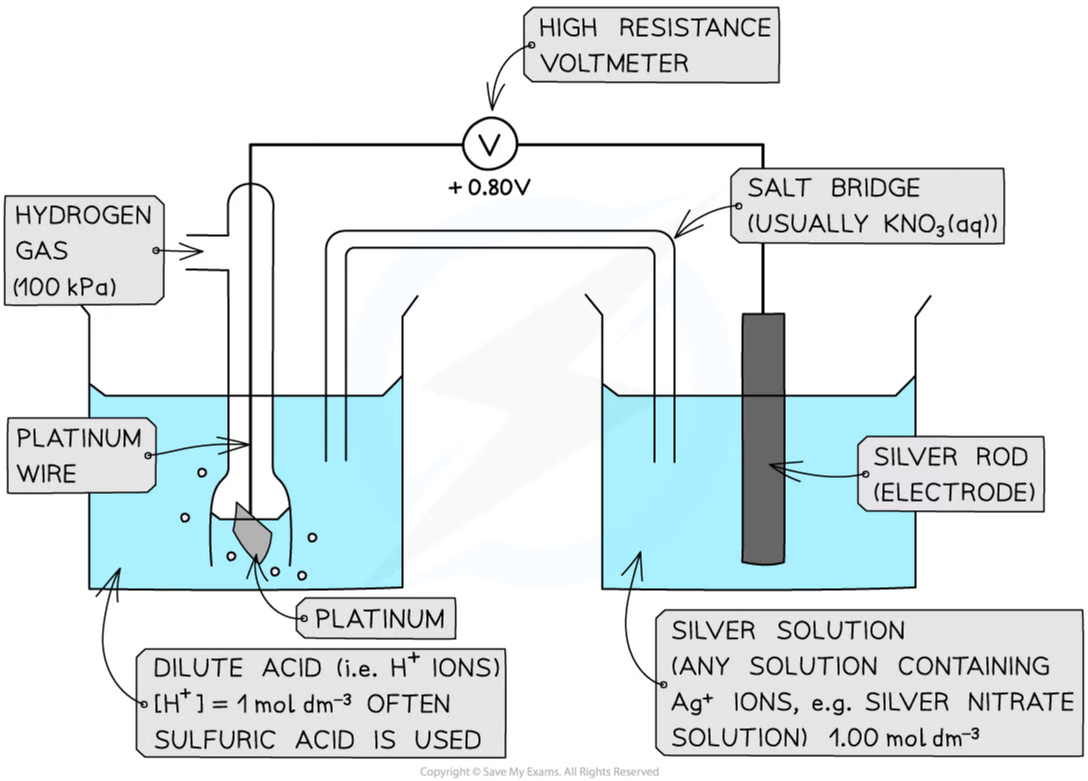
- When the standard hydrogen electrode is connected to another half-cell, the **standard electrode potential** of that half-cell can be read off a high resistance voltmeter



The standard electrode potential of a half-cell can be determined by connecting it to a standard hydrogen electrode

- There are three different types of half-cells that can be connected to a standard hydrogen electrode
  - A metal / metal ion half-cell
  - A non-metal / non-metal ion half-cell
  - An ion / ion half-cell (the ions are in different oxidation states)

Metal / metal-ion half-cell



Example of a metal / metal ion half-cell connected to a standard hydrogen electrode

- An example of a metal/metal ion half-cell is the Ag^+/ Ag half-cell
  - Ag is the metal
  - Ag^+ is the metal ion
- This half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

$$\mathbf{Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s) \qquad E^{\ominus} = +0.80\ V}$$

$$\mathbf{2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2(g) \qquad E^{\ominus} = 0.00\ V}$$

- Since the Ag^+/ Ag half-cell has a more positive $E^{\ominus}$ value, this is the **positive pole** and the H^+/H_2 half-cell is the **negative** pole
- The **standard cell potential (**$E_{cell}^{\ominus}$**)** is $\mathbf{E_{cell}^{\ominus} = (+0.80) - (0.00) = +0.80\ V}$
- The Ag^+ ions are more likely to get **reduced** than the H^+ ions as it has a greater $E^{\ominus}$ value
  - Reduction occurs at the **positive electrode**
  - Oxidation occurs at the **negative electrode**

Non-metal / non-metal ion half-cell

- In a **non-metal / non-metal ion** half-cell, **platinum** wire or foil is used as an electrode to make electrical contact with the solution
  - Like graphite, platinum is inert and does not take part in the reaction
  - The redox equilibrium is established on the platinum surface

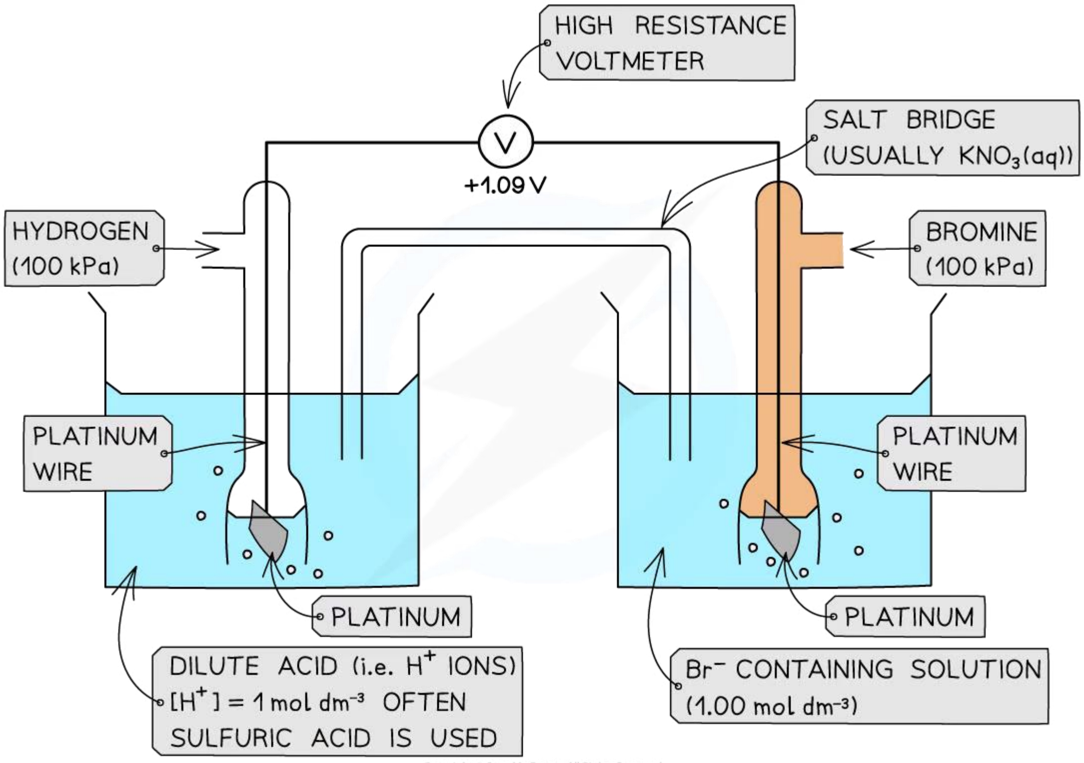
- An example of a non-metal / non-metal ion is the Br_2 / Br^- half-cell
    - Br_2 is the non-metal
    - Br^- is the non-metal ion

- The half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

$$Br_2\,(aq) + 2e^- \rightleftharpoons 2Br^-\,(aq) \qquad E^{\square} = +1.09\ V$$

$$2H^+\,(aq) + 2e^- \rightleftharpoons H_2\,(g) \qquad E^{\square} = 0.00\ V$$

- The Br_2 / Br^- half-cell is the **positive pole** and the H^+ / H_2 is the **negative** pole
- The $E_{cell}^{\square}$ is: $E_{cell}^{\square} = (+\ 1.09) - (0.00) = +\ 1.09\ V$
- The Br_2 molecules are more likely to get **reduced** than H^+ as they have a greater $E^{\square}$ value



Example of a non-metal / non-metal ion half-cell connected to a standard hydrogen electrode

Ion / Ion half-cell

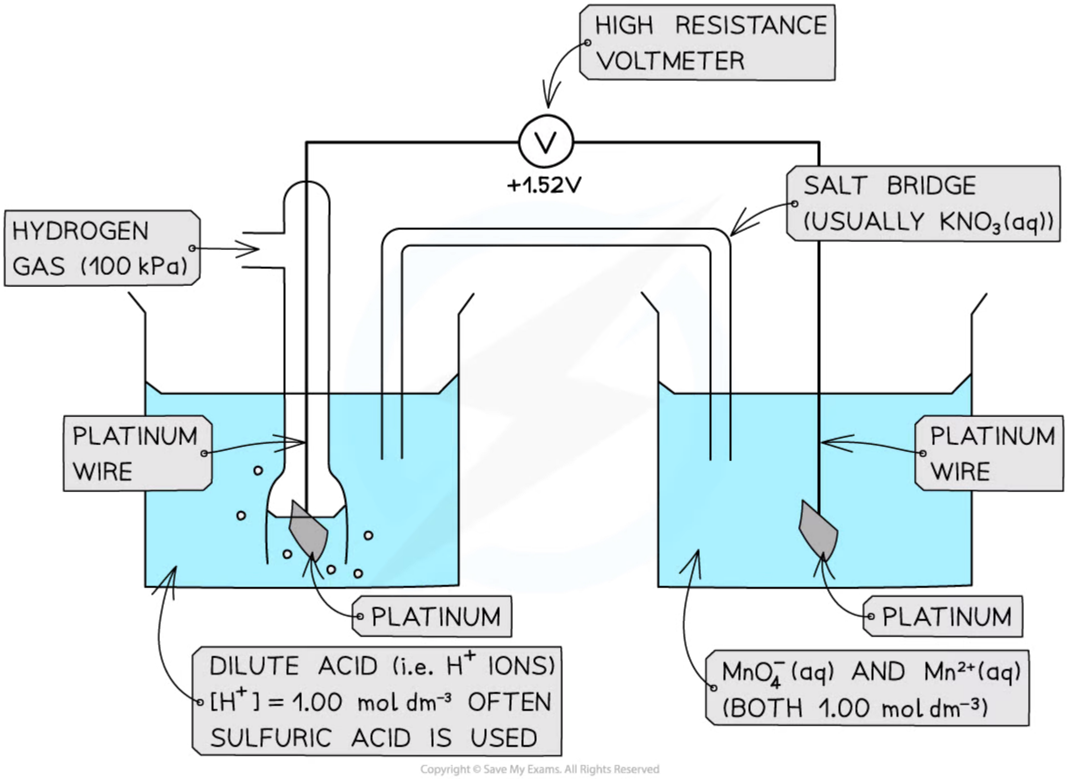
- A **platinum electrode** is again used to form a half-cell of ions that are in **different oxidation states**
- An example of such a half-cell is the MnO_4^- / Mn^{2+} half-cell
    - MnO_4^- is an ion containing Mn with oxidation state +7
    - The Mn^{2+} ion contains Mn with oxidation state +2

- This half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

MnO_4^- (aq) + $8H^+$ (aq) + $5e^-$ $\rightleftharpoons$ Mn^{2+} (aq) + $4H_2O$ (l) **$E^{\ominus}$ = +1.52 V**

$2H^+$ (aq) + $2e^-$ $\rightleftharpoons$ H_2 (g) **$E^{\ominus}$ = 0.00 V**

- The H^+ ions are also present in the half-cell as they are required to convert MnO_4^- into Mn^{2+} ions
- The MnO_4^- / Mn^{2+} half-cell is the **positive pole** and the H^+ / H_2 is the **negative** pole
- The $E_{cell}^{\ominus}$ is **$E_{cell}^{\ominus}$ = (+ 1.09) – (0.00) = + 1.09 V**



Ions in solution half cell

Conventional Representation of Cells

- Chemists use a type of shorthand convention to represent electrochemical cells
- In this convention:
  - A solid vertical (or slanted) line shows a **phase boundary**, that is an interface between a solid and a solution
  - A double vertical line (sometimes shown as dashed vertical lines) represents **a salt bridge**
    - A salt bridge has mobile ions that complete the circuit
    - Potassium chloride and potassium nitrate are commonly used to make the salt bridge as chlorides and nitrates are usually soluble
    - This should ensure that no precipitates form which can affect the equilibrium position of the half cells
  - The substance with the **highest oxidation state** in each half cell is drawn next to the salt bridge

  - The cell potential difference is shown with the **polarity of the right hand electrode**

- The cell convention for the zinc and copper cell would be

$Zn\ (s)|Zn^{2+}\ (aq)\ ||\ Cu^{2+}\ (aq)|Cu\ (s)$ $\qquad E_{cell} = +1.10\ V$

- This tells us the copper half cell is more positive than the zinc half cell, so that electrons would flow from the zinc to the copper
- The same cell can be written as:

$Cu\ (s)|Cu^{2+}\ (aq)\ ||\ Zn^{2+}\ (aq)|Zn\ (s)$ $\qquad E_{cell} = –1.10\ V$

- The polarity of the right hand half cell is negative, so we can still tell that electrons flow from the zinc to the copper half cell

Worked Example

Writing a cell diagram

If you connect an aluminium electrode to a zinc electrode, the voltmeter reads 0.94V and the aluminium is the negative. Write the conventional cell diagram to the reaction.

Answer

$Al\ (s)|Al^{3+}\ (aq)\ ||\ Zn^{2+}\ (aq)|Zn\ (s)$ $\qquad E_{cell} = +0.94\ V$

It is also acceptable to include phase boundaries on the outside of cells as well:

$|\ Al\ (s)|Al^{3+}\ (aq)\ ||\ Zn^{2+}\ (aq)|Zn\ (s)\ |$ $\qquad E_{cell} = +0.94\ V$

Exam Tip

Writing the cell representation is not a specific requirement of the syllabus, however questions will sometimes use cell representations to present information so it is useful to know what a cell representation is.

Students often confuse the redox processes that take place in electrochemical cells.

- Oxidation takes place at the negative electrode.
- Reduction takes place at the positive electrode.

Remember, oxidation is the loss of electrons, so you are losing electrons at the negative.

$|\ Al\ (s)|Al^{3+}\ (aq)\ ||Zn^{2+}\ (aq)|Zn\ (s)\ |$ $\qquad E_{cell} = +0.94\ V$

YOUR NOTES

5.5.4 Electrode Potential Calculations

Calculating Standard Cell Potential

- Once the $E^{\ominus}$ of a half-cell is known, the **potential difference** or **voltage** or **emf** of an **electrochemical cell** made up of any two half-cells can be calculated
  - These could be **any** half-cells and neither have to be a standard hydrogen electrode
- The **standard cell potential** ($E_{cell}^{\ominus}$) can be calculated by **subtracting** the **less positive** $E^{\ominus}$ from the **more positive** $E^{\ominus}$ value
  - The half-cell with the more positive $E^{\ominus}$ value will be the **positive** pole
    - By convention this is shown on the right hand side in a conventional cell diagram, so is termed $E_{right}^{\ominus}$
  - The half-cell with the less positive $E^{\ominus}$ value will be the **negative** pole
    - By convention this is shown on the left hand side in a conventional cell diagram, so is termed $E_{left}^{\ominus}$

$$E_{cell}^{\ominus} = E_{right}^{\ominus} - E_{left}^{\ominus}$$

  - Since oxidation is always on the left and reduction on the right, you can also use this version

$$E_{cell}^{\ominus} = E_{reduction}^{\ominus} - E_{oxidation}$$

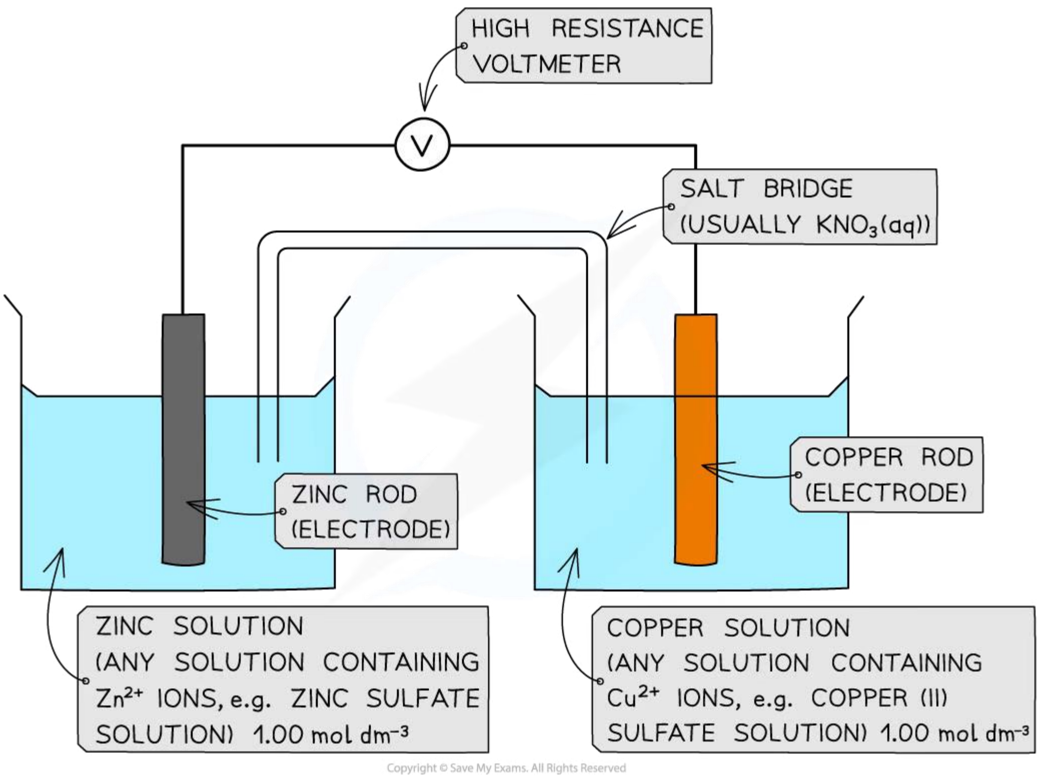
Worked Example

Calculating the standard cell potential

Calculate the standard cell potential for the electrochemical cell below and explain why the Cu^{2+} / Cu half-cell is the positive pole. The half-equations are as follows:

$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\ V$

$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\ V$



Answer

Step 1: Calculate the standard cell potential. The copper is more positive so must be the right hand side.

$$E_{cell}^{\square} = E_{right}^{\square} - E_{left}^{\square}$$

$$E_{cell}^{\square} = (+0.34) - (-0.76)$$

$$= +1.10 \text{ V}$$

The voltmeter will therefore give a value of +1.10 V

Step 2: Determine the positive and negative poles

The Cu^{2+} / Cu half-cell is the **positive** pole as its $E^{\square}$ is more positive than the $E^{\square}$ value of the Zn^{2+} / Zn half-cell

YOUR NOTES

Exam Tip

A helpful mnemonic for remembering redox in cells

Lio the lion goes Roor!

Lio stands for 'Left Is Oxidation' and he is saying ROOR because that is the order of species in the cell:

Reduced/Oxidised (salt bridge) Oxidised/Reduced

Feasibility & Standard Cell Potential

Feasibility

- The $E^{\ominus}$ values of a species indicate how **easily** they can get **oxidised** or **reduced**
- The **more** positive the value, the easier it is to reduce the species on the **left** of the half-equation
  - The reaction will tend to proceed in the **forward direction**
- The **less** positive the value, the easier it is to **oxidise** the species on the **right** of the half-equation
  - The reaction will tend to proceed in the backward direction
  - A reaction is **feasible** (likely to occur) when the $E_{cell}^{\ominus}$ is **positive**
- For example, two half-cells in the following electrochemical cell are:

$$Cl_2\,(g) + 2e^- \rightleftharpoons 2Cl^-\,(aq) \qquad E^{\ominus} = +1.36\ V$$

$$Cu^{2+}\,(aq) + 2e^- \rightleftharpoons Cu\,(s) \qquad E^{\ominus} = +0.34\ V$$

- Cl_2 molecules are **reduced** as they have a more positive $E^{\ominus}$ value
- The chemical reaction that occurs in this half cell is:

$$Cl_2\,(g) + 2e^- \rightarrow 2Cl^-\,(aq)$$

- Cu^{2+} ions are **oxidised** as they have a less positive $E^{\ominus}$ value
- The chemical reaction that occurs in this half cell is:

$$Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2e^-$$

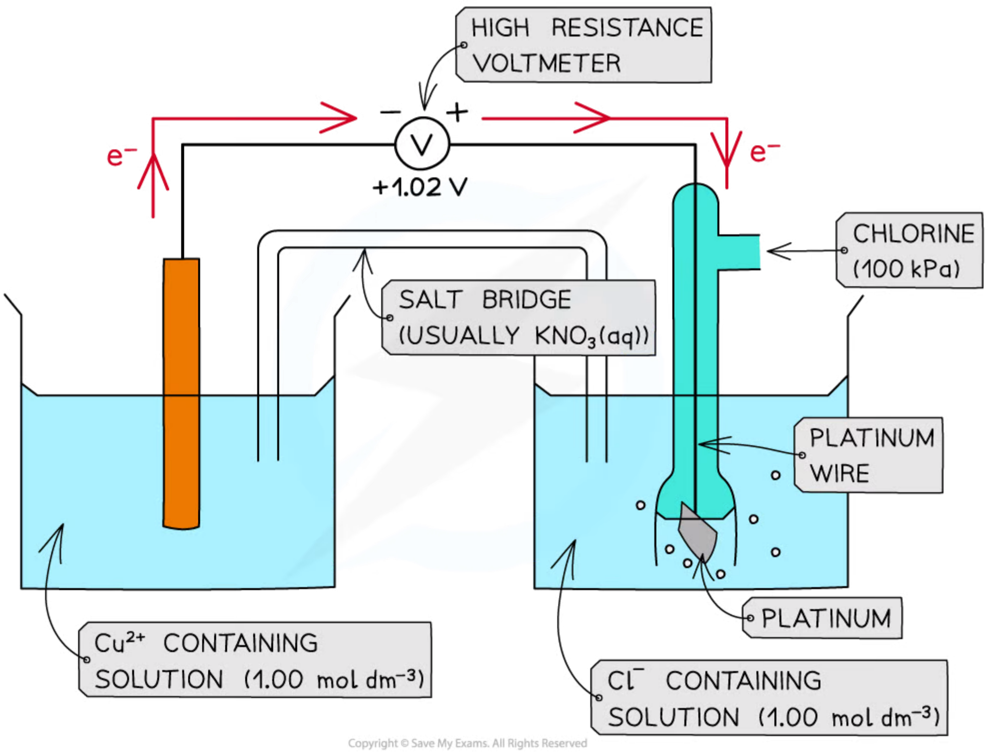
- The **overall equation** of the electrochemical cell is (after cancelling out the electrons):

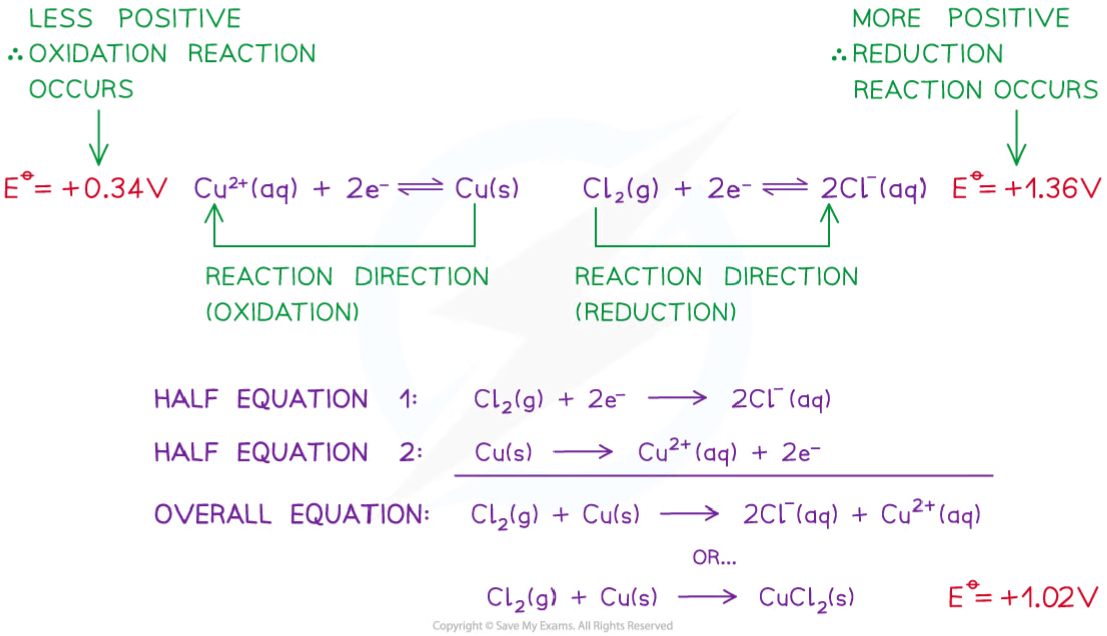
$$Cu\,(s) + Cl_2\,(g) \rightarrow 2Cl^-\,(aq) + Cu^{2+}\,(aq)$$

OR

$$Cu\,(s) + Cl_2\,(g) \rightarrow CuCl_2\,(s)$$

- The **forward** reaction is **feasible** (spontaneous) as it has a **positive** $E^{\ominus}$ value of +1.02 V ((+1.36) – (+0.34))
- The **backward** reaction is **not feasible** (not spontaneous) as it has a **negative** $E^{\ominus}$ value of –1.02 ((+0.34) – (+1.36))





A reaction is feasible when the standard cell potential E⦵ is positive

Exam Tip

You may have to apply your understanding (from the above worked example) to questions with more than 2 equations

- The process is still the same in terms of identifying the most positive / least negative value as the reduction reactions
- This reaction will also contain the oxidising agent on the left hand side

YOUR NOTES

Limitations of E^{θ} to predict reactions

- The thermodynamic feasibility of a reaction can be deduced from the electrode potential, however, it gives no information about the rate of reaction
- As standard electrode potentials are measured using solutions, we have to consider the le Châtelier's effect on concentration using non-standard conditions
    - For example, the redox equilibrium equation and standard electrode potential for the V^{3+} | V^{2+} system are:

$$V^{3+}\,(aq) + e^{-} \rightleftharpoons V^{2+}\,(aq) \qquad E^{\theta} = +0.26\ V$$

    - If the concentration of V^{3+} (aq) is greater than 1.0 mol dm^{-3}, then the equilibrium will shift to the right
        - This will remove electrons from the system, therefore, making the electrode potential less negative
    - If the concentration of V^{2+} (aq) is greater than 1.0 mol dm^{-3}, then the equilibrium will shift to the left
        - This will add electrons to the system, therefore, making the electrode potential more negative
    - Any change to the concentration will cause a change to the electrode potential and, therefore, to the overall cell potential
        - This is true of any change to the conditions that results in non-standard conditions
- Another, more basic limitation is the fact that many redox reactions are not aqueous

Storage Cells

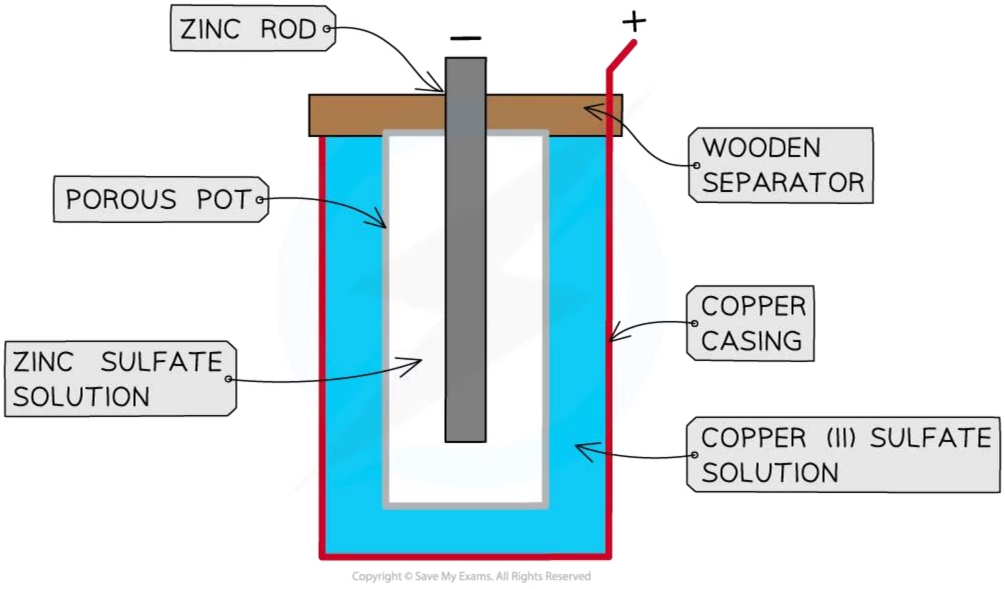
- Electrochemical cells can be used as a commercial source of electrical energy
- Cells can be described as **primary, secondary** or **fuel cells**
    - Primary cells are **non-rechargeable** (irreversible)
    - Secondary cells are **rechargeable**
- Type of cells used in commercial applications depend on
    - the **voltage** required
    - the **current** needed
    - the **size** of the cell
    - the **cost**

- Although it is commonly used incorrectly, the term *battery* should be used to refer to a *collection* of cells
- A car battery is correct, because it is a collection of six cells joined together

Primary cells

The Daniell cell

- The Daniell cell was one of the earliest electrochemical cells and consisted of a simple metal–metal ion system
- It was invented by British chemist John Daniell in 1836
- The cell consists of
    - a zinc rod immersed in a solution of zinc sulfate
    - a copper cylinder filled with copper sulfate solution
    - a porous pot that separates the copper sulfate from the zinc sulfate



A Daniell cell

- The zinc acts as the negative electrode and the copper is the positive electrode

- The half-cell reactions are

$\mathbf{Zn\ (s) \rightarrow\ Zn^{2+}(aq)\ +\ 2e^{-}}$ $\quad E^{\theta} = -0.76\ \mathrm{V}$

$\mathbf{Cu^{2+}(aq)\ +\ 2e^{-} \rightarrow Cu\ (s)}$ $\quad E^{\theta} = +0.34\ \mathrm{V}$

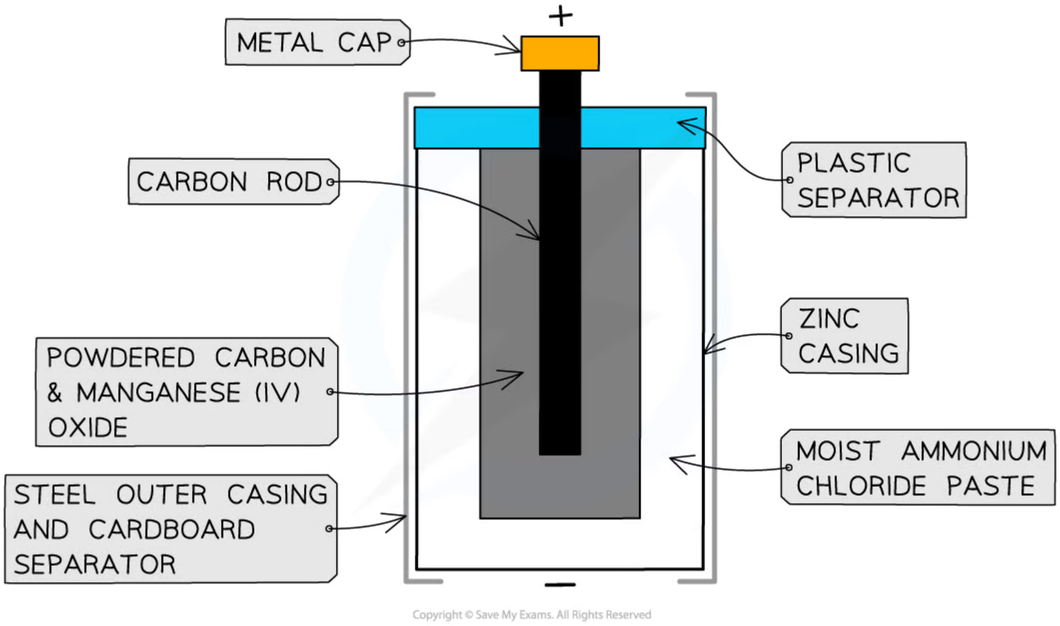
- The cell generates an EMF of 1.1 V and the overall reaction is

$\mathbf{Zn\ (s)\ +\ CuSO_4\ (aq) \rightarrow Cu\ (s)\ +\ ZnSO_4\ (aq)}$ $\quad E^{\theta}_{cell} = +1.10\ \mathrm{V}$

- However, the cell is impractical to use as a portable device because of the hazardous liquids in the cell

Zinc-carbon cells

- Zinc-carbon cells are the most common type of non-rechargeable cells, consisting of
  - a zinc casing which acts as the negative electrode
  - a paste of ammonium chloride which acts as an electrolyte as well as the positive electrode
  - a carbon rod which acts as an electron carrier in the cell



The zinc-carbon cell

- The half-cell reactions are

$\mathbf{Zn\ (s) \rightarrow\ Zn^{2+}(aq)\ +\ 2e^{-}}$ $\quad E^{\theta} = -0.76\ \mathrm{V}$

$\mathbf{2NH_4^{+}(aq) + 2e^{-} \rightarrow 2NH_3(g) + H_2(g)}$ $\quad E^{\theta} = +0.74\ \mathrm{V}$

- The cell generates an emf of 1.50 V and the overall reaction is

$\mathbf{2NH_4^{+}(aq) + Zn\ (s) \rightarrow 2NH_3\ (g) + H_2\ (g)\ +\ Zn^{2+}(aq)}$ $\quad E^{\theta}_{cell} = +1.50\ \mathrm{V}$

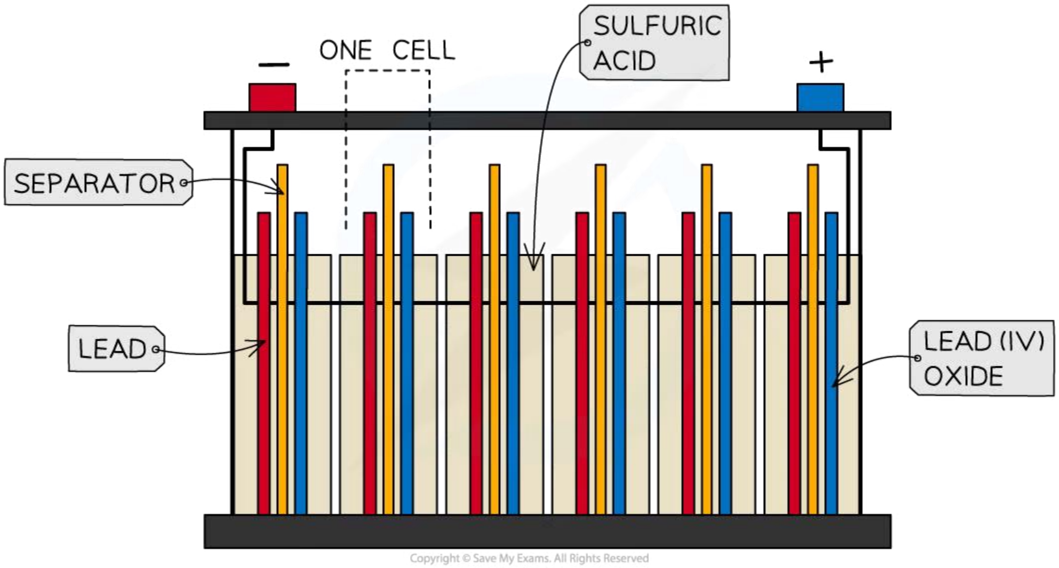
- As the cell discharges, the zinc casing eventually wears away and the corrosive contents of the electrolyte paste can leak out, which is an obvious disadvantage of zinc-carbon cells
- The cell provides a small current and is relative cheap compared to other cells
- Extra long life cells have a similar chemistry, but supply a higher current and use zinc chloride in the paste; they are suitable for torches, radios and clocks
- Another variation on the cell uses an alkaline paste in the electrolyte and they have a much longer operating life, but are noticeably more expensive than regular zinc-carbon cells

Secondary Cells

- Secondary / rechargeable cells employ chemical reactions which can be reversed by applying a voltage greater than the cell voltage, causing electrons to push in the opposite direction
- There are many types of rechargeable cells, but common ones include **lead-acid** batteries, **NiCad** cells and **lithium** cells which are covered in more detail in the next section

Lead-acid batteries

- Lead-acid batteries consist of **six cells** joined together **in series**
- The cells use **lead** metal as the **negative electrode** and and **lead(IV) oxide** as the **positive electrode**
- The electrolyte is sulfuric acid



A lead-acid battery

- The half-cell reactions are

$$Pb\ (s) + SO_4^{2-}\ (aq) \rightarrow PbSO_4\ (s) + 2e^- \qquad E^\theta = -0.36\ V$$

$$PbO_2\,(s) + 4H^+\,(aq) + SO_4^{2-}\,(aq) + 2e^- \rightarrow PbSO_4\,(s) + 2H_2O\,(l) \qquad E^\theta = +1.70\ V$$

- The cell generates an EMF of about 2 V and the overall reaction is

$$PbO_2\,(s) + 4H^+\,(aq) + 2SO_4^{2-}\,(aq) + Pb\,(s) \rightarrow 2PbSO_4\,(s) + 2H_2O\,(l)$$

$$E^\theta_{cell} = +2.06\ V$$

- In a commercial car battery, the six cells in series give a combined voltage of about 12 V
- When the car is in motion, the generator provides a push of electrons that reverses the reaction and regenerates lead and lead(IV) oxide
- Lead-acid batteries are designed to produce a **high current** for a short period of time, hence their use in powering a starter motor in car engines
- The disadvantage of lead-acid batteries is that:
  - They are very **heavy**
  - They contain **toxic** materials: lead and lead(IV) oxide
  - The sulfuric acid electrolyte is very **corrosive**

- This presents challenges of disposal when lead-acid batteries come to the end of their useful life

NiCad cells

- NiCad stands for nickel-cadmium and these cells are available in many standard sizes and voltages so they can replace almost any application of traditional zinc-carbon cells
- Although they are more expensive cells, the fact they can be recharged hundreds of times means they are commercially viable
- The positive electrode consists of cadmium and the negative electrode is made of a nickel(II) hydroxide-oxide system

- The half-cell reactions are

$$Cd\,(s) + 2OH^-\,(aq) \rightarrow Cd(OH)_2\,(s) + 2e^- \qquad E^\theta = -0.82\ V$$

$$NiO(OH)\,(s) + H_2O\,(l) + e^- \rightarrow Ni(OH)_2\,(s) + OH^-\,(aq) \qquad E^\theta = +0.38\ V$$

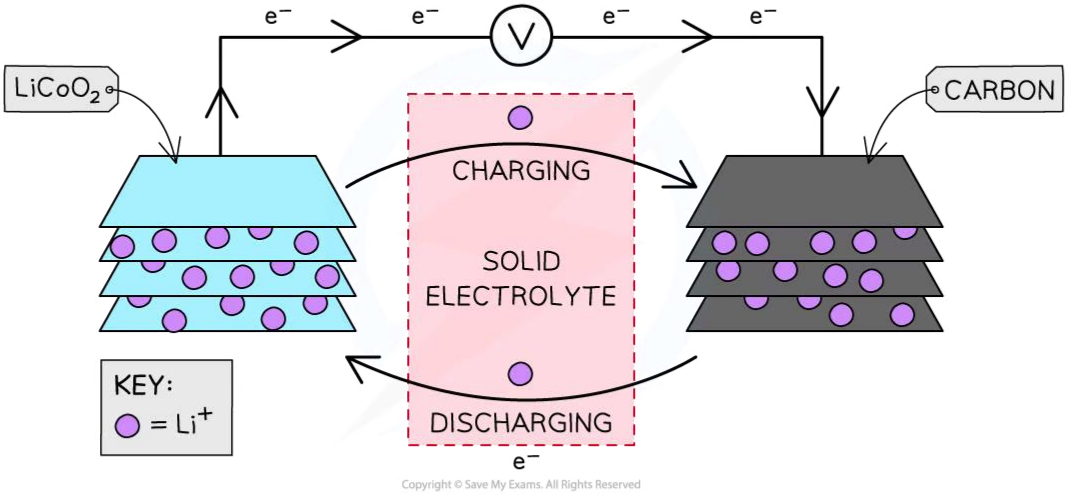
- The overall reaction in the cell is

$$2NiO(OH)\,(s) + 2H_2O\,(l) + Cd\,(s) \rightarrow 2Ni(OH)_2\,(s) + Cd(OH)_2\,(s) \qquad E^\theta = +1.2\ V$$

- Cadmium is a toxic metal so the disposal of old NiCad cells is also an environmental issue

- Lithium ion cells power the laptop or mobile device you are probably reading this on
- The Noble Prize for Chemistry in 2019 was awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino for their work on lithium ion cells that have revolutionised portable electronics

- Lithium is used because it has a very low density and relatively high electrode potential
- The cell consists of:
  - a positive lithium cobalt oxide electrode
  - a negative carbon electrode
  - a porous polymer membrane electrolyte
- The polymer electrolyte cannot leak since it is not a liquid or paste, which presents advantages over other types of cells



Lithium ion cell

- The cell consists of a sandwich of different layers of lithium cobalt oxide and carbon
- When the cell is charged and discharged the lithium ions flow between the negative and the positive through the solid electrolyte
- The half-cell reactions on discharge are:

$$\mathbf{Li\ (s) \rightarrow Li^+\ (s) + e^-} \qquad E^\theta = -3\ \mathrm{V}$$

$$\mathbf{Li^+\ (s) + CoO_2\ (s) + e^- \rightarrow Li^+(CoO_2)^-\ (s)} \qquad E^\theta = +1\ \mathrm{V}$$

- The cell generates an EMF of between 3.5 V and 4.0 V and the overall reaction is

$$\mathbf{Li\ (s) + CoO_2\ (s) \rightarrow Li^+(CoO_2)^-\ (s)} \qquad E^\theta_{cell} \sim +3.5$$

- NiCad cells have a problem called the memory effect in which they gradually begin to lose their charge after repeated charge cycles when the cell is not fully discharged. The cells appear to 'remember' their lower state of charge
- Lithium-ion cells do not have this problem so can be topped up without any loss of charge
- Some of the problems with lithium ion cells:
  - A global shortage of lithium is likely to make lithium ion cells unsustainable as the current demand for lithium exceeds the supply
  - If cells are not recycled but thrown away in landfills, then a huge amount of lithium becomes lost to future generations

- Reports of lithium ion cell fires have raised concern about the safety of these batteries in electronic devices; it is a reminder to us that lithium is a very reactive element in Group 1 of the periodic table, which is why it has a high electrode potential

Fuel Cells

- A fuel cell is an electrochemical cell in which a fuel **donates** electrons at one electrode and oxygen **gains** electrons at the other electrode
- These cells are becoming more common in the automotive industry to replace petrol or diesel engines
- As the fuel enters the cell it becomes oxidised which sets up a **potential difference** or voltage within the cell
- Different electrolytes and fuels can be used to set up different types of fuel cells
- An important cell is the **hydrogen-oxygen** fuel cell which combines both elements to release energy and water

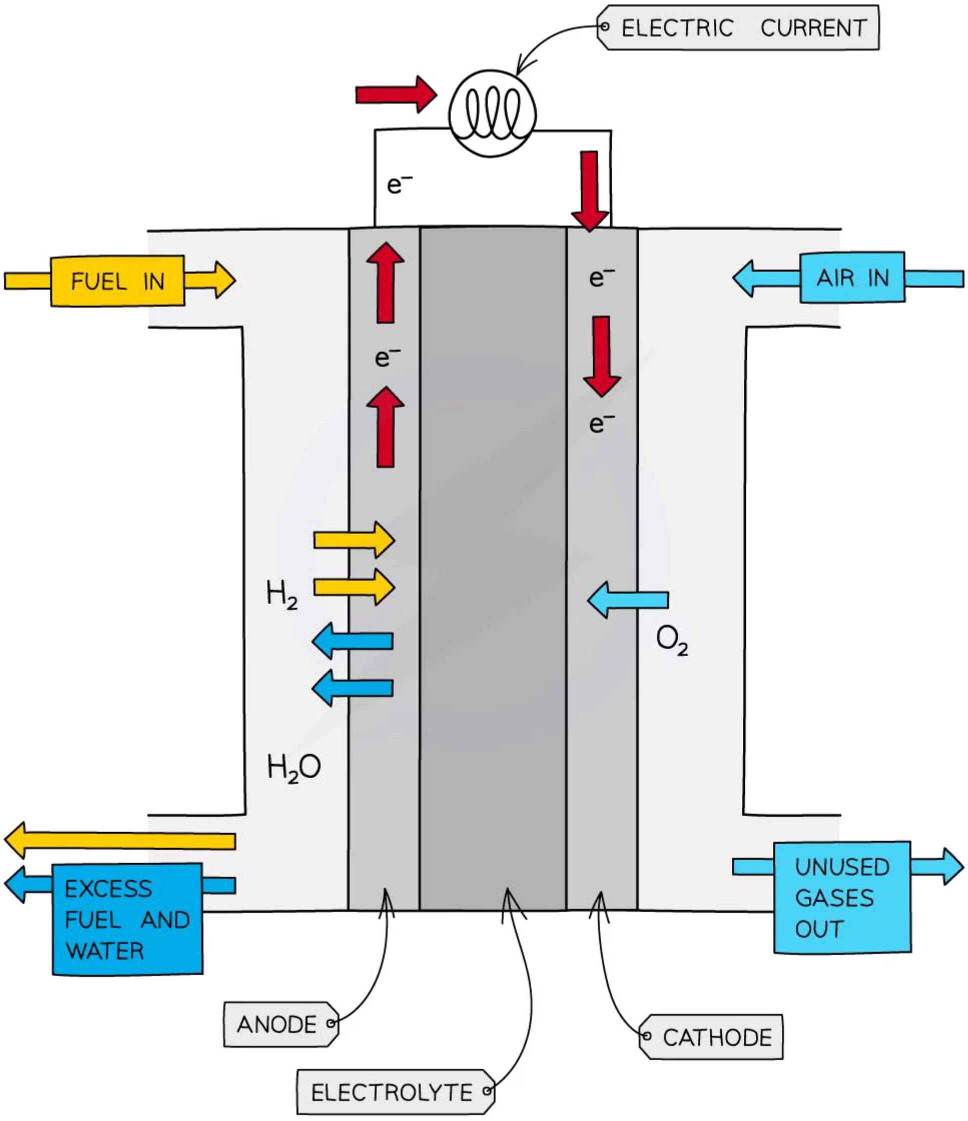


Diagram showing the movement of hydrogen, oxygen and electrons in a hydrogen-oxygen fuel cell

- The fuel cell consists of
  - a reaction chamber with separate inlets for hydrogen and oxygen gas
  - an outlet for the product - water
  - an electrolyte of aqueous sodium hydroxide
  - a semi-permeable membrane that separates the hydrogen and oxygen gases

- The half equations are

$$2H_2\,(g) + 4OH^-\,(aq) \rightarrow 4H_2O\,(l) + 4e^- \qquad E^\theta = -0.83\ V$$

$$O_2\,(g) + 2H_2O + 4e^- \rightarrow 4OH^-\,(aq) \qquad E^\theta = +0.40\ V$$

- The overall reaction is found by combining the two half equations and cancelling the common terms:

$$2H_2\,(g) + 4OH^-\,(aq) + O_2\,(g) + 2H_2O + 4e^- \rightarrow 42H_2O\,(l) + 4e^- + 4OH^-\,(aq)$$

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l) \qquad E^\theta = +1.23\ V$$

Benefits

- Water is the only reaction product, so fuel cells present obvious environmental advantages over other types of cells
- The reaction is the same as hydrogen combusting in oxygen, but since the reaction takes place at room temperature without combustion, all the bond energy is converted into electrical energy instead of heat and light
- There are no harmful oxides of nitrogen produced, which are usually formed in high temperature combustion reactions where air is present
- Fuel cells have been used on space craft, where the product can be used as drinking water for astronauts

Risks and problems

- Hydrogen is a highly flammable gas and the production and storage of hydrogen carries safety hazards
- Very thick walled cylinders and pipes are needed to store hydrogen which has economic impacts
- The production of hydrogen is a by-product of the crude oil industry, which means it relies on a **non-renewable, finite resource**
- Until a cheap way is found to make hydrogen, its widespread use in fuel cells will be limited
- Hydrogen has high energy density, that is, the amount of energy contained in 1g of the fuel is high compared to other fuels, but because it is a gas, its energy density per unit volume is low which means larger containers are needed compared to liquid fuels

Exam Tip

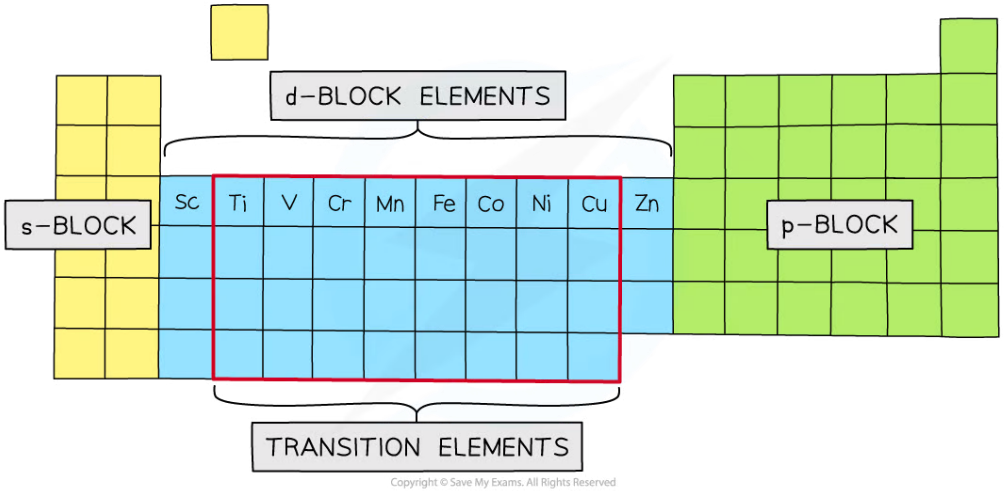
One difference between fuel cells and other cells is that the cell operates continuously as long as there is a supply of hydrogen and oxygen; the energy is not stored in the cell.

5.6 Transition Elements

5.6.1 Transition Elements

Electron Configuration of a Transition Element

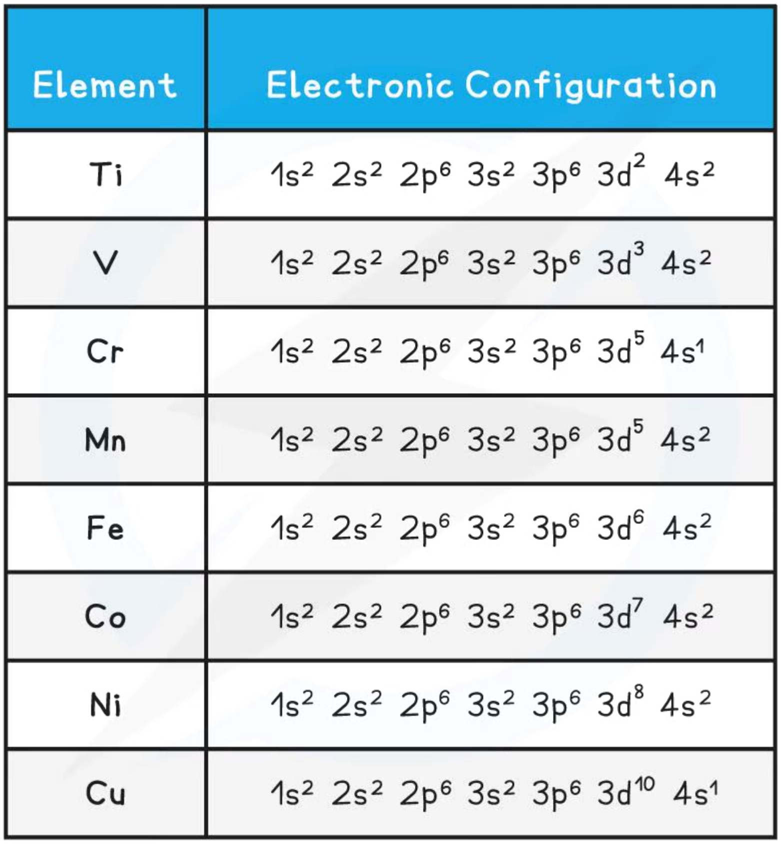
- Transition metals are elements with an incomplete d-subshell that can form at least one stable ion with an incomplete d-subshell
- This definition distinguishes them from d-block elements, because scandium and zinc do not fit the definition
    - Scandium only forms the ion **Sc^{3+}**, configuration **[Ar] $3d^0$**
    - Zinc only forms the ion **Zn^{2+}**, configuration **[Ar] $3d^{10}$**
- The elements of the first transition series are therefore titanium to copper



Electron Configuration

- The full electronic configuration of the first d-series transition metals is shown in the table below
- Following the **Aufbau Principle** electrons occupy the lowest energy subshells first
- The 4s overlaps with the 3d subshell so the 4s is filled first
- Remember that you can abbreviate the first five subshells, 1s-3p, as **[Ar]** representing the configuration of argon(known as the argon core)

Table showing the electronic configuration of the first d-series transition elements



Element	Electronic Configuration
Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
V	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Mn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

- From AS Chemistry you should recall two exceptions to the Aufbau Principle, chromium and copper
- In both cases an electron is promoted from the 4s to the 3d to achieve a half full and full d-subshell, respectively
- Chromium and copper have the following electron configurations, which are different to what you may expect:
  - Cr is [Ar] $3d^5\ 4s^1$ **not** [Ar] $3d^4\ 4s^2$
  - Cu is [Ar] $3d^{10}\ 4s^1$ **not** [Ar] $3d^9\ 4s^2$
- This is because the [Ar] $3d^5\ 4s^1$ and [Ar] $3d^{10}\ 4s^1$ configurations are **energetically more stable**
- The electronic configurations of an iron atom and its common ions, Fe^{2+} and Fe^{3+}, are shown below
  - Fe atom $1s^22s^22p^63s^23p^63d^64s^2$
  - Fe^{2+} ion $1s^22s^22p^63s^23p^63d^6$
  - Fe^{3+} ion $1s^22s^22p^63s^23p^63d^5$

Coloured Ions & Catalytic Behaviour

General properties

- Although the **transition elements** are metals, they have some properties unlike those of other metals on the periodic table, such as:
  - Variable **oxidation states**
  - Form **complex ions**
  - Form **coloured compounds**
  - Behave as **catalysts**

Variable Oxidation States

- Like other metals on the periodic table, the transition elements will lose electrons to form positively charged ions
- However, unlike other metals, transition elements can form more than one positive ion
  - They are said to have **variable oxidation states**
- Because of this, Roman numerals are used to indicate the oxidation state on the metal ion
  - For example, the metal sodium (Na) will only form Na^+ ions (no Roman numerals are needed, as the ion formed by Na will always have an oxidation state of +1)
  - The transition metal iron (Fe) can form Fe^{2+} (Fe(II)) **and** Fe^{3+} (Fe(III)) ions

Forming Complex ions

- Another property of transition elements caused by their ability to form variable oxidation states, is their ability to form **complex ions**
- A complex ion is a molecule or ion, consisting of a central metal atom or ion, with a number of molecules or ions surrounding it
- A molecule or ion surrounding the central metal atom or ion is called a **ligand**
- Due to the different oxidation states of the central metal ions, a different number and wide variety of ligands can form bonds with the transition element
  - For example, the chromium(III) ion can form $[Cr(NH_3)_6]^{3+}$, $[Cr(OH)_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$ complex ions

Forming coloured compounds

- Another characteristic property of transition elements is that their compounds are often **coloured**
  - For example, the colour of the $[Cr(OH)_6]^{3-}$ complex (where oxidation state of Cr is +3) is **dark green**
  - Whereas the colour of the $[Cr(NH_3)_6]^{3+}$ complex (oxidation state of Cr is still +3) is **purple**

Transition elements as catalysts

- Since transition elements can have variable oxidation states, they make excellent **catalysts**
- During catalysis, the transition element can change to various oxidation states by gaining electrons or donating electrons from reagents within the reaction

- Substances can also be adsorbed onto their surface and activated in the process
- There are two types of catalyst:
  - A **heterogeneous** catalyst is in a different physical state (phase) from the reactants
    - The reaction occurs at active sites on the surface of the catalyst
    - An example is the use of iron, Fe, in the Haber process for making ammonia

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

  - A **homogeneous** catalyst is in the same physical state (phase) as the reactants
- The decomposition of hydrogen peroxide is a common reaction in the study of chemical kinetics and uses manganese(IV) oxide as the catalyst

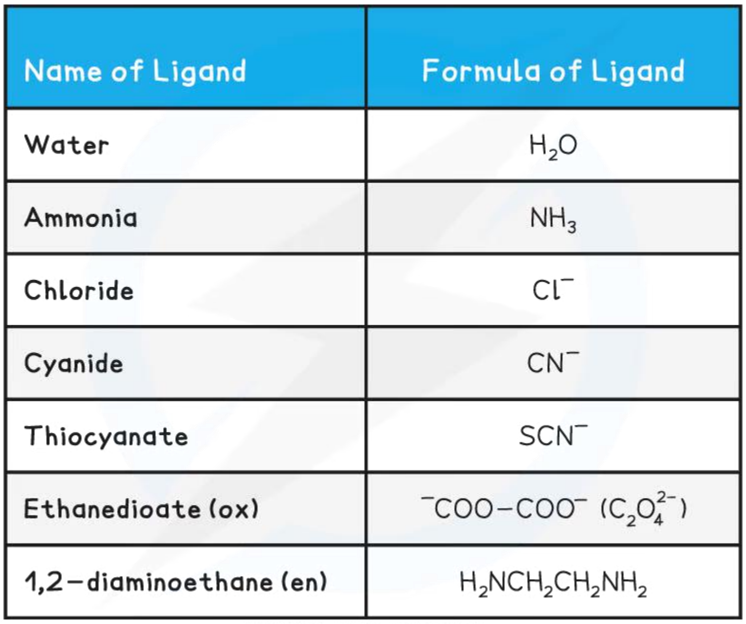
$$2H_2O_2\ (g) \rightarrow 2H_2O\ (aq) + O_2\ (g)$$

5.6.2 Ligands & Complex Ions

Structure & Bonding of Transition Element Complexes

- Transition element ions can form complexes which consist of a **central metal ion** and **ligands**
- A ligand is a molecule or ion that forms a co-ordinate bond with a transition metal by donating a pair of electrons to the bond
    - This is the definition of a Lewis base - electron pair donor
- This means ligands have a negative charge or a lone pair of electrons capable of being donated
    - This definition may seem familiar: a ligand is the same as a **nucleophile**
- Different **ligands** can form different numbers of dative bonds to the central metal ion in a complex
    - Some ligands can form **one** dative bond to the central metal ion
    - Other ligands can form **two** dative bonds, and some can form **multiple** dative bonds
- **Co-ordination number** is number of co-ordinate bonds to the central metal atom or ion

Examples of ligands Table

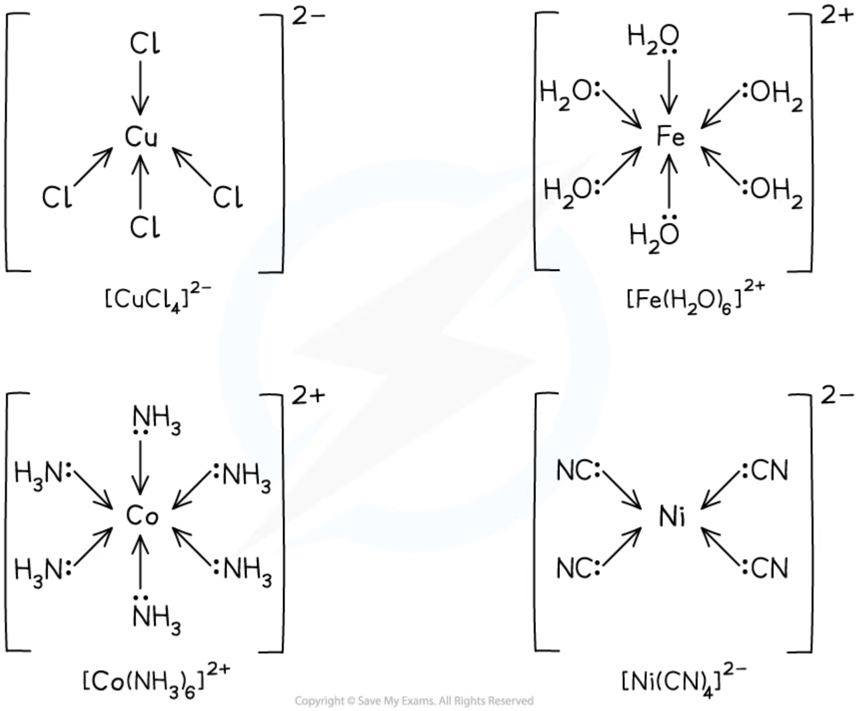


Name of Ligand	Formula of Ligand
Water	H_2O
Ammonia	NH_3
Chloride	Cl^-
Cyanide	CN^-
Thiocyanate	SCN^-
Ethanedioate (ox)	$^-COO-COO^-$ ($C_2O_4^{2-}$)
1,2-diaminoethane (en)	$H_2NCH_2CH_2NH_2$

Monodentate Ligands

- **Monodentate** ligands can form only **one** dative bond to the central metal ion
- Examples of monodentate ligands are:
    - Water (H_2O) molecules
    - Ammonia (NH_3) molecules
    - Chloride (Cl^-) ions

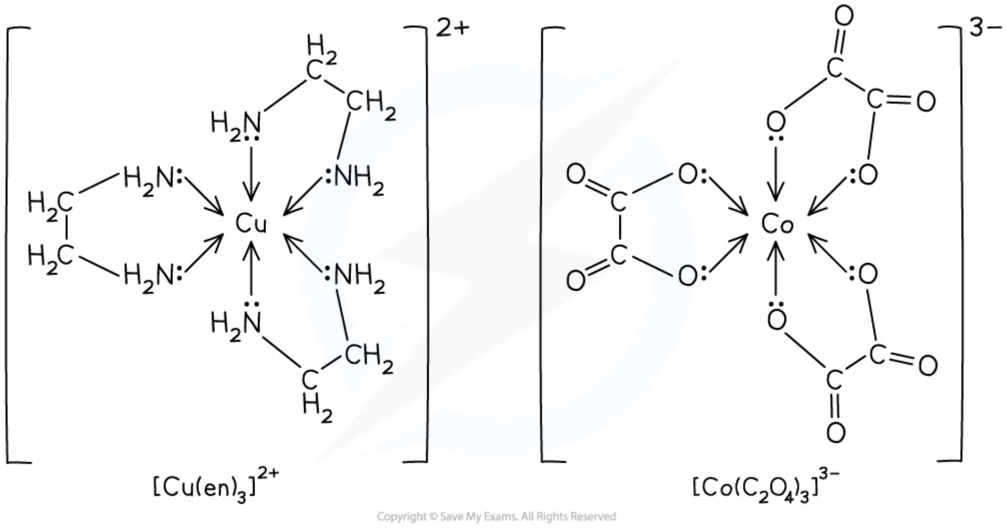
   - Cyanide (CN^-) ions



Examples of complexes with monodentate ligands

Bidentate Ligands

- **Bidentate** ligands can each form **two** dative bonds to the central metal ion
- This is because each ligand contains **two** atoms with lone pairs of electrons
- Examples of bidentate ligands are:
   - 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$) which is also written as **‘en’**
   - Ethanedioate ion ($C_2O_4^{2-}$) which is sometimes written as **‘ox’**



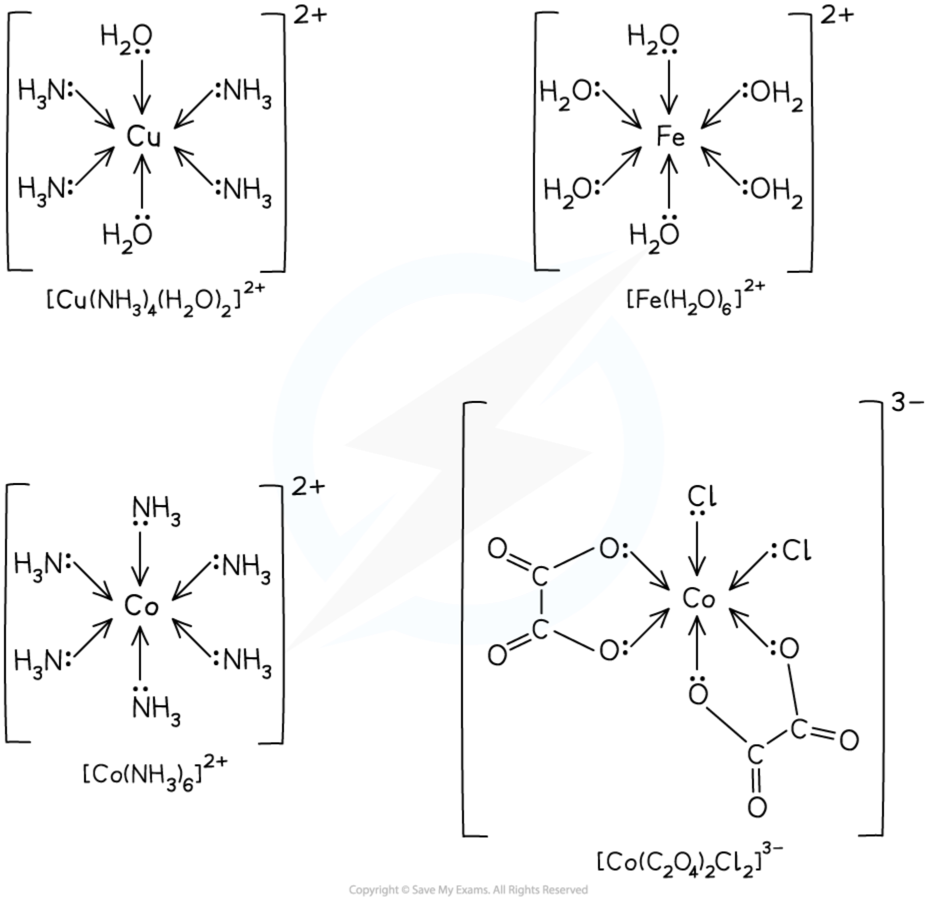
Examples of complexes with bidentate ligands

Shape & Coordination of Transition Element Complexes

- Depending on the **size of the ligands** and the **number of dative bonds** to the central metal ion, transition element complexes have different geometries
    - Dative bonds can also be referred to as **coordinate bonds**, especially when discussing the geometry of a complex

Six-coordinate complexes

- **Octahedral** complexes are formed when a central metal atom or ion forms **six coordinate bonds**
- This could be six coordinate bonds with **six** small, **monodentate** ligands
    - Examples of such ligands are **water** and **ammonia** molecules and **hydroxide** and **thiocyanate** ions
- It could be six coordinate bonds with **three bidentate** ligands
    - Each bidentate ligand will form two coordinate bonds, meaning six coordinate bonds in total
    - Examples of these ligands are **1,2-diaminoethane** and the **ethanedioate ion**
- The bond angles in an octahedral complex are 90°

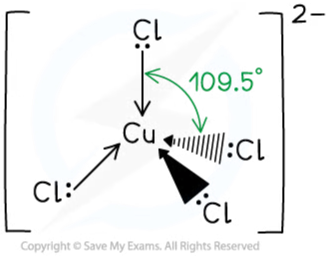


Examples of octahedral complexes

Four-coordinate complexes

Tetrahedral

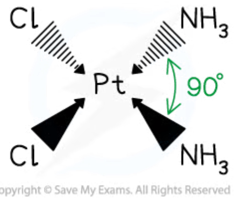
- When there are **four coordinate bonds** the complexes often have a **tetrahedral** shape
  - Complexes with four **chloride ions** most commonly adopt this geometry
  - Chloride ligands are large, so only four will fit around the central metal ion
- The bond angles in tetrahedral complexes are 109.5°



Example of a tetrahedral complex

Square planar

- Sometimes, complexes with **four coordinate bonds** may adopt a **square planar** geometry instead of a tetrahedral one
  - Cyanide ions (CN^-) are the most common ligands to adopt this geometry
  - An example of a square planar complex is **cisplatin**
- The bond angles in a square planar complex are 90°



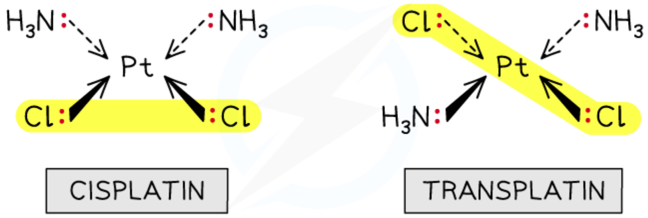
Cisplatin is an example of a square planar complex

Stereoisomerism in Transition Element Complexes

- Transition element complexes can exhibit **stereoisomerism**

Geometrical (*cis-trans*) isomerism

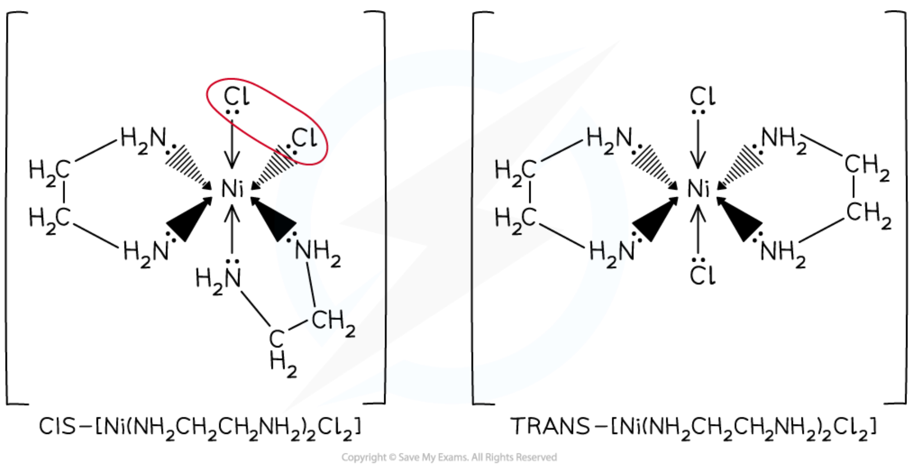
- Even though transition element complexes do not have a **double bond**, they can still have **geometrical isomers**
- **Square planar** and **octahedral** complexes with **two pairs of different** ligands exhibit *cis–trans* isomerism
- An example of a square planar complex with two pairs of ligands is the anti-cancer drug ***cis*-platin**
  - Whereas *cis*-platin has beneficial medical effects by binding to DNA in cancer cells, *trans*-platin cannot be used in cancer treatment



Cis-platin is an example of a square planar transition element complex that exhibits geometrical isomerism

- As long as a complex ion has two ligands attached to it that are different to the rest, then the complex can display geometric isomerism
- Examples of octahedral complexes that exhibit geometrical isomerism are the $[Co(NH_3)_4(H_2O)_2]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$ complexes
  - $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$ can also be written as $[Ni(en)_2(H_2O)_2]^{2+}$

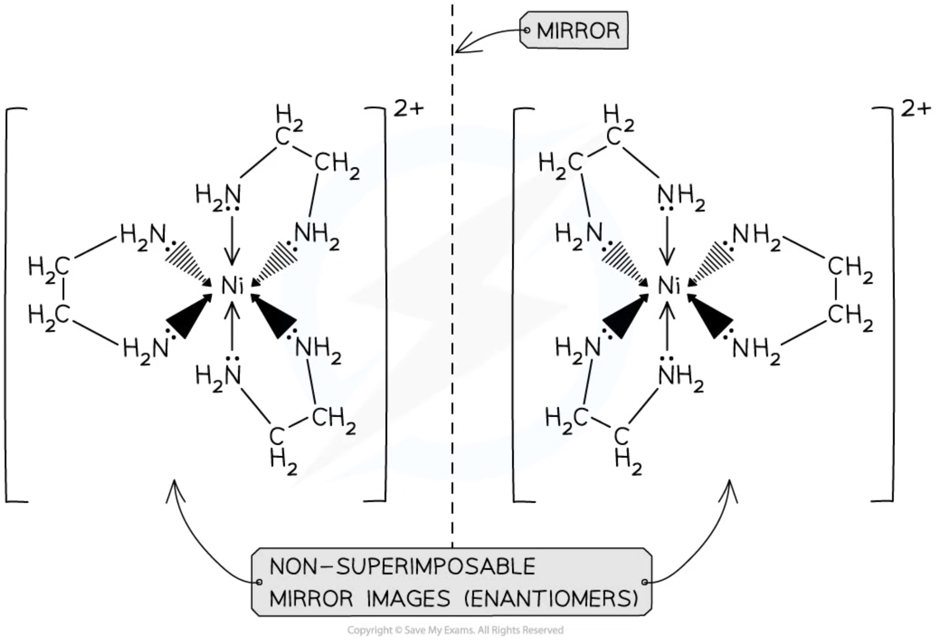
- Like in the square planar complexes, if the two 'different' ligands are next to each other then that is the 'cis' isomer, and if the two 'different' ligands are opposite each other then this is the 'trans' isomer
  - In $[Co(NH_3)_4(H_2O)_2]^{2+}$, the two water ligands are next door to each other in the cis isomer and are opposite each other in the trans isomer



Octahedral transition metal complexes exhibiting geometrical isomerism

Optical isomerism

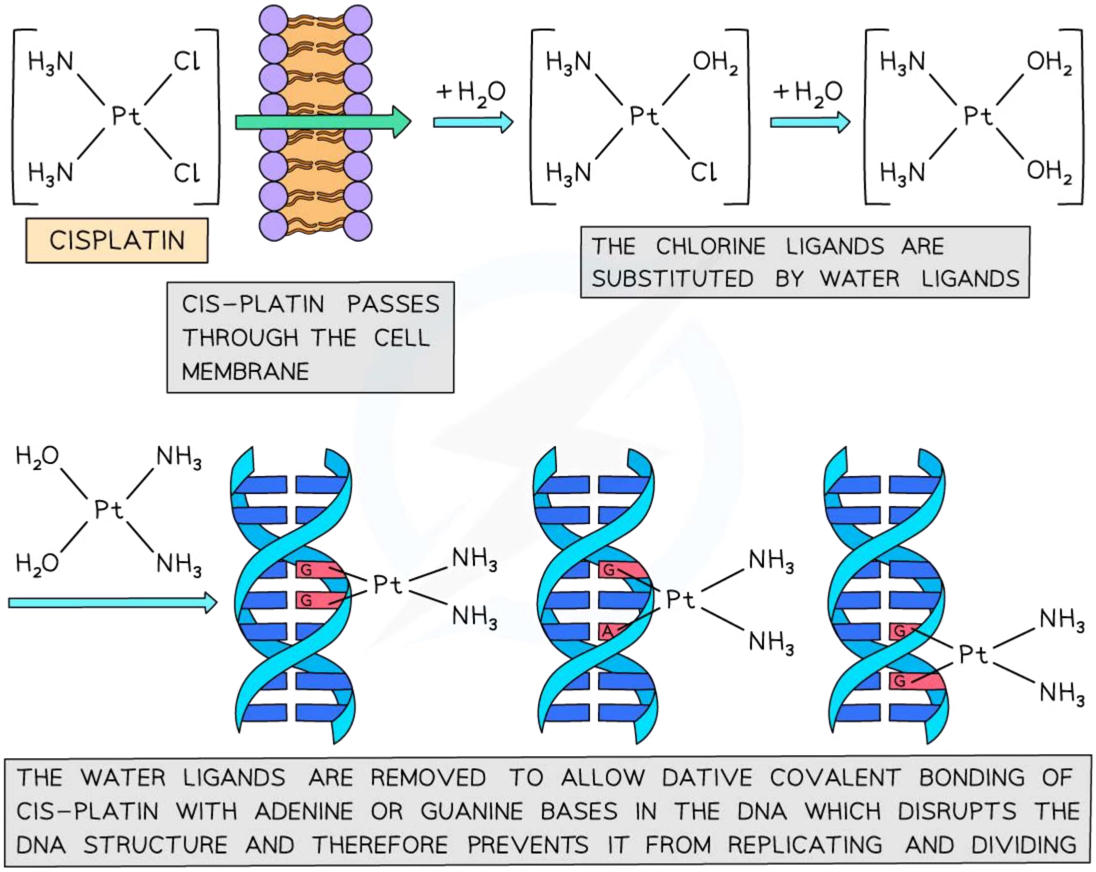
- **Octahedral** complexes with **bidentate ligands** also have **optical isomers**
- This means that the two forms are **non-superimposable mirror images** of each other
    - They have no plane of symmetry, and one image cannot be placed directly on top of the other
- The optical isomers only differ in their ability to rotate the plane of polarised light in opposite directions
- Examples of octahedral complexes that have optical isomers are the $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$ complexes
    - The ligand $H_2NCH_2CH_2NH_2$ can also be written as 'en' instead



Octahedral transition metal complexes exhibiting optical isomerism

Uses of cis-platin

- In the 1960's, the drug cis-platin was discovered
- Cis-platin has been extremely effective in treating a number of different types cancer such as testicular, ovarian, cervical, breast, lung and brain cancer
    - Cancer cells grow and replicate much faster than normal cells
- The cis-platin works by binding to the nitrogen atoms on the bases in DNA
- The cis-platin passes through the cell membrane and undergoes ligand exchange where the chlorines are replaced by water molecules
- The nitrogen is a better ligand than water and forms dative covalent bonds with the cis-platin
- The cis-platin distorts the shape of the DNA and prevents the DNA from replicating



CIS-PLATIN PASSES THROUGH THE CELL MEMBRANE

THE CHLORINE LIGANDS ARE SUBSTITUTED BY WATER LIGANDS

THE WATER LIGANDS ARE REMOVED TO ALLOW DATIVE COVALENT BONDING OF CIS-PLATIN WITH ADENINE OR GUANINE BASES IN THE DNA WHICH DISRUPTS THE DNA STRUCTURE AND THEREFORE PREVENTS IT FROM REPLICATING AND DIVIDING

Adverse Effects

- Cis-platin binds to healthy cells as well as cancerous cells, but affects cancer cells more as they are replicating faster
    - Unfortunately, this means that other healthy cells which replicate quickly, such as hair follicles, are also affected by cis-platin
    - This is why hair loss is a side-effect of people undergoing cancer treatment
- Despite this drawback, cis-platin is a highly effective drug and society needs to find a balance between the adverse effects of drugs and their therapeutic value

- New therapeutic pathways are constantly under development that aim to deliver drugs that target cancer cells while leaving healthy cells untouched

5.6.4 Ligand Substitution Reactions

Forming Solutions

- **Ligand substitution** (or **ligand exchange**) is when one **ligand** in a complex is replaced by another
- Ligand substitution forms a new complex that is **more stable** than the original one
- The ligands in the original complex can be **partially** or **entirely** substituted by others
- There are no changes in coordination number, or the geometry of the complex, if the ligands are of a **similar size**
- But, if the ligands are of a **different size**, for example water ligands and chloride ligands, then a change in coordination number and the geometry of the complex will occur

Substitution in copper(II) complexes

- When a transition element ion is in solution, it can be assumed that it exists as a **hexaaqua** complex ion (i.e. it has six water ligands attached to it)
    - For example **Cu^{2+}(aq) is $[Cu(H_2O)_6]^{2+}$(aq)**
- The $[Cu(H_2O)_6]^{2+}$ (aq) complex ion is **blue** in colour
- Upon **dropwise** addition of sodium hydroxide (NaOH) solution, a **light blue precipitate** is formed
- **Partial** ligand substitution of two water ligands by two hydroxide ligands has occurred

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(H_2O)_4\,(s) + 2H_2O\,(l)$$

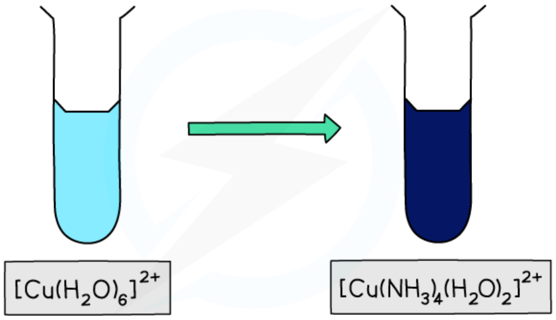
Blue solution Pale blue precipitate

- Upon addition of **excess concentrated** ammonia (NH_3) solution, the pale blue precipitate dissolves to form a **deep blue solution**
- Again, **partial** ligand substitution has occurred

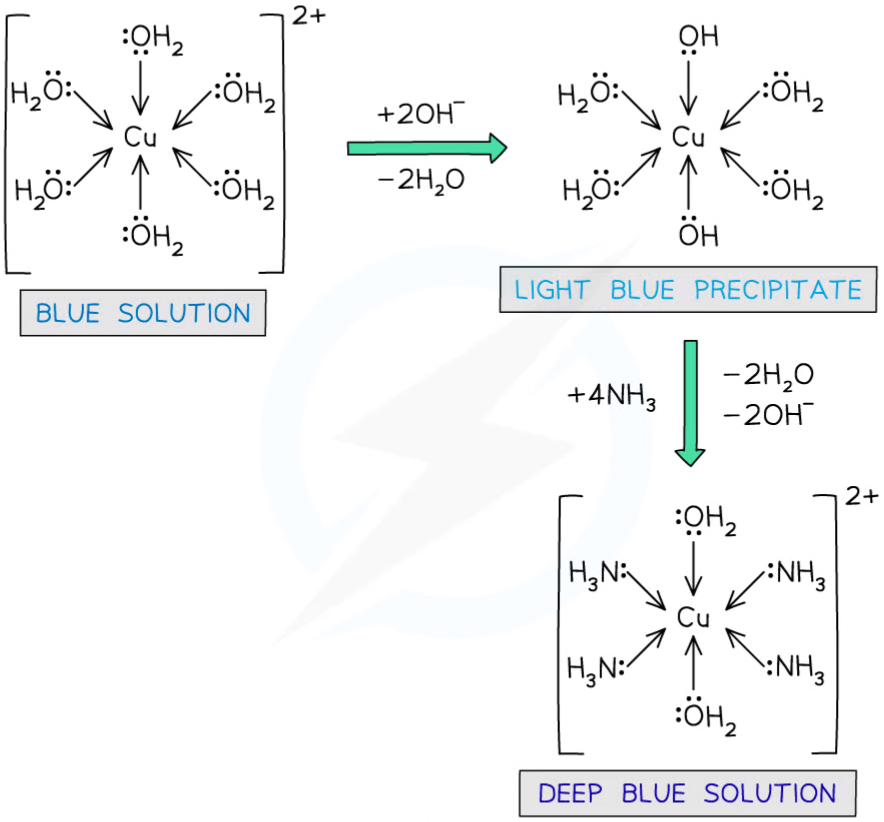
$$Cu(OH)_2(H_2O)_4(s) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-(aq)$$

Pale blue precipitate Deep blue solution

- If you were to add **concentrated ammonia** (NH_3) solution **dropwise** to the $[Cu(H_2O)_6]^{2+}$ (aq), rather than sodium hydroxide (NaOH) solution, the same **light blue precipitate** would form
- Again, the pale blue precipitate will **dissolve** to form a deep blue solution, if **excess** ammonia solution is then added



Addition of excess aqueous ammonia to the aqueous copper(II) ion results in a gorgeous deep blue complex

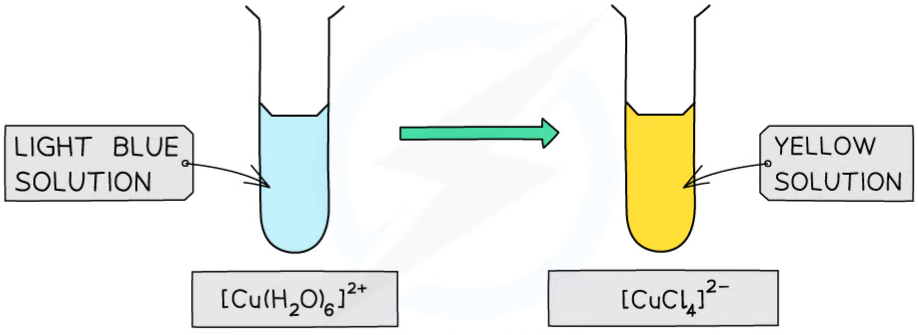


Water ligands are exchanged by hydroxide and ammonia ligands in the copper(II) complex

- The water ligands in $[Cu(H_2O)_6]^{2+}$ can also be substituted by **chloride** ligands, upon addition of **concentrated** hydrochloric acid (HCl)
- The **complete** substitution of the water ligands causes the **blue** solution to turn **yellow**

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

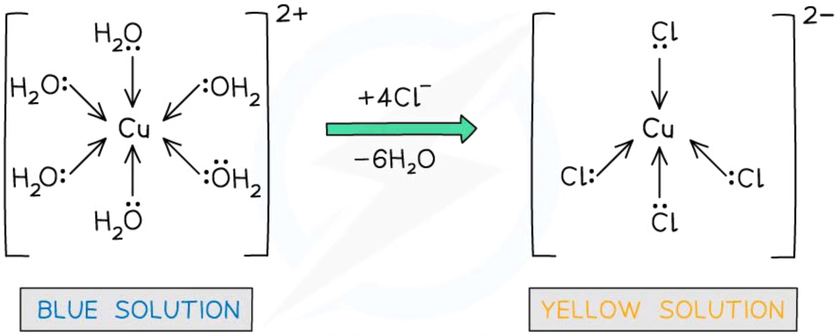
Blue solution Yellow solution



The colour changes from light blue to a yellow-green when copper(II) is treated with concentrated hydrochloric acid. The green appearance is due to the presence of unreacted aqueous copper(II) ions

- The **coordination number** has changed from **6 to 4**, because the chloride ligands are larger than the water ligands, so only 4 will fit around the central metal ion
- The geometry of the complex has also changed from **octahedral to tetrahedral**
- This is a reversible reaction, and some of the $[Cu(H_2O)_6]^{2+}$ complex ion will still be present in the solution
  - The mixture of blue and yellow solutions in the reaction mixture will give it a **green** colour

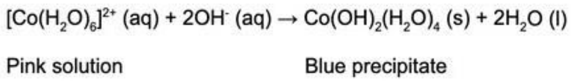
- Adding **water** to the solution will cause the **chloride** ligands to be **displaced by the water** molecules, and the $[Cu(H_2O)_6]^{2+}$ (aq) ion and **blue solution** will return



Water ligands are exchanged by chloride ligands in the copper(II) complex

Substitution in cobalt(II) complexes

- The $[Co(H_2O)_6]^{2+}$(aq) complex ion is **pink** in colour
- Upon **dropwise** addition of sodium hydroxide (NaOH) solution, a **blue** precipitate is formed
- **Partial** ligand substitution of two water ligands by two hydroxide (OH^-) ligands has occurred
  - If the alkali is added in **excess**, the blue precipitate will turn **red** when warmed



$$[Co(H_2O)_6]^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Co(OH)_2(H_2O)_4\ (s) + 2H_2O\ (l)$$

Pink solution Blue precipitate

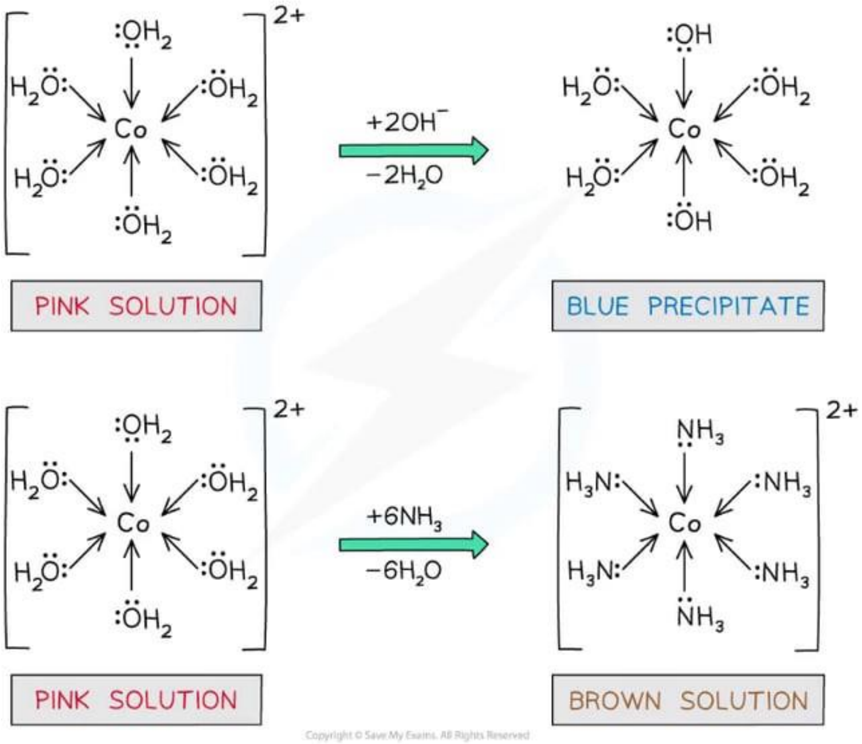
- If **excess concentrated** ammonia solution is added to $[Co(H_2O)_6]^{2+}$, a **brown** solution will also be formed
    - There will be no precipitate formed in this instance, as the ammonia has been added in excess and not dropwise

- **Complete** ligand substitution of the water ligands by ammonia ligands has occurred

$$[Co(H_2O)_6]^{2+}\,(aq) + 6NH_3\,(aq) \rightarrow [Co(NH_3)_6]^{2+}\,(aq) + 6H_2O\,(l)$$

Pink solution Brown solution

- The ammonia ligands make the cobalt(II) ion so **unstable** that it readily gets **oxidised** in air to cobalt(III), $[Co(NH_3)_6]^{3+}$ giving a brown or straw yellow solution



Water ligands are exchanged by hydroxide and ammonia ligands in the cobalt(II) complex

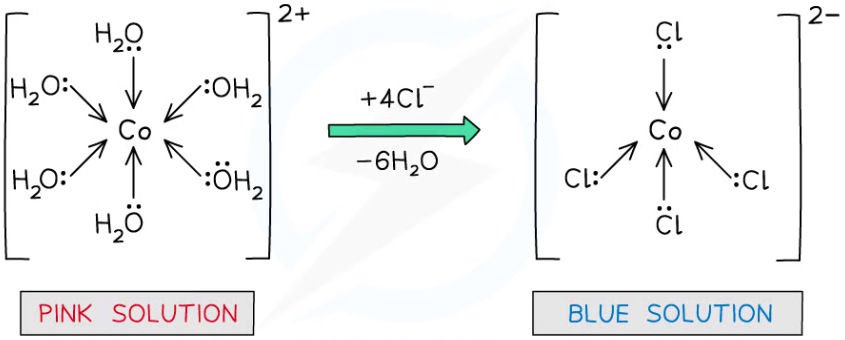
- The water ligands in $[Co[H_2O)_6]^{2+}$ can also be substituted by **chloride** ligands, upon addition of **concentrated** hydrochloric acid
- The **complete** substitution of the water ligands causes the **pink** solution to turn **blue**

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Pink solution Blue solution

- Like with $[Cu(H_2O)_6]^{2+}$ above, the **coordination number** has changed from **6 to 4**, because the chloride ligands are larger than the water ligands, so only 4 will fit around the central metal ion

- The geometry of the complex has also changed from **octahedral** to **tetrahedral**
- Adding **water** to the solution will cause the **chloride** ligands to be **displaced by the water** molecules, and the $[Co(H_2O)_6]^{2+}$ (aq) ion and **pink solution** will return



Water ligands are exchanged by chloride ligands in the cobalt(II) complex

Exam Tip

For copper(II) complexes, you only need to know the ligand substitution reaction and accompanying colour change for the addition of excess ammonia

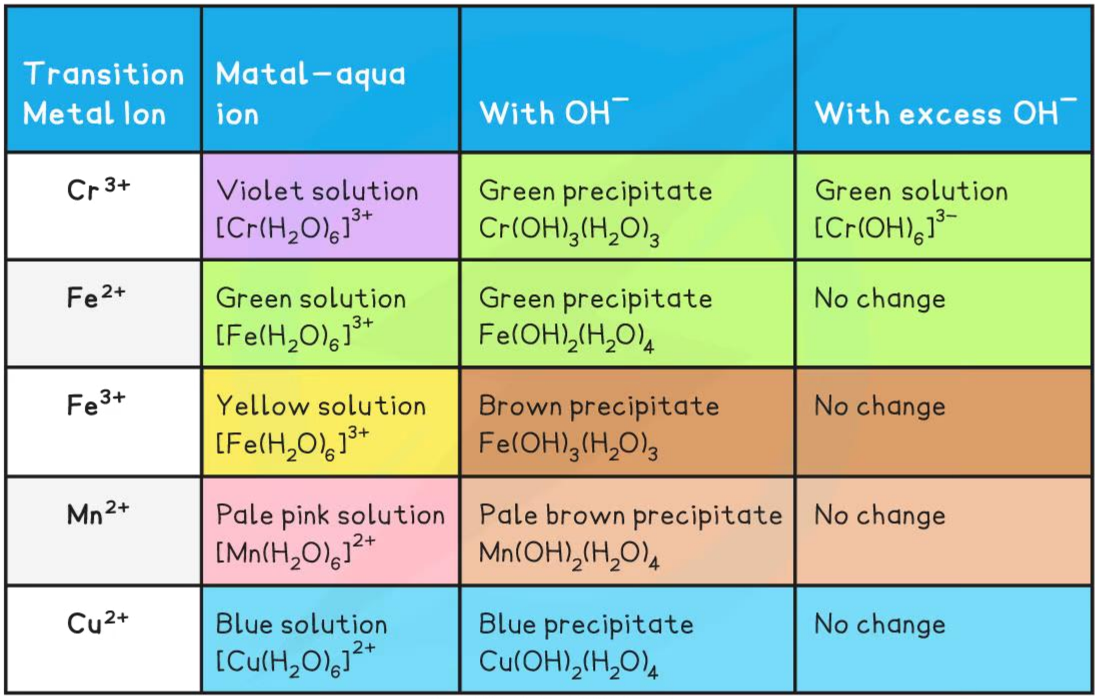
Be careful

If solid copper chloride (or any other metal) is dissolved in water, it forms the aqueous $[Cu(H_2O)_6]^{2+}$ complex and not the chloride $[CuCl_4]^{2-}$ complex!

Forming Precipitates

- When transition metal ions in aqueous solution react with aqueous sodium hydroxide and aqueous ammonia they form precipitates
- However some of these precipitates will dissolve in an excess of sodium hydroxide or ammonia to form complex ions in solution

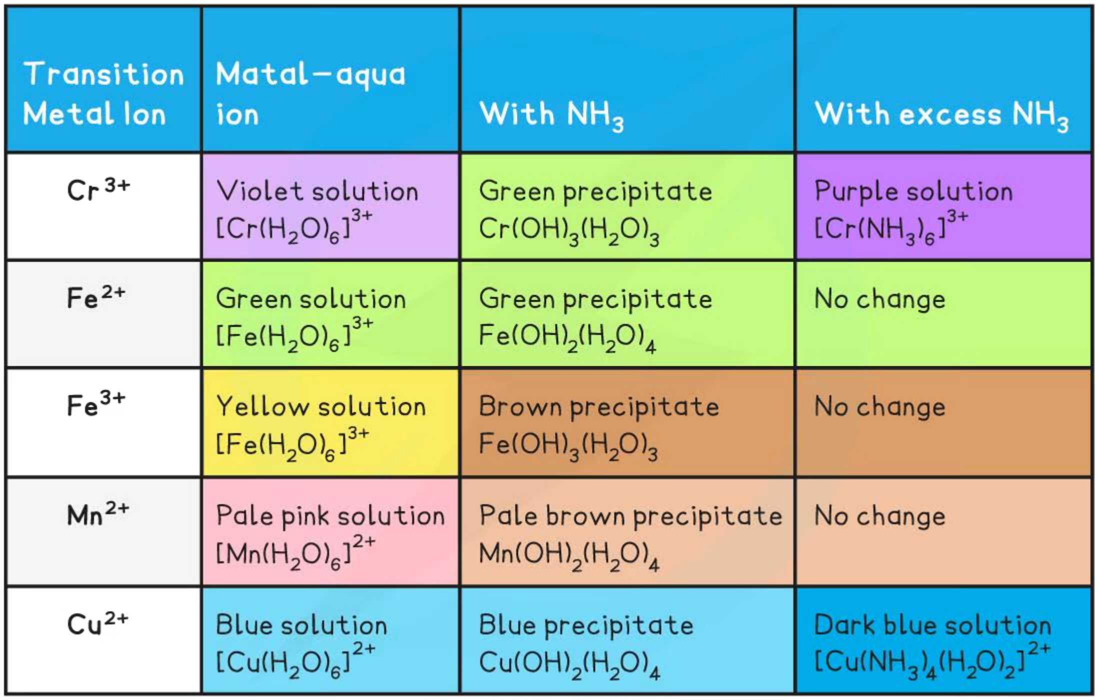
The reactions of aqueous transition metal ions with aqueous sodium hydroxide



Transition Metal Ion	Matal–aqua ion	With OH^-	With excess OH^-
Cr^{3+}	Violet solution $[Cr(H_2O)_6]^{3+}$	Green precipitate $Cr(OH)_3(H_2O)_3$	Green solution $[Cr(OH)_6]^{3-}$
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{3+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change
Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(OH)_3(H_2O)_3$	No change
Mn^{2+}	Pale pink solution $[Mn(H_2O)_6]^{2+}$	Pale brown precipitate $Mn(OH)_2(H_2O)_4$	No change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	No change

- Examples of ionic equations for the reactions in the table above
  - $[Fe(H_2O)_6]^{2+}$ (aq) + $2OH^-$ (aq) → $[Fe(H_2O)_4(OH)_2]$ (s) $+2H_2O$ (l)
  - $[Cu(H_2O)_6]^{2+}$ (aq) + $2OH^-$ (aq) → $[Cu(H_2O)_4(OH)_2]$ (s) $+2H_2O$ (l)
  - $[Fe(H_2O)_6]^{3+}$ (aq) + $3OH^-$ (aq) → $[Fe(H_2O)_3(OH)_3]$ (s) + $3H_2O$ (l)

The reactions of aqueous transition metal ions with ammonia



Transition Metal Ion	Matal−aqua ion	With NH_3	With excess NH_3
Cr^{3+}	Violet solution $[Cr(H_2O)_6]^{3+}$	Green precipitate $Cr(OH)_3(H_2O)_3$	Purple solution $[Cr(NH_3)_6]^{3+}$
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{3+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change
Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(OH)_3(H_2O)_3$	No change
Mn^{2+}	Pale pink solution $[Mn(H_2O)_6]^{2+}$	Pale brown precipitate $Mn(OH)_2(H_2O)_4$	No change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	Dark blue solution $[Cu(NH_3)_4(H_2O)_2]^{2+}$

- Examples of ionic equations for the reactions in the table above
    - $[Fe(H_2O)_6]^{2+}$ (aq) + $2NH_3$ (aq) → $[Fe(H_2O)_4(OH)_2]$ (s) + $2NH_4^+$ (aq)
    - $[Cu(H_2O)_6]^{2+}$ (aq) + $2NH_3$ (aq) → $[Cu(H_2O)_4(OH)_2]$ (s) + $2NH_4^+$ (aq)
    - $[Fe(H_2O)_6]^{3+}$ (aq) + $3NH_3$ (aq) → $[Fe(H_2O)_3(OH)_3]$ (s) + $3NH_4^+$ (aq)
    - $[Cu(H_2O)_4(OH)_2]$ (s) + $4NH_3$ (aq) → $[Cu(H_2O)_2(NH_3)_4]^{2+}$ (aq) + $2H_2O$ (l) + $2OH^-$ (aq)
- Solutions of metal aqua ions react as acids with aqueous ammonia, whilst some react further with excess ammonia
- Initially, ammonia acts as a base to remove one H^+ ion per ammonia molecule used
- With excess ammonia, some metal ions undergo ligand substitution with NH_3

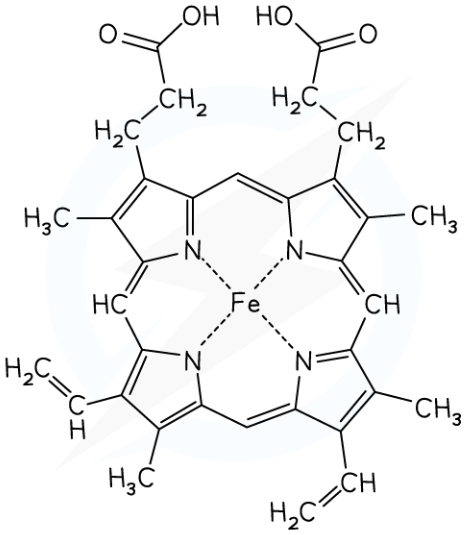
Exam Tip

It is easiest to remember the formulas of the precipitates by remembering that the number of OH− ions substituted is the same as the value of the charge on the initial ion

5.6.5 The Biochemical Importance of Iron in Haemoglobin

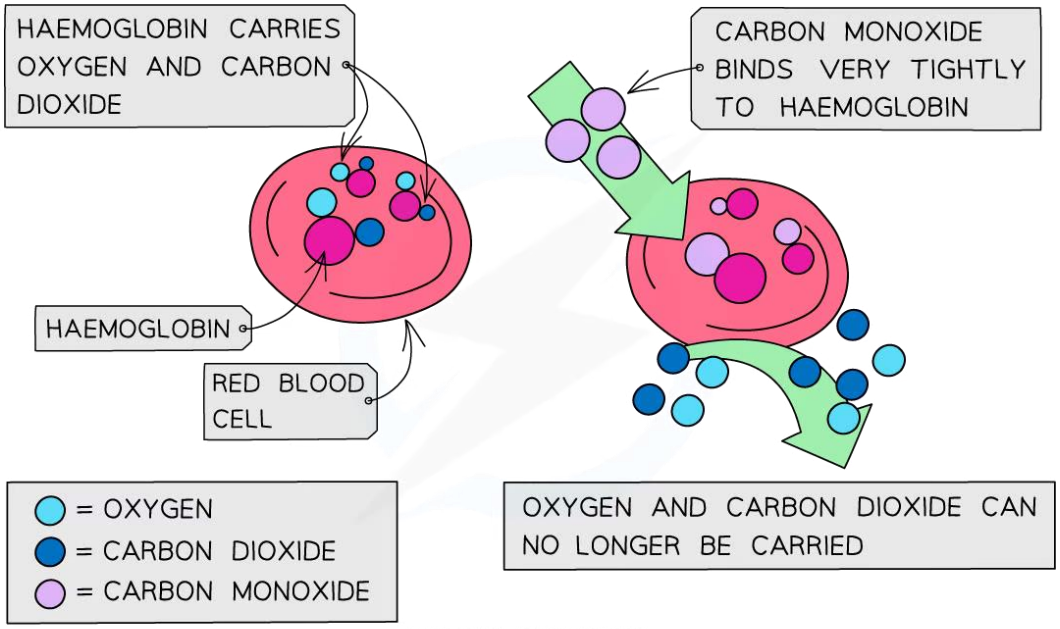
Ligand Substitution in Haemoglobin

- Haemoglobin is one of nature's complexes using a transition metal ion
- The haem molecule is a complex with iron(II) at its centre
- Oxygen atoms form a dative covalent bond with the Fe(II) which enables oxygen molecules to be transported around the body in the blood



The haem molecule with iron(II) at its centre

- Oxygen molecules are not very good ligands and bond weakly to the iron(II)
- The weak bonds allows them to break off easily and be transported into cells



- Carbon monoxide is toxic because it is a better ligand than oxygen and binds strongly and irreversibly to the iron(II) preventing oxygen from being carried to the cells
- If oxygen attached to the haemoglobin (oxyhaemoglobin) is replaced by carbon monoxide (carboxyhaemoglobin), a darker red colour is produced in the haem complex
    - A sign of carbon monoxide poisoning
- The condition anaemia occurs when a person does not have enough haemoglobin in their blood due to a loss of blood or deficiency in iron
    - Deficiency in iron can be restored by taking iron sulfate tables in the diet

5.6.6 Redox Reactions of Transistion Elements

Iron(II) & Iron(III) Ions

Oxidation of Fe^{2+} to Fe^{3+}

- A redox titration involves an **oxidising agent** being titrated against a **reducing agent**
- Electrons are transferred from one species to another
- In acid-base titrations indicators are used to show the endpoint of a reaction; however **redox titrations** using transition metal ions naturally change colour when changing oxidation state, so indicators are not always necessary
- They are said to be 'self-indicating'
- The redox reaction between iron (II) ions and manganate (VII) ions in acidic conditions is used as a basis for a redox titration
- In this reaction:
    - Fe^{2+} is oxidised to Fe^{3+}
    - MnO_4^- is reduced to Mn^{2+}
- **Potassium manganate(VII)** is commonly used which is an oxidising agent and is a deep purple colour
- In acidic solutions it is reduced to the almost colourless **manganese(II)** ion by the Fe^{2+}(aq)
- The equation for the reaction is:

$$\mathbf{MnO_4^-\,(aq) + 8H^+\,(aq) + 5Fe^{2+} \rightarrow Mn^{2+}\,(aq) + 5Fe^{3+} + 4H_2O\,(aq)}$$

purple *colourless*

Reduction of Fe^{3+} to Fe^{2+}

- An orange-brown solution of Fe^{3+}(aq) ions can be reduced to pale green Fe^{2+}(aq) ions by various reducing agents.
- A potassium iodide solution is commonly used
- The colour change can be masked by the formation of iodine which has a brown colour
- In this reaction
    - Fe^{3+} is reduced to Fe^{2+}
    - I^- is oxidised to I_2
- The equation for this reaction is:

$$\mathbf{2Fe^{3+}\,(aq) + 2I^+\,(aq) \rightarrow 2Fe^{2+} + I_2\,(aq)}$$

orange-brown *pale-green* *brown*

Chromium(III) & Dichromate Ions

Reduction of $Cr_2O_7^{2-}$ to Cr^{3+}

- Aqueous dichromate (VI) ions, $Cr_2O_7^{2-}$, have an orange colour whilst aqueous chromium (III) ions, Cr^{3+}(aq), have a green colour
- Acidified $Cr_2O_7^{2-}$ ions can be reduced to Cr^{3+}(aq) ions by the addition of zinc
- Zinc is a strong reducing agent and is capable of reducing both $Cr_2O_7^{2-}$ to Cr^{3+} and Cr^{3+} to Cr^{2+}
- The equation for this reaction is:

$$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 3Zn\,(s) \rightarrow 2Cr^{3+}\,(aq) + 7H_2O\,(l) + 3Zn^{2+}\,(aq)$$

orange green

- With an excess of zinc, chromium(III) ions are reduced further to chromium(II), which is a pale blue colour

$$Zn\,(s) + 2Cr^{3+}\,(aq) \rightarrow Zn^{2+}\,(aq) + 2Cr^{2+}\,(aq)$$

green *pale blue*

Exam Tip

Fe^{2+}(aq) is a weaker reducing agent than zinc and will only reduce the dichromate to Cr^{3+}

Standard electrode potentials can be used to compare the strength of reducing agents and you should be able to use $E^{\varnothing}$ to explain why certain redox reactions take place

Oxidation of Cr^{3+} to CrO_4^{2-}

- When transition metals in low oxidation states are in an alkaline solution, they are more easily oxidised than when in acidic solution
- Hot alkaline hydrogen peroxide, H_2O_2, is a powerful oxidising agent which can be used to oxidise chromium(III) to chromium(VI), CrO_4^{2-}
- The equation for this reaction is

$$3H_2O_2\,(aq) + 2Cr^{3+}\,(aq) + 10OH^-\,(aq) \rightarrow 2CrO_4^{2-}\,(aq) + 8H_2O\,(l)$$

dark green *yellow*

    - Chromium is oxidised from +3 in Cr^{3+} to +6 in CrO_4^{2-}
    - Oxygen is reduced from −1 in H_2O_2 to −2 in CrO_4^{2-}

Oxidation of CrO_4^{2-} to $Cr_2O_7^{2-}$

- Dilute sulfuric acid can be added to chromate (VI), CrO_4^{2-} (aq), solution to produce a dichromate (VI), $Cr_2O_7^{2-}$ (aq), solution
- The equation for this reaction is

$$2CrO_4^{2-}\,(aq) + 2H^+\,(aq) \rightarrow Cr_2O_7^{2-}\,(aq) + H_2O\,(l)$$

yellow *orange*

Exam Tip

Don't worry – you won't be expected to memorise and reproduce these full equations in exams.

You could be asked to construct and interpret redox equations from half equations and oxidation numbers though – so make sure you understand how to do it.

Reduction & Disproportionation of Copper Ions

Reduction of Cu^{2+} to Cu^{+}

- A pale blue solution of Cu^{2+} can be reduced to Cu^{+} by various reducing agents
- A potassium iodide solution is commonly used
- When excess iodide ions are present the following reaction occurs:

$$2Cu^{2+} (aq) + 4I^{-} (aq) \rightarrow 2CuI (aq) + I_2 (aq)$$

pale blue *white precipitate* *brown*

  - I^{-} is oxidised to brown iodine, I_2
  - Cu^{2+} is reduced to Cu^{+}, forming a white precipitate

Disproportionation of copper(I) ions

- When solid copper(I) oxide, Cu_2O, reacts with hot dilute sulfuric acid, a brown precipitate of copper is formed together with a blue solution of copper(II) sulfate
- In this reaction copper(I) ions, Cu^{+}, have been simultaneously oxidised and reduced
- As the same element has been reduced and oxidised, this reaction is disproportionation

$$Cu_2O (s) + H_2SO_4 (aq) \rightarrow Cu (s) + CuSO_4 (aq) + H_2O (l)$$

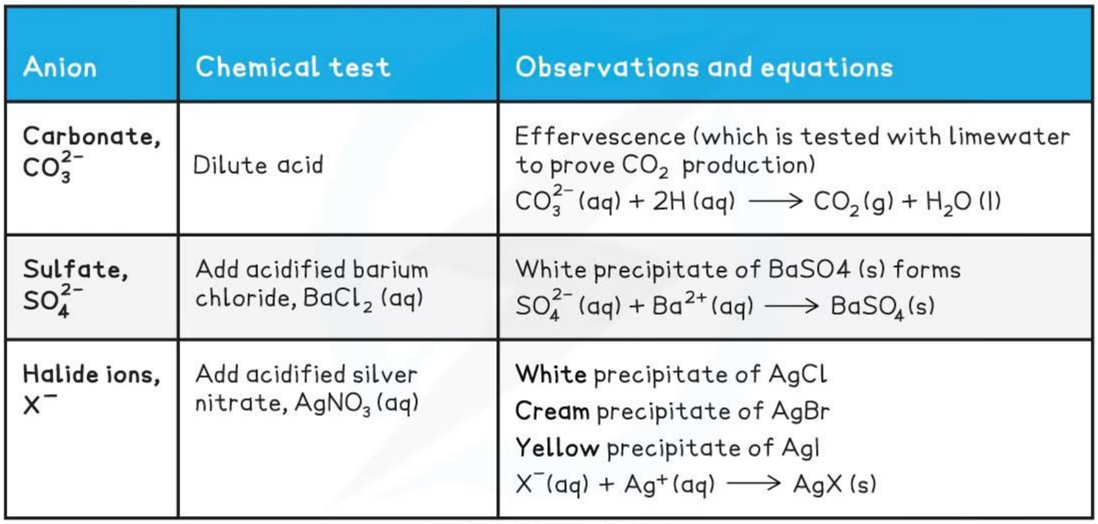
  - Copper has been reduced from +1 in Cu_2O to 0 in Cu
  - Copper has been oxidised from +1 in Cu_2O to +2 in $CuSO_4$

5.6.7 Qualitative Analysis

Testing for Anions

- Tests can be used to identify anions in solutions of unknown compounds.
- If multiple tests are being carried out on the same solution it is important to carry them out in the same order as in the table below

Tests for solutions containing one or more unknown anions



Anion	Chemical test	Observations and equations
Carbonate, CO_3^{2-}	Dilute acid	Effervescence (which is tested with limewater to prove CO_2 production) $CO_3^{2-}(aq) + 2H(aq) \longrightarrow CO_2(g) + H_2O(l)$
Sulfate, SO_4^{2-}	Add acidified barium chloride, $BaCl_2(aq)$	White precipitate of BaSO4 (s) forms $SO_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow BaSO_4(s)$
Halide ions, X^-	Add acidified silver nitrate, $AgNO_3(aq)$	**White** precipitate of AgCl **Cream** precipitate of AgBr **Yellow** precipitate of AgI $X^-(aq) + Ag^+(aq) \longrightarrow AgX(s)$

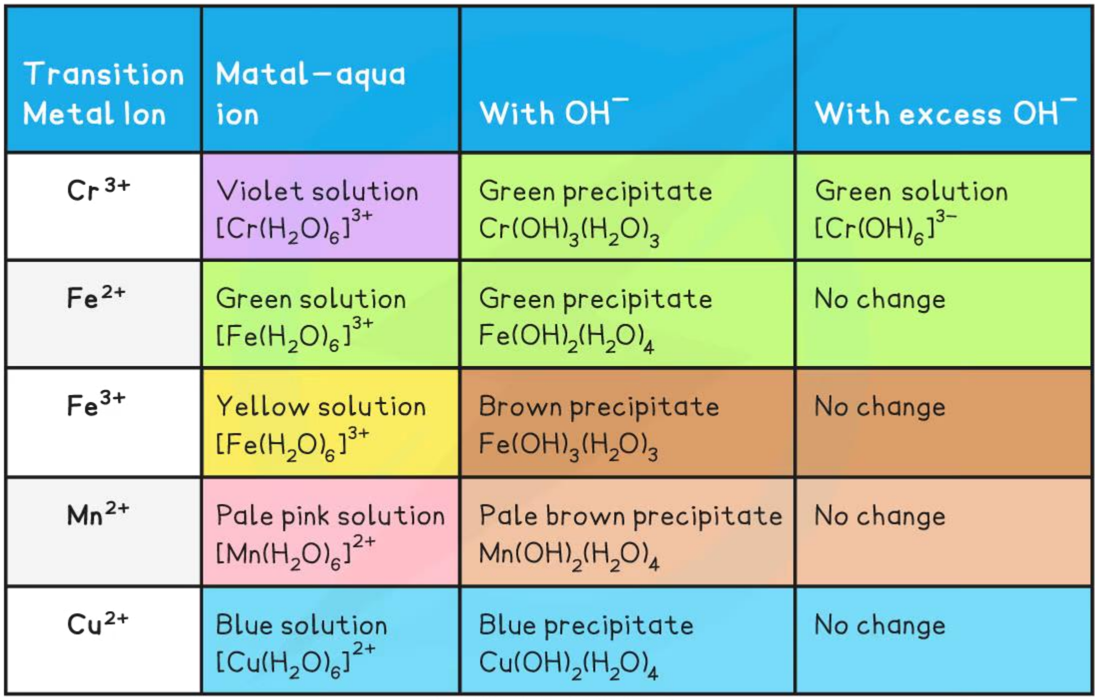
- Ammonia can help distinguish between the silver halide precipitates
  - Silver chloride dissolves in dilute ammonia
  - Silver bromide dissolves in concentrated ammonia
  - Silver iodide is insoluble in concentrated ammonia

Testing for Cations

Testing for transition metal ions

- Adding aqueous sodium hydroxide to various transition metal ions produces precipitates.
- These reactions can be used for identifying transition metal ions in an unknown solution

The reactions of aqueous transition metal ions with aqueous sodium hydroxide



Transition Metal Ion	Matal – aqua ion	With OH^-	With excess OH^-
Cr^{3+}	Violet solution $[Cr(H_2O)_6]^{3+}$	Green precipitate $Cr(OH)_3(H_2O)_3$	Green solution $[Cr(OH)_6]^{3-}$
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{3+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change
Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(OH)_3(H_2O)_3$	No change
Mn^{2+}	Pale pink solution $[Mn(H_2O)_6]^{2+}$	Pale brown precipitate $Mn(OH)_2(H_2O)_4$	No change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	No change

Testing for ammonium ions

- When heated with hydroxide ions ammonium ions react to produce ammonia gas

$$NH_4^+ (aq) + OH^- (aq) \rightarrow NH_3 (g) + H_2O (l)$$

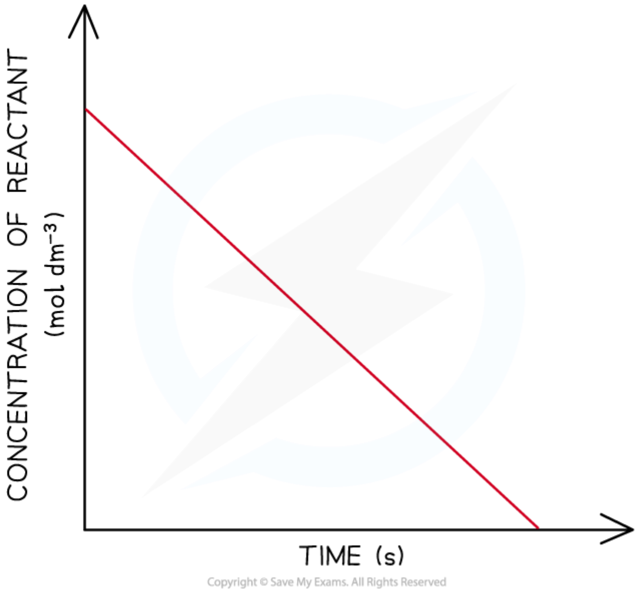
- Any ammonia produced will turn damp red litmus paper blue confirming the presence of ammonium ions in the original solution

5.1.2 Concentration–Time Graphs

Concentration–Time Graphs

Reaction Order Using Concentration–Time Graphs

- In a **zero-order** reaction, the concentration of the reactant is inversely proportional to time
  - This means that the reactant concentration decreases as time increases
  - The graph is a straight line going down as shown:

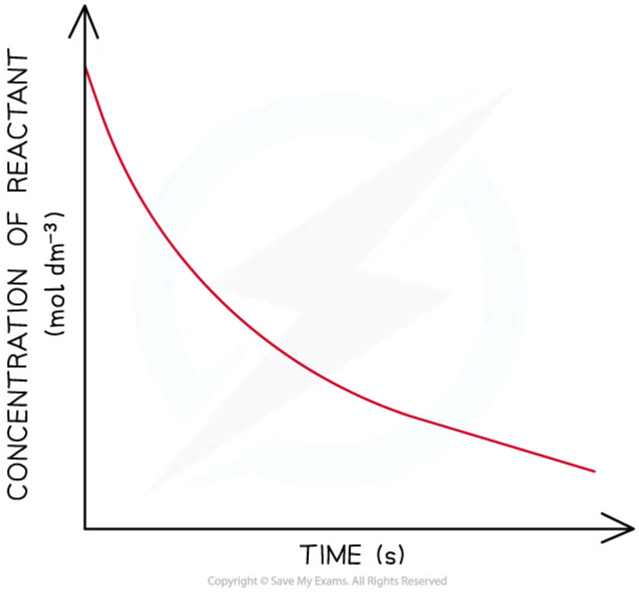


Concentration–time graph of a zero-order reaction

- The gradient of the line is the rate of reaction
  - Calculating the gradient at different points on the graph, will give a constant value for the rate of reaction
- When the order with respect to a reactant is 0, a change in the concentration of the reactant has no effect on the rate of the reaction
- Therefore:

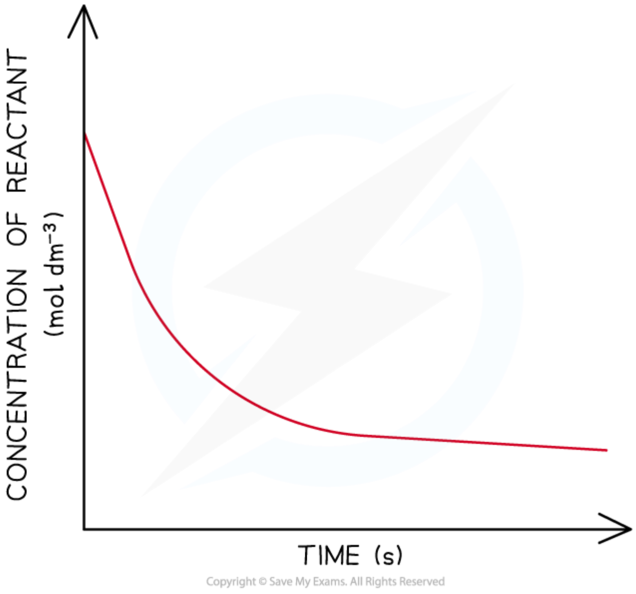
$$\textbf{Rate} = k$$

- This equation means that the gradient of the graph is the rate of reaction as well as the rate constant, k
- In a **first-order** reaction, the concentration of the reactant decreases with time
  - The graph is a curve going downwards and eventually plateaus:



Concentration–time graph of a first-order reaction

- In a **second-order** reaction, the concentration of the reactant decreases more steeply with time
  - The concentration of reactant decreases **more** with increasing time compared to a first-order reaction
  - The graph is a steeper curve going downwards:

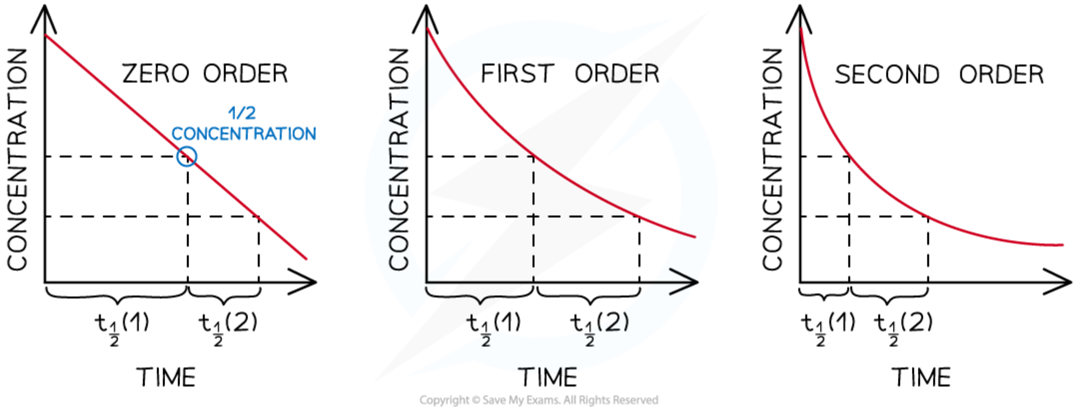


Concentration–time graph of a second–order reaction

Concentration–Time Graphs & Half-Life

Order of reaction from half-life

- The order of a reaction can also be deduced from its half-life **($t_{1/2}$)**
- For a zero-order reaction the successive half-lives decrease with time
    - This means that it would take less time for the concentration of reactant to halve as the reaction progresses
- The half-life of a first-order reaction remains constant throughout the reaction
    - The amount of time required for the concentration of reactants to halve will be the same during the entire reaction
- For a second-order reaction, the half-life increases with time
    - This means that as the reaction is taking place, it takes more time for the concentration of reactants to halve

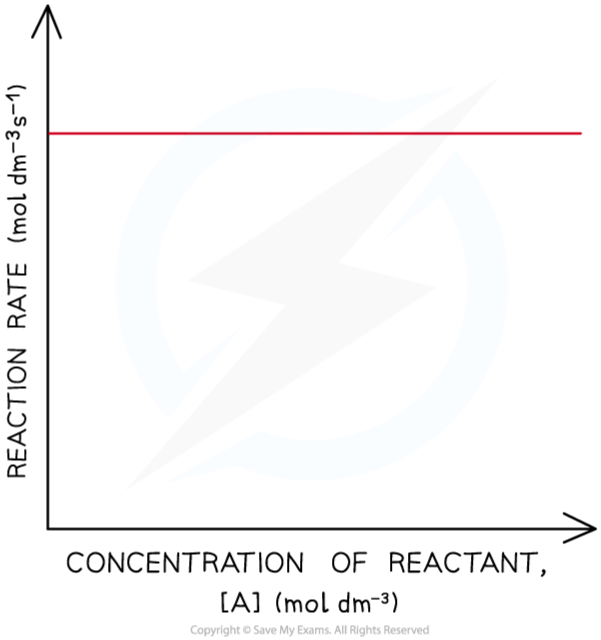


Half-lives of zero, first and second–order reactions

Rate-Concentration Graphs

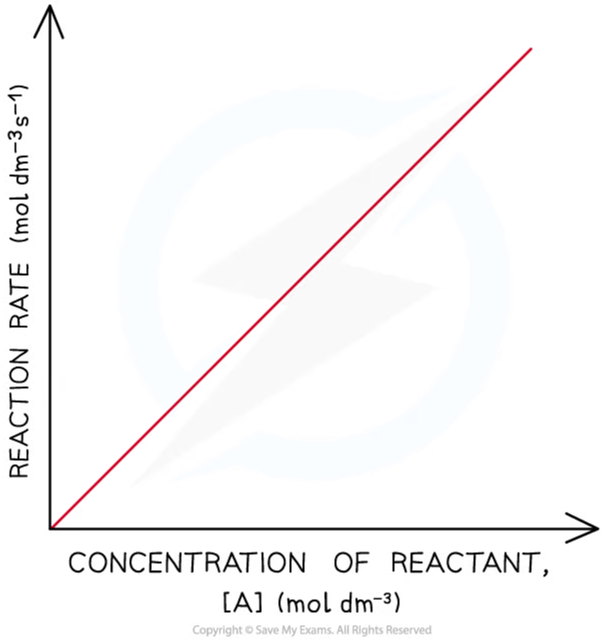
Reaction order using rate-concentration graphs

- In a **zero-order** reaction, the rate doesn't depend on the concentration of the reactant
  - The rate of the reaction therefore remains constant throughout the reaction
  - The graph is a horizontal line
  - The rate equation is **rate = *k***



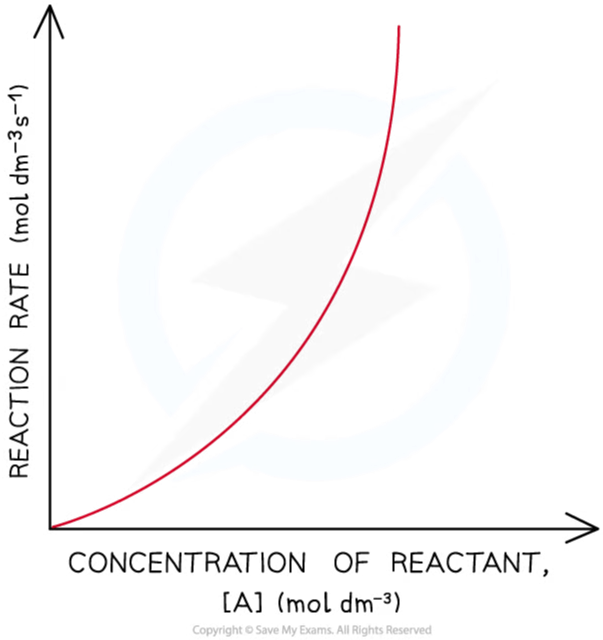
Rate-concentration graph of a zero-order reaction

- In a **first-order** reaction, the rate is directly proportional to the concentration of a reactant
  - The rate of the reaction increases as the concentration of the reactant increases
  - This means that the rate of the reaction decreases as the concentration of the reactant decreases when it gets used up during the reaction
  - The graph is a straight line
  - The rate equation is **rate = *k*[A]**



Rate–concentration graph of a first-order reaction

- In a **second-order** reaction, the rate is directly proportional to the square of concentration of a reactant
    - The rate of the reaction increases more as the concentration of the reactant increases
    - This means that the rate of the reaction decreases more as the concentration of the reactant decreases when it gets used up during the reaction
    - The graph is a curved line
    - The rate equation is **rate =** $k[A]^2$



Rate–concentration graphs of a second–order reaction

YOUR NOTES

Exam Tip

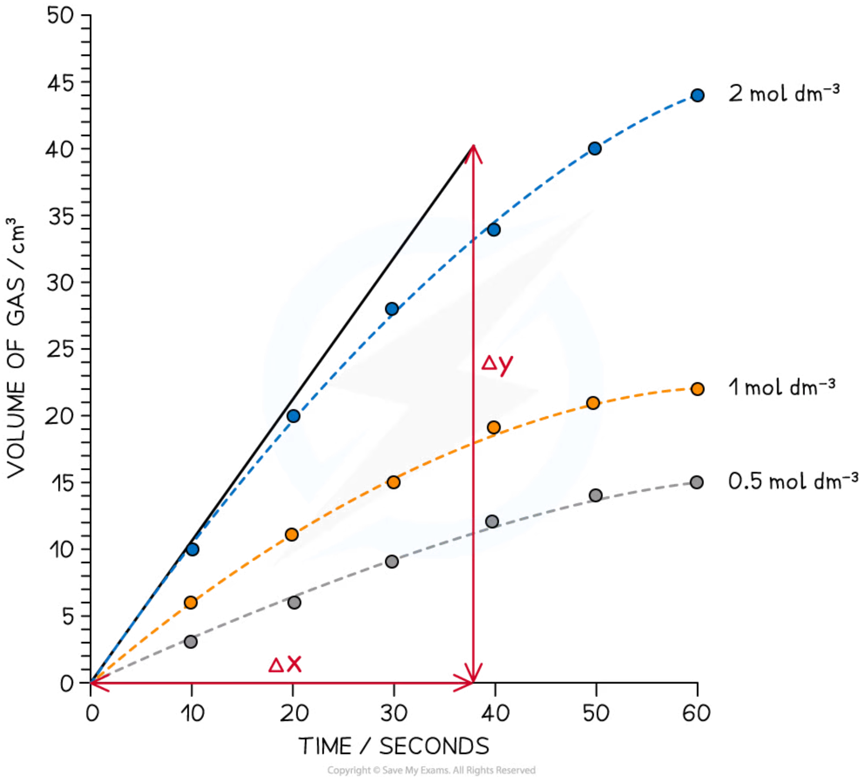
Careful – sometimes when asked to complete calculations for the rate constant, *k*, the exam question will give you a graph as well as tabulated data. Do not ignore the graph as this demonstrates the order of one of the reactants, while the tabulated data allows you to determine the order for the other reactants.

Initial Rates Methods

- The **initial rates method** determines the rate at the very start of the reaction when $t = 0$
- The initial rate can be found by:
  - Drawing a **concentration-time graph**
  - Adding a **tangent** at $t = 0$
  - Calculating the **gradient** of the tangent
- One example of measuring the initial rate could be the reaction of calcium carbonate with hydrochloric acid (similar to one of the PAG9 practicals)
  - The volume of carbon dioxide produced with different concentrations can be measured against time
  - The results are then plotted onto a graph
  - The tangent at $t = 0$ is then added
  - The gradient of the tangent can then be calculated to give the initial rate of the reaction

Worked Example

The concentration–time graph for the reaction of calcium carbonate with three different concentrations of hydrochloric acid is shown



Calculate the initial rate of reaction for the reaction of calcium carbonate with 2.0 mol dm^{-3} hydrochloric acid

Answer

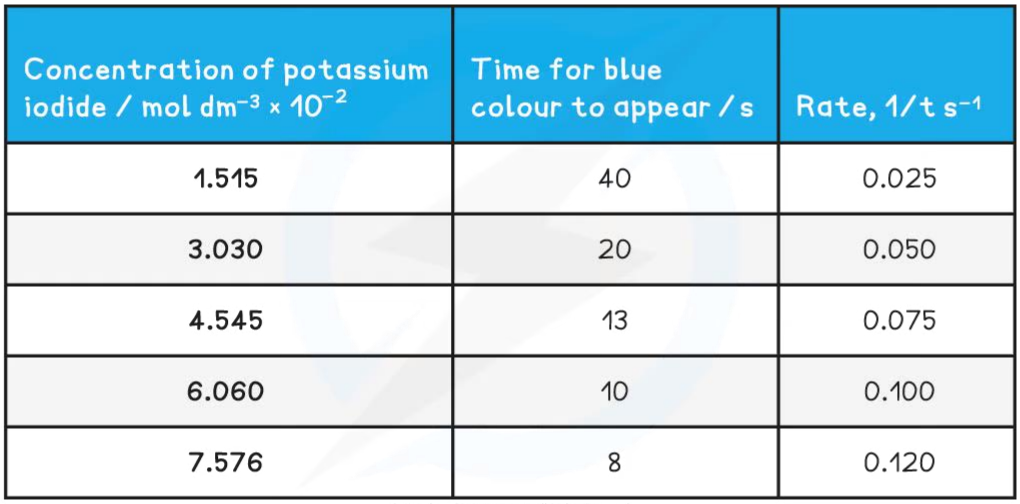
- Using the tangent drawn:
- Gradient $= \dfrac{\Delta y}{\Delta x} = \dfrac{40}{38} = 1.05$ mol dm^{-3} s^{-1}
- Therefore, the initial rate of reaction is 1.05 mol dm^{-3} s^{-1}

Clock reactions

- **Clock reactions** are a more convenient way of measuring the initial rate of reaction using a **single measurement**
- The time taken, *t*, for a specific visual change in the reaction to occur is measured
  - These changes could be a colour change or formation of a precipitate
- The major assumption that clock reactions depend on is:
  - That there is no significant change in the rate of reaction between the start of the reaction and the time when the measurement is taken
- The initial rate is then proportional to $\dfrac{1}{t}$

- The iodine clock experiment is a common clock reaction
    - This is covered in more detail in the PAG notes
- Here is a set of typical results for the iodine clock reaction:

Specimen results for the iodine clock reaction table



Concentration of potassium iodide / mol dm^{-3} x 10^{-2}	Time for blue colour to appear / s	Rate, 1/t s^{-1}
1.515	40	0.025
3.030	20	0.050
4.545	13	0.075
6.060	10	0.100
7.576	8	0.120

- The initial rate is a relatively simple calculation
    - E.g. For a concentration of 0.01515 mol dm^{-3}, the rate is $\frac{1}{40} = 0.025\ s^{-1}$
- A closer look at the results shows that as the concentration doubles, the rate also doubles
    - This can be linked back to the reaction being first order
- There are limitations to the accuracy of the clock reaction
    - These are, again, based on the assumption that the rate of reaction is constant
- As the reaction progresses, the concentration of the reactants decreases – typically on a curve
    - Therefore, when the time measured for the reaction to occur is short then there is a higher chance that the initial rate calculated will be closer to the true value
    - As the time taken for the reaction to occur, the value of the initial rate will become less accurate
- The initial rate measured during a clock reaction is an estimate

Continuous Monitoring

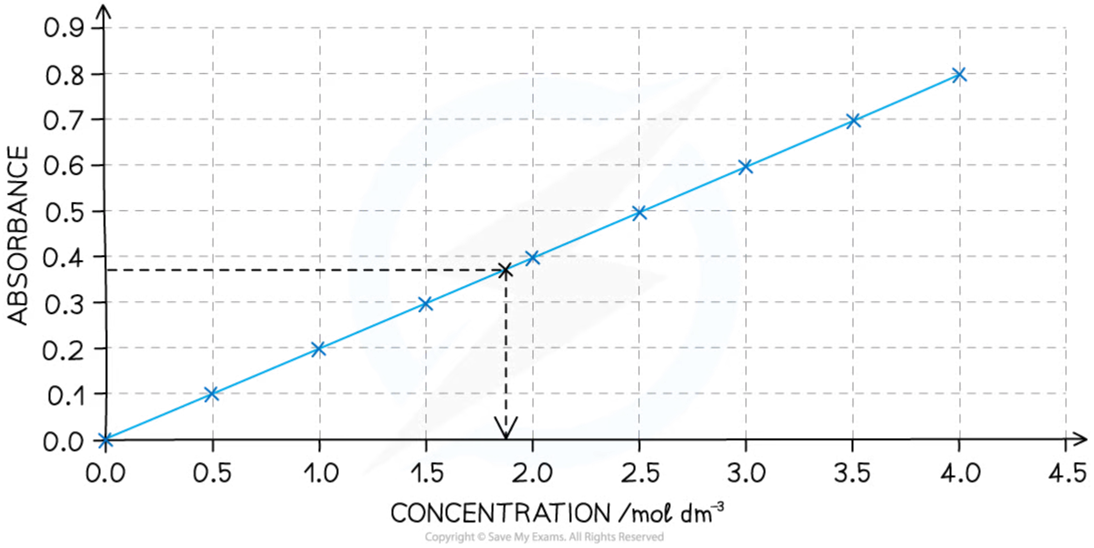
- **Continuous monitoring** involves collecting experimental data throughout the course of a reaction to plot a concentration-time graph
- Two of the most common ways to collect this data are by:
  - Measuring the volume / amount of gas evolved over time
  - Measuring the mass of reactants lost over time
- Another alternative method involves the use of colorimetry:

The iodination of propanone

- The iodination of propanone provides a suitable experiment in which the rate of reaction can be measured throughout the reaction by using a colorimeter
- The reaction is carried out using a catalyst of dilute sulfuric acid
- The iodine decolourises during the reaction as it turns into iodopropanone and hydrogen iodide:

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

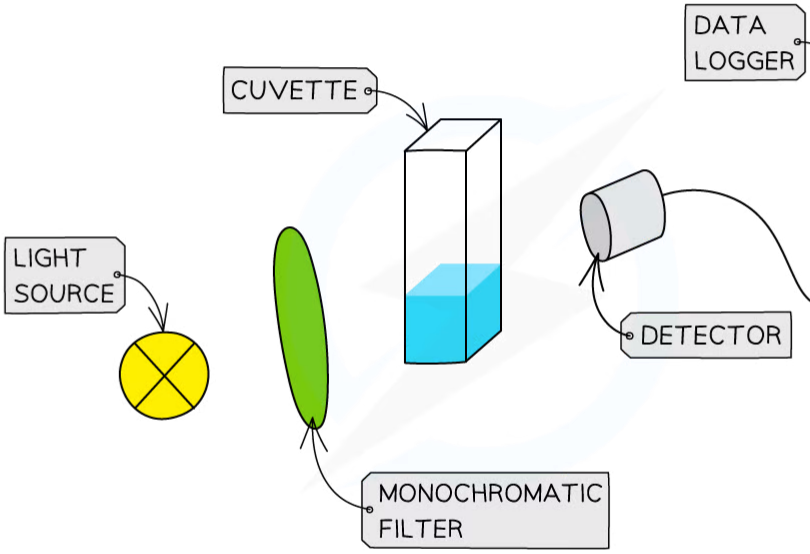
- The colorimeter measures colour absorbance which is proportional to the concentration of the coloured species
- Before the investigation begins it is necessary to measure the absorbance of a set of standard solutions of iodine and obtain a calibration curve
- For example, here is a calibration curve for a transition metal ion that allows you to convert colorimeter readings into concentrations:



A calibration curve showing the relationship between colour absorbance and concentration

- The colorimeter uses very small volumes of solutions, so four burettes can be filled with solutions of 0.02 mol dm^{-3} iodine, 1.0 mol dm^{-3} propanone and 1.0 mol dm^{-3} sulfuric acid and distilled water

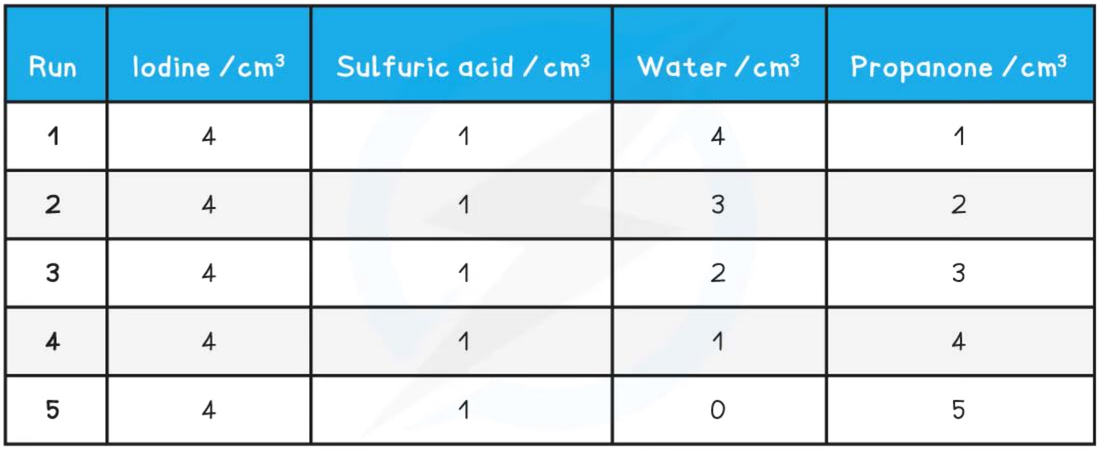
- By varying the volumes of solutions while maintaining a constant total volume with the use of distilled water, you can obtain a number of different concentrations
- The solutions are measured into a small beaker, leaving the iodine in a separate beaker – this starts the reaction, so it can be added when you start a timer or stop watch
- The iodine is added to the other liquids, the contents mixed and then quickly transferred into the cuvette (small receptacle) and the colorimeter / data logger started



The set up for using a colorimeter and data logger to continuously measure the rate of reaction

- A typical set of volume compositions could be as follows:

Volume Compositions Table

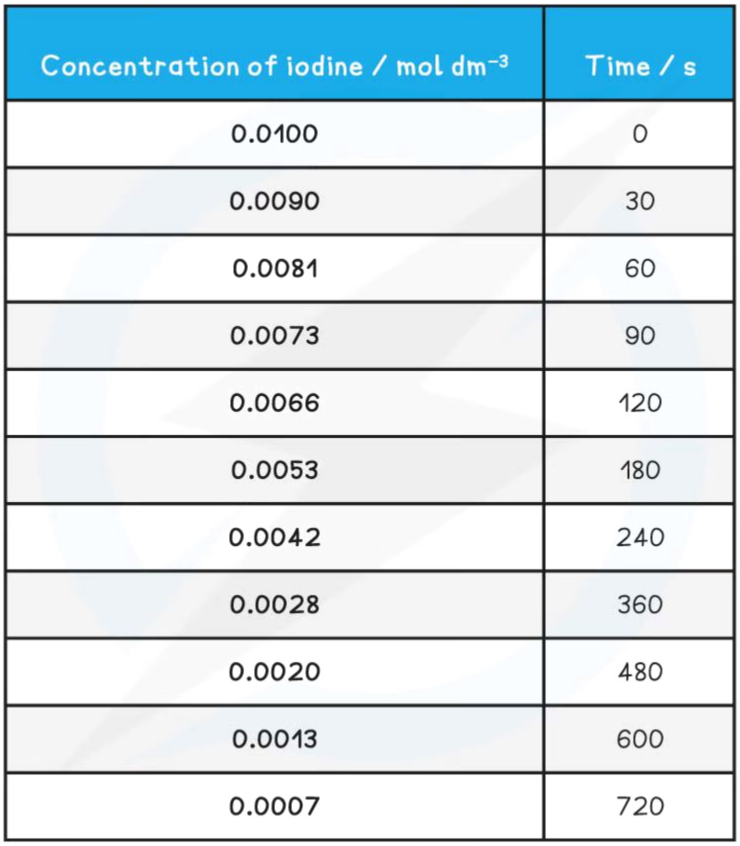


Run	Iodine / cm³	Sulfuric acid / cm³	Water / cm³	Propanone / cm³
1	4	1	4	1
2	4	1	3	2
3	4	1	2	3
4	4	1	1	4
5	4	1	0	5

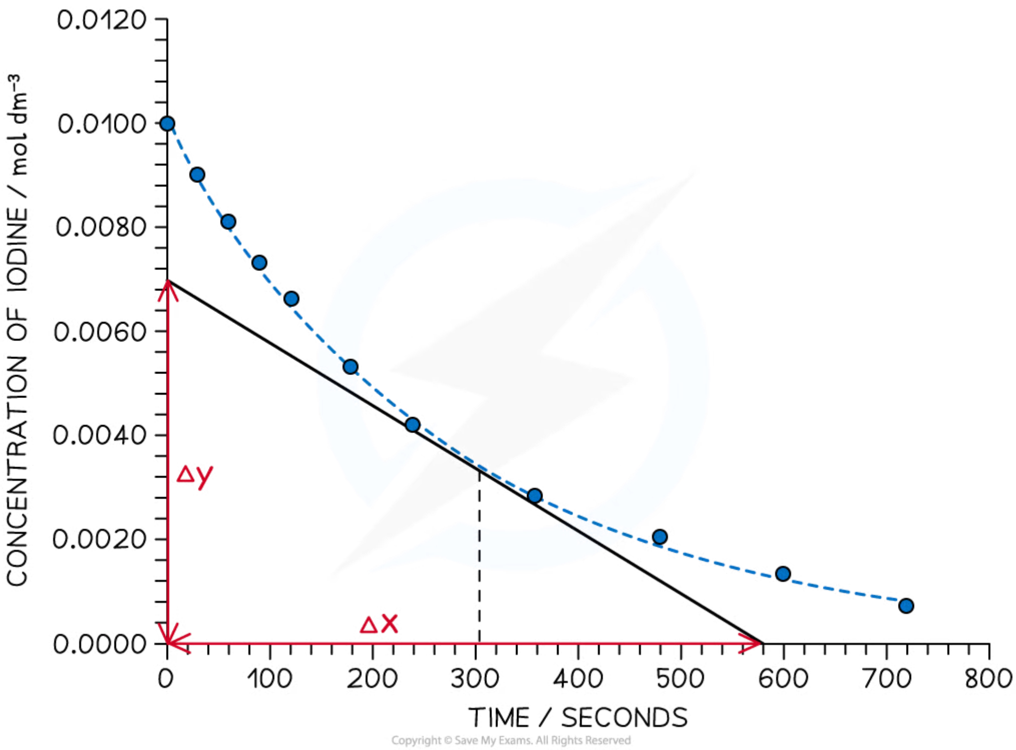
Practical tip

- Choose a filter that gives the strongest absorbance for the solution you are using – this will be the complementary colour to the colour of the solution under investigation

Specimen results table for the iodination of propanone



Concentration of iodine / mol dm^{-3}	Time / s
0.0100	0
0.0090	30
0.0081	60
0.0073	90
0.0066	120
0.0053	180
0.0042	240
0.0028	360
0.0020	480
0.0013	600
0.0007	720



Graph showing the change in concentration of iodine during the course of the reaction

Measuring rate

- To find the rate of reaction at any point, a tangent is drawn and the gradient is determined
- The gradient gives the rate of reaction
- For example, in the graph above, the rate of reaction at 300 seconds can be found
  - A vertical line is drawn from the 300 s mark until it meets the curve, then a tangent is drawn
  - Gradient $= \frac{\Delta y}{\Delta x} = \frac{0.0069}{580} = 1.19 \times 10^{-5}$ mol dm^{-3} s^{-1}
  - The gradient is the rate of reaction at that point

Exam Tip

Whichever rates experiments you carry out, make sure you can

- describe the steps in the procedure
- name all the apparatus used
- draw data tables which include headings and units
- draw graphs showing labels, units and best fit lines
- determine an initial gradient or at any point in the curve

Rate-determining Step

Rate-determining step & intermediates

- A chemical reaction can only go as fast as the slowest part of the reaction
    - So, the **rate-determining step** is the slowest step in the reaction
- If a reactant appears in the **rate-determining step**, then the concentration of that reactant will also appear in the **rate equation**
- For example, the rate equation for the reaction below is rate = $k\,[CH_3Br]\,[OH^-]$

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

- This suggests that **both** CH_3Br and OH^- take part in the **slow rate-determining step**

Predicting the reaction mechanism

- The **overall reaction equation** and **rate equation** can be used to predict a possible reaction mechanism of a reaction
    - This shows the individual reaction steps which are taking place
- For example, nitrogen dioxide (NO_2) and carbon monoxide (CO) react to form nitrogen monoxide (NO) and carbon dioxide (CO_2)
    - The overall reaction equation is:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

- The rate equation is:

$$\text{Rate} = k\,[NO_2]^2$$

- From the rate equation it can be concluded that the reaction is **zero order** with respect to CO (g) and **second order** with respect to NO_2 (g)
- This means that there are **two molecules** of NO_2 (g) involved in the **rate-determining step** and **zero molecules** of CO (g)
- A possible reaction mechanism could therefore be:

Step 1:

$2NO_2\,(g) \rightarrow NO\,(g) + NO_3\,(g)$ **slow** (rate-determining step)

Step 2:

$NO_3\,(g) + CO\,(g) \rightarrow NO_2\,(g) + CO_2\,(g)$ **fast**

Overall:

$$\cancel{2}NO_2\,(g) + \cancel{NO_3\,(g)} + CO\,(g) \rightarrow NO\,(g) + \cancel{NO_3\,(g)} + \cancel{NO_2\,(g)} + CO_2\,(g)$$

$$= \quad NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

Predicting the reaction order & deducing the rate equation

- The **order** of a reactant and thus the rate equation can be deduced from a reaction mechanism if the rate-determining step is known
- For example, the reaction of nitrogen oxide (NO) with hydrogen (H_2) to form nitrogen (N_2) and water

$$2NO\ (g) + 2H_2\ (g) \rightarrow N_2\ (g) + 2H_2O\ (l)$$

- The reaction mechanism for this reaction is:

Step 1:

$NO\ (g) + NO\ (g) \rightarrow N_2O_2\ (g)$ **fast**

Step 2:

$N_2O_2\ (g) + H_2\ (g) \rightarrow H_2O\ (l) + N_2O\ (g)$ **slow** (rate-determining step)

Step 3:

$N_2O\ (g) + H_2\ (g) \rightarrow N_2\ (g) + H_2O\ (l)$ **fast**

- The second step in this reaction mechanism is the **rate-determining step**
- The rate-determining step consists of:
  - N_2O_2 which is formed from the reaction of **two NO molecules**
  - **One H_2 molecule**

- The reaction is, therefore, **second order** with respect to NO and **first order** with respect to H_2
- So, the **rate equation** becomes:

$$\text{Rate} = k\ [NO]^2\ [H_2]$$

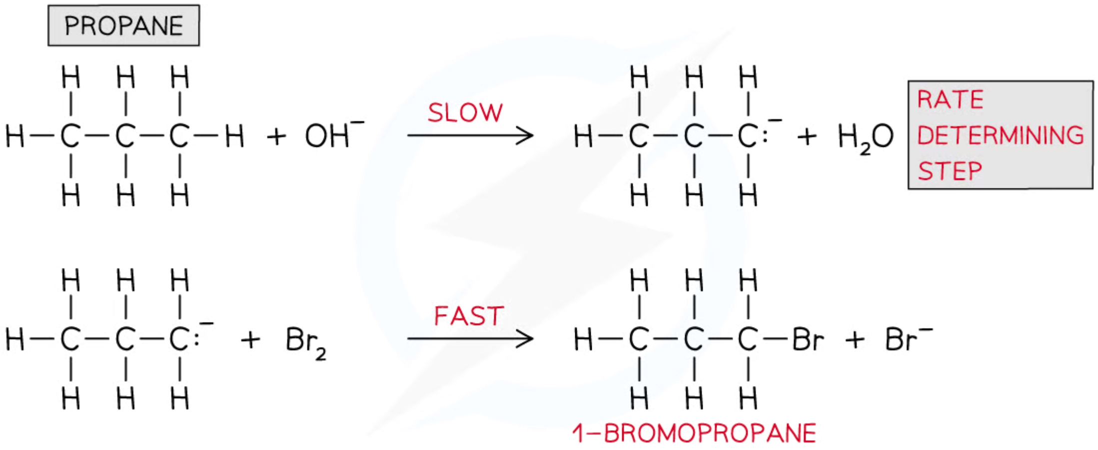
- The reaction is, therefore, **third order overall**

Identifying the rate-determining step

- The rate-determining step can be identified from a rate equation given that the reaction mechanism is known
- For example, propane ($CH_3CH_2CH_3$) undergoes bromination under alkaline solutions
- The overall reaction is:

$$CH_3CH_2CH_3 + Br_2 + OH^- \rightarrow CH_3CH_2CH_2Br + H_2O + Br^-$$

- The reaction mechanism is:



Reaction mechanism for the bromination of propane under alkaline conditions

- The rate equation is:

$$\textbf{Rate} = k\,[CH_3CH_2CH_3]\,[OH^-]$$

- From the rate equation, it can be deduced that only $CH_3CH_2CH_3$ and OH^- are involved in the **rate-determining step** and not bromine (Br_2)
- $CH_3CH_2CH_3$ and OH^- are only involved in the first step of the reaction mechanism, therefore the **rate-determining step** is:
  - $CH_3CH_2CH_3 + OH^- \rightarrow CH_3CH_2CH_2^- + H_2O$

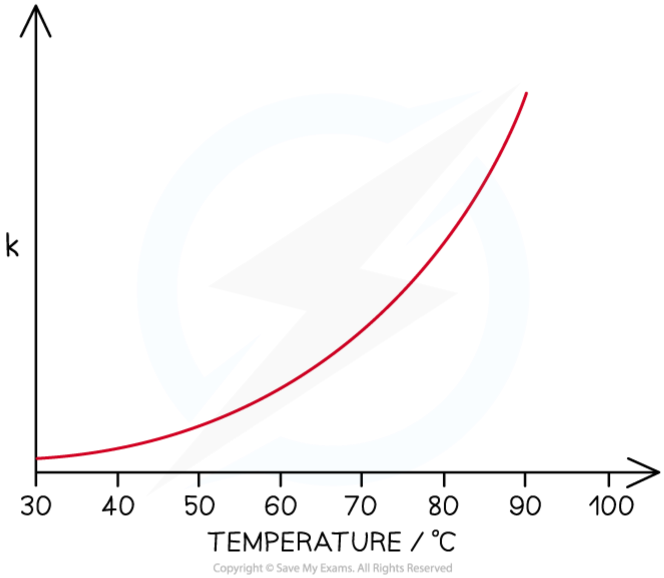
The Effect of Temperature on Rate Constants

- The following general reaction and rate equation will be used to discuss the effect of temperature on the rate constant, *k*:

$$A + B \rightarrow C + D$$

$$\text{Rate of reaction} = k[A][B]$$

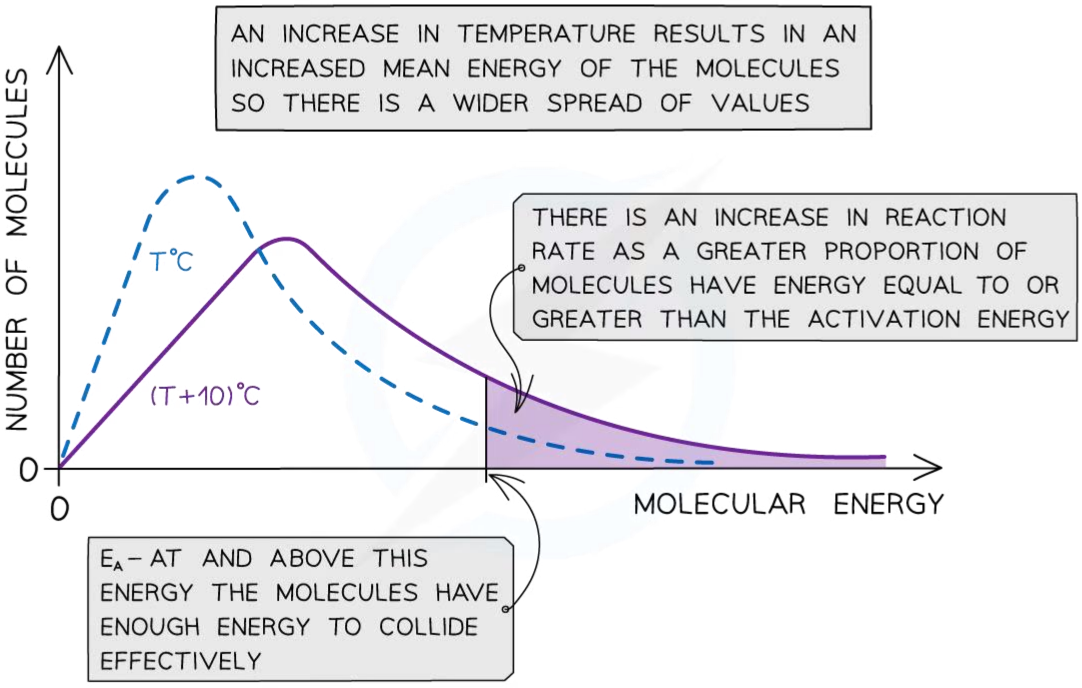
- The rate equation shows that rate of reaction depends on the rate constant, *k*, and the concentration of the reactants
  - As the rate of reaction increases the rate constant will increase
- Increasing the temperature of a reaction increases the rate of a chemical reaction
  - Remember: this does not necessarily increase the yield of a chemical reaction depending on whether a reaction is endothermic or exothermic according to Le Châtelier's principle
- Therefore, increasing the temperature also increases the value of the rate constant, *k*, assuming that the concentration of the reactants remains unchanged
- An exponential relationship between the rate of reaction and temperature is observed when seen on a graph:



Relationship between temperature and rate constant, k

- The graph shows that the rate of reaction roughly doubles with an increase of 10 °C
  - This general relationship does not apply to all reactions
  - Also, it is not necessarily every 10 °C, the rate may double every 9 °C or 11 °C

  - The number of degrees needed to double the rate also changes gradually as temperature increases
- When the temperature of a reaction mixture increases, there are two contributing factors to the increased rate and rate constant:
  - Increasing temperature causes the particles to move around faster resulting in more **frequent collisions**
  - Furthermore, the proportion of **successful collisions** increases, meaning a higher **proportion** of the particles possess the minimum amount of energy (activation energy) to cause a chemical reaction



The Maxwell-Boltzmann distribution curve at T ºC and when the temperature is increased by 10 ºC

- Therefore, an increase in temperature causes an increased rate of reaction due to:
  - There being **more effective collisions** as the particles have **more kinetic energy**, making them move around faster
  - A **greater proportion** of the molecules having **kinetic energy** greater than the **activation energy**
- The increase in proportion of molecules having kinetic energy greater than the activation has a greater effect on the rate of reaction than the increase in effective collisions

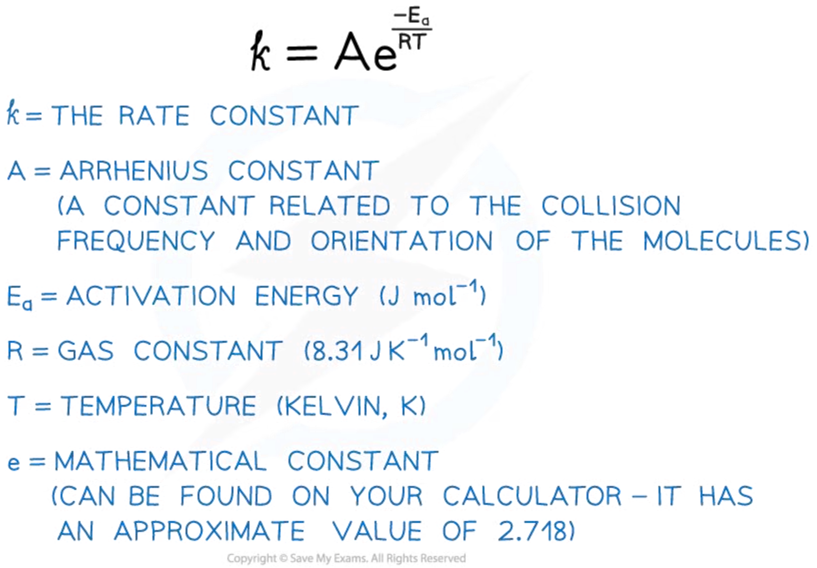
5.1.7 The Arrhenius Equation

Describing the Arrhenius Equation

- The rate equation shows how each of the reactants in a reaction effects the rate of the reaction and it includes the rate constant, *k*
- However, *k* only remains constant if the concentration of the reactants is the only factor which is changed
    - If the temperature is changed or a catalyst is used or changed, then the rate constant, *k*, changes

- At higher temperatures, a greater proportion of molecules have energy greater than than the activation energy
- Since the **rate constant** and **rate of reaction** are **directly proportional** to the fraction of molecules with energy equal or greater than the activation energy, then at higher temperatures:
    - The **rate of reaction** increases
    - The **rate constant** increases

- The relationship between the rate constant, the temperature and also the activation energy is given by the Arrhenius equation:



$$k = Ae^{\frac{-E_a}{RT}}$$

k = THE RATE CONSTANT

A = ARRHENIUS CONSTANT
(A CONSTANT RELATED TO THE COLLISION FREQUENCY AND ORIENTATION OF THE MOLECULES)

E_a = ACTIVATION ENERGY (J mol^{-1})

R = GAS CONSTANT (8.31 J K^{-1} mol^{-1})

T = TEMPERATURE (KELVIN, K)

e = MATHEMATICAL CONSTANT
(CAN BE FOUND ON YOUR CALCULATOR – IT HAS AN APPROXIMATE VALUE OF 2.718)

- E_a and *A* are constants that are characteristic of a specific reaction
    - *A* does vary slightly with temperature but it can still be considered a constant

- *R* is a fundamental physical constant for all reactions
- *k* and *T* are the only variables in the Arrhenius equation

- The Arrhenius equation is used to describe reactions that involve gases, reactions occurring in solution or reactions that occur on the surface of a catalyst

Using Arrhenius Plots

YOUR NOTES

Finding the Activation Energy

- Very often, the Arrhenius equation is used to calculate the activation energy of a reaction
- A question will either give sufficient information for the Arrhenius equation to be used or a graph can be plotted and the calculation done from the plot

Using the Arrhenius Equation

- The Arrhenius equation is easier to use if you take natural logarithms of each side of the equation, which results in the following equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

- The Arrhenius Equation can be used to show the effect that a change in temperature has on the rate constant, *k*, and thus on the overall rate of the reaction
  - An increase in temperature (higher value of *T*) gives a greater value of ln *k* and therefore a higher value of *k*
  - Since the rate of the reaction depends on the rate constant, *k*, an increase in *k* also means an increased rate of reaction
- The equation can also be used to show the effect of increasing the activation energy on the value of the rate constant, *k*
  - An increase in the activation energy, E_a, means that the proportion of molecules which possess at least the activation energy is less
  - This means that the rate of the reaction, and therefore the value of *k*, will decrease
- The values of *k* and *T* for a reaction can be determined experimentally
  - These values of *k* and *T* can then be used to calculate the activation energy for a reaction
  - This is the most common type of calculation you will be asked to do on this topic

Worked Example

Calculate the activation energy of a reaction which takes place at 400 K, where the rate constant of the reaction is 6.25 x 10^{-4} s^{-1}.

A = 4.6 x 10^{13} and R = 8.31 J mol^{-1} K^{-1}.

Answer

$$\ln k = \ln A - \frac{E_a}{RT}$$

REARRANGE THE EQUATION FOR E_a:

$$\frac{E_a}{RT} + \ln k = \ln A$$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$\longrightarrow E_a = (\ln A - \ln k) \times RT$$

INSERT VALUES FROM THE QUESTION:

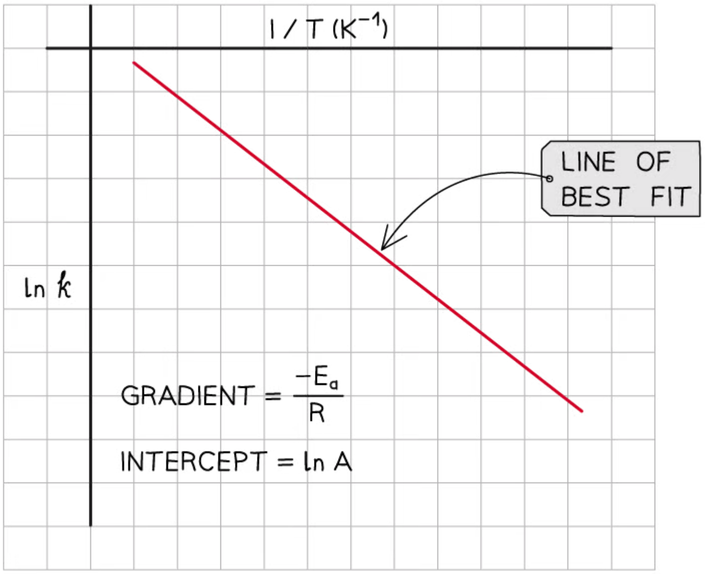
$$\begin{aligned} E_a &= [(\ln 4.6 \times 10^{13}) - (\ln 6.25 \times 10^{-4})] \times (8.31 \times 400) \\ &= [(31.4597) - (-7.3778)] \times (3324) \\ &= 129{,}095.85\ \text{J} \end{aligned}$$

REMEMBER, E_a HAS THE UNIT kJ...

$$E_a = 129\ \text{kJ}$$

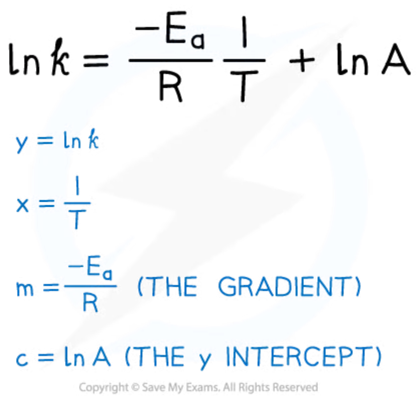
Using an Arrhenius plot:

- A graph of ln *k* against 1/*T* can be plotted, and then used to calculate E_a
  - This gives a line which follows the form y = mx + c



The graph of ln k against 1/T is a straight line with gradient -E_a/R

- From the graph, the equation in the form of y = mx + c is as follows:



$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$

$y = \ln k$

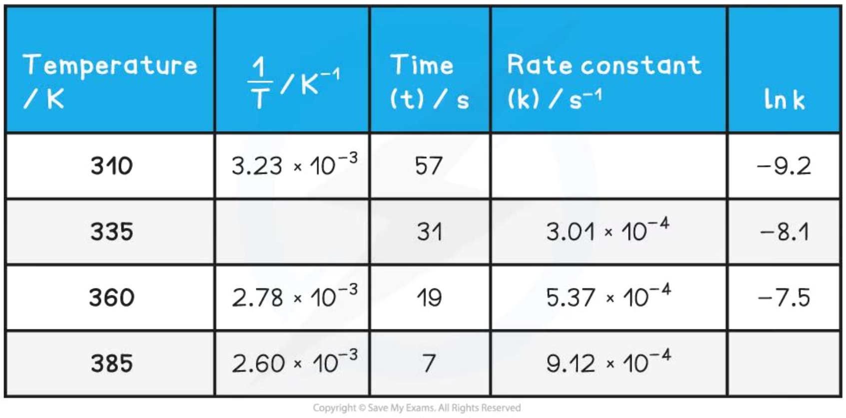
$x = \frac{1}{T}$

$m = \frac{-E_a}{R}$ (THE GRADIENT)

$c = \ln A$ (THE y INTERCEPT)

Worked Example

1. Complete the following table
2. Plot a graph of ln k against $1/T$
3. Use this to calculate the activation energy, E_a, and the Arrhenius constant, A, of the reaction.



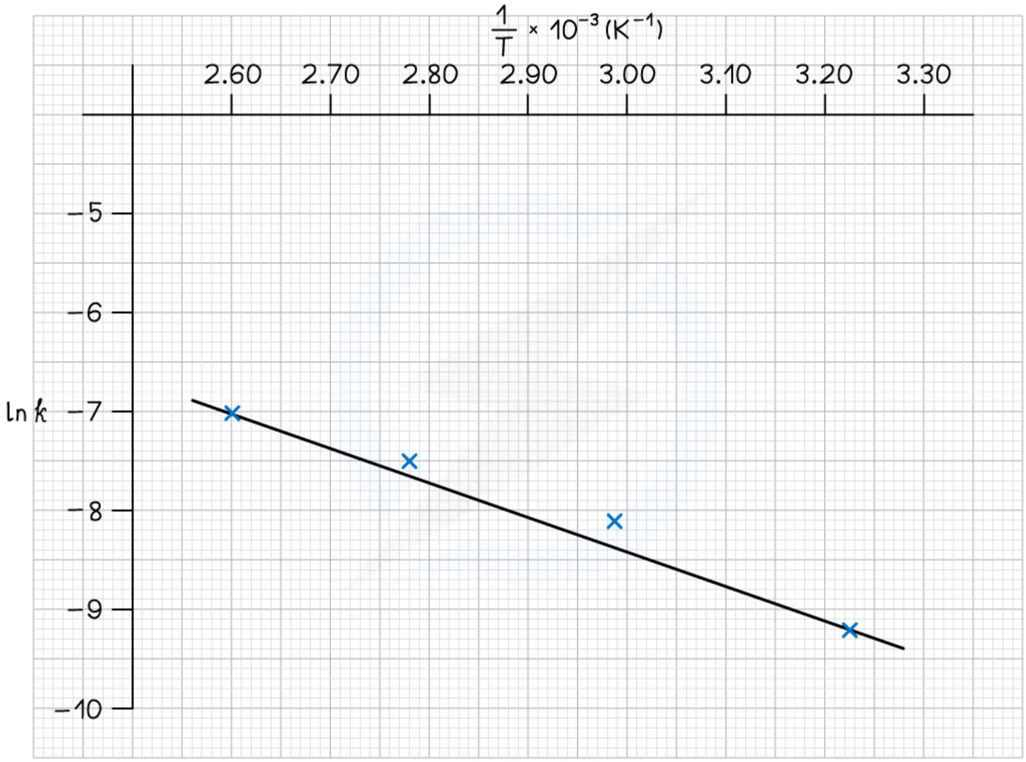
Temperature / K	$\frac{1}{T}$ / K^{-1}	Time (t) / s	Rate constant (k) / s^{-1}	ln k
310	3.23×10^{-3}	57		−9.2
335		31	3.01×10^{-4}	−8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	−7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	

Answers

Answer 1:

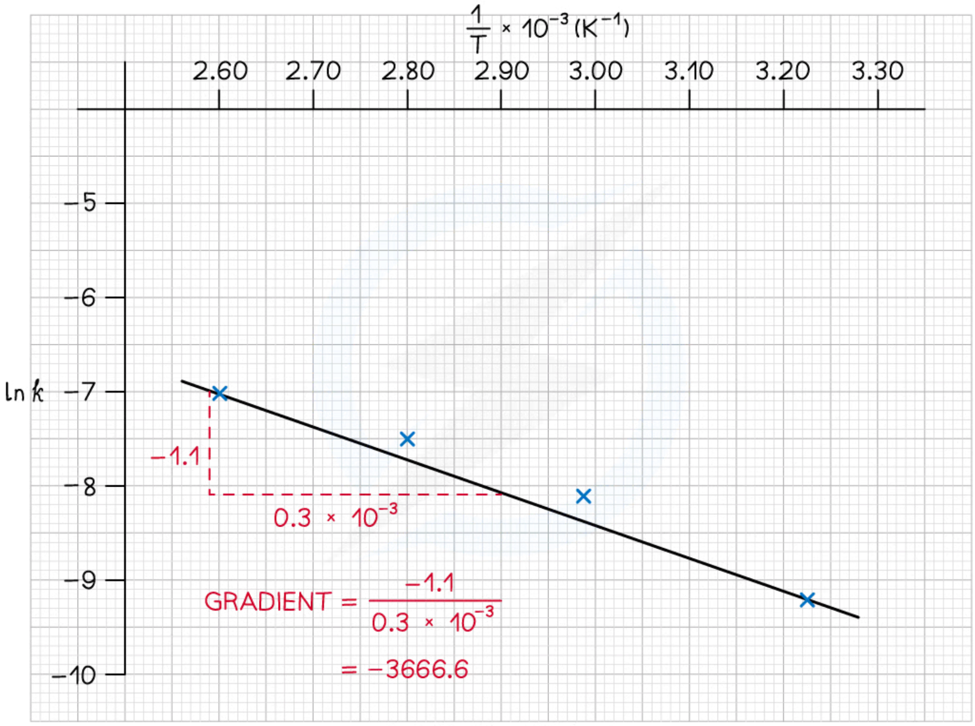
Temperature / K	$\frac{1}{T}$ / K^{-1}	Time (t) / s	Rate constant (k) / s^{-1}	ln k
310	3.23×10^{-3}	57	1.01×10^{-4}	−9.2
335	2.99×10^{-3}	31	3.01×10^{-4}	−8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	−7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	−7.0

Answer 2:



Answer 3:

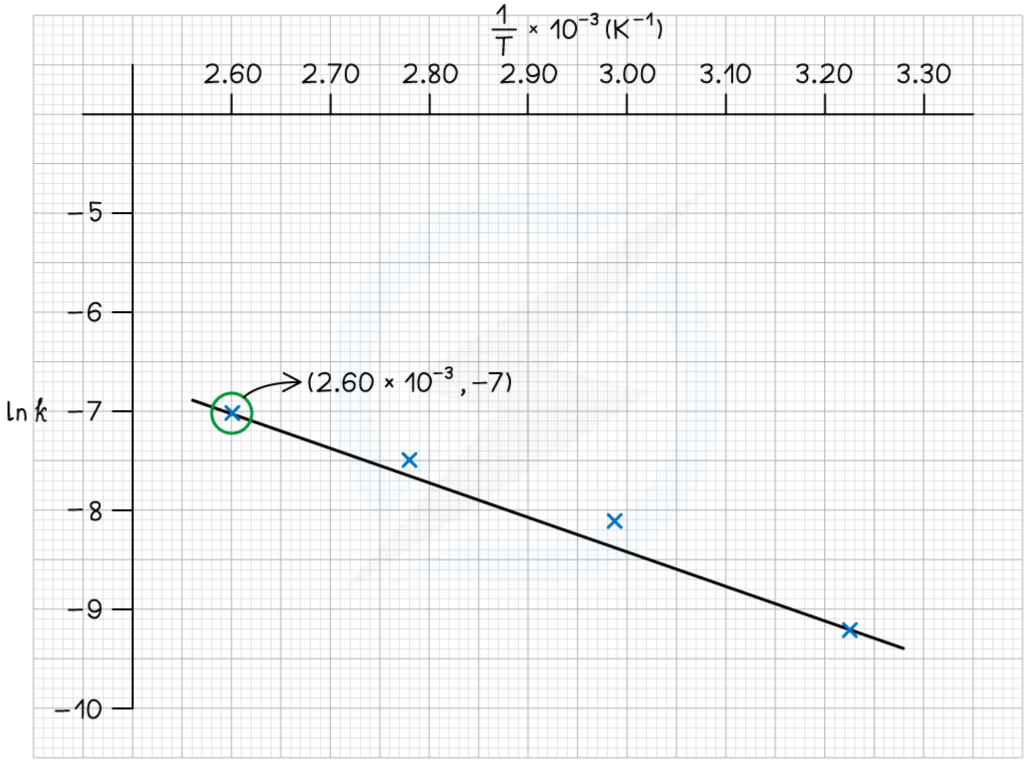
CALCULATE THE ACTIVATION ENERGY:



$$\text{GRADIENT} = \frac{-E_a}{R} = -3666.6$$

$$E_a = -(-3666.6 \times 8.31)$$
$$= 30{,}469 \text{ J mol}^{-1}$$
$$= 30.5 \text{ kJ mol}^{-1}$$

CALCULATE A:



CHOOSE A POINT ON THE GRAPH

$(2.60 \times 10^{-3}, -7.0)$

USE THE FOLLOWING EQUATION:

$$\begin{array}{ccccccc} y & = & m & x & + & c \\ \ln k & = & \frac{-E_a}{R} & \frac{1}{T} & + & \ln A \end{array}$$

$$\left.\begin{array}{l} \ln k = -7.0 \\ \frac{1}{T} = 2.60 \times 10^{-3} \end{array}\right\} \text{FROM THE POINT CHOSEN ON THE GRAPH}$$

$$\frac{-E_a}{R} = \frac{-1.1}{0.3 \times 10^{-3}}$$

$$= -3666.6$$

SO: $-7.0 = (-3666.6 \times 2.60 \times 10^{-3}) + \ln A$

$-7.0 = -9.53 + \ln A$

$\therefore \ln A = -7.0 + 9.53$

$= 2.53$

$A = e^{2.53}$

$A = 12.55$