

**WJEC**  

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**CBAC**

**AS/A LEVEL**  
**GCE in Chemistry**

**REVISION AID**

**CH5**

## **UNIT CH5 Physical and inorganic chemistry**

This unit develops ideas of redox, kinetics, energy changes and equilibria.  
The inorganic chemistry of some elements in various sections of the Periodic Table is studied.

### **Topic 15**

**15.1 Redox and standard electrode potential**

**15.2 Redox reactions**

**15.3 Applications**

### **Topic 16**

**16.1 General Chemistry of the p – block**

**16.2 Group 3 (13)**

**16.3 Group 4 (14)**

**16.4 Group 7 (17)**

### **TOPIC 17 - d-block transition elements**

### **TOPIC 18 - Chemical kinetics**

### **TOPIC 19 - Energy changes**

**19.1 Enthalpy changes for solids and solutions**

**19.2 Entropy and feasibility of reactions**

### **TOPIC 20 – Equilibria**

**20.1 General Equilibria**

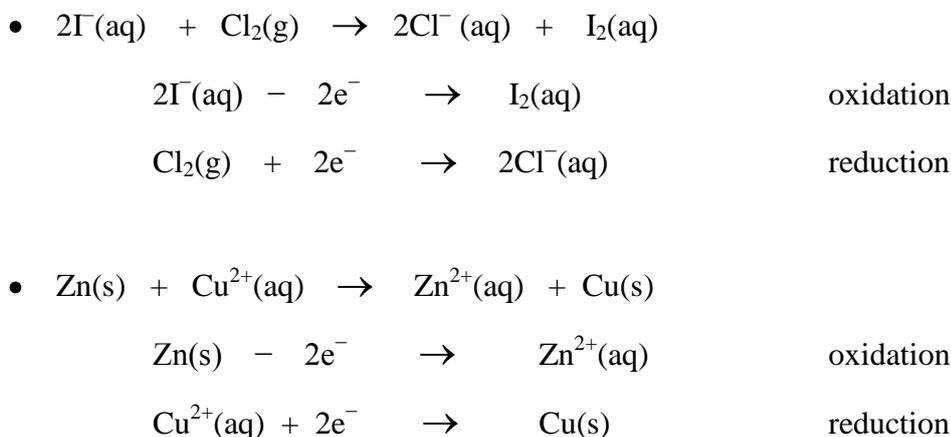
**20.2 Acid-Base Equilibria**

**Topic 15****Topic 15.1 Redox and standard electrode potential****Topic 15.2 Redox reactions****(a) Redox****Candidates should be able to:**

*describe redox in terms of electron transfer, use oxidation states (numbers) to identify redox reactions and decide which species have been oxidised and which reduced;*

Oxidation may be defined as electron loss and reduction as electron gain.

The following equations represent examples of redox reactions and the half equations clearly show the transfer of electrons.

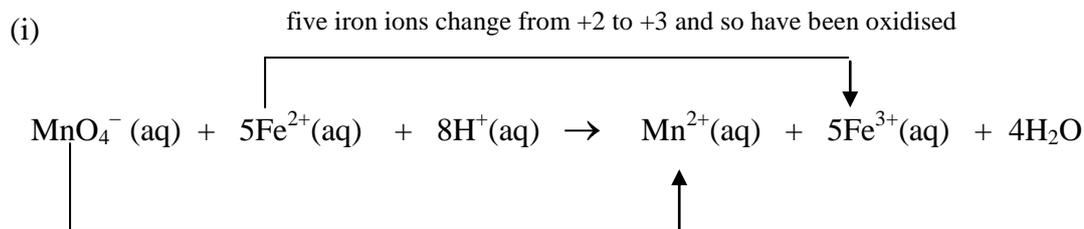
**Oxidation state or oxidation number**

This concept was introduced in **Topic 6.1(d)**

Oxidation is an increase in oxidation number and reduction is a decrease in oxidation number.

**Examples**

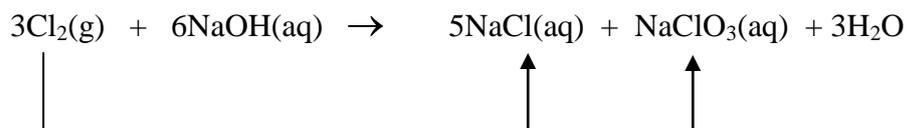
Consider the changes in oxidation state (number) in the following



the element manganese changes from +7 to +2 and so has been reduced.

Summary	Manganese	+7	→	+2	change -5
	Iron	5 × +2	→	5 × +3	change +5

(ii)



Oxidation state



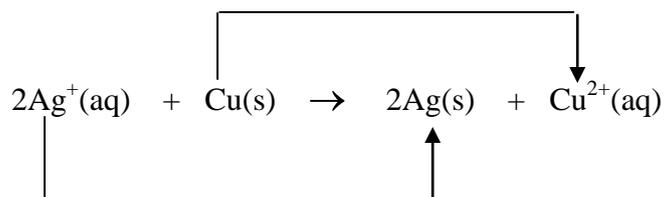
Six chlorine atoms oxidation state zero change to five chloride ions oxidation state  $-1$  and chlorine in one  $\text{ClO}_3^-$  ion with oxidation state  $+5$

Chlorine is simultaneously oxidised and reduced. This is called **disproportionation**.

Summary    Chlorine     $6 \times 0 \rightarrow (5 \times -1) + (1 \times +5)$     change zero

(iii)

one copper atom changes from 0 to  $+2$  so has been oxidised



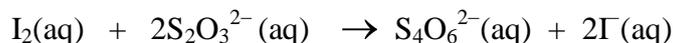
two silver ions change from  $+1$  to  $0$  so have been reduced

Summary    Silver     $2 \times +1 \rightarrow 0$     change  $-2$   
               Copper     $0 \rightarrow +2$     change  $+2$





Hence the overall reaction between iodine and sodium thiosulfate is



### The use of potassium manganate(VII) in volumetric analysis

The aqueous potassium manganate(VII) is placed in the burette and the reducing agent pipetted into the conical flask with an excess of aqueous sulfuric acid. These titrations require no external indicator. As soon as all the reducing agent has been oxidised, the next drop of potassium manganate imparts a pink colour to the contents of the flask.

The aqueous potassium manganate(VII) must always be standardised by titration with a standard solution of a reducing agent such as ammonium iron(II) sulphate.

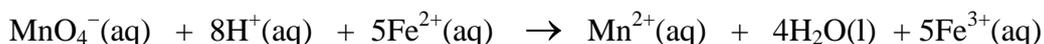
The ion-electron half equation is:



The ion-electron half equation for  $\text{MnO}_4^-$  is:



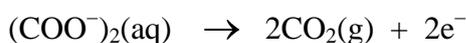
Since the total number of electrons lost must be equal to the number gained, the overall equation is:



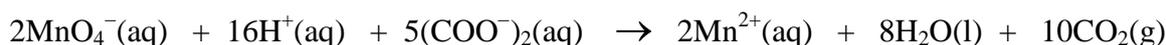
**1 mol  $\text{MnO}_4^-$  (aq) reacts with 5 mol  $\text{Fe}^{2+}$  (aq)**

Other reducing agents whose concentration may be determined by potassium manganate(VII) titrations are

(i) ethanedioate ions and ethanedioic acid



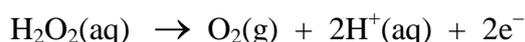
The overall equation is:



**2 mol  $\text{MnO}_4^-$  (aq) reacts with 5 mol  $(\text{COO}^-)_2$  (aq)**

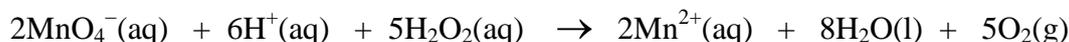
*(This reaction proceeds very slowly at room temperature and must be heated to about 70 °C to proceed at a reasonable rate but once started, it is catalysed by the  $\text{Mn}^{2+}$  ions produced and no more heat is required)*

(ii) aqueous hydrogen peroxide



(Note hydrogen peroxide is reacting as a reducing agent rather than as an oxidising agent)

The overall equation is:



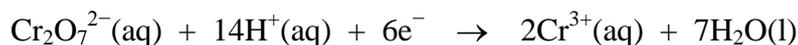
**2 mol  $\text{MnO}_4^-(\text{aq})$  reacts with 5 mol  $\text{H}_2\text{O}_2(\text{aq})$**

**The use of potassium dichromate(VI) in volumetric analysis**

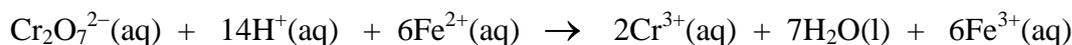
Here the orange aqueous potassium dichromate(VI) is placed in the burette but this time an indicator is required e.g. during the oxidation of aqueous iron(II) ions.



Since the ion-electron half equation for  $\text{Cr}_2\text{O}_7^{2-}$  is:

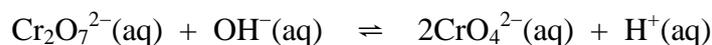


The overall equation is:



**1 mol  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$  reacts with 6 mol  $\text{Fe}^{2+}(\text{aq})$**

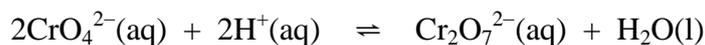
Note that the interconversion of dichromate(VI),  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ , and chromate(VI),  $\text{CrO}_4^{2-}(\text{aq})$ , is **NOT** redox as the chromium does not change its oxidation number.



orange

yellow

**or**



yellow

orange

The oxidation number of the chromium is +6 in both of these ions.

This is an acid/base equilibrium and shows that dichromate(VI) ions are stable in acidic solution and chromate(VI) is stable in alkaline solution.

### The use of sodium thiosulfate(VI) in volumetric analysis

Aqueous sodium thiosulfate(VI) is oxidised by aqueous iodine.

The concentration of oxidising agents can be determined by reaction with excess aqueous iodide ions, and then titrating the iodine released with aqueous sodium thiosulfate. The aqueous sodium thiosulfate is placed in the burette; the oxidising agent is pipetted into the conical flask which contains excess aqueous potassium iodide. The sodium thiosulfate solution is run into the flask until the colour due to iodine fades to a pale straw colour. At this point starch solution is added as indicator, turning the mixture dark blue. The end point is reached when the blue colour is completely discharged.

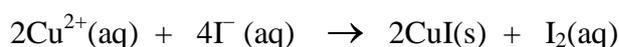
The ion-electron half equation is:



Here are some oxidising agents which can be determined by sodium thiosulfate titrations.

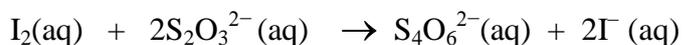
#### (i) Aqueous copper(II) salts

Aqueous copper(II) ions oxidise aqueous iodide ions



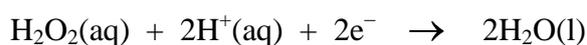
blue solution

buff coloured ppt

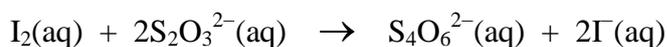
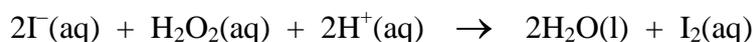


**1 mol Cu<sup>2+</sup>(aq) requires 1 mol S<sub>2</sub>O<sub>3</sub><sup>2-</sup>(aq)**

#### (ii) Aqueous hydrogen peroxide



The potassium iodide must be acidified with dilute sulfuric acid.

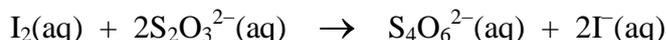
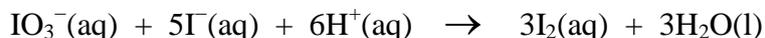


**1 mol H<sub>2</sub>O<sub>2</sub>(aq) requires 2 mol of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>(aq)**

## (iii) Aqueous potassium iodate(V)

As potassium iodate(V) can be obtained in a very pure state, it can be used to standardise aqueous sodium thiosulfate.

In the presence of excess acid, potassium iodate(V) will oxidise aqueous iodide ions.



**1 mol  $\text{IO}_3^-(\text{aq})$  requires 6 mol  $\text{S}_2\text{O}_3^{2-}(\text{aq})$**

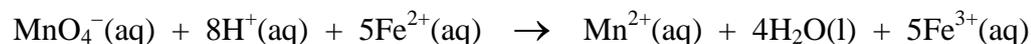
The specification requires, “use titration and other data to carry out appropriate calculations”.

## Examples of worked calculations

(i) 25.0 cm<sup>3</sup> of aqueous iron(II) sulfate of concentration 25.00 g FeSO<sub>4</sub>·7H<sub>2</sub>O per dm<sup>3</sup> and containing excess aqueous sulfuric acid, were pipetted into a conical flask. On titrating with aqueous potassium manganate(VII), 25.55 cm<sup>3</sup> of the potassium manganate(VII) solution were required for complete oxidation. Calculate the concentration of aqueous potassium manganate(VII) in mol dm<sup>-3</sup>.

Molar mass of FeSO<sub>4</sub>·7H<sub>2</sub>O = 278.0 g

Concentration of Fe<sup>2+</sup>(aq) ions = 25.00/278.0 mol dm<sup>-3</sup> = 0.08993 mol dm<sup>-3</sup>



Number of mol of Fe<sup>2+</sup>(aq) ions used = volume (dm<sup>3</sup>) × concentration

$$= (25.0 \times 0.08993)/1000 = 2.248 \times 10^{-3} \text{ mol}$$

Therefore 25.55 cm<sup>3</sup> of potassium manganate(VII) solution contains (2.248 × 10<sup>-3</sup>)/5 mol MnO<sub>4</sub><sup>-</sup>

Concentration of potassium manganate(VII) = (1000/25.55) × (2.248 × 10<sup>-3</sup>)/5 = 0.0176 mol dm<sup>-3</sup>

Note that the volume of iron(II) sulfate solution was only given to three significant figures which was the least accurate figure quoted, so final concentration is given to three significant figures.

Any correct manipulation of data will gain credit in the examination.

Some candidates may substitute in a rote equation.

e.g.

$$\frac{v_1 \times c_1}{n_1} = \frac{v_2 \times c_2}{n_2}$$

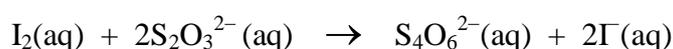
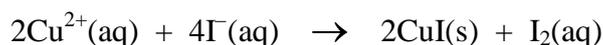
If such a method is employed, marks may be lost if errors are made, as no credit can be given for explanations or method.

(ii) 10.200 g of the contents of a bottle labelled “copper(II) ethanoate,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ”, were dissolved in water and the solution made up to  $500 \text{ cm}^3$  in a volumetric flask.  $25.0 \text{ cm}^3$  of this solution were pipetted into a conical flask containing excess aqueous potassium iodide. The liberated iodine was titrated against aqueous sodium thiosulfate of concentration  $0.1000 \text{ mol dm}^{-3}$ , using starch as indicator near the end-point.

The volume of aqueous sodium thiosulfate required was  $24.95 \text{ cm}^3$ .

Calculate the percentage purity of the copper(II) ethanoate.

Relevant equations are



2 mol of sodium thiosulfate reacts with the iodine formed by 2 mol of copper(II) ions.

Number of mol of sodium thiosulfate in the titre =  $(24.95 \times 0.1000)/1000 = 2.495 \times 10^{-3} \text{ mol}$

therefore the number of mol of  $\text{Cu}^{2+}(\text{aq})$  in  $25.0 \text{ cm}^3$  of the copper(II) ethanoate solution

is  $2.495 \times 10^{-3} \text{ mol}$ .

Number of mol of  $\text{Cu}^{2+}(\text{aq})$  in  $500 \text{ cm}^3$  of solution =  $(2.495 \times 10^{-3} \times 20) \text{ mol} = 4.99 \times 10^{-2} \text{ mol}$

Molar mass of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O} = 199.63 \text{ g mol}^{-1}$

Thus mass of copper(II) ethanoate,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  in  $500 \text{ cm}^3 = 199.63 \times 4.99 \times 10^{-2} \text{ g}$

$$= 9.962 \text{ g}$$

Purity of copper(II) ethanoate,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O} = (9.962/10.200) \times 100 = 97.7\%$

**(b) Electrode processes****Candidates should be able to:**

*show awareness that electrode processes represent oxidations and reductions;*

Electrode processes involve oxidations and reductions e.g. during electrolysis, oxidation takes place at the anode and reduction takes place at the cathode.

Many industrial processes involve electrolysis e.g. reactive metals such as sodium and aluminium are extracted electrolytically, the metal ions gaining electrons at the cathodes of the electrolytic cells.

**(d), (e), (f) Recall, use and describe redox systems****Candidates should be able to:**

*(c) recall and use the redox systems specified below, including the appropriate colour change and ion/electron half-equations.*

$\text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s}); \text{Zn}^{2+}(\text{aq}) \mid \text{Zn}(\text{s}); \text{H}^{+}(\text{aq}) \mid \text{H}_2(\text{g}) \text{ Pt}; \text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq}) \mid \text{Pt};$   
 $\text{MnO}_4^{-}(\text{aq}), \text{Mn}^{2+}(\text{aq}) \mid \text{Pt}; \text{X}_2(\text{g}) \mid 2\text{X}^{-}(\text{aq}) (\text{X} = \text{Cl}^{-}, \text{Br}^{-}, \text{I}^{-});$

*(d) use redox systems in addition to those in (d), for which all relevant information is supplied;*

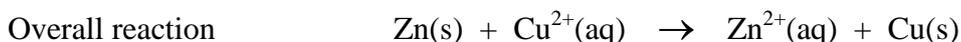
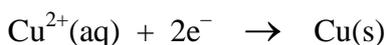
*(f) describe simple electrochemical cells involving;*

*(i) metal/metal ion electrodes, and*

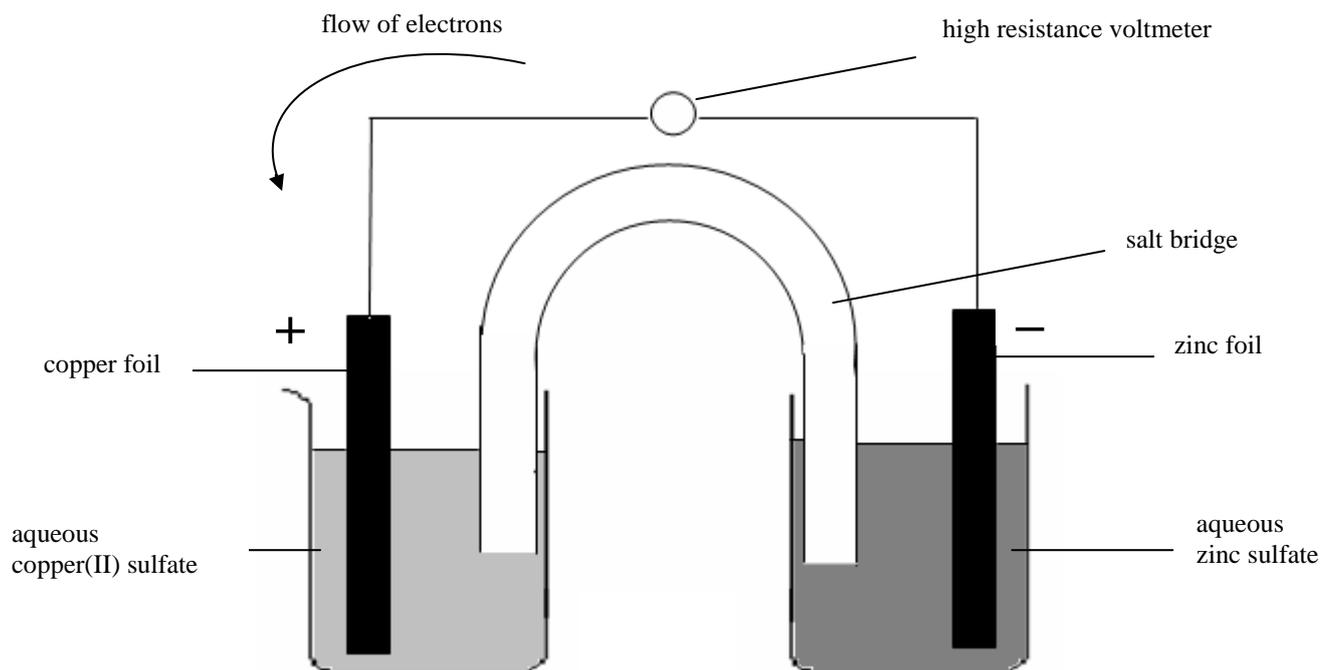
*(ii) electrodes based on different oxidation states of the same element.*

Consider the changes that occur when small pieces of zinc metal are dropped into aqueous copper(II) sulfate. If the mixture is stirred, gradually the blue colour of the solution begins to fade and a reddish deposit is seen on the pieces of zinc and at the bottom of the beaker.

A redox reaction has taken place.



The aqueous zinc ion is colourless and the blue colour of the aqueous copper(II) ion disappears as the ions are reduced to the metal. If the two halves of the reaction are kept separate, chemical energy is changed into electrical energy producing a voltage.



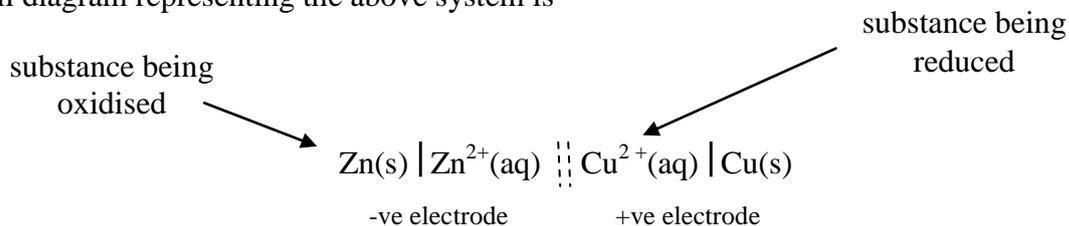
The salt bridge is needed to allow ions to flow from one solution to the other while the two solutions themselves are kept separate.

Electrons are released at the zinc electrode and will flow through the external wire to the copper electrode where copper ions accept electrons.

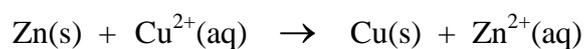
The emf of this cell is of the order of 1.1 volts.

By convention the cell is represented by a cell diagram *but note that a cell diagram is not the same as a diagram of a cell* which is the diagram above.

This cell diagram representing the above system is



This cell diagram represents



### (g) The standard hydrogen electrode

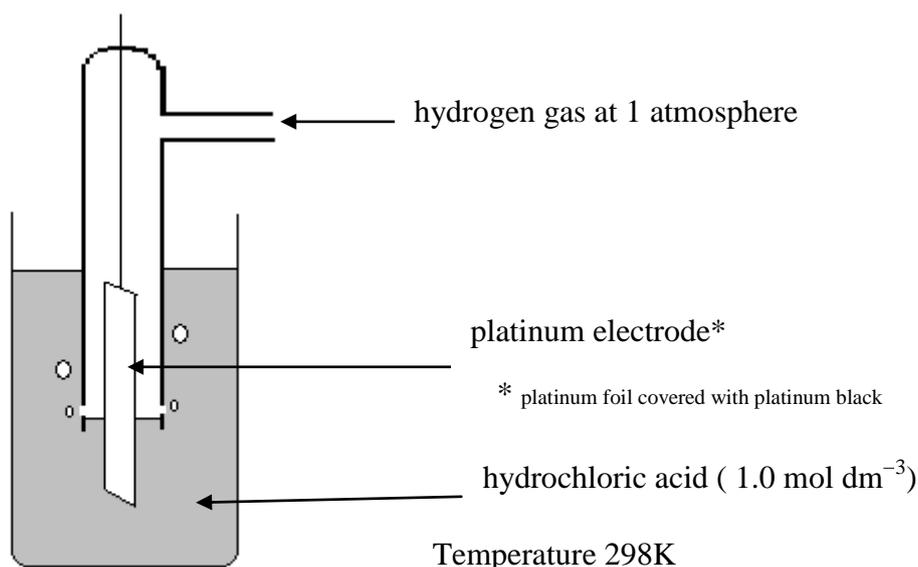
#### Candidates should be able to:

*explain and use the term standard electrode potential especially*

- (i) *the use of the standard hydrogen electrode in determining standard electrode potential;*
- (ii) *to calculate standard potentials of cells formed by combining different electrodes and;*
- (iii) *to predict the feasibility of specified reactions.*

As can be seen above a combination of two electrodes produces an emf.

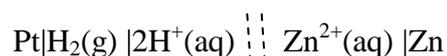
By convention all such emfs are measured with respect to the standard hydrogen electrode.



By convention the electrode process at the platinum electrode  $2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{H}_2(\text{g})$  is taken as the standard and other potentials are measured with respect to it.

#### Electrode potential

By definition, the electrode potential of a half cell, say  $\text{Zn} | \text{Zn}^{2+}(\text{aq})$ , is the emf of a cell represented by the cell diagram



When conditions are standard i.e. 298K and unit concentrations (1.0 mol dm<sup>-3</sup>) the emf is called the **Standard Electrode Potential ( $E^\ominus$ )**.

The sign of the electrode potential is the sign of the right hand electrode in the cell diagram.

The emf of a cell is measured using a high resistance voltmeter which takes no current itself. The emf is the potential difference across the cell when it takes no current. The emf is a measure of the maximum amount of energy which can be given by the cell.

### Some Standard Electrode Potentials

Reaction	$E^\ominus / \text{V}$
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K}(\text{s})$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca}(\text{s})$	-2.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.41
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.23
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.04
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	+0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}^+(\text{aq})$	+0.16
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.52
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l})$	+0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Hg}(\text{l})$	+0.85
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Hg}_2^{2+}(\text{aq})$	+0.90
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.07
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ce}^{3+}(\text{aq})$	+1.44
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.78
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Co}^{2+}(\text{aq})$	+1.82
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.87

Note that some standard electrode potentials above are given for cells containing ions in different oxidation states e.g.  $\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ .

Physically these cells use an inert platinum electrode to allow the passage of electrons.

The cell diagram for determining the standard electrode potential is written

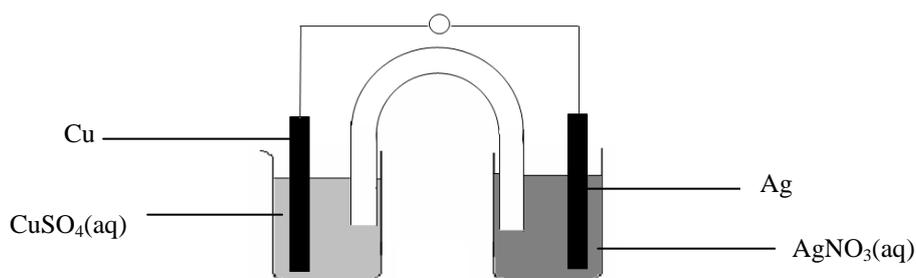


and standard conditions apply.

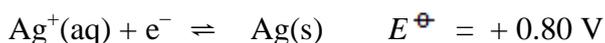
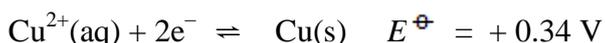
### The uses of standard electrode potentials

To calculate the emf of a cell made by combining different electrodes.

Consider the following practical setup.

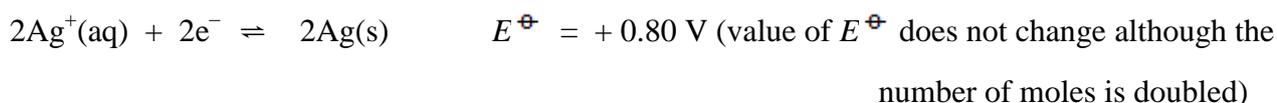


From the table above

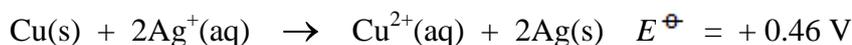


Careful observation shows that silver is deposited on the silver electrode and the copper electrode starts to dissolve. The reaction with the more positive  $E^{\ominus}$  will proceed in the forward direction because reduction is more favourable.

The overall reactions are



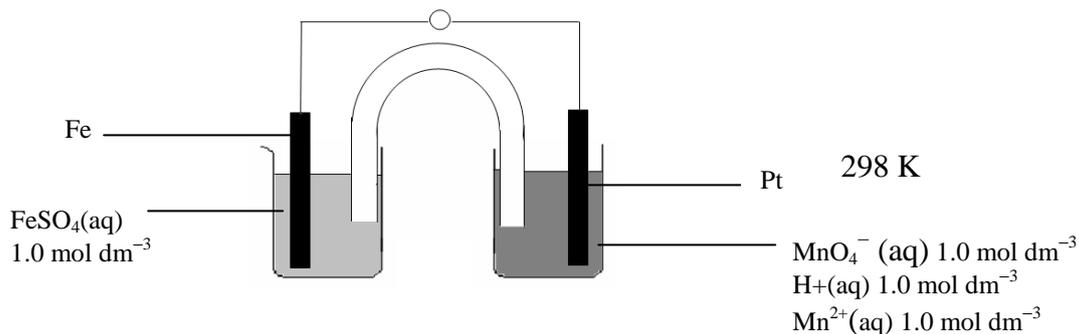
Overall we can add the two equations to obtain the overall redox equation and also add the  $E^{\ominus}$  values



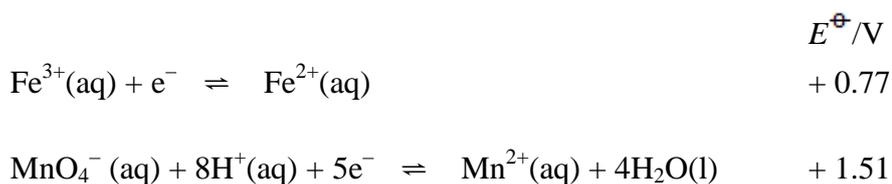
This value agrees with the experimentally determined value under standard conditions and a positive value for  $E^{\ominus}$  means that the reaction is feasible.

### Other examples of redox cell chemistry

(i)

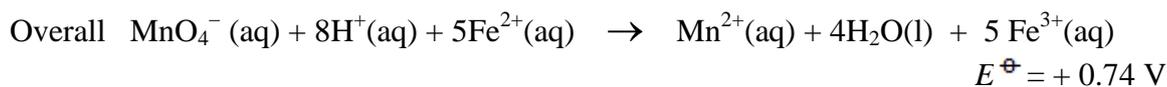
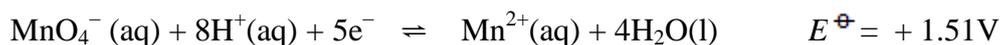


From the table above



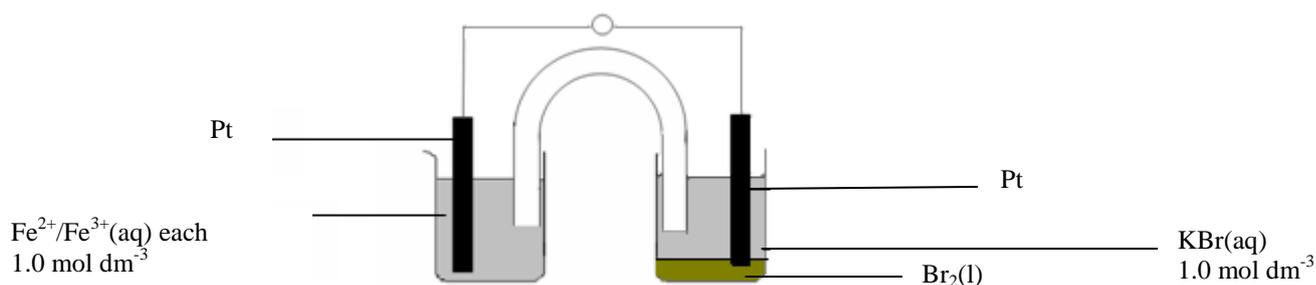
$MnO_4^{-}$  has the more positive  $E^{\ominus}$  value so this reaction proceeds in the forward direction and acidified potassium manganate(VII) oxidises iron(II).

Rearranging

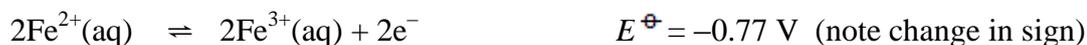
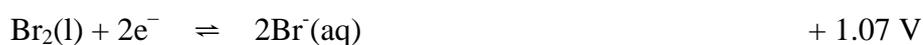


The Fe electrode is negatively charged and the Pt electrode is positively charged meaning that electrons would flow from the iron to the platinum if the cell were short circuited.

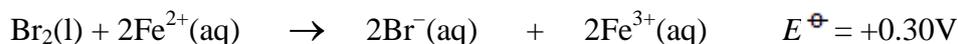
(ii) State what the spontaneous reaction would be in the following set up.



From the table of standard redox potentials



The spontaneous reaction is



### Topic 15.3 Applications

Candidates should be able to:

(1) appreciate the very wide range of occurrence of redox processes in chemistry;

Redox processes occur widely in chemistry. In the organic chemistry of Unit 4 a number of reactions involving oxidation or reduction have already been encountered. Candidates should be familiar with these and be able to quote them under the more general heading of redox.

Very few metals occur uncombined or as “native” metals (gold and silver, and to some extent copper, occur as the metal).

Mercury can be obtained by heating its oxide. Most metals are obtained from their ores by reduction.

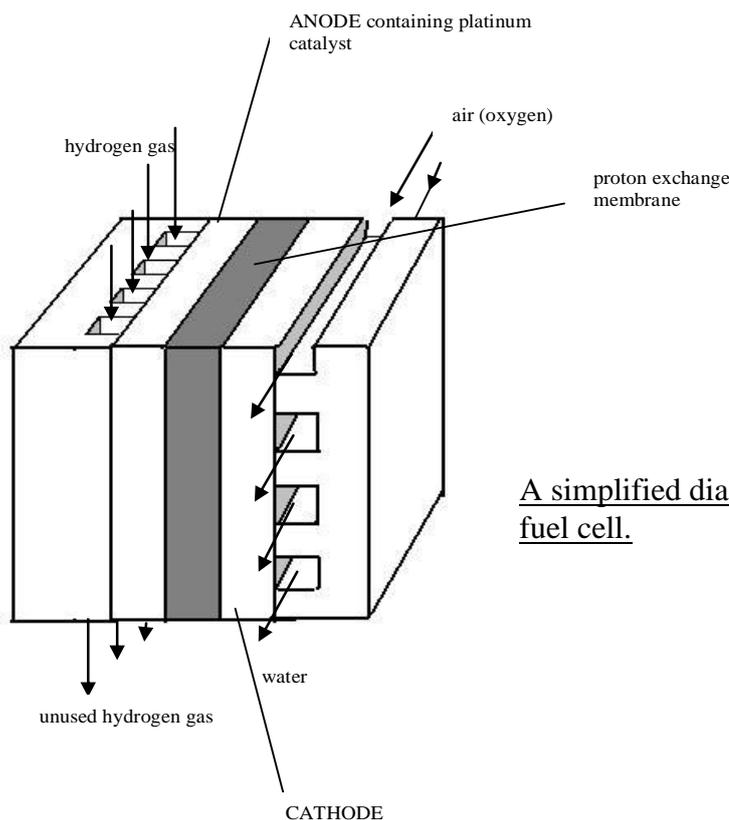
Metals such as iron and copper are obtained by chemical reduction whereas very reactive metals such as sodium, potassium and aluminium are extracted by electrolytic reduction.

Electrolysis is important in other industrial processes, e.g. in the extraction of the halogens fluorine, chlorine and bromine in which the halide ions are oxidised to the halogen by electrolysis.

## The Hydrogen Fuel Cell

Candidates should be able to:

- (m) *explain the principles underlying the operation of the hydrogen fuel cell in terms of the electrode half reactions  $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$  and  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$  in the presence of a platinum catalyst, its potential use for storing energy and generating electricity and heat, and the benefits and drawbacks of its use (details of cell construction not required).*



A simplified diagram of a hydrogen fuel cell.

**This diagram is for information only and its recall will not be required for the examination**

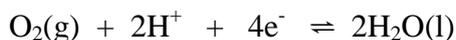
Hydrogen gas is fed into the anode on one side of the cell while oxygen from the air is fed to the cathode on the other side.

Under the influence of the platinum catalyst, the hydrogen gas is oxidised.



The polymer/electrolyte membrane only allows the passage of positive ions to the cathode and the electrons are forced to the cathode via an external circuit. This means that the electrons power the external electrical device.

At the cathode oxygen, protons and electrons form the waste product of the device which is water.



A typical cell gives an emf of about 0.6 V but they can be connected in series to give a higher voltage or in parallel to give a higher current density in a **fuel cell stack**.

### **Advantages of hydrogen fuel cells**

- Clean technology – water is the only waste product
- High efficiency – fuel cells convert chemical energy directly to electrical energy with no combustion process
- Quiet operation
- Relatively simple construction
- In recent years there has been a large increase in power density

### **Disadvantages of hydrogen fuel cells**

- They are expensive
- Storage of hydrogen poses problems as hydrogen is a very flammable and explosive gas
- Present cells are not economically viable because they last for a short time.
- There is a net energy loss since the energy required to produce the hydrogen is more than that produced in its use

## Topic 16.1 Chemistry of the p-block

### (a) The p-block elements and their electronic configurations

Candidates should be able to:

derive the electron configurations of the p-block elements up to Ar and the general outer configuration for each p block group ( $s^2p^1$ ,  $s^2p^2$ ,  $s^2p^3$  etc);

Group 3 (13)		Group 4 (14)		Group 5 (15)		Group 6 (16)		Group 7 (17)		Group 0	
										4	<b>He</b> helium $1s^2s^2$
5	<b>B</b> boron $1s^22s^22p^1$	6	<b>C</b> carbon $1s^22s^22p^2$	7	<b>N</b> nitrogen $1s^22s^22p^3$	8	<b>O</b> oxygen $1s^22s^22p^4$	9	<b>F</b> fluorine $1s^22s^22p^5$	10	<b>Ne</b> neon $1s^22s^22p^6$
13	<b>Al</b> aluminium [Ne] $3s^23p^1$	14	<b>Si</b> silicon [Ne] $3s^23p^2$	15	<b>P</b> phosphorus [Ne] $3s^23p^3$	16	<b>S</b> sulfur [Ne] $3s^23p^4$	17	<b>Cl</b> chlorine [Ne] $3s^23p^5$	18	<b>Ar</b> argon [Ne] $3s^23p^6$
31	<b>Ga</b> gallium [Ar] $3d^{10}4s^24p^1$	32	<b>Ge</b> germanium [Ar] $3d^{10}4s^24p^2$	33	<b>As</b> arsenic [Ar] $3d^{10}4s^24p^3$	34	<b>Se</b> selenium [Ar] $3d^{10}4s^24p^4$	35	<b>Br</b> bromine [Ar] $3d^{10}4s^24p^5$	36	<b>Kr</b> krypton [Ar] $3d^{10}4s^24p^6$
49	<b>In</b> indium [Kr] $4d^{10}5s^25p^1$	50	<b>Sn</b> tin [Kr] $4d^{10}5s^25p^2$	51	<b>Sb</b> antimony [Kr] $4d^{10}5s^25p^3$	52	<b>Te</b> tellurium [Kr] $4d^{10}5s^25p^4$	53	<b>I</b> iodine [Kr] $4d^{10}5s^25p^5$	54	<b>Xe</b> xenon [Kr] $4d^{10}5s^25p^6$
81	<b>Tl</b> thallium [Xe] $4f^{14}5d^{10}6s^26p^1$	82	<b>Pb</b> lead [Xe] $4f^{14}5d^{10}6s^26p^2$	83	<b>Bi</b> bismuth [Xe] $4f^{14}5d^{10}6s^26p^3$	84	<b>Po</b> polonium [Xe] $4f^{14}5d^{10}6s^26p^4$	85	<b>At</b> astatine [Xe] $4f^{14}5d^{10}6s^26p^5$	86	<b>Rn</b> radon [Xe] $4f^{14}5d^{10}6s^26p^6$

Candidates may be required to derive the electronic configurations of the elements up to Ar (atomic number 18 and shaded above) and know the general outer electronic configuration of each p-block element.

### (b) The inert pair effect

Candidates should be able to:

show knowledge of the increasing stability of the inert pair ( $ns^2$ ) cations on descent of Groups 3, 4 and 5;

This applies to Groups 3, 4 and 5.

The effect refers to the fact that the lower valencies become more stable as the group is descended.

## Group 4

All of the elements in the group have the outer electronic structure  $ns^2np^2$ .

The oxidation state of IV is where all these outer electrons are directly involved in the bonding.

Closer to the bottom of the Group, there is an increasing tendency for the  $s^2$  pair not to be used in the bonding. This is often known as the inert pair effect – and is dominant in **lead** chemistry.

In Group 4, the II oxidation state is more stable for lead and tin than for germanium. Carbon and silicon exhibit oxidation state  $C^{IV}$  and  $Si^{IV}$  (carbon monoxide is an exception).

The reasons for this increasing stability of the lower oxidation state are complex and are beyond the scope of this specification.

The lower valency states have a greater percentage of ionic bonding.

It should be remembered that for germanium, although  $Ge^{II}$  exists  $Ge^{IV}$  is the more stable.

$Sn^{II}$  and  $Sn^{IV}$  have similar stabilities but that  $Pb^{II}$  is more stable than  $Pb^{IV}$ .

$Sn^{2+}$  and  $Pb^{2+}$  occur in predominantly ionic compounds.

In Group 3,  $In^+$  and  $Tl^+$  exist but in Group 5 only  $Bi^{3+}$  appears as predominantly ionic.

### (c) Maximum covalency rule

#### Candidates should be able to:

*show understanding of why the maximum number of electron pairs which can surround a central atom is greater in Row 3 (Na-Ar) than in Row 2 (Li-Ne), using examples drawn from the Group 5 halides;*

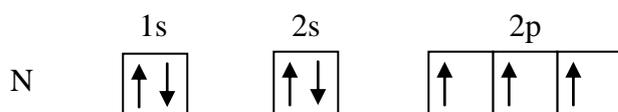
In the first period of the Periodic Table the maximum covalency of the elements is four, with a maximum of four electron pairs.

In the second period compounds such as  $PCl_5$  and  $SF_6$  are formed in which the covalency, the number of covalent bonds formed, is greater than four, with up to six electron pairs.

The reason for this increase is that in the third quantum shell there are d-electron levels which can be involved in bonding.

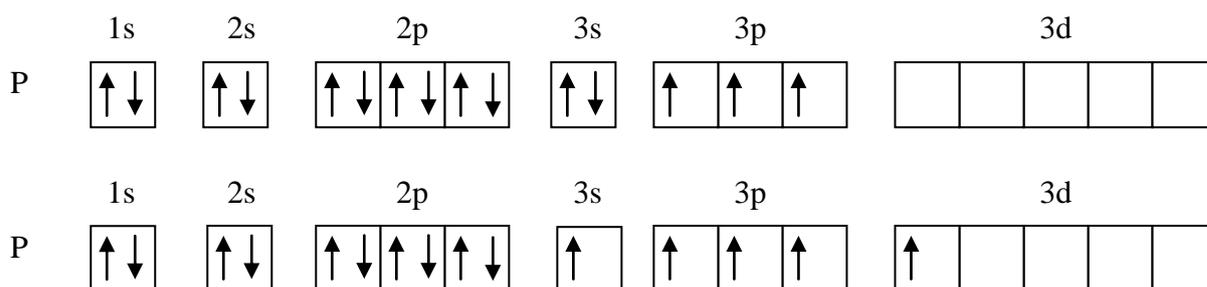
Consider the Group 5 halides.

Nitrogen has only 3 electrons available for bonding e.g. in  $NCl_3$ .



The three unpaired 2p electrons can each form a bond but the 2s electrons cannot as there are no '2d' orbitals into which one of the 2s electrons can be promoted.

Phosphorus can show valencies of 3 and 5 e.g. in  $\text{PCl}_3$  and  $\text{PCl}_5$ .



By promoting an electron from the 3s orbital to the 3d orbital, phosphorus now has 5 unpaired electrons available for bonding.

#### (d) Amphoteric behaviour

**Candidates should be able to:**

*explain the term amphoteric behaviour and illustrate this behaviour using reactions of  $\text{Al}^{3+}$  and  $\text{Pb}^{2+}$*

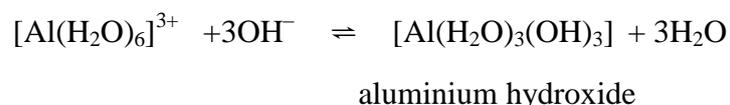
An element, a compound or an ion is said to be amphoteric if it reacts with both acids and alkalis.

Consider the aluminium ion,  $\text{Al}^{3+}$ , in aqueous solution.

The  $\text{Al}^{3+}$  ion is small and highly charged and so will be extensively hydrated in aqueous solution. The aqueous ion may be considered to be  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ .

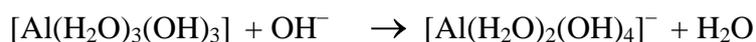
If aqueous sodium hydroxide is added to a solution containing aqueous  $\text{Al}^{3+}$  ions, the  $\text{OH}^-$  ions will remove protons from the hydrated aluminium ion.

This can be represented as



The aluminium hydroxide forms as a white gelatinous precipitate.

If more sodium hydroxide solution is added, the precipitate dissolves to give a colourless solution containing the aluminate ion.



The equation is simplified by omitting the water molecules.

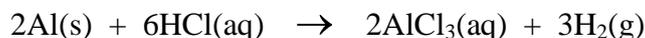


The series of reactions may be reversed by addition of acid to the aluminate solution.

Aluminium hydroxide is an amphoteric hydroxide.

It reacts with dilute acids to form salt solutions and with aqueous sodium or potassium hydroxide to form the aluminate ion.

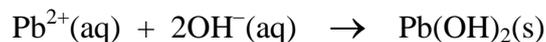
The amphoteric nature of aluminium metal itself may be illustrated by its reaction with hydrochloric acid and with hot aqueous sodium hydroxide.



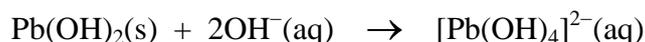
Amphoteric nature of  $\text{Pb}^{\text{II}}$

The reactions of the lead(II) ion are usually illustrated using lead(II) nitrate which is the most common soluble salt of divalent lead.

When aqueous sodium hydroxide is added to aqueous lead(II) nitrate, a white precipitate of lead(II) hydroxide is formed.



On addition of excess aqueous sodium hydroxide, the white precipitate dissolves to give a colourless solution containing the plumbate(II) ion.



Addition of acid to the solution containing the plumbate(II) ion will re-precipitate the lead(II) hydroxide which in turn will dissolve in more acid to form aqueous  $\text{Pb}^{2+}$  ions.

## Topic 16.2

### (e), (f) Group 3 (13)

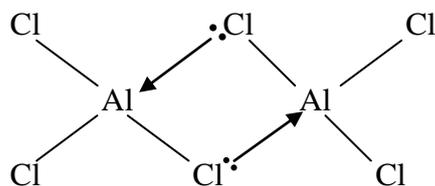
**Candidates should be able to:**

- (e) *understand the electron deficient nature of Group 3 systems such as  $\text{BF}_3$ ,  $\text{BCl}_3$  and monomeric  $\text{AlCl}_3$  and their electron acceptor properties;*
- (f) *explain the ready formation of the  $\text{Al}_2\text{Cl}_6$  dimer, its structure and its bonding;*

The compounds of the Group 3 elements can demonstrate electron deficiency.

Boron has the electronic configuration  $1s^2 2s^2 2p^1$ . It has three valency electrons and so when it combines with a halogen such as fluorine it forms three bonding pairs of electrons and the  $\text{BF}_3$  molecule adopts a trigonal planar shape. Since the molecule has only six valency electrons rather than the normal octet, it is said to be *electron deficient*.

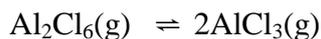
In the same way aluminium chloride,  $\text{AlCl}_3$ , will be electron deficient. However, in anhydrous conditions, the  $\text{AlCl}_3$  molecules dimerises to the  $\text{Al}_2\text{Cl}_6$  molecule by each monomer accepting a non-bonding pair of electrons from a chlorine atom.



The arrows represent coordinate, or dative covalent, bonds.

Note that the spatial arrangement of the bonds around the aluminium atoms changes from trigonal planar in the monomer to tetrahedral in the dimer.

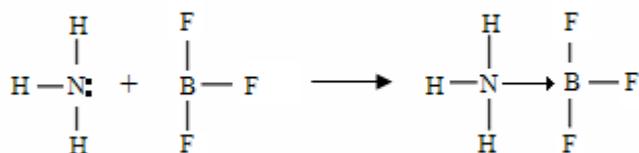
Above  $200^\circ\text{C}$ , the dimer dissociates



**(g) Know that electron deficiency can lead to the formation of addition compounds.**

**Candidates should be able to:**

*understand the formation of donor-acceptor compounds such as  $\text{NH}_3 \cdot \text{BF}_3$ ;*



The non-bonding pair of electrons in ammonia forms a coordinate bond with the electron deficient boron trifluoride.

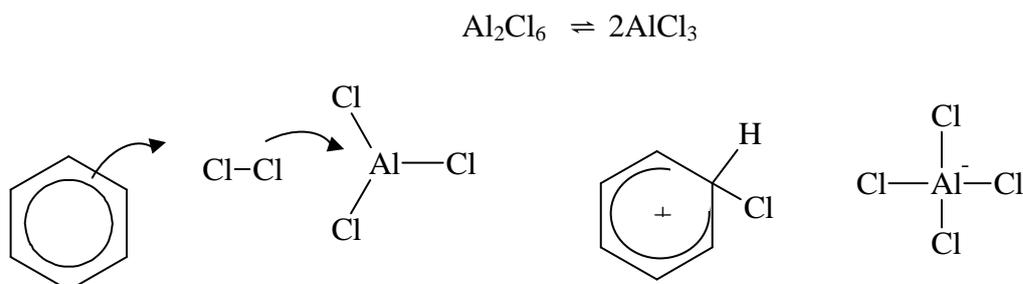
**(h) Candidates should be able to:**

*recall that the affinity of  $\text{AlCl}_3$  for chlorine species results in industrially important catalysts such as*

- (i) the chlorination of benzene and*
- (ii) low melting temperature ionic liquids, containing the chloroaluminate(III) ion,  $\text{AlCl}_4^-$ , which are being developed as “clean technology” solvents and catalysts for processes such as the polymerisation of alkenes;*

In the chlorination of benzene by electrophilic substitution and in the Friedel-Crafts reaction anhydrous aluminium chloride behaves as a catalyst (sometimes called a halogen carrier). It is thought that the mechanism involves the heterolytic fission of the Cl-Cl bond in molecular chlorine.

The mechanism can be pictured as



The intermediate then loses a proton and forms chlorobenzene.

The recall of this mechanism is not required for the CH5 unit.

### Ionic Liquids

In recent years room temperature ionic liquids have been developed to replace volatile organic compounds (VOCs) and produce cleaner solvents and “vehicles” for catalytic processes such as polymerisation of alkenes. Several of these ionic liquids contain the anion  $\text{AlCl}_4^-$ .

Two prominent ones are formed from

- 1-butylpyridiniumchloride and aluminium chloride
- 1-ethyl-3-methylimidazolium chloride and aluminium chloride.

Candidates are not expected to know the names or structures of the organic cations in these liquids only that the anion is  $\text{AlCl}_4^-$

The advantages of ionic liquids are that

- they have a very small vapour pressure and they are non-volatile so do not evaporate during use
- they are often easier to separate from the catalyst and product than conventional VOCs.

**(i), (j) Boron nitride, BN****Candidates should be able to:**

- (i) explain how boron nitride, BN, forms hexagonal and cubic structures corresponding to graphite and diamond respectively and, because of its hardness, chemical inertness, high melting temperature and semiconductor properties, is finding increasing use as lubricant, as wear-resistant coating and as nanotubes for wire sleeving, catalyst support and semiconduction;
- (j) recognise that in none of the cases (f) to (i) above is the compound electron deficient.

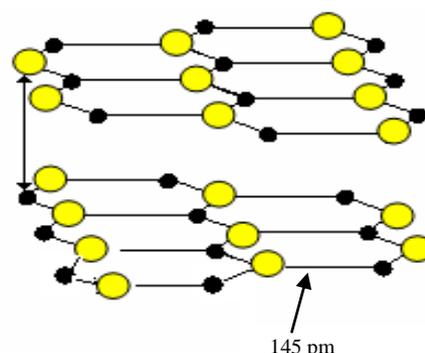
Visit <http://www.accuratus.com/boron.html>

Boron nitride is a giant covalent structure that has the same number of electrons as graphite and diamond. They are said to be isoelectronic.

Boron nitride exists in two forms

- hexagonal boron nitride with a graphite structure

330 picometres



- cubic boron nitride with a diamond structure.

The nitrogen – boron bond length is 157 picometres or 0.157 nanometers.

**Properties and uses of h-boron nitride**

Hexagonal boron nitride is sometimes called ‘white graphite’ because of its excellent lubricating properties. Unlike graphite, hexagonal boron nitride is an insulator and finds applications which depend upon this property. There are limitations to its use however, as it tends to oxidise at high temperatures.

It is chemically inert and can be used as reaction vessels, crucibles etc. although oxidation must be prevented.

After hot pressing, hexagonal boron nitride can be machined, using conventional metal cutting equipment, into complex shapes. Modern techniques have been developed to form boron nitride nanotubes up to 120 microns long. One use of these tubes has been to form insulating sheaths for single-walled carbon nanotubes acting as conducting wires. One technique involves packing a boron nitride nanotube with fullerene spheres ( $C_{60}$ ) and then exposing the assembly to an intense beam of electrons. The result is the insulated conducting wire.

Visit <http://www.lbl.gov/Science-Articles/Archive/MSD-nano-insulation.html>

### Properties and uses of c-boron nitride

Cubic boron nitride is the second hardest material known. It has high thermal conductivity and is chemically inert. It is wear resistant. It is used for cutting tools and abrasives and is especially suitable for low carbon ferrous metals. It has been used for mounting high power electronic components utilising its high thermal conductivity to allow efficient heat dissipation. Cubic boron nitride wear resistant coatings have also been developed. Boron nitride powders with high surface area have been used as supports for catalysts in a number of processes. Chemical inertness and high thermal conductivity make BN particularly suitable.

### Topic 16.3

#### (k) Group 4 (14)

#### Candidates should be able to:

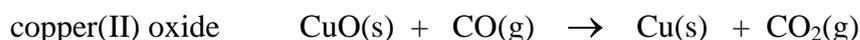
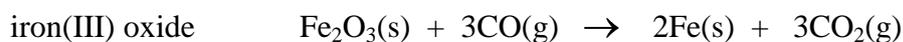
*describe the change in relative stability of oxidation states II and IV down Group 4, as shown by reactions of CO as a reducing agent with oxides and Pb(IV) as an oxidising agent in the reaction of PbO<sub>2</sub> with concentrated hydrochloric acid;*

Element	Oxidation State II	Oxidation State IV
C	Example CO Carbon monoxide is an exception	Example CO <sub>2</sub> C <sup>IV</sup> is the stable oxidation state
Si	Si <sup>II</sup> does not exist under normal conditions	Example SiCl <sub>4</sub> SiO <sub>2</sub> Si <sup>IV</sup> is more stable than Si <sup>II</sup>
Ge	Example GeCl <sub>2</sub> Ge <sup>II</sup> is less stable than Ge <sup>IV</sup>	Example GeCl <sub>4</sub> Ge <sup>IV</sup> is more stable than Ge <sup>II</sup>
Sn	Example SnCl <sub>2</sub> Sn <sup>II</sup> and Sn <sup>IV</sup> have similar stabilities	Example SnCl <sub>4</sub> Sn <sup>II</sup> and Sn <sup>IV</sup> have similar stabilities
Pb	Example PbCl <sub>2</sub> Pb(NO <sub>3</sub> ) <sub>2</sub> Pb <sup>II</sup> is more stable than Pb <sup>IV</sup>	Example PbO <sub>2</sub> Pb <sup>II</sup> is more stable than Pb <sup>IV</sup>

Carbon monoxide is a strong **reducing agent**.

It is involved in the reduction of metallic ores.

e.g.



Since  $\text{Pb}^{\text{II}}$  is more stable than  $\text{Pb}^{\text{IV}}$ , some lead(IV) compounds are oxidising agents being reduced in the reaction to  $\text{Pb}^{\text{II}}$ .

The example quoted in the specification is lead(IV) oxide. When heated with concentrated hydrochloric acid, lead(IV) oxide oxidises the chloride ion to give chlorine gas.



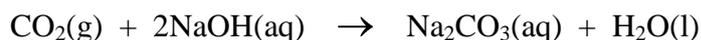
### (I) Carbon dioxide

**Candidates should be able to:**

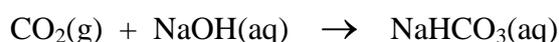
*recall the nature, physical and acid-base properties of  $\text{CO}_2$  and  $\text{PbO}$ ;*

Carbon dioxide is a covalent, colourless gas. It is readily soluble in water to give an acidic solution. Solid carbon dioxide (dry ice) sublimates at  $-78^\circ\text{C}$ .

When passed into aqueous sodium hydroxide, sodium carbonate is formed if the alkali is in excess.



If carbon dioxide is in excess then sodium hydrogencarbonate is formed

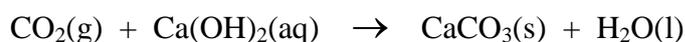


This acidic nature is used in the limewater test for carbon dioxide.

Limewater is a saturated solution of calcium hydroxide, which is only slightly soluble in water.

On passing carbon dioxide into limewater, calcium carbonate is formed as a white precipitate.

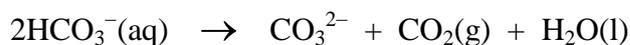
Scientifically it is more correct to state that a white precipitate is formed, rather than using the common expression “*the limewater turns milky*”.



On continuing to pass carbon dioxide through the mixture, a colourless solution forms.



It is incorrect to say the calcium hydrogencarbonate is formed. A solution containing calcium ions and hydrogencarbonate ions is formed. Any attempt to isolate calcium hydrogencarbonate results in the decomposition of the hydrogencarbonate ion and the precipitation of calcium carbonate.

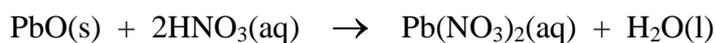


This reaction takes place in the formation of kettle fur and stalactites and stalagmites.

### Lead(II) oxide

Lead(II) oxide, PbO, has predominantly ionic character and exists in two forms – one a red solid and the other a yellow solid. The difference lies in the crystal structures of the two forms. The red form is called litharge and the yellow form massicot.

Lead(II) oxide is amphoteric as can be illustrated by its reaction with nitric acid. Since lead(II) sulfate is insoluble and lead(II) chloride only sparingly soluble in the cold, it is best to form the soluble lead(II) nitrate.



When heated with aqueous sodium hydroxide, sodium plumbate(II) is formed as a colourless solution.



The plumbate(II) ion is  $\text{Pb}(\text{OH})_4^{2-}$  although  $\text{PbO}_2^{2-}$  will be acceptable giving sodium plumbate(II) the formula  $\text{Na}_2\text{PbO}_2$ .

### (m) Some chlorides of Group 4

#### Candidates should be able to:

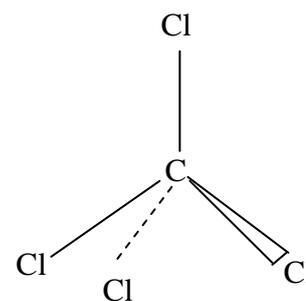
*describe the types of bonding in the chlorides  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{PbCl}_2$  and their reactions with water ;*

Tetrachloromethane,  $\text{CCl}_4$

Sometimes called carbon tetrachloride, tetrachloromethane is a colourless liquid which is more dense than water and immiscible with it.

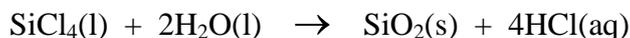
Unlike all the other tetrachlorides of the group it is not hydrolysed by water. Being in the first period, carbon cannot utilise d orbitals for attack by the nucleophilic water molecule.

The molecule, as predicted by VSEPR theory, is tetrahedral.



Silicon tetrachloride,  $\text{SiCl}_4$

This is a colourless liquid which fumes on contact with air as it is hydrolysed by atmospheric moisture. Silicon tetrachloride reacts vigorously with water being hydrolysed to silicon dioxide. The lone pair from a water molecule can attack the silicon atom which can expand its octet being in the second period.

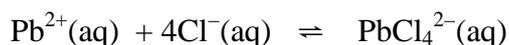


The  $\text{SiCl}_4$  molecule is tetrahedral.

Lead(II) chloride,  $\text{PbCl}_2$

Lead(II) chloride is a white solid which is sparingly soluble in cold water but much more soluble in hot water. The compound has a significant amount of ionic character, its aqueous solutions containing the  $\text{Pb}^{2+}$  ion.

Lead(II) chloride will dissolve in concentrated hydrochloric acid forming a tetrachlorolead(II) ion. Hydrochloric acid provides water and a high concentration of chloride ions.



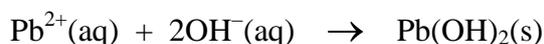
### (n) Some reactions of the aqueous $\text{Pb}^{2+}$ ion

**Candidates should be able to:**

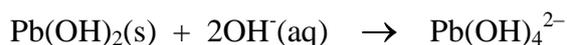
*recall the reactions of  $\text{Pb}^{2+}(\text{aq})$  with aqueous  $\text{NaOH}$ ,  $\text{Cl}^{-}$  and  $\text{I}^{-}$ .*

- With aqueous sodium hydroxide

When aqueous sodium hydroxide is added to aqueous lead(II) nitrate, a white precipitate is formed which reacts with excess sodium hydroxide to form a colourless solution.



lead(II) hydroxide

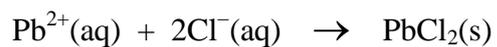


plumbate(II) ion

- With aqueous chloride ions

When aqueous sodium chloride is added to aqueous lead(II) nitrate, a white precipitate is formed.

This precipitate of lead(II) chloride is more soluble in hot water than in cold.

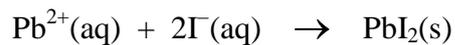


The white precipitate is soluble in concentrated hydrochloric acid as shown previously in (m).

- With aqueous iodide ions

When aqueous potassium iodide is added to aqueous lead(II) nitrate, a bright yellow precipitate is formed.

This precipitate of lead(II) iodide is soluble in hot water to give a colourless solution.



## Topic 16.4 Group 7 (17)

### (o) The halogens

Candidates should be able to:

explain the trends in oxidising power of the halogens and displacement reactions in terms of position in the group and  $E^\ominus$  values;

Halogen	Description and state at room temperature		Reduction process	$E^\ominus / \text{V}$
Fluorine	pale yellow gas	↓ <b>Oxidising Power</b> ↓ <b>Decreases</b>	$\frac{1}{2}\text{F}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{F}^-(\text{aq})$	+2.87
Chlorine	greenish-yellow gas		$\frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq})$	+1.36
Bromine	red-brown liquid		$\frac{1}{2}\text{Br}_2(\text{l}) + \text{e}^- \rightleftharpoons \text{Br}^-(\text{aq})$	+1.07
Iodine	lustrous grey-black solid		$\frac{1}{2}\text{I}_2(\text{s}) + \text{e}^- \rightleftharpoons \text{I}^-(\text{aq})$	+0.54

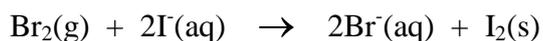
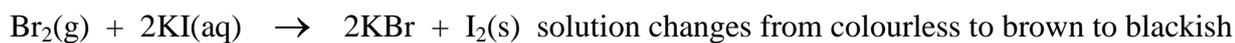
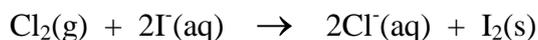
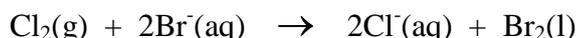
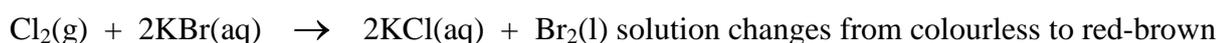
The strongest oxidising halogen is fluorine which has the most positive  $E^\ominus$  value.

Fluorine is so strong an oxidising agent that it oxidises water.

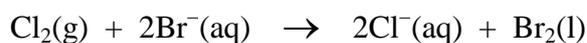
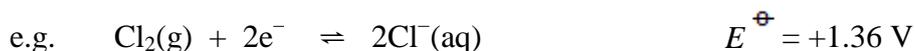
For this reason it would be an error to include fluorine when discussing the displacement reactions of one halogen by another in aqueous solution.

Chlorine displaces both bromine and iodine from aqueous solutions of their respective halides.

Candidates should be able to write stoichiometric or ionic equations.



The feasibility of these displacement reactions can be predicted from the  $E^\ominus$  values above.



$E^\ominus = +0.29 \text{ V}$  is positive so the reaction is feasible

**(p) Reactions of chlorine with aqueous sodium hydroxide**

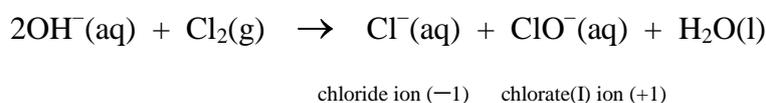
**Candidates should be able to:**

*recall the reactions of chlorine, Cl<sub>2</sub>, with both cold and warm aqueous NaOH and the various disproportionation reactions involved;*

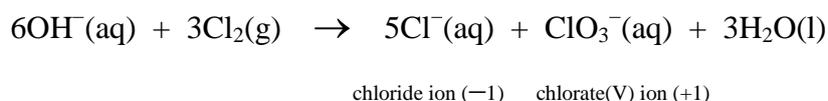
Cold dilute aqueous sodium hydroxide.

Chlorine reacts with cold dilute aqueous sodium hydroxide to give a mixture of sodium chloride and sodium chlorate(I).

This is an example of **disproportionation**. Chlorine is simultaneously oxidised from oxidation state zero to oxidation state +1 and reduced from oxidation state zero to oxidation state -1.



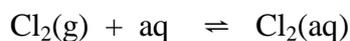
With warm concentrated aqueous sodium hydroxide, the disproportionation is from oxidation state zero to oxidation state -1 and +5.

**(q) Antibacterial and bleaching action of chlorine**

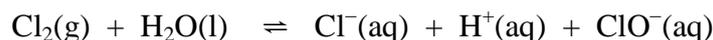
**Candidates should be able to:**

*show a knowledge of the relationship of the bleaching and bacterial action of Cl<sub>2</sub> and chlorate(I) (ClO<sup>-</sup>) to their oxidising power and the use of chlorate(V) as a weed killer;*

When chlorine is bubbled into water some chlorine molecules remain as the dissolved gas



and some chlorine reacts with the water



Chlorine is used to sterilise public water supplies. It is a broad spectrum bactericide and destroys most micro-organisms and bacterial spores. It is relatively inexpensive.

It is likely that the effective agent is the chlorate(I) ion attacking the bacterium.

Household bleaches are about 5.2% solutions of sodium chlorate(I) which can be made by the action of chlorine on cold dilute sodium hydroxide (see above).

These are used as disinfectants and bleaching agents.

The bleaching action is brought about by oxidation of the dye by the chlorate(I) ion.

Sodium chlorate(V),  $\text{NaClO}_3$ , is an effective weed killer, sold under a variety of trade names. Once used, the ground cannot be cultivated for some time. It is a white crystalline solid with a melting point of  $248^\circ\text{C}$ . It is a powerful oxidising agent; mixtures with organic materials are potentially explosive. It has to be treated with caution.



### (r) The action of concentrated sulfuric acid on sodium halides

Candidates should be able to:

*recall the behaviour of sodium halides ( $\text{NaCl}$ ,  $\text{NaBr}$  and  $\text{NaI}$  only) with concentrated sulfuric acid (the formation and subsequent reactions of  $\text{HX}$ , the products and their oxidation states) and explain the differences in terms of  $E_o$  values; (Equations not required)*

#### Sodium chloride

When concentrated sulfuric acid is added to sodium chloride, white misty fumes of hydrogen chloride are observed.



Hydrogen chloride is not a strong enough reducing agent to affect the concentrated sulfuric acid.

#### Sodium bromide

When concentrated sulfuric acid is added to sodium bromide, white misty fumes of hydrogen bromide are observed together with brown fumes of bromine.

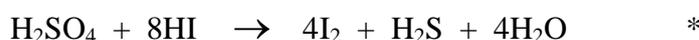
The reason is that hydrogen bromide is a strong enough reducing agent to react with concentrated sulfuric acid.



Hydrogen bromide reduces sulfur from oxidation state +6 in  $\text{H}_2\text{SO}_4$  to +4 in  $\text{SO}_2$ .

#### Sodium iodide

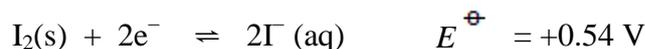
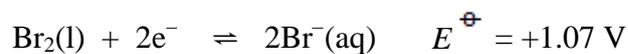
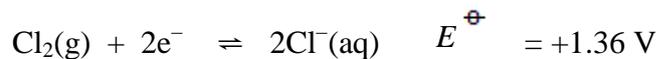
When concentrated sulfuric acid is added to sodium iodide, on warming purple fumes of iodine are observed together with the smell of hydrogen sulfide.



Hydrogen iodide is the strongest reducing agent of the three hydrogen halides and reduces sulfur from +6 in  $\text{H}_2\text{SO}_4$  to -2 in  $\text{H}_2\text{S}$ .

\* The specification states that **equations are not required** and candidates are only required to recall the behaviour of the sodium halides with concentrated sulfuric acid.

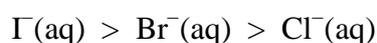
The standard electrode potentials for the three halogens are



The strongest oxidising agent has the most positive  $E^\ominus$  value so the relative oxidising powers of the three halogens are



Therefore the reducing powers of the halide ions is



and of the hydrogen halides is



### (s) Commercial and industrial uses of the halogens and their compounds

**Candidates should be able to:**

*show an awareness of the very wide range of halogen containing compounds of commercial and industrial importance.*

#### **Fluorine compounds**

Hydrofluoric acid is used to etch glass.

Chlorofluorocarbons are odourless and non-poisonous liquids or gases such as Freon, and were used as dispersing agents in aerosol sprays and as refrigerants. Now they have been replaced by compounds which do not affect the ozone layer.

PTFE, Teflon, poly(tetrafluoroethene) is very resistant to most chemical action, is widely used to make products such as motor gaskets and dashboard accessories in the automobile industry. It is also used as a coating on the inner surface of frying pans and other kitchen utensils to reduce the need for fat in cooking. Uranium hexafluoride, the only volatile compound of uranium is used in the gaseous diffusion process to enrich uranium fuel in the fissionable isotope. Compounds containing fluoride are added to drinking water and toothpaste to prevent dental caries.

**Chlorine and chlorine compounds**

Chlorine is used on a large scale for the sterilisation of drinking water and it is also used as a bleaching agent. Chlorine is used in the production of a wide range of organo-chlorine compounds.

Some examples are polymers such as poly(chloroethene) PVC, solvents such as tetrachloromethane and trichloroethene, antiseptics such as Dettol and TCP, bleaches such as sodium chlorate(I), weed killers such as sodium chlorate(V), pesticides such as DDT, Dieldrin and Aldrin (now restricted in use), fungicides and pharmaceutical products

**Bromine compounds**

Silver bromide has been used in photography for many years as a light sensitive medium on plates and films. Bromine and some of its compounds are used for water purification.

Bromine compounds are used as dyes and in many medicines

**Iodine compounds**

Potassium iodide has been used in the treatment of goitre and stores of potassium iodide are kept near nuclear installations in case of leakage of  $^{131}\text{I}$ , a radioactive  $\beta$ -emitter. The population would take potassium iodide tablets so that normal iodine would reduce the concentration of radioactive iodine in the body. Tincture of iodine is a solution of iodine in ethanol which is an antiseptic.

Silver iodide is used in photography and a range of iodine compounds are used as catalysts and in inks, dietary supplements and pharmaceuticals.

## Topic 17 d-block transition elements

(a) Candidates should be able to:

recall that transition elements (except Cu) possess partly filled d-orbitals and derive the electronic configuration of any first row transition metal ion using a Periodic Table;

<i>Element</i>	<i>Symbol</i>	<i>Ground state electronic configuration</i>
Scandium	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ *
Manganese	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ *
Zinc	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

The transition elements are shaded

\* Note the special cases of chromium and copper

- chromium has half filled d-orbitals with only one 4s electron
- copper has completely filled d-orbitals with only one 4s electron

A half-filled set of d-orbitals and a complete set of d-orbitals confer extra stability on the configuration.

A transition element may be defined as one which possesses, or forms an ion which possesses, an incomplete set of d-orbitals.

**(b) Candidates should be able to:**

*recall that 4s electrons are lost more readily than 3d electrons in ion formation;*

In the formation of ions, the 4s electrons are lost more readily than the 3d electrons.

Some ions of the first transition series of elements.

<i><b>Ion</b></i>	<i><b>Electronic configuration of ion</b></i>
$\text{Sc}^{3+}$ *	$1s^2 2s^2 2p^6 3s^2 3p^6$
$\text{Ti}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
$\text{Ti}^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$
$\text{V}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
$\text{V}^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
$\text{Cr}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$
$\text{Cr}^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
$\text{Mn}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
$\text{Mn}^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$
$\text{Fe}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
$\text{Fe}^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
$\text{Co}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$
$\text{Co}^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
$\text{Ni}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$
$\text{Cu}^+$ *	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
$\text{Cu}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

only nickel<sup>II</sup> occurs in the common chemistry of nickel.

\* these ions are **not** considered as transition metal ions as they do not have an incomplete set of d orbitals

**(c) Candidates should be able to:**

*explain why various oxidation states are possible in transition elements;*

As can be seen from the above table, the transition elements have more than one oxidation state. The reason is that successive ionisation energies for the transition elements tend to increase gradually without large jumps in value. The energies of the d-orbitals are very similar. The number of different oxidation states reaches a maximum in the centre of the series.

Oxidation states are shown below - the most common for each element are in bold and underlined.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
<u><b>3</b></u>	<u><b>4</b></u>	<u><b>5</b></u>	6	7	6	4	4	<u><b>2</b></u>
	3	4	<u><b>3</b></u>	6	<u><b>3</b></u>	3	<u><b>2</b></u>	1
	2	3	2	4	2	<u><b>2</b></u>		
		2		3				
				<u><b>2</b></u>				

**(d) Catalytic action of transition elements**

**Candidates should be able to:**

*recall that transition metals and their compounds are often good catalysts, give an example, and explain why this is so in terms of partially filled d-shells and variable oxidation states;*

<i>Catalyst</i>	<i>Process</i>
TiCl <sub>3</sub> or TiCl <sub>4</sub>	Ziegler-Natta catalysts in the polymerisation of ethene
V <sub>2</sub> O <sub>5</sub>	Contact process $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$
Fe	Haber Process $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$
Ni	Catalytic hydrogenation of oils $>\text{C}=\text{C}< + \text{H}_2 \rightarrow >\text{CH}-\text{CH}<$

The

catalytic activity of the transition elements depends on the ability to exhibit variable valency and the availability of vacant d-orbitals. The reactants use vacant d-orbitals to form temporary bonds with the catalyst which holds the reactants so that reaction can take place. Most catalysts are heterogeneous catalysts.

## Examples of transition metal catalysts

## (e), (f) Complex ions

## Candidates should be able to:

- (e) recall that many complexes are formed by co-ordinate bonding between transition metal ions and ligands;
- (f) describe the bonding, colour and formulae of the approximately octahedral complex ions  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ , the approximately tetrahedral ion  $[\text{CuCl}_4]^{2-}$ , and other complexes where relevant information is supplied;

A complex ion is a central metal ion surrounded by atoms or groups of atoms linked by a coordinate bond. The surrounding groups are called ligands. If an atom or group of atoms forms only one coordinate bond it is said to be a monodentate ligand. e.g. ammonia  $\text{:NH}_3$ .

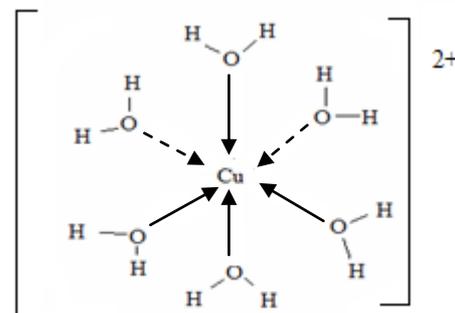
Notice that ligands are able to donate a lone pair of electrons into available orbitals of the central metal ion. Some molecules such as  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  can form two coordinate bonds and are bidentate ligands. An important species called EDTA is a polydentate ligand forming several coordinate bonds.

Transition metal ions in aqueous solution are hydrated.

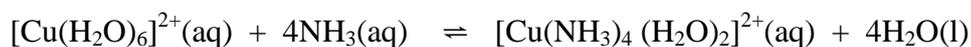
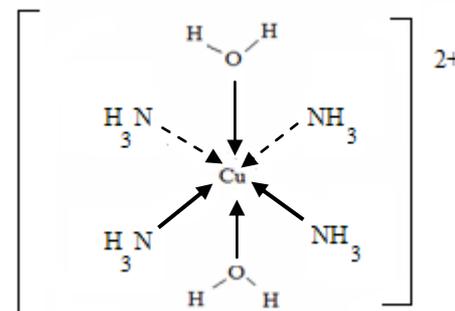
Water molecules act as ligands.

The familiar blue colour of copper(II) sulfate solution is caused by the hexaaquacopper(II) ion,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . It is common for six ligands to surround the central metal ion and form an octahedral complex ion.

In fact, the hexaaquacopper(II) ion,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is a slightly distorted octahedron with two water molecules being further away than the other four.

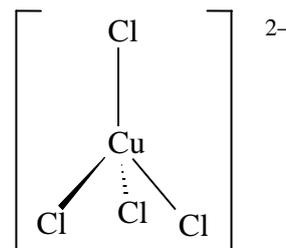


There is often competition between ligands. When aqueous ammonia is added in excess to aqueous copper(II) sulfate, a royal blue solution is obtained. The ammonia molecules replace four of the water molecules in the hexaaquacopper(II) ion.



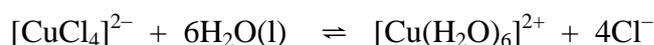
tetraamminocopper(II) ion

If copper(II) carbonate is dissolved in concentrated hydrochloric acid, a yellow-green or yellow-brown solution is formed containing the tetrachlorocuprate(II) ion,  $[\text{CuCl}_4]^{2-}$ . This is a tetrahedral ion.

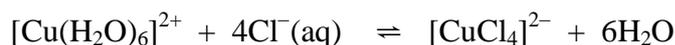


Once again it is easy to demonstrate competition by ligands.

If the solution obtained by the action of concentrated hydrochloric acid on copper(II) carbonate is steadily diluted with water, there is a gradual change in colour until with a large excess of water the typical blue colour of  $\text{Cu}^{2+}(\text{aq})$  is formed.



Likewise, if concentrated hydrochloric acid is added to aqueous copper(II) sulfate, the solution rapidly turns green.

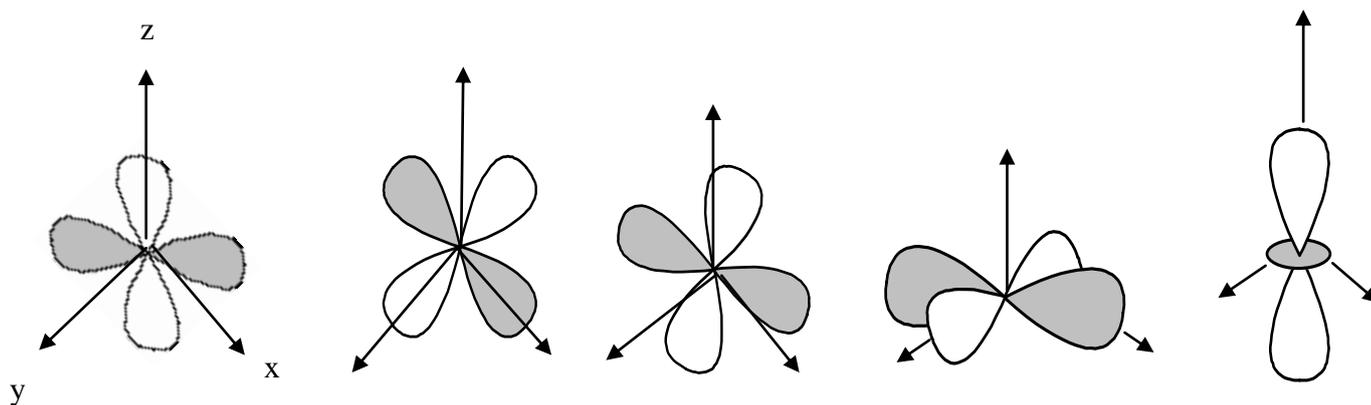


**(g) Candidates should be able to:**

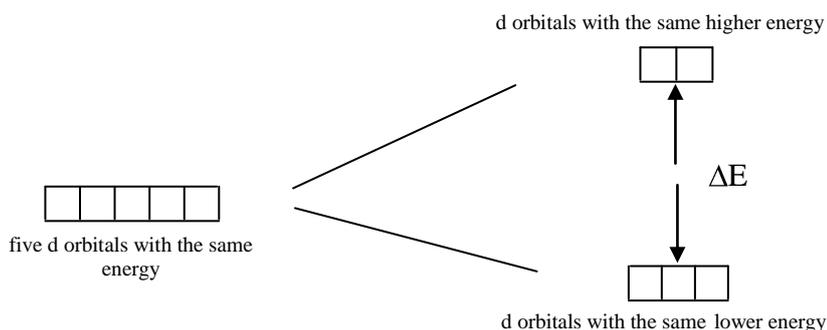
- (i) *explain the origins of colour in transition metal complexes and give a qualitative account of this for octahedral 6-coordinate species in terms of the splitting of the d-orbitals involved, and;*
- (ii) *show understanding of the spectroscopic consequences of (i) above and explain that in many cases the colours of such transition metal complexes arise from d-d transitions between the split d-orbital levels \*;*

The d-orbitals have complicated shapes which *candidates do not need to remember*.

In an isolated atom all five orbitals have the same energy and are said to be degenerate.



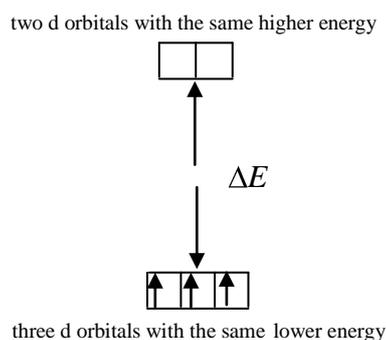
In octahedral complexes, the electrostatic field from the ligands split the orbitals into two levels.



Take the ion  $\text{Cr}^{3+}$  with configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ .

The three d-electrons will occupy the lowest energy levels in the ground state.

This can be represented by the following diagram where the three electrons occupy the 3 lower energy orbitals with parallel spins.



Excitation of the ion may promote one or more of these electrons to the higher energy orbitals.

Such a transition is called a d-d transition and involves the energy jump labelled  $\Delta E$ .

The value of  $\Delta E$  will depend upon

- the identity of the metal
- its oxidation state
- the nature of the ligands in the octahedral complex

For many d-d transitions the value of  $\Delta E$  corresponds to the energy of a photon of visible light.

$$\Delta E = hf$$

Where  $h$  is Planck's constant and  $f$  is the frequency of the visible radiation.

Thus when white light falls on such a complex, some wavelengths will be absorbed giving rise to d-d transitions and producing colour.

It is one of the characteristic properties of transition elements that many of their compounds are coloured. Zinc compounds however are not coloured because  $\text{Zn}^{2+}$  has fully occupied 3d orbitals and scandium compounds are not coloured because  $\text{Sc}^{3+}$  has no 3d electrons.

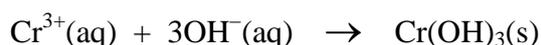
**(h) Reactions of transition metal ions with aqueous sodium hydroxide and aqueous ammonia**

**Candidates should be able to:**

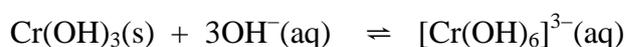
*describe the reactions of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  with excess aqueous  $\text{OH}^-$  ;*

**(i) Chromium<sup>III</sup>  $\text{Cr}^{3+}(\text{aq})$** 

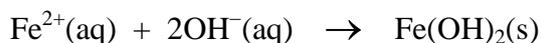
With aqueous sodium hydroxide, the blue-violet solution containing  $\text{Cr}^{3+}(\text{aq})$  gives a grey-green gelatinous precipitate of chromium(III) hydroxide.



On addition of excess sodium hydroxide the chromium(III) hydroxide dissolves and a green solution containing the chromate(III) ion is formed.

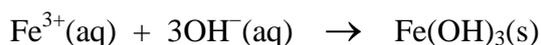
**(ii) Iron<sup>II</sup> and Iron<sup>III</sup> -  $\text{Fe}^{2+}(\text{aq})$  and  $\text{Fe}^{3+}(\text{aq})$** 

When aqueous sodium hydroxide is added to a pale green solution containing  $\text{Fe}^{2+}(\text{aq})$  ions, a dirty green precipitate of iron(II) hydroxide is formed.



The precipitate undergoes oxidation to iron(III) hydroxide so it turns brown at the surface.

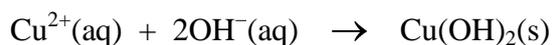
When aqueous sodium hydroxide is added to a yellow solution containing  $\text{Fe}^{3+}(\text{aq})$  ions, a reddish-brown precipitate of iron(III) hydroxide is formed.



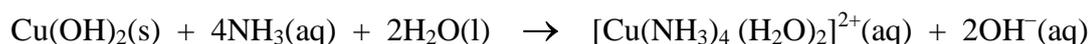
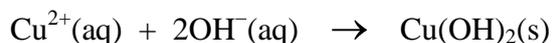
The precipitate is insoluble in excess sodium hydroxide solution.

**(iii) Copper<sup>II</sup>  $\text{Cu}^{2+}(\text{aq})$** 

When aqueous sodium hydroxide is added to a blue solution containing  $\text{Cu}^{2+}(\text{aq})$  ions, a blue precipitate of copper(II) hydroxide is formed. The precipitate is not soluble in excess sodium hydroxide solution.



When solutions containing  $\text{Cu}^{2+}(\text{aq})$  are treated with aqueous ammonia, copper(II) hydroxide is precipitated, as a basic salt. This precipitate dissolves in excess to form a deep royal blue solution containing the tetraamminecopper(II) ion.



### (i) Trace elements in living systems

#### Candidates should be able to:

*show an awareness of the economic importance of transition metals and their importance as trace elements in living systems, and give one example of economic importance and one example of trace element importance.*

*Note:*

*\*The simple electrostatic model is adequate to account for the d-orbital splitting. Candidates should be able appropriately to allocate electrons to the split d-orbitals using the arrows in boxes technique but consideration of the factors leading to high or low spin behaviour will not be required.*

The d-block elements are important in many biological systems as trace elements. The reactions being based on typical redox and coordination chemistry. The ligands involved in transition element chemistry in living systems include water, simple organic molecules, porphyrin and the side chains of amino acids.

Candidates are not required to go into great detail but should be able to recall one example of trace element importance

- Vanadium. This is found in some marine creatures.
- Manganese. Is found in bones, tissues and some organs. It is present in many enzyme systems. Like many trace elements the daily requirement is vague being about 3 mg per day. Major sources are nuts and unrefined cereals.
- Iron. Iron is present in the blood in haemoglobin. The iron occupies a similar place in the porphyrin structure in haemoglobin, to magnesium in the porphyrin structure in chlorophyll. It is present in all tissues and organs and is excreted slowly by the body so that iron is a necessary part of a healthy diet. Large intakes of iron are to be avoided although at such times as pregnancy iron supplements are usually prescribed by doctors. Common forms of iron supplements are in the form of iron(II) sulfate, iron(II) fumarate and iron(II) gluconate. Iron deficiency leads to anaemia.
- Cobalt. This is a component of vitamin B<sub>12</sub>
- Chromium. This is a cofactor in the insulin hormone system which regulates blood glucose levels.
- Copper. This is important in the formation of haemoglobin so that among the symptoms of copper deficiency is anaemia.
- Zinc. This is found in many enzyme systems and is important in the metabolism of glucose.

### The economic importance of the transition elements

Element	Economic importance
Scandium	It is used in mercury vapour lamps to produce natural daylight lighting. Can be alloyed with aluminium to form metal baseball bats.
Titanium	Titanium is used in high tensile steels and helicopter rotors. The oxide is an important pigment. $TiCl_3$ and $TiCl_4$ are Ziegler Natta catalysts in the polymerisation of ethene. Titanium is used to make spectacle frames. It is used in making surgical plates which are unreactive towards body fluids.
Vanadium	The biggest use of vanadium is in vanadium steels which are rust resistant and useful in machine tools. Vanadium(V) oxide is used in ceramics and as the catalyst in the Contact Process for making sulfuric acid.
Chromium	Chromium is used in the manufacture of stainless steel. Heat resistant chromium alloys are used in high temperature chemical apparatus. Chromium plating gives base metals an attractive and corrosion resistant finish. Addition to glass imparts an emerald green colour.
Manganese	Manganese steels are tough and important in improving rolling and forging properties. Manganese dioxide is used in dry batteries.
Iron	The main use of iron is in iron and steel manufacture. Iron is used as the catalyst in the Haber process for the manufacture of ammonia.
Cobalt	Cobalt is used as an alloying element in high temperature super alloys used for casting airfoils and structural parts in jet turbine engines. Cobalt improves the properties of rechargeable batteries. Cobalt is essential in the manufacture of permanent magnets. Permanent magnets are found in a large variety of electrical instruments from loudspeakers to galvanometers.
Nickel	Nickel is an important chemical catalyst in such processes as the hydrogenation of vegetable oils and reforming hydrocarbons. Nickel electroplating protects base metals, often applied prior to chromium plating. Nickel alloys are used in the manufacture of spectacle frames. Nickel deposited from solution without an electric current is used in computer hard disks. It is a component of stainless steel.
Copper	Copper is essential for all electrical apparatus and is essential in computer manufacture and operation. It is essential for printed circuit boards, integrated circuits, chip construction, wire and power supplies. Copper is found in many applications in the motor car.

## Topic 18 Chemical kinetics

### (a) Candidates should be able to:

describe in outline the variety of methods for studying reaction kinetics e.g. the iodine clock reaction, colorimetry and other spectroscopic techniques, pressure and volume changes;

Candidates should know that there are a variety of methods for following how quickly a reaction proceeds. We need to find some property (chemical or physical) which changes as the reaction takes place.

Here are some examples

Example of reaction	Means of following the reaction
$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$	measure volume of gas evolved over time
$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$	measure change in mass over time
$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	measure concentration of acid by sampling at set time intervals and titration
$\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$	measure change in colour over time with a colorimeter
$2\text{KI} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$	use iodine clock technique/or use colorimeter

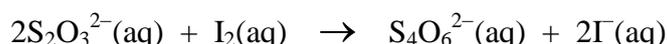
In addition to the simple techniques above, spectroscopic methods can be used. NMR has been used to study the rates at which drugs act within the body.

Candidates should understand the “iodine clock” technique.

This method is used in reactions which produce iodine.

Included in the reaction mixture is a small but constant amount of sodium thiosulfate and some starch indicator.

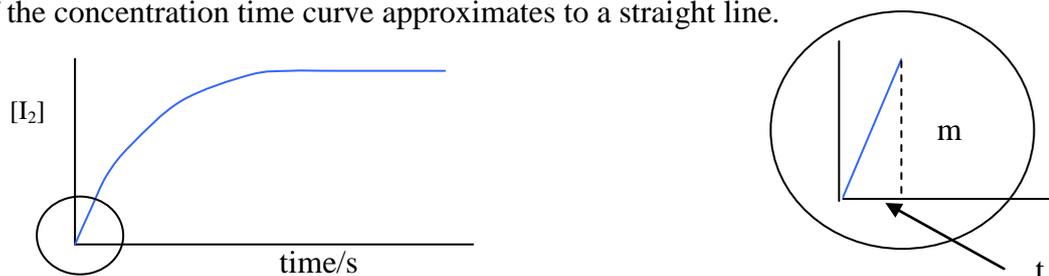
When the reaction begins the first iodine that is formed reacts with sodium thiosulfate



and only when the thiosulfate is used up does the iodine produce the dark blue colour with starch. The time (t) taken from mixing the reactants to the formation of the dark blue starch complex gives a measure of the **initial rate** of reaction.

$$\text{Initial rate} \propto 1/t$$

If the amount of sodium thiosulfate used is small and is equivalent to  $m \text{ mol dm}^{-3}$  of iodine, then the beginning of the concentration time curve approximates to a straight line.

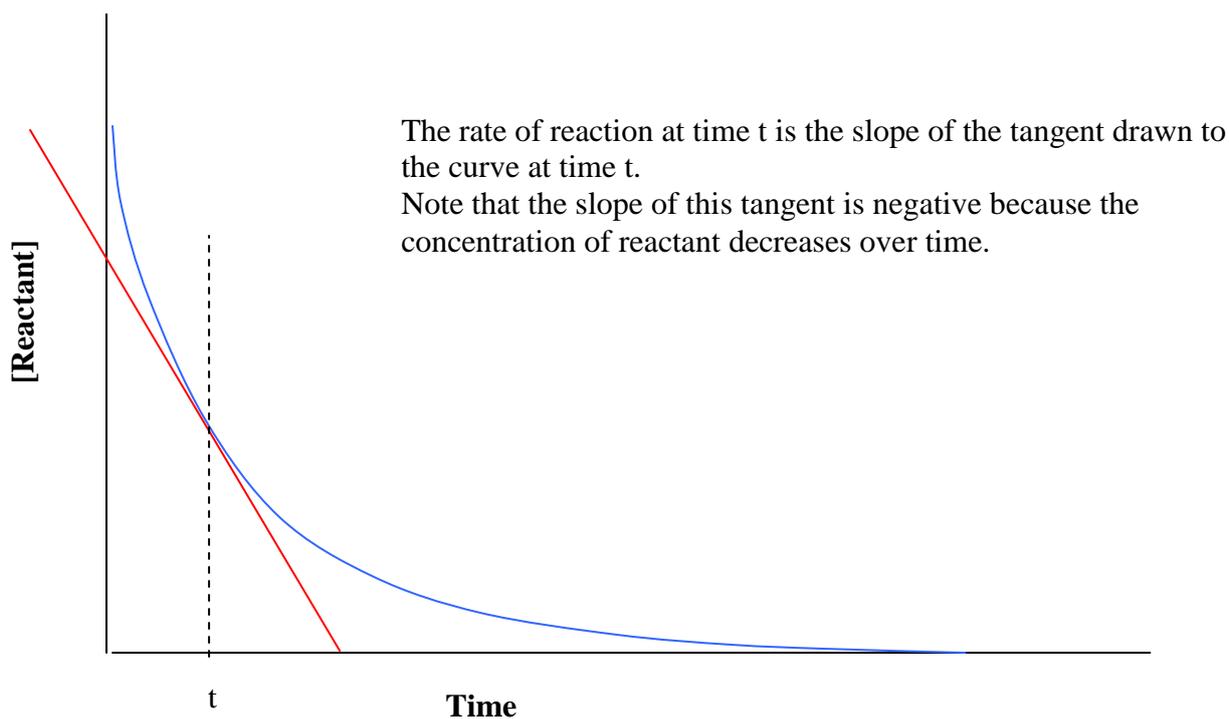


The initial rate of reaction is given by the gradient of this line which is equal to  $m/t \text{ mol dm}^{-3}\text{s}^{-1}$ .

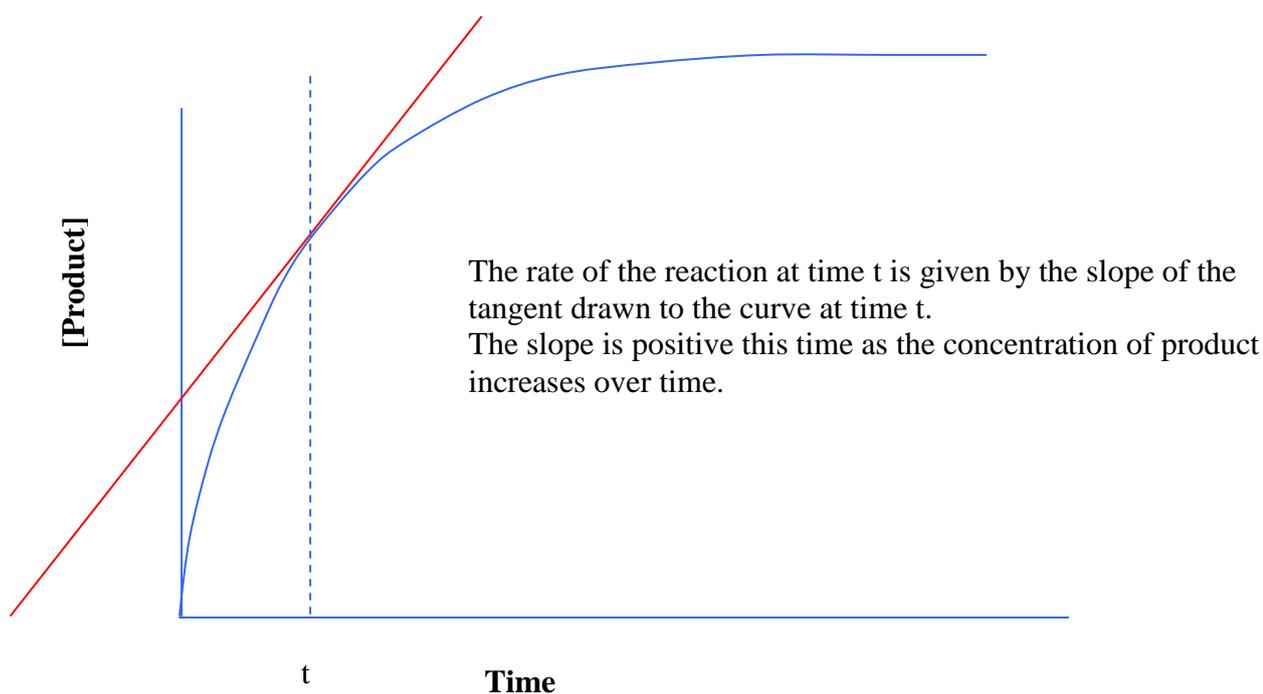
**(b) Candidates should be able to:**

*calculate rates from numerical or graphical data (including drawing tangents to concentration-time curves);*

As a reaction proceeds its rate constantly changes and can be shown on concentration - time curve. If the concentration of the reactant is plotted, then a curve similar to that below is obtained. The rate decreases over time as the reactant is used up.



A curve of the concentration of the product against time can also be drawn.

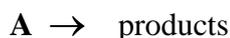


**(c) Rate equations****Candidates should be able to:**

recall and apply the general rate equation,  $\text{rate} = k[A]^m [B]^n$ , define rate, rate constant and reaction order, and give the units of rate constants up to, and including, second order;

**Rate equations can only be determined by experiment and cannot be deduced from the stoichiometric equation for the reaction.**

If it is found that the rate of a reaction



is connected to the concentration of a reactant by  $\text{Rate} \propto [A]^x$ , then the reaction is said to have order 'x' with respect to reactant A.

The rate equation is  $\text{Rate} = k[A]^x$  where  $k$  is the rate constant.

The value of  $x$  may be 0, 1 or 2 corresponding to zero order, first order and second order.

For a reaction,  $A + B \rightarrow \text{products}$ , the rate equation is

$$\text{Rate} = k[A]^x[B]^y$$

The order of the reaction is  $(x + y)$  and is order  $x$  with respect to A and order  $y$  with respect to B.

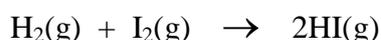
**Units**

Rate of reaction is measured in  $\text{mol dm}^{-3}\text{s}^{-1}$

For a zero order reaction the rate constant,  $k$ , would have the units  $\text{mol dm}^{-3}\text{s}^{-1}$

For a first order reaction the rate constant,  $k$ , has the units  $\text{s}^{-1}$

For a second order reaction the rate constant,  $k$ , has the units  $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

**Some examples**

second order

$$\text{Rate} = k[\text{H}_2(\text{g})][\text{I}_2(\text{g})]$$

units of  $k$   $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$



first order

$$\text{Rate} = k[\text{N}_2\text{O}_5(\text{g})]$$

units of  $k$   $\text{s}^{-1}$



This reaction may be considered second order as it is zero order with respect to  $\text{H}^+(\text{aq})$

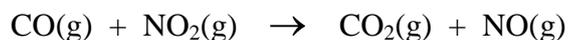
$$\text{Rate} = k[\text{KI}(\text{aq})][\text{H}_2\text{O}_2(\text{aq})]$$

units of  $k$   $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$

Often candidates will be supplied with kinetic data from which they will have to draw conclusions. Here are some examples.

### Example 1

The reaction between carbon monoxide and nitrogen dioxide is shown by the equation



Experiments at a temperature of 600K produced the following results.

Initial rate of reaction / mol dm <sup>-3</sup> s <sup>-1</sup>	Initial concentration NO <sub>2</sub> / mol dm <sup>-3</sup>	Initial concentration CO / mol dm <sup>-3</sup>
$1.12 \times 10^{-4}$	0.050	0.050
$2.24 \times 10^{-4}$	0.050	0.100
$4.48 \times 10^{-4}$	0.100	0.100
$8.96 \times 10^{-4}$	0.100	0.200

Determine the order of reaction with respect to NO<sub>2</sub> and the order with respect to CO and state the rate equation for this reaction.

Calculate the value of the rate constant,  $k$ , and give its units.

### Solution

The reaction is first order with respect to NO<sub>2</sub> because doubling its initial concentration doubles the rate of the reaction. It is also first order with respect to CO.

Rate equation      Rate =  $k[\text{NO}_2][\text{CO}]$

The rate equation is rearranged to calculate the value of rate constant,  $k$ .

$$k = \frac{\text{Rate}}{[\text{NO}_2][\text{CO}]}$$

$$k = 4.48 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

**Example 2**

A number of experiments were carried out for the following reaction at 283K



The following results were obtained.

Experiment	Initial concentration of NOBr(g)/ mol dm <sup>-3</sup>	Initial rate of reaction/ mol dm <sup>-3</sup> s <sup>-1</sup>
I	0.010	$8 \times 10^{-5}$
II	0.020	$3.2 \times 10^{-4}$
III	0.040	$1.28 \times 10^{-3}$

Calculate the order of reaction with respect to nitrosyl bromide, NOBr.

Write the rate equation and calculate the value of the rate constant and state its units.

**Solution**

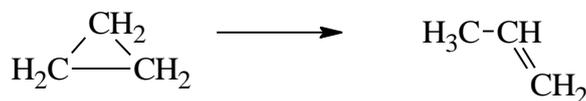
Second order with respect to NOBr, as doubling [NOBr] increases the rate by a factor of 4

Rate equation is  $\text{Rate} = k[\text{NOBr}]^2$

Rate constant,  $k$ , is  $0.80 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

**Example 3**

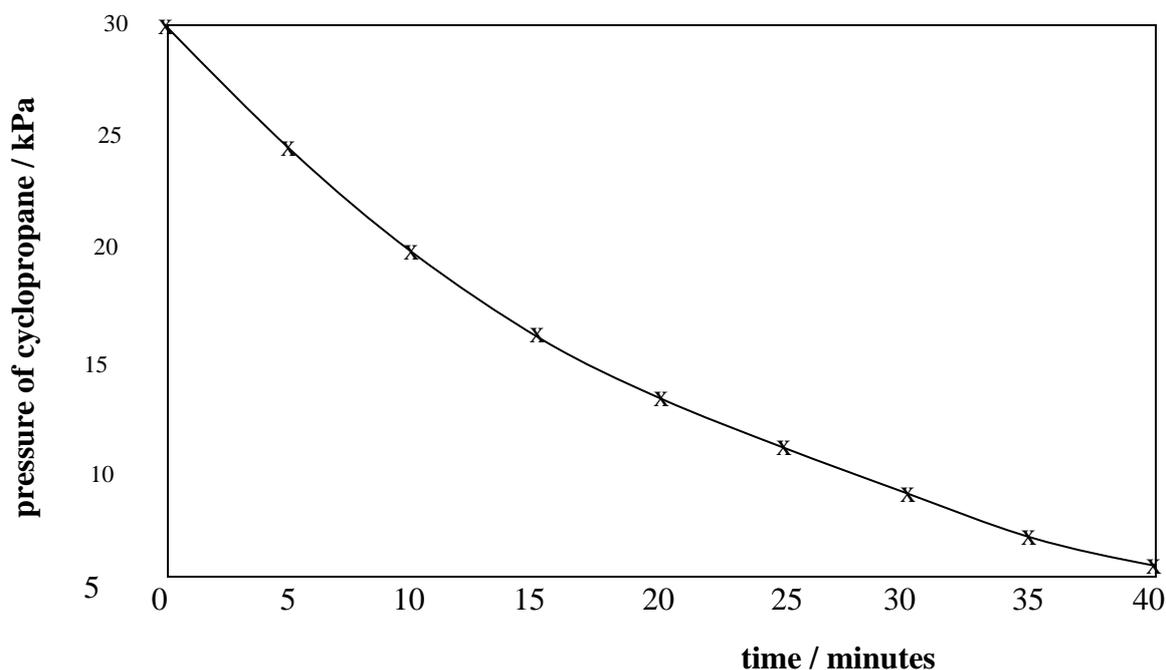
The following results were obtained from experiments on the isomerisation of cyclopropane to propene at 773K.



Time/min	Pressure of cyclopropane/ kPa
0	30
5	24.5
10	20.0
15	16.4
20	13.4
25	11.0
30	8.95
35	7.32
40	5.99

Plot a graph of pressure of cyclopropane against time.

Measure the gradient of the curve at four different points and plot these values against the corresponding pressures and hence deduce the order of the reaction. State the half life of the reaction.

**Solution**

The plot of gradient against pressure should be a straight line showing the reaction to be first order and the half life should be about 17.2 minutes.

**(d), (e) Rate and equilibrium****Candidates should be able to:**

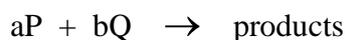
- (d) (i) *calculate rate constants and integral orders of reaction (0, 1 or 2) from given rate data;*  
(ii) *appreciate that orders of reaction may only be found through rate measurement and not from stoichiometric equations;*
- (e) *distinguish clearly between rate and equilibrium and between the effects of temperature change on rates and on the position of equilibrium;*

Chemical kinetics (rates of reaction) is concerned with how fast reactions proceed.

Chemical equilibria are concerned with how far reactions proceed.

They are distinct branches of chemistry and must not be mixed up.

For a reaction

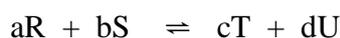


the following rate equation applies

$$\text{Rate} = k[P]^a[Q]^b$$

a and b are the orders of the reaction with respect to P and Q and (a + b) is the overall order.

For a reversible reaction of the type



the relationship  $K_c = \frac{[T]^c[U]^d}{[R]^a[S]^b}$  holds, where  $K_c$  is the equilibrium constant.

$K_c$  has a constant value at a given temperature.

An increase in temperature increases the rate of a chemical reaction.

This can be explained in terms of the fraction of molecules having energy equal to, or greater than, the activation energy for the reaction.

For an equilibrium, an increase in temperature increases the rates of both the forward and reverse reactions. This means that equilibrium is attained more quickly but the effect on the position of equilibrium cannot be determined from kinetic data.

The effect on the value of the equilibrium constant depends upon the enthalpy change for the forward reaction and can be predicted using Le Chatelier's Principle.

If  $\Delta H$  for the forward reaction is negative (an exothermic reaction), an increase in temperature will decrease the amounts of products and the value of  $K_c$  will decrease. For an endothermic forward reaction ( $\Delta H$  is positive), an increase in temperature will increase the value of  $K_c$ .

**(f) Candidates should be able to:**

*explain and use the concept of rate determining step;*

The order of a reaction with respect to a particular reactant may give some information as to the mechanism of the reaction. Most reactions take place by a number of simple steps, the sequence being known as the reaction **mechanism**. The reaction cannot proceed faster than the slowest of these simple steps. The slowest step in the mechanism is called the **rate-determining step**.

Consider the following reactions which compare the rates of hydrolysis of a primary and tertiary halogenoalkane.



From experimental data, the rate equation for reaction **I** is



and for reaction **II** is



So in reaction **I** it is assumed that the slowest step, the rate-determining step, must involve both 1-bromobutane and the hydroxide ion.

The reaction mechanism is thought to consist of two steps.

Step 1



Step 2



The reaction is classed as  $\text{S}_{\text{N}}2$  – nucleophilic substitution by a bimolecular process where there are two species in the rate determining step.

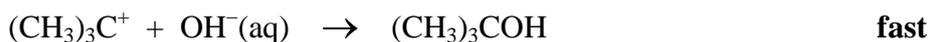
In reaction **II**

The rate-determining step only involves only 2-chloro-2-methylpropane.

Step 1



Step 2



This reaction is classed as  $\text{S}_{\text{N}}1$ ; nucleophilic substitution by a unimolecular process where there is one species in the rate determining step.

**(g) Determining a possible reaction mechanism****Candidates should be able to:**

*deduce the kinetics that would apply to a suggested mechanism or, conversely, suggest a mechanism consistent with a determined or given reaction order in simple cases and show an understanding of how kinetic evidence may support a proposed mechanism.*

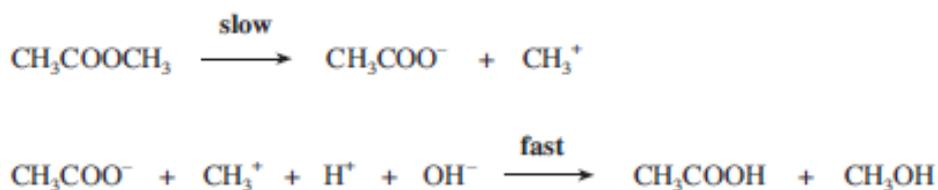
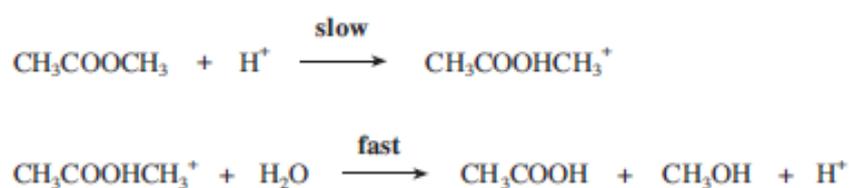
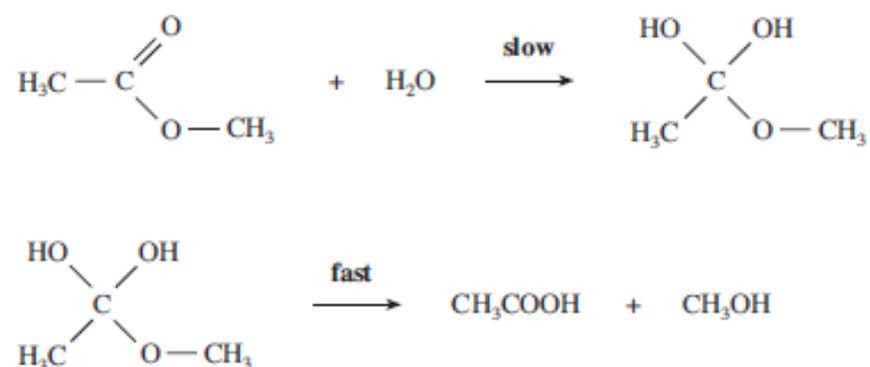
The ester methyl ethanoate,  $\text{CH}_3\text{COOCH}_3$ , hydrolyses slowly when dissolved in dilute hydrochloric acid.



Experiments show that the following rate equation applies to the reaction.

$$\text{Rate} = k[\text{CH}_3\text{COOCH}_3][\text{HCl}]$$

You should be able to suggest which one of the following three mechanisms is compatible with the rate equation.

**Mechanism 1****Mechanism 2****Mechanism 3**

The rate equation shows that the reaction is first order with respect to  $\text{CH}_3\text{COOCH}_3$  and first order with respect to  $\text{HCl}$ , i.e. the concentrations of both affect the rate of reaction. As the rate of a reaction is determined by its slowest step, it is reasonable to assume that the correct reaction mechanism will include a rate-determining step that involves both  $\text{CH}_3\text{COOCH}_3$  and  $\text{HCl}$ .

The rate-determining step in Mechanism 1 does not include  $\text{HCl}$  suggesting that if the reaction proceeded in this way, its rate would not be affected by changing the  $\text{HCl}$  concentration.

The same is true of Mechanism 3.

The rate-determining step in Mechanism 2 includes both  $\text{CH}_3\text{COOCH}_3$  and  $\text{H}^+$  (from  $\text{HCl}$ ) suggesting that this may indeed be the way that the reaction occurs.

## Topic 19 Energy changes

### 19.1 Enthalpy changes for solids and solutions

#### (a) Candidates should be able to:

*understand the use of the terms enthalpy change of atomisation, lattice formation and breaking, hydration and solution (formal definitions are not required);*

Formal definitions of the following enthalpy changes are not required but will be given for completeness.

#### **Enthalpy change of atomisation of an element, $\Delta H_{\text{at}}^{\ominus}$ .**

This is the enthalpy change when one mole of gaseous atoms at 298K and 1 atmosphere, is formed from the element in its standard state.

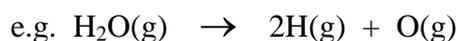
Element	$\Delta H_{\text{at}} / \text{kJ mol}^{-1}$
carbon, $\text{C(s)} \rightarrow \text{C(g)}$	715
chlorine, $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$	121*
hydrogen, $\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H(g)}$	218*
oxygen, $\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O(g)}$	249*
sodium, $\text{Na(s)} \rightarrow \text{Na(g)}$	107

Note that all these enthalpy changes are positive since they are endothermic processes.

\* These values are half of the bond dissociation energy for the diatomic molecule.

One mole of a diatomic molecule dissociates into two moles of atoms.

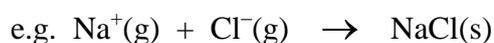
For compounds, atomisation refers to breaking the bonds in the molecule to form isolated gaseous atoms.



This can be calculated from bond dissociation enthalpy changes.

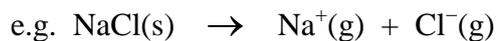
#### **Enthalpy change of lattice formation, $\Delta H_{\text{lat}}^{\ominus}$ .**

This is the enthalpy change when one mole of an ionic solid is formed from its gaseous ions under standard conditions, 298K, 1 atmosphere.



Note that such an enthalpy change is always negative.

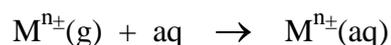
The **enthalpy change of lattice breaking** is that associated with changing one mole of a solid ionic compound into its gaseous ions under standard thermodynamic conditions.



This has the same value as the enthalpy change of lattice formation but is always positive. The values of enthalpy changes of lattice formation may be determined experimentally or theoretically.

**Enthalpy change of hydration,  $\Delta H_{\text{hyd}}^{\oplus}$**

Most simply, the enthalpy change of hydration refers to the process



The values of  $\Delta H_{\text{hyd}}^{\oplus}$  are negative – the hydration is exothermic.

**Enthalpy change of solution,  $\Delta H_{\text{sol}}$**

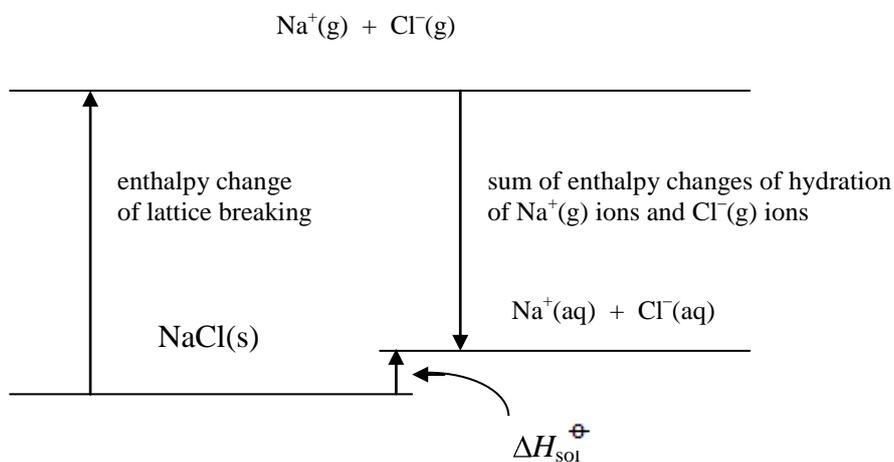
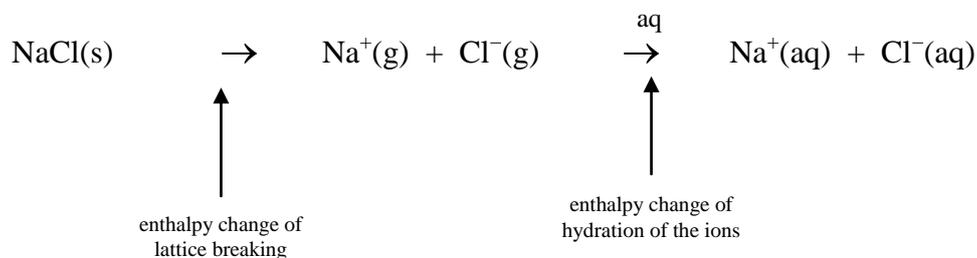
This refers to the process in which  $\oplus$  one mole of solid dissolves in water to form a solution at infinite dilution.



**(b) Candidates should be able to:**

explain how enthalpy changes of solution are related to lattice breaking enthalpies and hydration enthalpies of the ions;

Another way of approaching this is to consider that  $\Delta H_{\text{sol}}^{\oplus}$  is the overall enthalpy change for



$$\Delta H_{\text{sol}}^{\oplus} = -\Delta H_{\text{lat}}^{\oplus} + \Delta H_{\text{hyd}}^{\oplus}$$

**(c) Candidates should be able to:**

show understanding of the way in which the solubilities of ionic solids in water depend upon the balance between the lattice breaking enthalpies and the hydration enthalpies of the ions;

For an ionic solid to dissolve exothermically in water, the energy absorbed to break the lattice into gaseous ions must be less than the energy evolved in hydrating the ions.

Taking values for sodium chloride

$$\Delta H_{\text{lat}}^{\oplus} = -771 \text{ kJ mol}^{-1}, \Delta H_{\text{hyd}}^{\oplus} \text{ for } \text{Na}^{\oplus}(\text{g}) = -405 \text{ kJ mol}^{-1}, \Delta H_{\text{hyd}}^{\oplus} \text{ for } \text{Cl}^{\ominus}(\text{g}) = -364 \text{ kJ mol}^{-1}$$

This makes  $\Delta H_{\text{sol}}^{\oplus}$  for sodium chloride just positive and its dissolution is slightly endothermic.

$$\Delta H_{\text{sol}}^{\oplus} = -(-771) + (-769) = +2 \text{ kJ mol}^{-1}$$

If we consider enthalpy changes only, ionic compounds which have highly exothermic enthalpy changes of solution would be expected to be highly soluble in water.

This may be seen to be true for compounds such as Group 1 hydroxides.

This argument breaks down for salts such as ammonium nitrate and potassium iodide which dissolve endothermically but are readily soluble.

To explain this we must look at the role of entropy (Topic 19.2) and free energy.

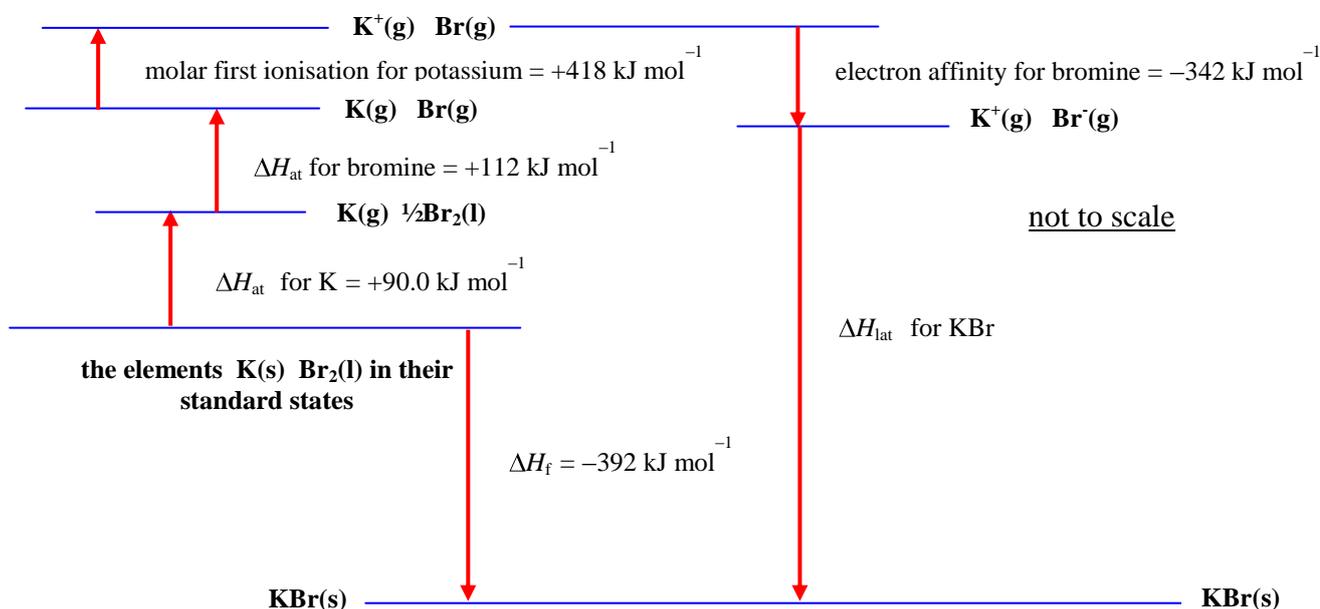
#### (d) The Born-Haber cycle

Candidates should be able to:

*apply Hess's Law (Born-Haber cycle) to the formation of simple ionic compounds and carry out appropriate calculations (data will be supplied as necessary);*

This is an application of Hess's Law and is applied to ionic compounds.

A Born-Haber cycle for potassium bromide, KBr.



In examples of a Born-Haber cycle, all data will be given except one item which may be calculated by applying Hess's law. In the example above, all values are given except the enthalpy change of lattice formation for KBr.

Applying Hess's law

$$+90.0 + 112 + 418 - 342 + \Delta H_{\text{lat}} = -392$$

$$\text{Hence } \Delta H_{\text{lat}} = -392 - 90.0 - 112 - 418 + 342 = -670 \text{ kJ mol}^{-1}$$

**(e) Candidates should be able to:**

appreciate that the exothermicity or endothermicity of  $\Delta H_f^\ominus$  may be used as a qualitative indication of the stability of the compound in question and recognise that the most stable ionic compounds will be those formed most exothermically from their elements.

Candidates should realise that the values of  $\Delta H_f^\ominus$  are a rough guide to the stability of compounds.

A negative value for  $\Delta H_f^\ominus$  is a good indication that the compound is more stable than a compound with a positive value.

For ionic compounds, those with the most negative values for  $\Delta H_f^\ominus$  are the most stable.

Take as an example the sodium halides.

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$\Delta H_{\text{lat}} / \text{kJ mol}^{-1}$
sodium fluoride	-569	-902
sodium chloride	-411	-771
sodium bromide	-360	-733
sodium iodide	-288	-684

**Topic 19.2 Entropy and feasibility of reactions****(f), (g), (h) and (i) Candidates should be able to:**

- (f) appreciate that the entropy,  $S$ , of a chemical system is to a large degree determined by the freedom possessed by the molecules or atoms within the system, and that for all natural changes entropy increases towards a maximum (definitions not required);
- (g) recognise that molecules or atoms in a solid have much more restricted freedom than in a gas and that, other factors being equal, entropy increases in the sequence  $S(\text{solid}) < S(\text{liquid}) < S(\text{gas})$ ;
- (h) apply the equation relating free energy change,  $\Delta G$ , to the entropy change,  $\Delta S$ ,  

$$\Delta G = \Delta H - T\Delta S$$
and understand that, for a reaction:  
if  $\Delta G$  is negative the reaction occurs spontaneously;  
if  $\Delta G$  is positive the reaction does not occur spontaneously;
- (i) understand that, because of the entropy change, endothermic processes such as the boiling of liquids, the solution of some salts and the thermal decomposition of oxysalts may still occur spontaneously.

The question must be answered as to why endothermic changes take place at all. The system resulting from an endothermic change is at a higher energy level than the system before the change.

There must be another factor, which determines whether an endothermic process is feasible.

The quantity that determines whether a change is feasible **is not** the change in enthalpy,  $\Delta H$ , but the change in **free energy**,  $\Delta G$ .

If  $\Delta G$  is negative then a change is feasible. (*It should be emphasised that thermodynamics only deals with the feasibility of a reaction and gives no information about the kinetics of a reaction. Many reactions that are energetically feasible do not take place under ordinary conditions since the activation energy for the reaction is too high for reaction to occur*).

The change in free energy is related not only to  $\Delta H$ , the change in enthalpy, but also to the temperature and the change in another quantity called **entropy**,  $S$ .

Entropy is related to the disorder of a system. In solid sodium chloride the ions are in an ordered arrangement in the crystal lattice but in molten sodium chloride the ions are far less ordered being free to move in the liquid state. Molten sodium chloride has larger entropy than solid sodium chloride.

In general, the entropy of a gaseous substance is greater than that of the liquid which, in turn, is greater than that of the solid. The specification refers to the disorder of the particles in a system as

*“the freedom possessed by the molecules or atoms within the system”*.

The relationship between  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  is

$$\Delta G = \Delta H - T\Delta S \quad \text{where } T \text{ is the Kelvin temperature.}$$

As stated previously for a reaction to be feasible and proceed spontaneously,  $\Delta G$  must be negative. It is therefore possible to list combinations which will show whether the value of  $\Delta G$  is negative or positive.

$\Delta H$	$\Delta S$	$\Delta G$	Feasibility of reaction
Negative	Positive	Negative	Reaction always feasible
Negative	Negative	Negative or positive depending upon the magnitude of $T\Delta S$	Reaction may or may not be feasible
Positive	Positive	Negative or positive depending upon the magnitude of $T\Delta S$	Reaction may or may not be feasible
Positive	Negative	Positive	Reaction is never feasible

Let us look at some endothermic processes.

The salt ammonium nitrate is very soluble in water but dissolves endothermically.

$$\Delta H_{\text{sol}} = +25.8 \text{ kJ mol}^{-1}$$

As the salt dissolves spontaneously, the term  $T\Delta S$  must be greater in magnitude than  $\Delta H$  so that  $\Delta G$  is negative. It is the large increase in entropy that makes the salt soluble.

The solubility of ammonium nitrate varies with temperature from about 118 g per 100g of water at 0°C to about 870 g per 100g of water at 100°C.

### The thermal decomposition of calcium carbonate



The values of  $\Delta H_f^\circ$  for  $\text{CaCO}_3(\text{s})$ ,  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$  respectively are

$$-1207, -635 \text{ and } -394 \text{ kJ mol}^{-1}.$$

Applying Hess's law, the enthalpy change for the decomposition of calcium carbonate is endothermic.

$$-635 - 394 + 1207 = +178 \text{ kJ mol}^{-1}$$

From thermodynamic tables, the change in entropy,  $\Delta S^\ominus$ , is  $+163.5 \text{ J mol}^{-1} \text{ K}^{-1}$ .

From this data it should be possible to estimate the temperature at which calcium carbonate will undergo thermal decomposition.

$$\Delta G = \Delta H - T\Delta S$$

For the reaction to proceed  $\Delta G$  must be negative.

If  $\Delta G$  is given the value of zero,

$$\text{then } 0 = +178\,000 - T \times 163.5$$

$$\text{hence } T = 1090 \text{ K}$$

Calcium carbonate will not decompose until the temperature is greater than 1090K (816 °C).

## Topic 20 Equilibria

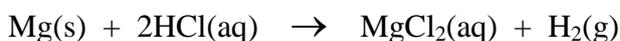
### Topic 20.1 General Equilibria

(a) and (b) Candidates should be able to:

- (a) deduce expressions for the equilibrium constants,  $K_p$  and  $K_c$  in terms of partial pressures or of concentrations, as appropriate;
- (b) appreciate that  $K_p$  or  $K_c$  are constant for a given system at any fixed temperature and understand the effect of temperature changes on  $K_p$  or  $K_c$  for exothermic and endothermic reactions;

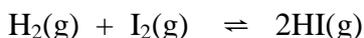
Many of the reactions studied in the laboratory appear to go to completion.

For example the reaction between hydrochloric acid and magnesium ribbon continues until one of the reactants is used up.



There are reactions which do not go to completion.

If an equal number of moles of hydrogen and iodine are placed in a sealed tube at 500 °C and left for some time, a point will be reached when the tube contains gaseous iodine, gaseous hydrogen and gaseous hydrogen iodide.

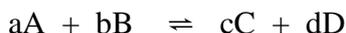


Furthermore, the concentration of each substance remains constant. On a macro scale the reaction seems to have ceased. On the molecular scale the forward and the reverse reactions are still proceeding but the rate of formation of hydrogen iodide is equal to the rate at which it decomposes into its elements. This is called a **dynamic equilibrium**.

The reaction is reversible and the symbol “ $\rightleftharpoons$ ” is used.

#### The Equilibrium Law

For a reaction of the type



when at equilibrium at a given temperature  $\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$  is a constant.

[ ] represents the concentration of the species **at equilibrium** in mol dm<sup>-3</sup>.

The constant is called the equilibrium constant,  $K_c$ .

For the reaction:  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$

$$K_c = \frac{[\text{HI(g)}]^2}{[\text{H}_2\text{(g)}][\text{I}_2\text{(g)}]}$$

For gaseous reactions, the concentrations in  $\text{mol dm}^{-3}$  may be replaced by the partial pressures of the gases. The equilibrium constant is then denoted by  $K_p$ .

$$K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} p_{\text{I}_2}} \text{ where } p \text{ represents the partial pressure.}$$

The partial pressure of a gas is the pressure that the gas would exert if it alone occupied that volume. If three gases A, B and C occupy a container and the total pressure is P, then

$$P = p_A + p_B + p_C$$

$$P = \sum p$$

### Le Chatelier's Principle

This was stated in Topic 2.1

In 1888 Henri Le Chatelier put forward his principle which dealt with the effects of constraints upon a system in equilibrium.

If the conditions of a reversible reaction are changed and disturb the equilibrium, the composition of the mixture will tend to change to restore the equilibrium and to minimize the effect of altering the conditions.

For a given reaction at a given temperature the value of  $K_c$  or  $K_p$  is constant.

The value of  $K_c$  or  $K_p$  varies with temperature.

The shift in the position of equilibrium with change in temperature can be deduced by applying Le Chatelier's principle.

Take the oxidation of sulfur dioxide in the contact process.



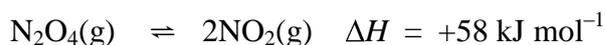
The forward reaction is exothermic. If the temperature of an equilibrium mixture is raised, then the reverse endothermic reaction is favoured and there will be less  $\text{SO}_3$  in the equilibrium mixture. This means that the values of  $K_p$  and  $K_c$  will be smaller.

For this reaction, the value of  $K_p$  at  $25^\circ\text{C}$  is of the order of  $4 \times 10^{24} \text{ atm}^{-1}$  and at  $425^\circ\text{C}$  is of the order of  $3 \times 10^4 \text{ atm}^{-1}$ .

Of course, at the lower temperature the rate at which equilibrium would be established would be very slow and the reaction between sulfur dioxide and oxygen would not be appreciable. In the industrial process, a catalyst of vanadium(V) oxide is used and a temperature of about  $450^\circ\text{C}$ .

Catalysts do not alter the value of the equilibrium constant but only speed up the rate at which equilibrium is attained.

Dinitrogen tetraoxide decomposes endothermically.



An increase in temperature on the system at equilibrium will increase the amount of nitrogen dioxide in the new equilibrium mixture. The equilibrium constant  $K_p$  will increase.

At 25°C, the value is 0.115 atm but at 77°C it is 3.7 atm.

If an equilibrium mixture of  $\text{N}_2\text{O}_4(\text{g})/\text{NO}_2(\text{g})$  in a sealed tube is heated from 0°C to 60°C the mixture goes much darker as the almost colourless gas containing mainly  $\text{N}_2\text{O}_4$  molecules decomposes to form the dark brown gas containing many more  $\text{NO}_2$  molecules.

In summary, for an exothermic reaction an increase in temperature decreases  $K_c/K_p$  and conversely for an endothermic reaction an increase in temperature increases  $K_c/K_p$ .

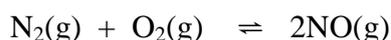
### (c) Calculations on equilibria

**Candidates should be able to:**

*calculate values of  $K_p$  and  $K_c$  or of quantities present at equilibrium, given appropriate data (no manipulations of mole fraction or of degree of dissociation will be required);*

Worked examples

1. Nitrogen monoxide, NO, can be formed in small amounts when a mixture of nitrogen and oxygen is heated strongly.



At a temperature of 1500K,  $K_p$  has a value of  $1.0 \times 10^{-5}$ . Calculate the partial pressure (in atm) of nitrogen monoxide present at equilibrium if the partial pressures of nitrogen and oxygen at equilibrium are each 1.2 atm.

$$K_p = \frac{p(\text{NO}(\text{g}))^2}{p(\text{N}_2(\text{g})) \times p(\text{O}_2(\text{g}))}$$

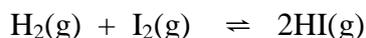
$$p(\text{NO}(\text{g}))^2 = K_p \times p(\text{N}_2(\text{g})) \times p(\text{O}_2(\text{g}))$$

$$p(\text{NO}(\text{g}))^2 = 1.0 \times 10^{-5} \times 1.2 \times 1.2$$

$$p(\text{NO}(\text{g})) = \sqrt{1.0 \times 10^{-5} \times 1.2 \times 1.2}$$

$$p(\text{NO}(\text{g})) = 3.79 \times 10^{-3} \text{ atm}$$

2. Hydrogen iodide is a covalent compound formed from its elements according to the following equation.



In an experiment, hydrogen gas and iodine vapour having initial partial pressures of 15 atm and 10 atm respectively, were allowed to reach equilibrium at a given temperature. The equilibrium partial pressure of the hydrogen iodide gas formed was 18 atm.

Calculate the equilibrium pressures of hydrogen and iodine and use these to calculate a value for  $K_p$  at this temperature.

A good method of tackling this type of question is to write down the initial pressures and the equilibrium pressures.

Initial partial pressures in atm	15	10	0	
	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$			
Eq <sup>m</sup> partial pressures in atm			18	

Because there are two moles of gas on both sides of the equation, the total pressure at equilibrium must be equal to the total initial pressure, meaning that the sum of the equilibrium partial pressures of  $\text{H}_2$  and  $\text{I}_2$  must be 7 atm. As reaction involves equal numbers of moles of  $\text{H}_2$  and  $\text{I}_2$ , the equilibrium partial pressure of  $\text{H}_2$  will still be 5 atm greater than that of  $\text{I}_2$ .

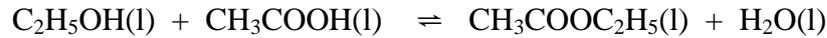
Equilibrium partial pressure of  $\text{H}_2$  gas must therefore be 6 atm and that of  $\text{I}_2$  must be 1 atm.

These values are substituted into the expression for  $K_p$  as follows.

$$K_p = \frac{p(\text{HI}(\text{g}))^2}{p(\text{H}_2(\text{g})) \times p(\text{I}_2(\text{g}))}$$

$$K_p = \frac{18^2}{6 \times 1} = 54$$

3. The esterification reaction between ethanol and ethanoic acid is a liquid-phase equilibrium. When equal numbers of moles of ethanol ( $1.00 \text{ mol dm}^{-3}$ ) and ethanoic acid ( $1.00 \text{ mol dm}^{-3}$ ) are allowed to reach equilibrium at  $100^\circ\text{C}$ , two-thirds of the ethanoic acid reacts according to the equation



Calculate the value of  $K_c$  at  $100^\circ\text{C}$ .

If two-thirds of the ethanoic acid reacts then two-thirds of the ethanol must also do so and one-third of the initial amount of each must be present at equilibrium. One molecule of ester is formed from each ethanoic acid molecule so the equilibrium concentration of the ester must be two-thirds of the initial acid concentration i.e.  $0.667 \text{ mol dm}^{-3}$ .

Initial concentrations ( $\text{mol dm}^{-3}$ )	1.00	1.00	0	0
	$\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$			
Eq <sup>m</sup> concentrations ( $\text{mol dm}^{-3}$ )	0.333	0.333	0.667	0.667

The value of  $K_c$  may now be calculated using the following expression.

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})] [\text{H}_2\text{O}(\text{l})]}{[\text{C}_2\text{H}_5\text{OH}(\text{l})] [\text{CH}_3\text{COOH}(\text{l})]}$$

$$K_c = \frac{0.667 \times 0.667}{0.333 \times 0.333} = 4.0$$

4. For the reaction,



at a certain temperature and at a total pressure of  $101\,300 \text{ Pa}$ , the equilibrium partial pressures of  $\text{PCl}_3(\text{g})$  and  $\text{Cl}_2(\text{g})$  are equal and twice the equilibrium partial pressure of  $\text{PCl}_5(\text{g})$ . Calculate the value of  $K_p$  for the reaction at that temperature.

$$K_p = \frac{p_{\text{PCl}_3} p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$$

Let  $p$  be the partial pressure of  $\text{PCl}_5(\text{g})$  then partial pressures of  $\text{PCl}_3(\text{g})$  and  $\text{Cl}_2(\text{g})$  are  $2p$ .

$$K_p = (2p \times 2p) / p = 4p$$

$$\text{Total pressure} = 101\,300 = p + 2p + 2p = 5p$$

$$\text{Hence } p = 20\,260 \text{ Pa}$$

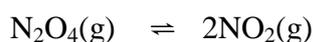
$$K_p = 81040 \text{ Pa}$$

**(d) Candidates should be able to:**

*show ability to use given or calculated values of  $K_p$  and  $K_c$  to estimate qualitatively the location of the position of equilibrium for a system;*

The value of the equilibrium constant at a given temperature can be used to estimate, in a qualitative way, where the position of equilibrium lies.

Take for example



Temperature/ $^{\circ}\text{C}$	$K_p$ /atmospheres
25	0.115
75	3.54
125	44.7

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$

At  $25^{\circ}\text{C}$  the denominator (bottom line) for the expression for  $K_p$  must be much larger than the numerator (top line). This means that the equilibrium lies to the left. From the values at  $75^{\circ}\text{C}$  and  $125^{\circ}\text{C}$ , the equilibrium moves further to the right as the temperature increases.

This could have been predicted by applying le Chatelier's principle knowing that the enthalpy change,  $\Delta H_{\text{forward reaction}}$  is  $+58 \text{ kJ mol}^{-1}$ .

**(e) Relationship between  $K_c/K_p$  and  $\Delta G$** **Candidates should be able to:**

*recognise that for a reaction with  $\Delta G$  negative (see 19.2 (h))  $K_p$  and  $K_c$  will have large values as the products predominate and that for a reaction with  $\Delta G$  positive  $K_p$  and  $K_c$  will have small values as the reactants predominate;*

In general, if  $\Delta G$  is negative then products predominate in the equilibrium mixture and the values of  $K_c$  and  $K_p$  will be relatively large.

If  $\Delta G$  is positive then the equilibrium constant must be less than 1 and the reactants will predominate in the equilibrium mixture.

## (f) Equilibrium data and kinetic data

### Candidates should be able to:

appreciate the distinction between what may be deduced from **equilibrium** data and what may be deduced from **kinetic** data;

It is vital that candidates are able to distinguish between what information is given by equilibrium data and what by kinetic data.

Equilibrium data tells us **how far** a reaction goes.

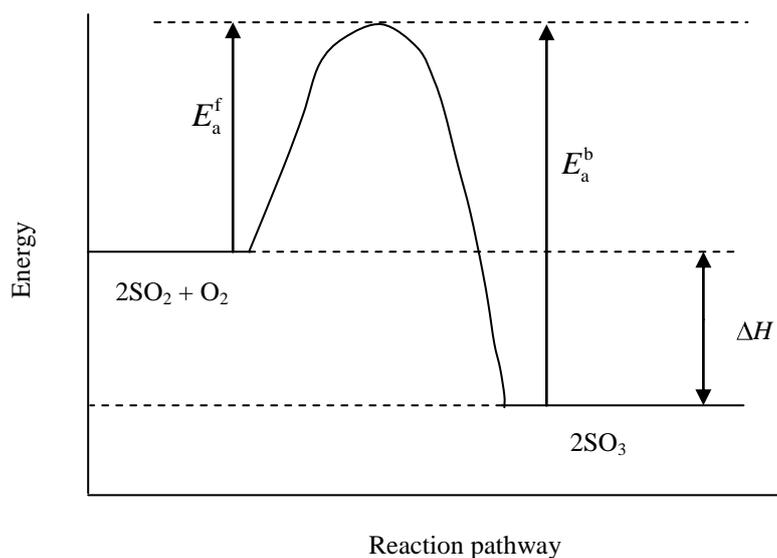
Kinetic data tells us **how fast** a reaction proceeds.

Equilibrium data is governed by the values of equilibrium constants,  $K_p$  or  $K_c$ , at a given temperature.

Kinetic data is governed by the values of the rate constant,  $k$ , at a given temperature.

This may be summed up by a reaction profile.

Take, for example,  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$



Equilibrium is only concerned with the value of  $\Delta H$  and the balanced equation. Predictions can be made by le Chatelier's Principle as to changes in equilibrium caused by changes in temperature or pressure.

Kinetics is concerned with the activation energies  $E_a^f$  and  $E_a^b$ . All reactions go faster if the temperature increases.\*

\* Not true of enzyme-catalysed reactions which may slow down at higher temperatures due to the increase in temperature destroying the enzyme.

**Remember also that the equilibrium constant for a reaction always depends on the stoichiometry of the reaction but the rate equation does not.**

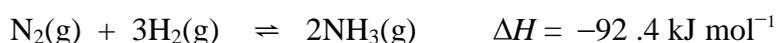
**(g) Candidates should be able to:**

*integrate and evaluate supplied kinetics, energetics and equilibria data for environmental and industrial chemical processes.*

Candidates will be expected to evaluate and integrate given equilibrium and kinetic data for industrial and environmental processes. Classic examples are the Haber process for ammonia manufacture and the Contact process for sulfuric acid manufacture.

**The Haber process**

The reaction is



Applying Le Chatelier's Principle, an increase in pressure will favour the formation of ammonia since there are fewer gas molecules on the product side of the equation than on the reactant side.

An increase in temperature will favour the reactants since the forward reaction is exothermic and the equilibrium will adjust by favouring the endothermic reverse reaction.

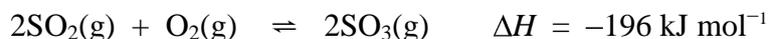
Although low temperatures favour the yield of ammonia, low temperatures mean that equilibrium is established too slowly.

In practice a temperature of 400-450°C (an optimum temperature) is used in conjunction with an iron catalyst. Ammonia is removed as it is formed and unused nitrogen and hydrogen recycled.

Full details can be obtained from the Internet.

**The Contact process**

The reaction is



An increase in temperature reduces the amount of sulfur trioxide in the equilibrium mixture since the forward reaction is exothermic. In practice a temperature of 450°C is chosen in conjunction with a catalyst of vanadium(V) oxide,  $\text{V}_2\text{O}_5$ . This allows the reaction to proceed at a reasonable rate without reducing the yield too much.

An increase in pressure favours the yield of sulfur trioxide but only a small increase in pressure is used. This is sufficient to drive the gases through the plant. Higher pressure would be expensive and unnecessary as a 99% conversion of sulfur dioxide can be obtained without it.

Full details can be obtained from the Internet.

## Topic 20.2 Acid-base Equilibria

### (h) Brønsted-Lowry Theory

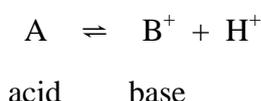
#### Candidates should be able to:

*understand and apply the Lowry-Brønsted theory of acids and bases (limited to aqueous solutions);*

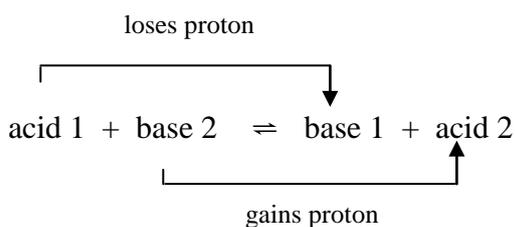
This theory states that an acid is an ion or molecule which can donate a proton and a base is a molecule or ion which can accept a proton.

When a Brønsted-Lowry acid donates a proton it immediately becomes a base.

A Brønsted-Lowry base accepts a proton to become an acid.



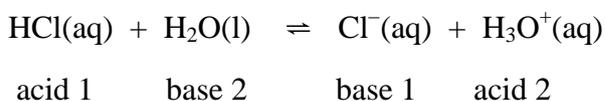
In a neutralisation reaction one substance donates a proton to another substance, often a molecule of water.



acid 1 and base 1 are described as a conjugate acid-base pair.

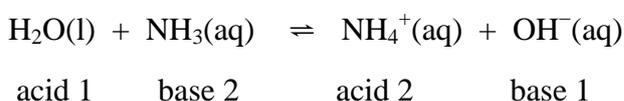
#### Examples

1. Water can act as a Brønsted-Lowry **base**



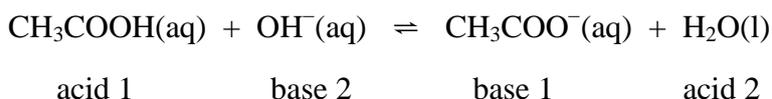
HCl(aq) is a strong acid i.e. it is almost completely ionised so its conjugate base, Cl<sup>-</sup>(aq), is a weak base having little tendency to accept a proton.

2. Water can also act as a Brønsted-Lowry **acid**



Water is said to be amphoteric.

3. The neutralisation of ethanoic acid.



Ethanoic acid and water are weak acids, the ethanoate ion and hydroxide ion are strong bases. The equilibrium lies to the product side.

### (i) pH

**Candidates should be able to:**

*recall the definition of pH and calculate pH values from those of  $[\text{H}^+(\text{aq})]$  and vice versa;*

The term pH was introduced by Sørensen, a Danish chemist, as a way of measuring acidity.

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

The advantage of the pH scale is that instead of measuring  $[\text{H}^+]$ , which is usually a very small number such as  $1 \times 10^{-3} \text{ mol dm}^{-3}$ , the corresponding pH value is 3. This is much more readily understood and used by the general public.

Modern calculators make the manipulation of pH calculations very easy.

### Examples

The table below shows the pH values of solutions containing various hydrogen ion concentrations.

$[\text{H}^+(\text{aq})]/\text{mol dm}^{-3}$	pH
$1.0 \times 10^{-7}$	7
$2.78 \times 10^{-5}$	4.56
$6.51 \times 10^{-2}$	1.19
$3.20 \times 10^{-9}$	8.49

Use $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$
--------------------------------------------------------

Students should be familiar with carrying out determining pH values from given hydrogen ion concentrations.

The following table shows the hydrogen ion concentrations calculated from given pH values.

pH	$[\text{H}^+(\text{aq})]/\text{mol dm}^{-3}$
2.5	$3.16 \times 10^{-3}$
5.6	$2.5 \times 10^{-6}$
7.9	$1.26 \times 10^{-8}$
10	$1.0 \times 10^{-10}$

Use  
 $[\text{H}^+(\text{aq})] = \text{antilog}(-\text{pH})$

### (j) Aqueous solutions of acids and bases

#### Candidates should be able to:

*understand and appreciate the distinction between the terms concentrated/dilute and strong/weak and explain the differences in behaviour between strong and weak acids and bases, using  $K_a$ ;*

#### Concentration

If a large amount of solute is dissolved in the solution it is said to be **concentrated**.

If a small amount of solute is dissolved in the solution it is said to be **dilute**.

#### Strength of acids and bases

An acid or base is said to be strong if, when dissolved in water, it is almost completely ionised.

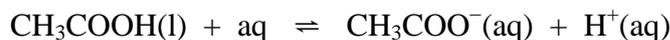


Hydrogen chloride (its solution is hydrochloric acid) is a strong acid.

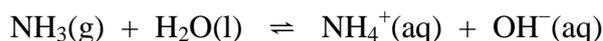


Sodium hydroxide is a strong base.

If an acid or base is only partially ionised in aqueous solution it is said to be weak.



Ethanoic acid is a weak acid



Ammonia is a weak base.

Remember that

$1 \times 10^{-4} \text{ mol dm}^{-3}$  HCl is a dilute solution of a strong acid

$10 \text{ mol dm}^{-3}$  CH<sub>3</sub>COOH is a concentrated solution of a weak acid

For weak acids, application of the equilibrium law gives

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

where  $K_a$  is the acid dissociation constant and has the units  $\text{mol dm}^{-3}$

For strong acids the value of  $K_a$  is very large.

### (k) The Ionisation of Water

#### Candidates should be able to:

*appreciate the significance of the ionic product of water,  $K_w$ , and understand that neutralisation involves  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ ;*

Water self-ionises according to the following equation.



The ionisation is very small.

Applying the equilibrium law

$$K_c = \frac{[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}]}$$

Since the ionisation is so small,  $[\text{H}_2\text{O}]$  may be considered constant and a new constant called the ionic product of water may be defined.

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

Like all equilibrium constants its value varies with temperature.

At 298 K,  $K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

As  $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ ,

At 298 K,  $[\text{H}^+(\text{aq})] = \sqrt{(1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6})} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$

At 298 K, the pH of water = 7.

Applying le Chatelier's principle, the ionisation will be greater as temperature increases, the value of  $K_w$  will increase and the pH will decrease.

At 313 K,  $K_w = 2.9 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

$$[\text{H}^+] = \sqrt{(2.9 \times 10^{-14})} = 1.7 \times 10^{-7} \text{ mol dm}^{-3}$$

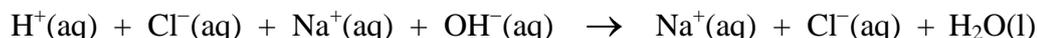
$$\text{pH} = 6.77$$

## Neutralisation

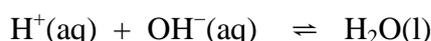
When a strong acid and strong base react to form a salt and water, the reaction is said to be neutralisation.



in terms of ions



Omitting the sodium and chloride ions which do not take part in the reaction (spectator ions) gives the ionic equation



This is the equation for all neutralisations involving a strong acid and a strong base.

Evidence to support this is that the enthalpy changes of neutralisation for different strong acid/strong base reactions are the same; approximately  $-57 \text{ kJ mol}^{-1}$ .

This is not true if the strong acid is replaced by a weak acid.

## (I) Calculations involving strong and weak acids and strong and weak bases

**Candidates should be able to:**

*explain and use pH,  $K_w$  and  $K_a$  in calculations involving strong and weak acids, and use pH and  $K_w$  in calculations involving strong bases;*

### Strong acids

Since strong acids are fully ionised it is easy to calculate the pH of a solution of known concentration.

e.g. Find the pH of a solution of hydrochloric acid of concentration  $0.0125 \text{ mol dm}^{-3}$ .

Since hydrochloric acid is fully ionised,  $[\text{H}^+(\text{aq})] = 0.0125 \text{ mol dm}^{-3}$ .

$$\text{pH} = -\log(0.0125) = 1.90$$

### Strong bases

To obtain the pH of an aqueous solution of a strong base,  $K_w$  must first be used in order to find  $[\text{H}^+]$ .

e.g. Find the pH of a solution of sodium hydroxide of concentration  $0.045 \text{ mol dm}^{-3}$ .

Since sodium hydroxide is a strong base,  $[\text{NaOH}] = [\text{OH}^-]$

$$[\text{OH}^-] = 0.045 \text{ mol dm}^{-3}$$

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

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

$$1 \times 10^{-14} = [\text{H}^+][0.045]$$

$$[\text{H}^+] = 2.22 \times 10^{-13} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 2.22 \times 10^{-13} = 12.7$$

### Weak acids

Since weak acids are not fully dissociated, the original acid concentration will not equal  $[H^+]$ . To take into account the amount of dissociation that has occurred,  $K_a$  must be used.

It can be shown that if the amount of dissociation is small

$$\boxed{[H^+] = \sqrt{K_a [\text{acid}]}} \quad \text{or} \quad \boxed{K_a = \frac{[H^+]^2}{[\text{acid}]}}$$

These equations can be used in calculations involving weak acids.

### Example

Calculate the pH of an aqueous solution of ethanoic acid of concentration  $0.100 \text{ mol dm}^{-3}$  at 298 K.

$$K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3} \text{ at } 298 \text{ K.}$$

### Solution

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

$$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.1}$$

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

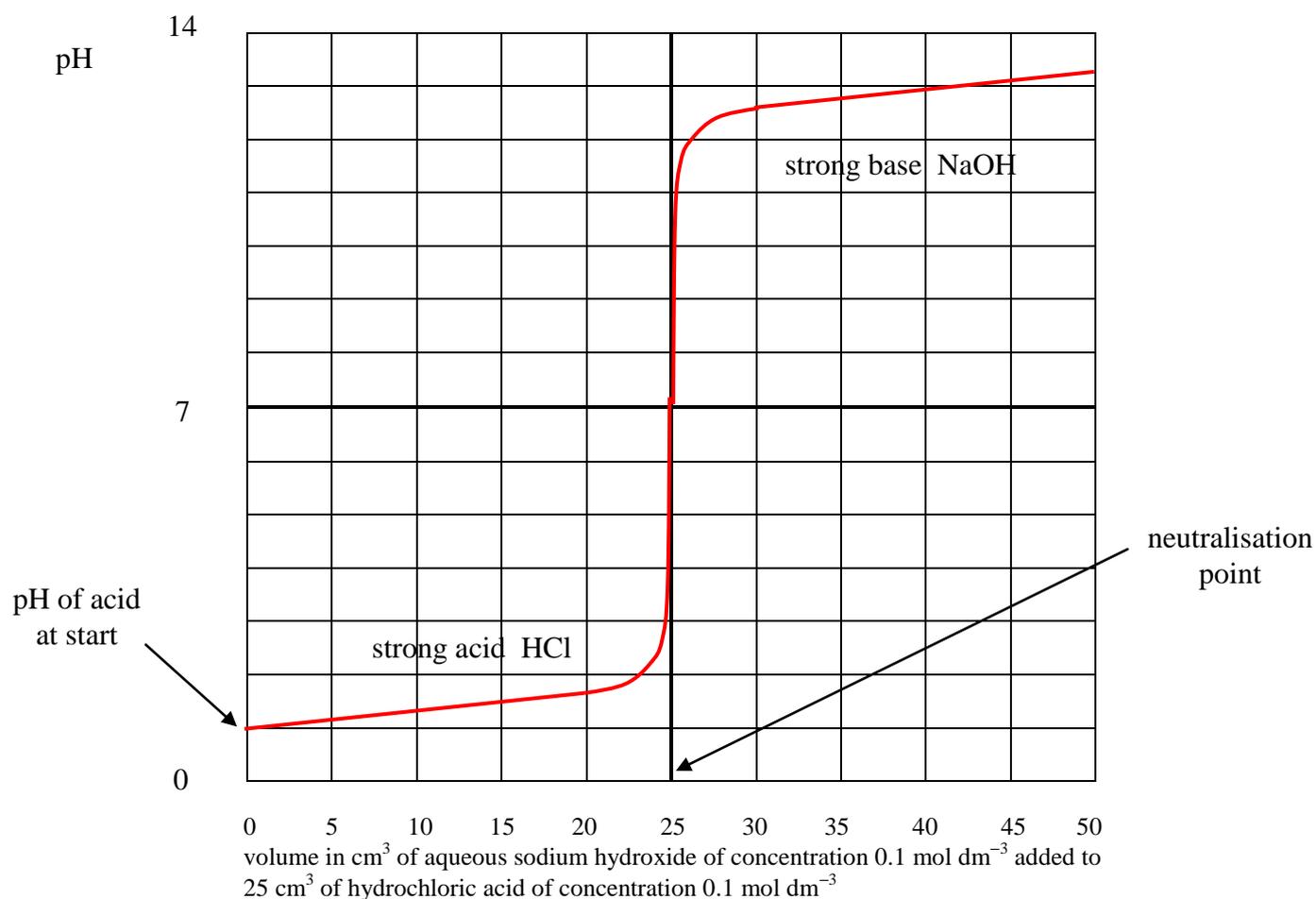
$$\text{pH} = -\log [H^+]$$

$$\text{pH} = -\log 1.32 \times 10^{-3} = 2.88$$

**(m) Titration curves****Candidates should be able to:**

recall the forms of the acid - base titration curves for the systems: strong acid /strong base (e.g.  $\text{HCl}/\text{NaOH}$ ), strong acid/ weak base (e.g.  $\text{HCl}/\text{NH}_3$ ) and weak acid/strong base (e.g.  $\text{CH}_3\text{COOH}/\text{NaOH}$ ), explaining these in terms of the appropriate acid and base strengths;

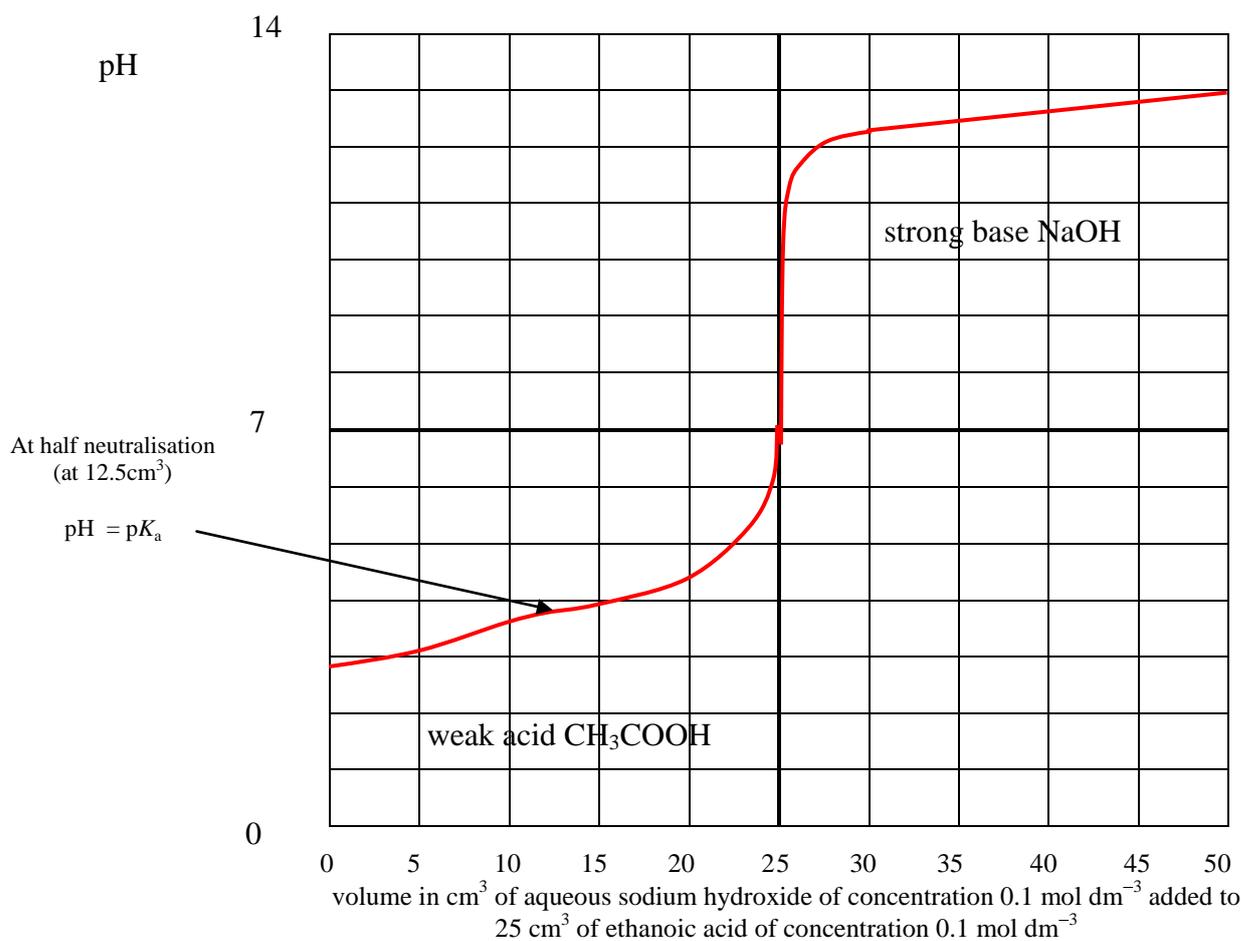
When aqueous sodium hydroxide is slowly added to aqueous hydrochloric acid there is a gradual change in pH and this may be shown on a titration curve.



The point to note on this curve is that there is a very sharp rise in pH from 24.9 cm<sup>3</sup> added (pH  $\approx$  3.7) to 25.1 cm<sup>3</sup> added (pH  $\approx$  10.3).

This means that any acid-base indicator that changes in the pH range 3–11 can be used in a titration of a strong acid with a strong base. (See acid-base indicators below).

For a weak acid against a strong base the shape of the titration curve changes.



Notice the sharp change in pH now takes place in the alkaline region and a suitable indicator must change colour over a pH range in this region.

The acid dissociation constant of ethanoic acid is given by the expression

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

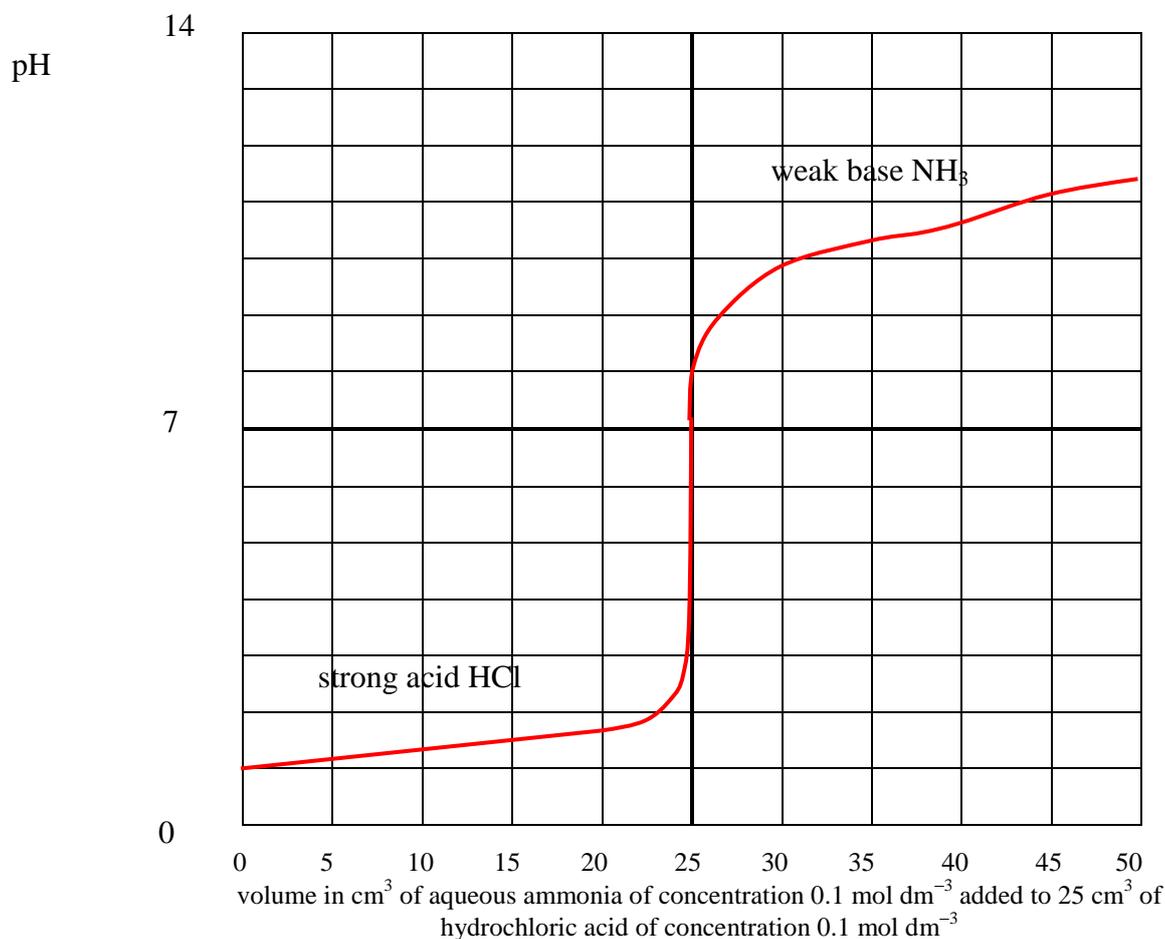
When sodium hydroxide is added to ethanoic acid sodium ethanoate is formed.



The concentration of ethanoate ion from the sodium ethanoate far outweighs that from the dissociation of the weak acid. When half the acid has been neutralised, the amount of salt formed is equal to the amount of acid remaining.

It is useful to remember that at the point of half neutralisation,  $\text{pH} = \text{p}K_a$ .

## Strong acid against a weak base



Note that a suitable indicator must operate in the acid region in a pH range less than 7.

**(n) Buffer solutions****Candidates should be able to:**

*understand the mode of action of buffer solutions, exemplified by the  $\text{CH}_3\text{COONa} / \text{CH}_3\text{COOH}$  and  $\text{NH}_3/\text{NH}_4^+$  systems, appreciate their importance, and carry out appropriate calculations using pH,  $K_w$  and  $K_a$ ;*

A buffer solution is one that resists a change in its pH when contaminated with small amounts of acid or alkali. Buffer solutions are used in many biochemical experiments where it is vital to keep pH constant while measuring such things as enzyme activity.

### The ethanoic acid/sodium ethanoate buffer

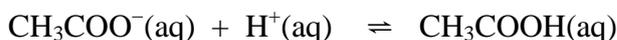
Ethanoic acid is a weak acid



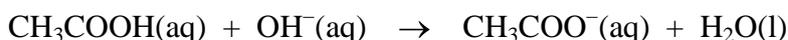
Sodium ethanoate is a fully ionised salt existing in solution as  $\text{CH}_3\text{COO}^-(\text{aq})$  and  $\text{Na}^+(\text{aq})$

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

If a small amount of acid is added to the buffer solution, the large reservoir of ethanoate ions from the sodium ethanoate will remove the extra hydrogen ions to form undissociated ethanoic acid molecules, and the pH will remain almost the same.



If a small amount of alkali is added, the hydroxide ions will react with ethanoic acid molecules and the concentration of hydrogen ions and hence the pH will remain almost the same.



### To find the pH of a buffer solution

$[\text{CH}_3\text{COO}^-(\text{aq})]$  will approximate very closely to the concentration of the salt, sodium ethanoate.

By le Chatelier's principle, the addition of ethanoate ions from the sodium ethanoate will suppress the ionisation of the ethanoic acid.  $[\text{CH}_3\text{COOH}(\text{aq})]$  will approximate to the concentration of the aqueous ethanoic acid used.

Rearranging the expression for the acid dissociation constant,  $K_a$ , allows  $[\text{H}^+]$  and subsequently pH to be calculated.

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

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

**Example**

Calculate the pH of a solution made by dissolving 16.4 g of sodium ethanoate in 1 dm<sup>3</sup> of ethanoic acid of concentration 0.100 mol dm<sup>-3</sup>. The acid dissociation constant,  $K_a = 1.74 \times 10^{-5}$  mol dm<sup>-3</sup>

**Solution**

16.4 g of sodium ethanoate = 16.4/82 mol = 0.20 mol

Assuming no change in volume on adding the salt,  $[\text{CH}_3\text{COONa}(\text{aq})] = 0.20 \text{ mol dm}^{-3}$

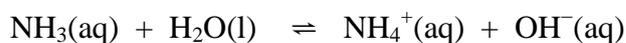
$$[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

$$[\text{H}^+] = 1.74 \times 10^{-5} \times \frac{0.100}{0.20} = 8.7 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = 5.1 \text{ (correct to 2 significant figures)}$$

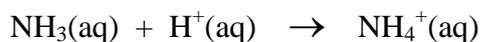
**Ammonia/ammonium chloride buffer**

Aqueous ammonia is a weak base.

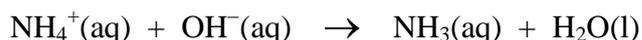


Ammonium chloride ionises fully in aqueous solution as  $\text{NH}_4^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ .

If a small amount of acid is added to an ammonia/ammonium chloride buffer, it will be neutralised by the ammonia molecules and the concentration of  $\text{H}^+(\text{aq})$  and the pH will be almost unchanged.



If a small amount of alkali is added, the  $\text{OH}^-(\text{aq})$  ions will be removed by the reservoir of ammonium ions from the ammonium chloride and the pH will remain almost the same.



**(o) Salt hydrolysis****Candidates should be able to:**

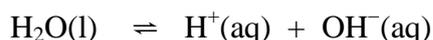
*recall, and explain qualitatively, typical pH values exhibited by solutions of salts of*

*strong acid / strong base (e.g. NaCl)  
strong acid / weak base (e.g. NH<sub>4</sub>Cl) and  
weak acid / strong base (e.g. CH<sub>3</sub>COONa);*

Salt hydrolysis is a term applied to the fact that solutions of some salts are not neutral.

When we have the salt of a strong acid and a strong base e.g. sodium chloride, an aqueous solution has a pH of 7. In solution, the component ions of the salt separate and exist as Na<sup>+</sup>(aq) and Cl<sup>-</sup>(aq).

Water is slightly dissociated



but there is no tendency for the sodium ion or the chloride ion to interact with the ions from water and the pH of the solution is the same as that of water.

On the other hand, a salt of a weak base and a strong acid such as ammonium chloride forms an aqueous solution that is not neutral.

In solution, the component ions of the salt separate and exist as NH<sub>4</sub><sup>+</sup>(aq) and Cl<sup>-</sup>(aq).

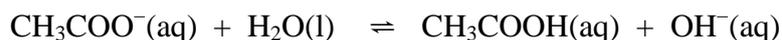
The acidic ammonium ion reacts with a water molecule.



Therefore [H<sup>+</sup>(aq)] > [OH<sup>-</sup>(aq)] and the pH is less than 7 – the solution is acidic.

For the salt of a weak acid and a strong base such as sodium ethanoate, its aqueous solution is alkaline.

The salt exists in aqueous solution as CH<sub>3</sub>COO<sup>-</sup>(aq) and Na<sup>+</sup>(aq).



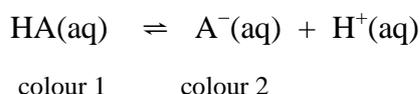
Therefore [OH<sup>-</sup>(aq)] > [H<sup>+</sup>(aq)] and the pH is greater than 7.

**(p) Indicators****Candidates should be able to:**

*understand the working of an indicator and select suitable indicators for specified acid-base titrations, given appropriate pH values.*

Acid-base indicators are weak acids or weak bases that have different forms in acidic and alkaline conditions, the different forms having different colours.

Consider a weak acid, HA, which is an indicator. In water there will be the usual equilibrium set up.



Adding acid pushes the equilibrium to the left and colour 1 predominates. Adding alkali removes  $\text{H}^{\oplus}$ , pushing the equilibrium to the right so that colour 2 predominates.

For litmus, colour 1 is red and colour 2 is blue.

A rough guide concerning the colour observed from a mixture of two species of different colours is that one colour will predominate when the number of particles producing that colour is ten times greater than the number of particles producing the other colour. It follows that an indicator will change colour over about two pH units.

**Some common indicators**

Indicator	pH range	colour in acid	colour in alkali
methyl orange	3.1–4.4	red	yellow
bromophenol blue	3.0–4.6	yellow	blue
methyl red	4.2–6.3	red	yellow
bromothymol blue	6.8–8.4	yellow	blue
phenolphthalein	8.3–10	colourless	red
thymolphthalein	9.3–10.5	colourless	blue

As can be seen from the table above, the approximation of a change in colour over two pH units is a fair one.

**Choosing an indicator**

To find a suitable indicator for a particular titration it is necessary to look at the titration curves.

The pH range of the indicator must lie on the very steep part of the curve where the addition of one drop of acid or alkali causes a significant change in pH value.

For a strong acid titrated with a strong base, most of the indicators above could be used.

For a weak acid titrated with a strong base, the steep portion of the curve lies above pH 7 and so an indicator such as phenolphthalein or thymolphthalein would be suitable.

For a strong acid and a weak base, the steep portion lies in the acidic region and methyl orange or bromophenol blue would be suitable. Methyl red is often chosen for titrations of carbonates with strong acids such as hydrochloric acid.

There are no suitable indicators for weak acid against weak base and another technique must be used.