




# SL IB Chemistry

  
Your notes

## Electron Transfer Reactions

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- \* Oxidation & Reduction
- \* Half Equations
- \* Relative Ease of Oxidation & Reduction
- \* Acids with Reactive Metals
- \* Primary Cells
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- \* Oxidation of Alcohols
- \* Reduction of Carboxylic Acids, Aldehydes & Ketones
- \* Reduction of Unsaturated Compounds



Your notes

## Oxidation & Reduction

### Oxidation & Reduction

#### Oxidising agent

- An **oxidising agent** is a substance that **oxidises** another atom or ion by causing it to lose electrons
- An oxidising agent itself gets **reduced** – **gains electrons**
- Therefore, the **oxidation number** of the oxidising agent **decreases**

#### H<sub>2</sub>O<sub>2</sub> acting as the oxidising agent

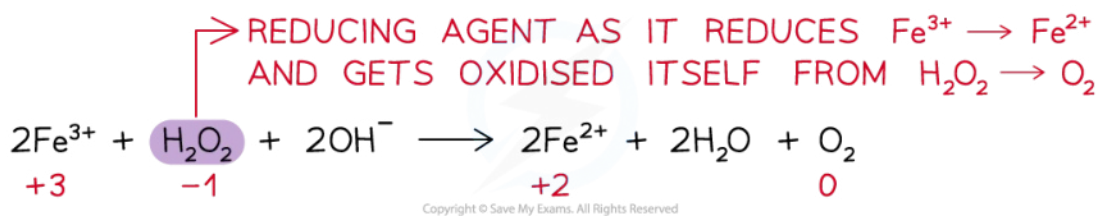


*Example of an oxidising agent in a chemical reaction*

#### Reducing agent

- A **reducing agent** is a substance that **reduces** another atom or ion by causing it to gain electrons
- A reducing agent itself gets **oxidised** – **loses/donates electrons**
- Therefore, the **oxidation number** of the reducing agent **increases**

#### H<sub>2</sub>O<sub>2</sub> acting as a reducing agent



*Example of a reducing agent in a chemical reaction*

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

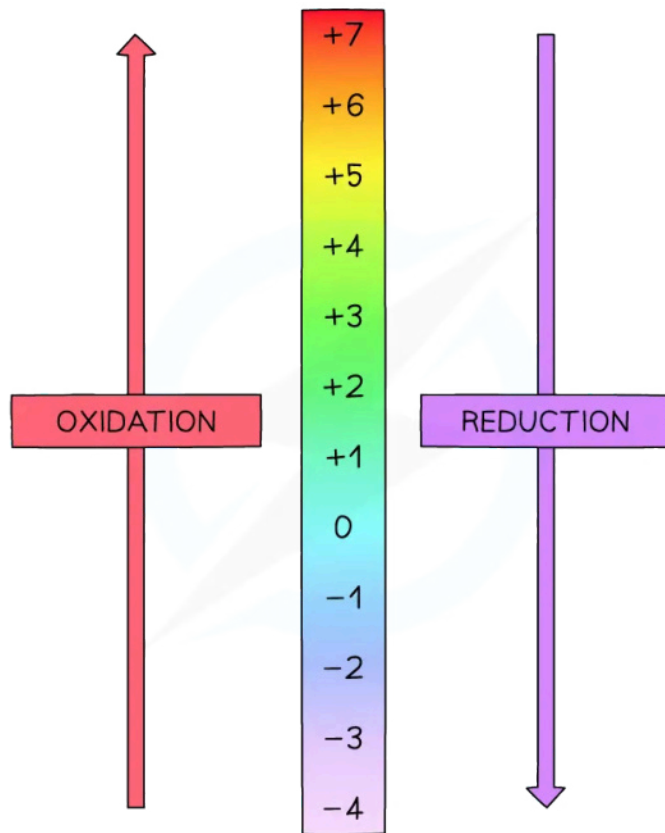
#### Oxidising & Reducing Agents Table

Oxidising agents...	Reducing agents...
---------------------	--------------------

.... oxidise other species	.... reduce other species
.... accept electrons	.... donate electrons
.... are themselves reduced	.... are themselves oxidised

- Applying the definitions of oxidising and reducing agents allows you to identify them in chemical equations
- By deducing the oxidation numbers of the species you can determine whether it has been oxidised or reduced

### Oxidation number of redox line



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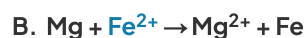
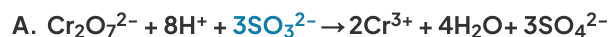
***A visual reminder of oxidation numbers and redox. This is like an elevator in a building going up to higher floors is oxidation and going down to the basement is reduction***



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### Worked example

Four reactions are shown. In which reaction is the species in blue acting as an oxidising agent?



**Answer:**

- The correct option is **B**.
  - Oxidising agents are substances that oxidise other species, gain electrons and are themselves reduced.
  - Write down the oxidation numbers of each species in the reaction



- In equation B,  $\text{Fe}^{2+}$  oxidises  $\text{Mg}(0)$  to  $\text{Mg}^{2+}(+2)$  and is itself reduced from  $\text{Fe}^{2+}(+2)$  to  $\text{Fe}(0)$

### Examiner Tip

- Don't forget:
  - Oxidation is the gain of oxygen or the loss of hydrogen
  - Reduction is the loss of oxygen or the gain of hydrogen
- Using these other definitions can make it quicker / easier to spot which species is being reduced or oxidised

## Half Equations



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## Half Equations

### How to balance a redox equation

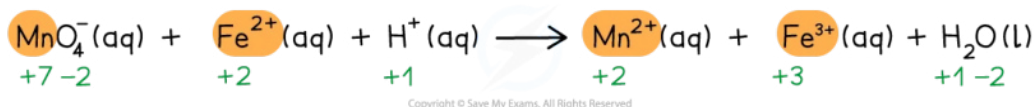
- Oxidation numbers can be used to balance chemical equations
- Go through these steps to balance a redox equation:
  1. **Write the unbalanced equation and identify the atoms which change in ox. no.**
  2. **Deduce the oxidation number changes**
  3. **Balance the oxidation number changes**
  4. **Balance the charges**
  5. **Balance the atoms**

### Worked example

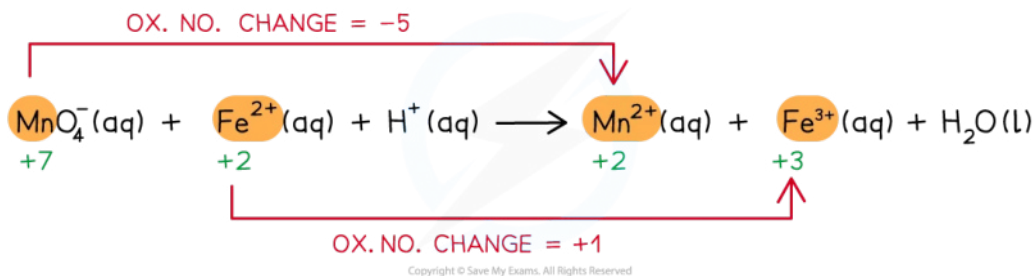
Manganate(VII) ions ( $\text{MnO}_4^-$ ) react with  $\text{Fe}^{2+}$  ions in the presence of acid ( $\text{H}^+$ ) to form  $\text{Mn}^{2+}$  ions,  $\text{Fe}^{3+}$  ions and water. Write the overall redox equation for the reaction

Answer:

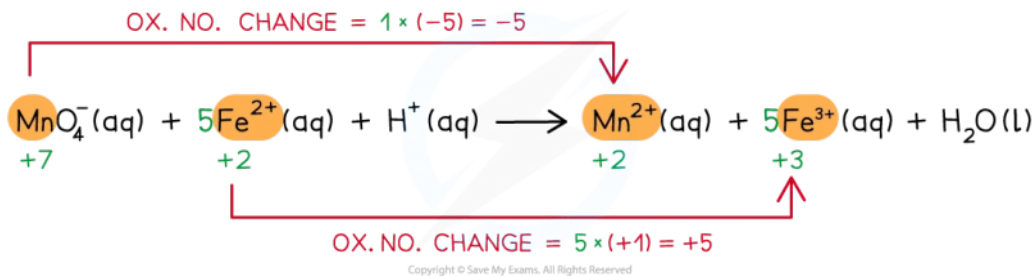
- Write the unbalanced equation and identify the atoms which change in oxidation number



- Deduce the oxidation number changes



- Balance the oxidation number changes



- Balance the charges



IGNORING  $\text{H}^+$

• TOTAL  $\oplus$  CHARGE =  $(5 \times 2+) = 10+$

• TOTAL  $\ominus$  CHARGE =  $1-$

TOTAL CHARGE REACTANTS =  $9+$

• TOTAL  $\oplus$  CHARGE =  $5 \times (3+) + (2+) = 17+$

• TOTAL  $\ominus$  CHARGE =  $0$

TOTAL CHARGE PRODUCTS =  $17+$

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

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5. Balance the atoms



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## Redox titrations

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

### Manganate(VII) titrations

- A redox reaction occurs between acidified manganate(VII) ions and iron(II) ions:
 
$$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{Fe}^{2+} (\text{aq}) \rightarrow \text{Mn}^{2+} (\text{aq}) + 5\text{Fe}^{3+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$$
- This reaction needs no indicator as the manganate(VII) is a strong purple colour which disappears at the endpoint, so the titration is self-indicating
- This reaction is often used for the analysis of iron for example in iron tablets (health supplements)

### Iodine-thiosulfate titrations

- A redox reaction occurs between iodine and thiosulfate ions:
 
$$2\text{S}_2\text{O}_3^{2-} (\text{aq}) + \text{I}_2 (\text{aq}) \rightarrow 2\text{I}^- (\text{aq}) + \text{S}_4\text{O}_6^{2-} (\text{aq})$$
- The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions
- When the solution is a straw colour, **starch** is added to clarify the endpoint
- The solution turns blue/black until all the iodine reacts, at which point the colour disappears.
- This titration can be used to determine the concentration of an **oxidising agent**, which **oxidises** iodide ions to iodine molecules
- The amount of iodine is determined from **titration** against a known quantity of sodium thiosulfate solution
- This reaction can be used for the analysis of chlorine in bleach



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### Worked example

A health supplement tablet containing iron(II)sulfate was analysed by titration. A tablet weighing 2.25 g was dissolved in dilute sulfuric acid and titrated against  $0.100 \text{ mol dm}^{-3} \text{ KMnO}_4$ . The titration required  $26.50 \text{ cm}^3$  for a complete reaction. Calculate the percentage by mass of iron in the table.

#### Answer:

1. Write the balanced equation for the reaction

- oxidation:  $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
- reduction:  $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
- overall:  **$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 5\text{Fe}^{3+}(\text{aq})$**

2. Determine the amount of  $\text{MnO}_4^-$  used in the titration

- moles of  $\text{MnO}_4^- = 0.0265 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = \mathbf{0.00265 \text{ mol}}$

3. Determine the amount of iron in the reaction

- From the equation for the reaction, we know the reacting ratio  $\text{MnO}_4^- : \text{Fe}^{2+} = 1 : 5$
- $\therefore$  moles of  $\text{Fe}^{2+} = 0.00265 \text{ mol MnO}_4^- \times 5 = \mathbf{0.01325 \text{ mol}}$

4. Convert moles into the mass of iron

- Mass of iron =  $0.01325 \text{ mol} \times 55.85 \text{ gmol}^{-1} = \mathbf{0.740 \text{ g}}$

5. Find the percentage of iron in the tablet

- $\therefore$  % Fe in the tablet =  $(0.740 / 2.25) \times 100 = \mathbf{32.9\%}$





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## Relative Ease of Oxidation & Reduction

### Relative Ease of Oxidation & Reduction

- Depending on the position in a group, a metal (in Group 1 or Group 2) will be more or less likely to be oxidised
- When lithium reacts with water hydrogen gas and lithium hydroxide are formed
$$2\text{Li (s)} + 2\text{H}_2\text{O (l)} \rightarrow 2\text{LiOH (aq)} + \text{H}_2 \text{(g)}$$
- Lithium is oxidised from Li to Li<sup>+</sup>
  - The oxidation number changes from 0 to +1
- This reaction is vigorous, though down Group 1 the reaction becomes even more vigorous and violent
- Therefore down the group, the relative ease of oxidation **increases**
- The same pattern also occurs in Group 2
  - For example, magnesium reacts very slowly with water and calcium reacts much more quickly
    - $\text{Mg (s)} + 2\text{H}_2\text{O (l)} \rightarrow \text{Mg(OH)}_2 \text{(s)} + \text{H}_2 \text{(g)}$  = very slow reaction
    - $\text{Ca (s)} + 2\text{H}_2\text{O (l)} \rightarrow \text{Ca(OH)}_2 \text{(s)} + \text{H}_2 \text{(g)}$  = very quick reaction

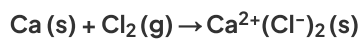


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## Reduction of Halogens

### Oxidising power of the Group 17 elements

- Halogens react with metals by accepting an electron from the metal atom to become an ion with 1- charge



- Halogens are therefore **oxidising agents**:
- Halogens **oxidise** the metal by removing an electron from the metal (the oxidation number of the metal increases)
- Halogens become **reduced** as they gain an extra electron from the metal atom (the oxidation number of the halogen decreases)
- The **oxidising power** of the halogens **decreases** going **down the group** (the halogens get less reactive)

#### The relative oxidising power of the halogens

F <sub>2</sub>	strongest oxidising agent most readily becomes reduced
Cl <sub>2</sub>	↑
Br <sub>2</sub>	
I <sub>2</sub>	weakest oxidising agent least readily becomes reduced

### Reaction of the halogens with halide ions in displacement reactions

- A halogen **displacement** occurs when a **more** reactive halogen displaces a **less** reactive halogen from an aqueous solution of its halide
- The reactivity of Group 17 non-metals increases as you move up the group
- Out of the 3 halogens, chlorine, bromine and iodine, chlorine is the most reactive and iodine is the least reactive

#### Aqueous Solution Colour of Halogens

Aqueous solution	Colour
Chlorine	Very pale green, but usually appears colourless as it is very dilute
Bromine	Orange but will turn yellow when very dilute
Iodine	Brown

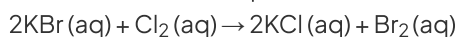


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## Halogen displacement reactions

### Chlorine and bromine

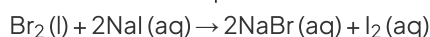
- If you add chlorine solution to colourless potassium bromide solution, the solution becomes orange as bromine is formed
- Chlorine is **above** bromine in Group 17 so it is more reactive
- Chlorine will therefore **displace** bromine from an aqueous solution of a metal bromide



potassium bromide + chlorine → potassium chloride + bromine

### Bromine and iodine

- Bromine is **above** iodine in Group 17 so it is **more** reactive
- Bromine will therefore **displace** iodine from an aqueous solution of a metal iodide



bromine + sodium iodide → sodium bromide + iodine

### Worked example

Which of the statements below are correct?

- I. Potassium chloride solution will react with fluorine to form chlorine.
- II. Sodium chloride solution will react with iodine to form chlorine.
- III. Lithium iodide solution will react with bromine to form iodine.

- A. I and II only
- B. I and III only
- C. II and III only
- D. I, II and III

**Answer:**

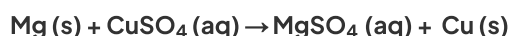
- The correct option is **B**.
  - Fluorine will displace chlorine as it is higher up in the group
  - Bromine will displace iodine for the same reason.
  - Iodine is below chlorine so cannot displace chlorine from sodium chloride



Your notes

## Metal & Metal Ion Reactions

- Metals can be ranked in order of reactivity
  - This is called the **reactivity series** or just **activity series**
- Metals higher in reactivity can **displace** less reactive metals from their compounds in solutions or from their oxides
- An example of a **metal displacement reaction** occurs between magnesium and aqueous copper (II) sulfate solution



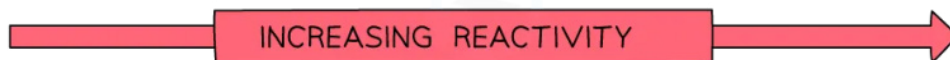
- What are the **redox processes** going on here?
  - If we split the equation into half equations it's easy to see which species is **oxidised** and which is **reduced**:



- The more reactive metal acts as a **reducing agent**
- This allows metals to be ranked from most reactive (**strongest reducing agents**) to least reactive:

### The metal activity series

Pt Au Ag Cu Pb Fe Zn Al Mg Ca Na K



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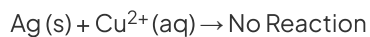
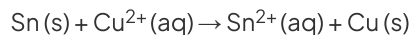
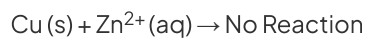
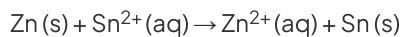
*The more reactive a metal is the better it is at pushing electrons onto less reactive metal ions.  
Magnesium is better at pushing electrons onto copper(II) ions than copper is at pushing electrons onto magnesium ions*



Your notes

### Worked example

What is the order of decreasing reactivity of the metals (most reactive first)?



- A. Zn > Cu > Sn > Ag
- B. Sn > Zn > Ag > Cu
- C. Ag > Cu > Zn > Sn
- D. Zn > Sn > Cu > Ag

#### Answer:

- The correct option is **D**.
  - The first reaction tells you that zinc is more reactive than tin (Zn > Sn):
$$\text{Zn (s)} + \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Sn (s)}$$
  - The second reaction tells you that zinc is more reactive than copper (Zn > Cu):
$$\text{Cu (s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{No Reaction}$$
  - The third reaction tells you that tin is more reactive than copper (Sn > Cu):
$$\text{Sn (s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{Cu (s)}$$
  - The fourth reaction tells you that copper is more reactive than silver (Cu > Ag):
$$\text{Ag (s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{No Reaction}$$



Your notes

## Acids with Reactive Metals

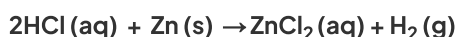
### Acids with Reactive Metals

#### Metals and acids

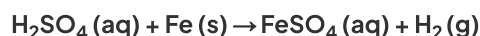
- The typical reaction of a metal and an acid can be summarised as  

$$\text{acid} + \text{metal} \rightarrow \text{salt} + \text{hydrogen}$$

- For example:



hydrochloric acid + zinc → zinc chloride\* + hydrogen



sulfuric acid + iron → iron(II) sulfate\* + hydrogen

\*zinc chloride and iron(II) sulfate are salts

- A salt is an ionic compound formed when the hydrogen of an acid is replaced by a metal or another positive ion
- Clearly, the extent of the reaction depends on the **reactivity** of the metal and the **strength** of the acid
- Very reactive metals would react dangerously with acids and these reactions are not usually carried out
- Metals low in **reactivity** do not react at all
  - For instance, copper does not react with dilute acids
- Stronger acids** will react **more vigorously** with metals than weak acids
- What signs of reaction would be expected to be different between the two?
  - Faster reaction seen as:
    - more effervescence
    - the metal dissolves faster

#### Ionic Equations

- The reactions of acids and metals can be written as ionic equations showing only the species that has changed in the reaction
- Zinc reacts with hydrochloric acid to give a salt and hydrogen
  - Zinc metal is being oxidised to a zinc ion as shown in the table


Full equation	$2\text{HCl}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})$
Ionic equation	$2\text{H}^+(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ $2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + \text{H}_2(\text{g})$



Your notes

Reducing agent	Zn(s) Zn is being oxidised to Zn <sup>2+</sup> (0 to +2)
Oxidising agent	H <sup>+</sup> (aq) in HCl (aq) H <sup>+</sup> is being reduced to H <sub>2</sub> (+1 to 0)

Table to show the relative reducing power of metals

Mg	<b>strongest reducing agent - most readily becomes oxidised</b>
Al	
Zn	
Fe	
Pb	
H	
Cu	
Ag	<b>weakest oxidising agent - least readily becomes oxidised</b>



Your notes

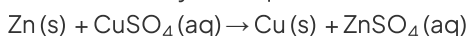
## Primary Cells

### Primary Cells

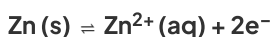
- We have seen previously that **redox** reactions involve simultaneous **oxidation** and **reduction** as electrons flow from the **reducing agent** to the **oxidising agent**
- Which way electrons flow depends on the reactivity of the species involved
- Redox chemistry has very important applications in **electrochemical cells**, which come in two types:
  - Voltaic cells
  - Electrolytic cells

### Voltaic cells

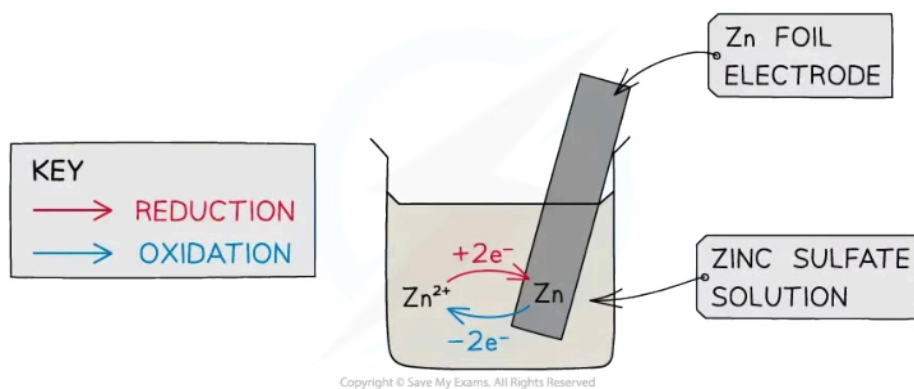
- A **voltaic cell** generates a potential difference known as an **electromotive force** or **EMF**
- The EMF is also called the **cell potential** and is given the symbol **E**
- The absolute value of a cell potential cannot be determined only the difference between one cell and another
  - This is analogous to arm-wrestling; you cannot determine the strength of an arm-wrestler unless you compare them to the other competitors
- Voltaic (or Galvanic) cells generate electricity from spontaneous redox reactions, e.g.



- Instead of electrons being transferred directly from the zinc to the copper ions, a cell is built which separates the two redox processes
- Each part of the cell is called a **half-cell**
- If a rod of metal is dipped into a solution of its own ions, an equilibrium is set up
  - For example



#### Zinc metal in a solution of zinc sulfate



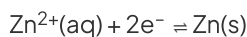
**When a metal is dipped into a solution containing its ions, an equilibrium is established between the metal and its ions**





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- This is a **half-cell** and the strip of metal is an **electrode**
- The position of the equilibrium determines the **potential difference** between the metal strip and the solution of metal
- The Zn atoms on the rod can deposit two electrons on the rod and move into solution as  $\text{Zn}^{2+}$  ions:  
$$\text{Zn(s)} = \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$$
  - This process would result in an accumulation of negative charge on the zinc rod
- Alternatively, the  $\text{Zn}^{2+}$  ions in solution could accept two electrons from the rod and move onto the rod to become Zn atoms:



- This process would result in an accumulation of positive charge on the zinc rod
- In both cases, a potential difference is set up between the rod and the solution
  - This is known as an electrode potential
- A similar electrode potential is set up if a copper rod is immersed in a solution containing copper ions (eg  $\text{CuSO}_4$ ), due to the following processes:

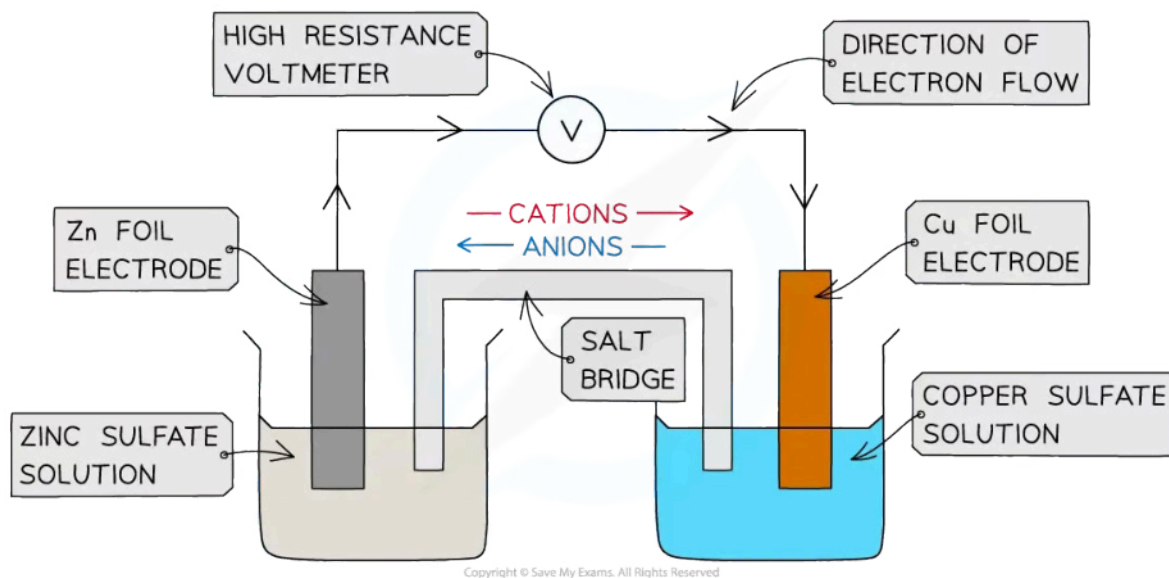


- Note that a chemical reaction is not taking place – there is simply a potential difference between the rod and the solution

## Creating an EMF

- If two different electrodes are connected, the potential difference between the two electrodes will cause a current to flow between them
- Thus an **electromotive force (EMF)** is established and the system can generate electrical energy
- A typical electrochemical cell can be made by combining a zinc electrode in a solution of zinc sulfate with a copper electrode in a solution of copper sulfate

### Electrochemical cell



**The zinc-copper voltaic cell (also known as the Daniell Cell)**

- The circuit must be completed by allowing ions to flow from one solution to the other
- This is achieved by means of a **salt bridge**
  - This is often a piece of filter paper saturated with a solution of an **inert electrolyte** such as  $\text{KNO}_3(\text{aq})$
- The EMF can be measured using a **voltmeter**
  - Voltmeters have a high resistance so that they do not divert much current from the main circuit
- The two half cells are said to be *in series* as the same current is flowing through both cells
- The combination of two electrodes in this way is known as a voltaic cell and can be used to generate electricity

## Conventional Representation of Cells

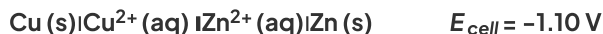
- Chemists use a type of shorthand convention to represent electrochemical cells
- In this convention:
  - A solid vertical (or slanted) line shows a **phase boundary**, which is an interface between a solid and a solution
  - A double vertical line (sometimes shown as dashed vertical lines) represents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





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



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

### Worked example

#### Writing a cell diagram

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

#### Answer:

- $\text{Al (s)} \mid \text{Al}^{3+} \text{ (aq)} \parallel \text{Zn}^{2+} \text{ (aq)} \mid \text{Zn (s)} \quad E_{\text{cell}} = +0.94 \text{ V}$
- It is also acceptable to include phase boundaries on the outside of cells as well:
- $\mid \text{Al (s)} \mid \text{Al}^{3+} \text{ (aq)} \parallel \text{Zn}^{2+} \text{ (aq)} \mid \text{Zn (s)} \mid \quad E_{\text{cell}} = +0.94 \text{ V}$

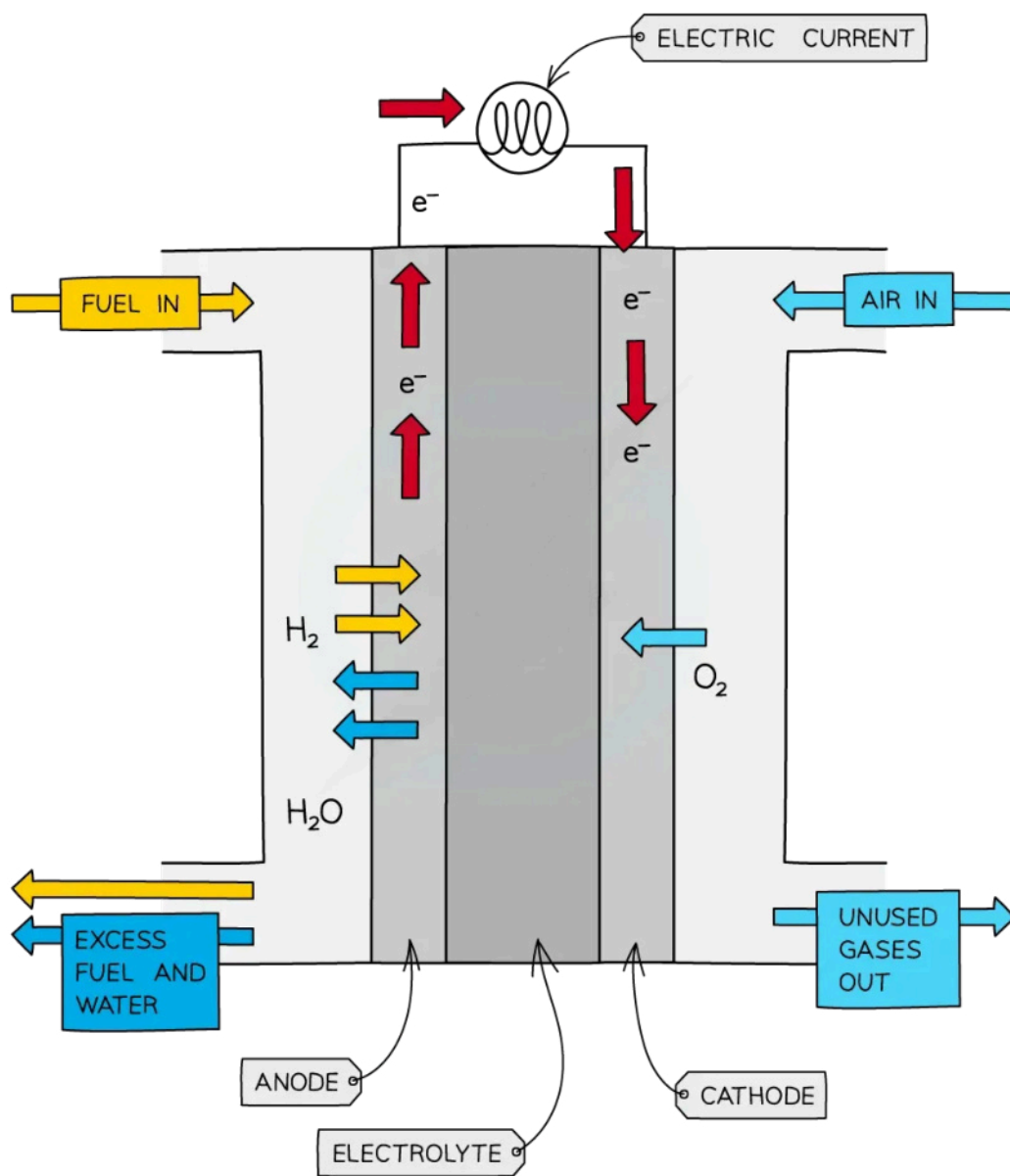
### Examiner Tip

- Students often confuse the redox processes that take place in electrochemical cells
  - Oxidation takes place at the negative electrode
  - Reduction takes place at the positive electrode
- Remember, oxidation is the loss of electrons, so you are losing electrons at the negative
- $\mid \text{Al (s)} \mid \text{Al}^{3+} \text{ (aq)} \parallel \text{Zn}^{2+} \text{ (aq)} \mid \text{Zn (s)} \mid \quad E_{\text{cell}} = +0.94 \text{ V}$

## Fuel cells

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

### The hydrogen-oxygen fuel cell



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***A hydrogen-oxygen fuel cell combines both elements to release energy and water***

- The fuel cell consists of
  - A reaction chamber with separate inlets for hydrogen and oxygen gas
  - An outlet for the product - water
  - An electrolyte of aqueous sodium hydroxide

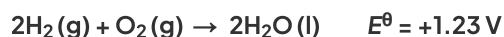


Your notes

- A semi-permeable membrane that separates the hydrogen and oxygen gases
- The half equations are



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



## Benefits of fuel cells

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

## Risks and problems of fuel cells

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

### Examiner Tip

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



Your notes

## Redox in Voltaic Cells

- Electrochemical cells can be either **voltaic** (galvanic) or **electrolytic** cells
  - Voltaic cells generate electricity from chemical reactions
    - This is a spontaneous reaction which drives electrons around a circuit
  - Electrolytic cells drive chemical reactions using electrical energy
    - An electric current reverses the normal directions of chemical change and this is non-spontaneous
    - Stable compounds such as sodium chloride or lead bromide can be broken down into their elements
- Oxidation takes place at the anode and reduction will occur at the cathode
  - Depending on the type of cell, the polarity changes
    - In voltaic cells the anode is negative
    - In electrolytic cells the anode is positive

**Comparing Voltaic & Electrolytic Cells Summary Table**

	Negative	Positive
Voltaic cell	anode	cathode
	oxidation	reduction
Electrolytic cell	cathode	anode
	reduction	oxidation

### Examiner Tip

- Students often confuse the redox processes that take place in voltaic cells and electrolytic cells
- An easy way to remember is the phrase **RED CAT**:
  - **RED**uction takes place at the **CAT**hode!



Your notes

## Secondary Cells

### Secondary Cells

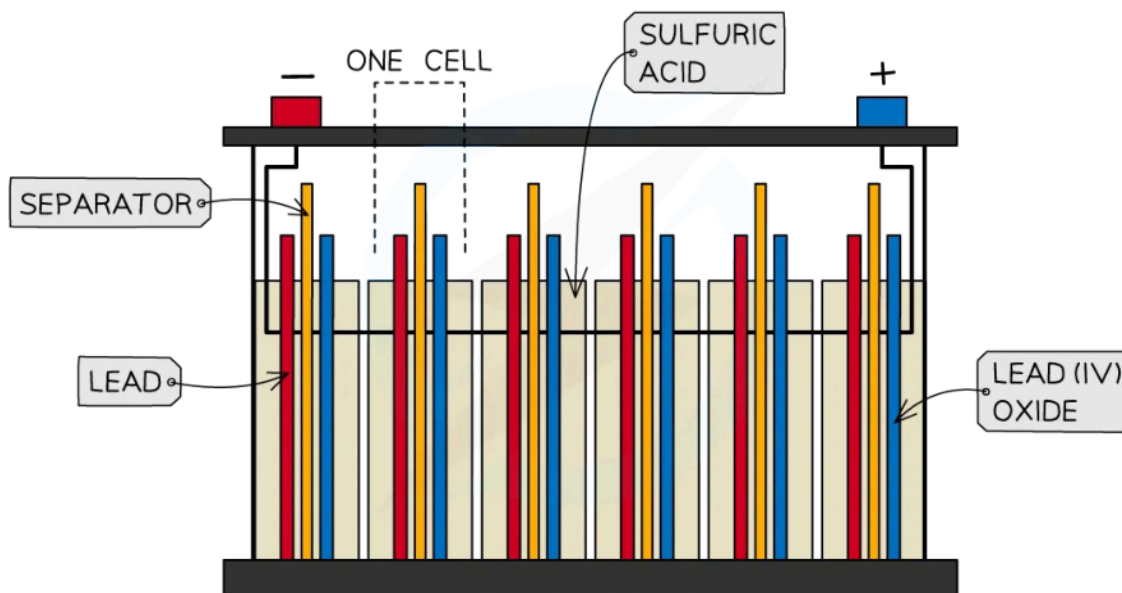
#### Secondary Cells

- Secondary / rechargeable cells employ chemical reactions which can be reversed by applying a voltage greater than the cell voltage, causing electrons to push in the opposite direction
- There are many types of rechargeable cells, but common ones include:
  - Lead-acid batteries,
  - Nickel-cadmium / NiCad cells
  - Lithium cells

#### Lead-acid batteries

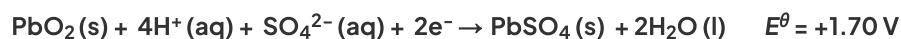
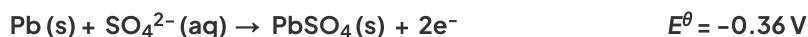
- Lead-acid batteries consist of **six cells** joined together **in series**
- The cells use **lead** metal as the **negative electrode** and **lead(IV) oxide** as the **positive electrode**
- The electrolyte is sulfuric acid

A lead-acid battery



**A lead acid battery is made by placing negative lead and positive lead dioxide electrodes into the sulfuric acid electrolyte**

- The half-cell reactions are



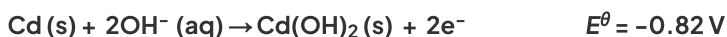


Your notes

- The cell generates an EMF of about 2 V and the overall reaction is
 
$$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) + \text{Pb}(\text{s}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \quad E^\theta_{\text{cell}} = +2.06 \text{ V}$$
- In a commercial car battery, the six cells in series give a combined voltage of about 12 V
  - When the car is in motion, the generator provides a push of electrons that reverses the reaction and regenerates lead and lead(IV) oxide
- Lead-acid batteries are designed to produce a **high current** for a short period of time, hence their use in powering a starter motor in car engines
- The disadvantage of lead-acid batteries is that:
  - They are very **heavy**
  - They contain **toxic** materials: lead and lead(IV) oxide
  - The sulfuric acid electrolyte is very **corrosive**
- This presents challenges of disposal when lead-acid batteries come to the end of their useful life

## NiCad cells

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



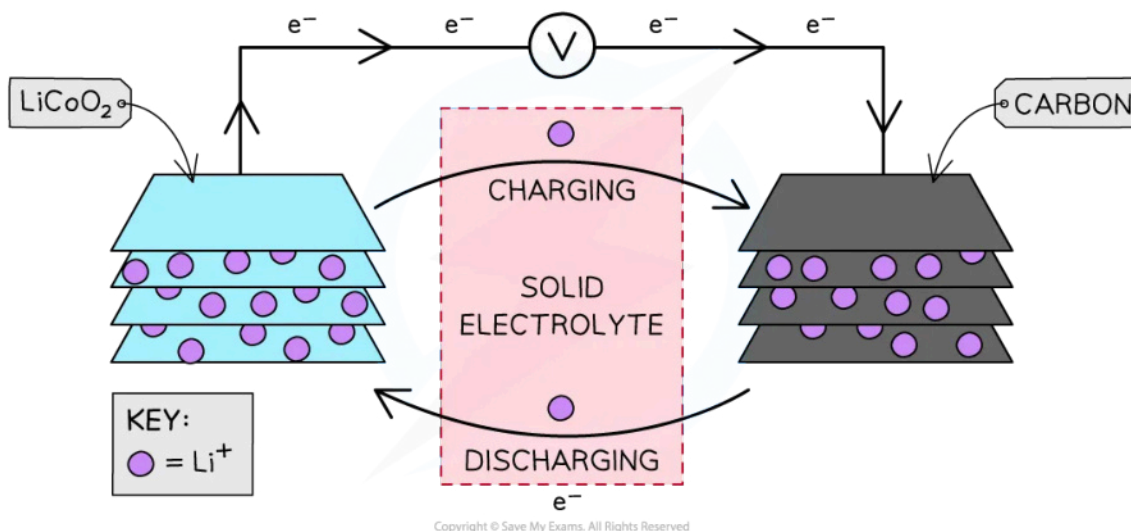
- The overall reaction in the cell is
 
$$2\text{NiO}(\text{OH})(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{Cd}(\text{s}) \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s}) \quad E^\theta = +1.2 \text{ V}$$
- Cadmium is a toxic metal so the disposal of old NiCad cells is also an environmental issue

## Lithium-ion cell

- Lithium ion cells power the laptop or mobile device you are probably reading this on
- The Noble Prize for Chemistry in 2019 was awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino for their work on lithium ion cells that have revolutionised portable electronics
- Lithium is used because it has a very low density and relatively high electrode potential
- The cell consists of:
  - A positive lithium cobalt oxide electrode
  - A negative carbon electrode
  - A porous polymer membrane electrolyte
- The polymer electrolyte cannot leak since it is not a liquid or paste, which presents advantages over other types of cells

### Lithium-ion cell





The lithium-ion cell consists of a positive lithium cobalt oxide electrode and a negative carbon electrode

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



- The cell generates an EMF of between 3.5 V and 4.0 V and the overall reaction is
- $$\text{Li (s)} + \text{CoO}_2 \text{ (s)} \rightarrow \text{Li}^+ \text{ (CoO}_2\text{)}^- \text{ (s)} \quad E^\theta_{\text{cell}} \sim +3.5$$
- NiCad cells have a problem called the memory effect in which they gradually begin to lose their charge after repeated charge cycles when the cell is not fully discharged. The cells appear to 'remember' their lower state of charge
  - Lithium-ion cells do not have this problem so can be topped up without any loss of charge
  - Some of the problems with lithium-ion cells:
    - A global shortage of lithium is likely to make lithium-ion cells unsustainable as the current demand for lithium exceeds the supply
    - If cells are not recycled but thrown away in landfills, then a huge amount of lithium becomes lost to future generations
    - Reports of lithium-ion cell fires have raised concern about the safety of these batteries in electronic devices; it is a reminder to us that lithium is a very reactive element in Group 1 of the periodic table, which is why it has a high electrode potential

### Summary of primary and secondary cells



Your notes

Type of cell		Advantages	Disadvantages
Primary	General	Inexpensive Lightweight Long shelf life	Single-use which increases landfill and causes environmental impacts Only delivers small currents
	Fuel cell	Reduced pollution if hydrogen used as fuel Hydrogen has a low density More efficient than combustion as more chemical energy converted to electrical energy	Safety issues with hydrogen gas Hydrogen must be transported using heavy containers Expensive Only delivers small currents Technical issues due to catalytic failures, leaks and corrosion
Rechargeable / secondary	General	Materials can be regenerated Can deliver high current	
	Lead-acid	Can deliver large amounts of energy over short periods	Heavy mass Lead and sulfuric acid could cause pollution
	Cadmium-nickel	Longer life than lead-acid batteries	Cadmium is very toxic Produces a low voltage Expensive
	Lithium-ion	Low density of lithium No toxic heavy metals High voltage	Limited life span Expensive

## Electrolytic Cells



Your notes

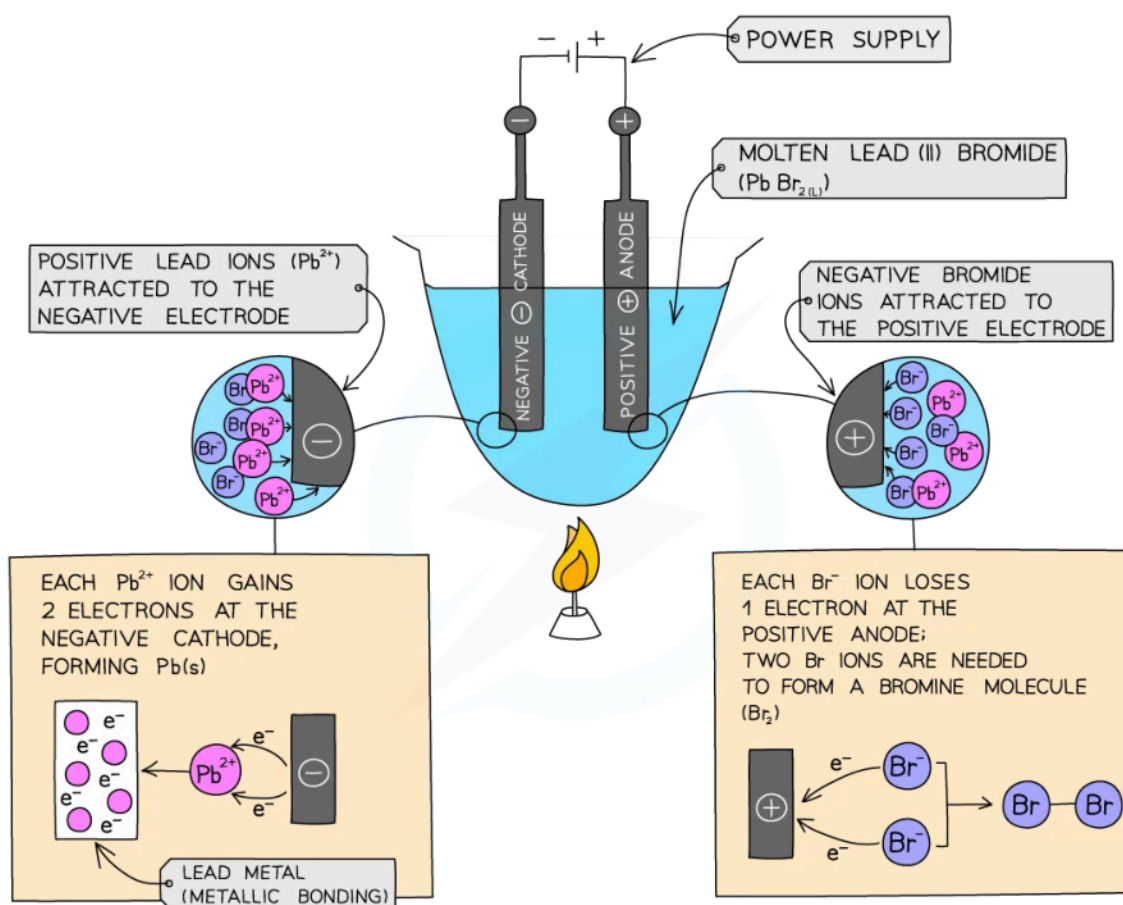
### Electrolytic Cells

- An ionic compound conducts electricity when it is molten or in solution
- The current causes the ionic compound to split up and form new substances.
- This process is called **electrolysis**, a word which comes from Greek and means “splitting by electricity”
- **Electrolysis** has many uses, including:
  - Purifying copper
  - Plating metals with silver and gold
  - Extracting reactive metals, such as aluminium
  - Making chlorine, hydrogen and sodium hydroxide

### Electrolytic cells

- Electrolytic cells can be constructed using a beaker or crucible as the cell depending on whether the ionic compound is in solution or molten

#### Lead bromide electrolytic cell



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**Electrolysis of a binary ionic compound, when molten, produces the component elements**

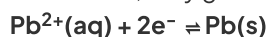
- In electrolysis, the substance that the current passes through and splits up is called the **electrolyte**
- The electrolyte contains positive and negative ions

**What happens to the ions during electrolysis?**

- **Negative ions** move to the **anode** and lose electrons - this is **oxidation**
- **Positive ions** move to the **cathode** and gain electrons - this is **reduction**
- Electrically neutral atoms or molecules are released

**Electrolysis of molten lead bromide**

- The reactions which take place at the electrodes can be shown by half equations
- When the positive lead ions move to the **cathode**, they gain electrons in a **reduction** reaction:



- Similarly, when the negative bromide ions move to the **anode** they lose electrons in an **oxidation** reaction:



- Sometimes oxidation reactions are written with '+2e<sup>-</sup>' on the right of the arrow instead of '-2e<sup>-</sup>' on the left
- In this case, the alternative half equation is:



- Since metals are always **cations** and non-metal **anions**, it is easy to predict the products of electrolysis of molten salts:
  - **Metals** will always be formed at the **cathode** and **non-metals** at the **anode**



Your notes



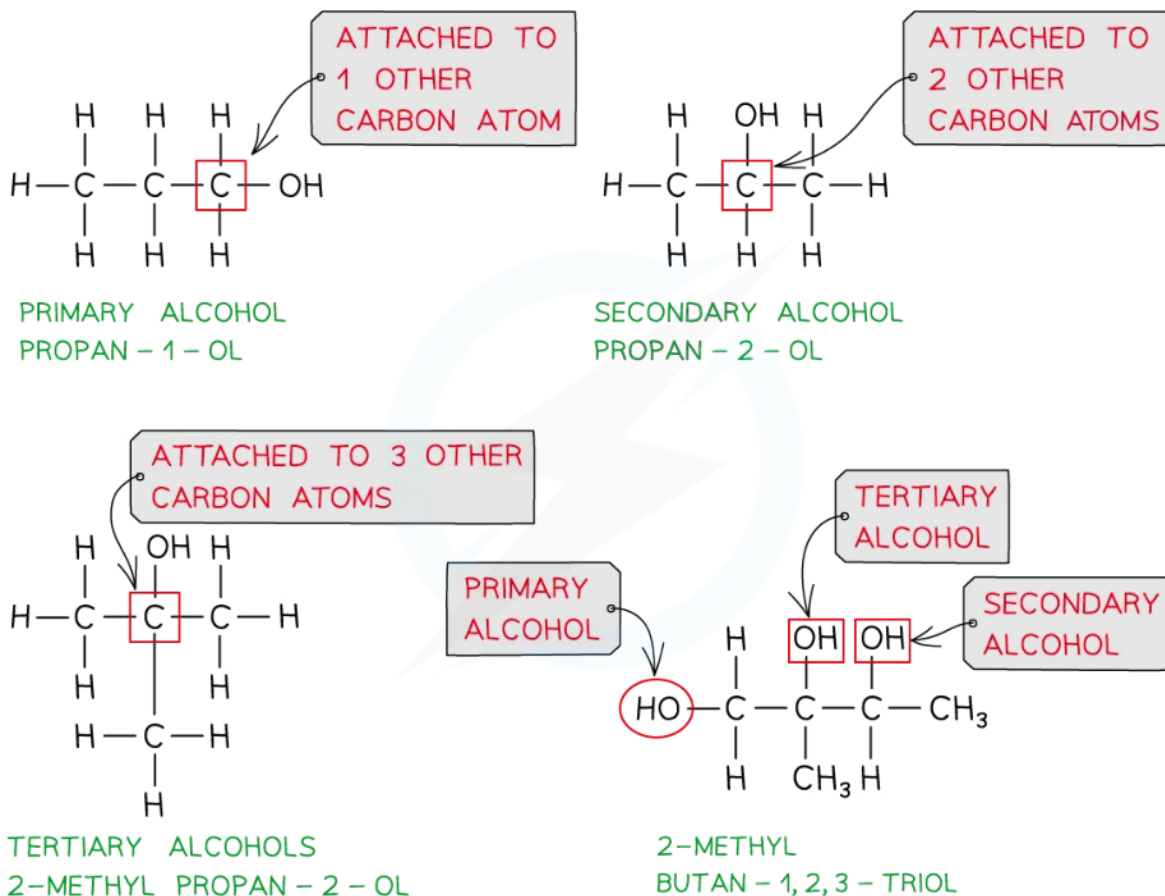
Your notes

## Oxidation of Alcohols

### Oxidation of Alcohols

- The products of oxidation of **alcohols** depends on the class of **alcohols**
- Here is a reminder of the three classes of alcohols:

#### The three classes of alcohols



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### Classification of primary, secondary and tertiary alcohols

#### Primary alcohols

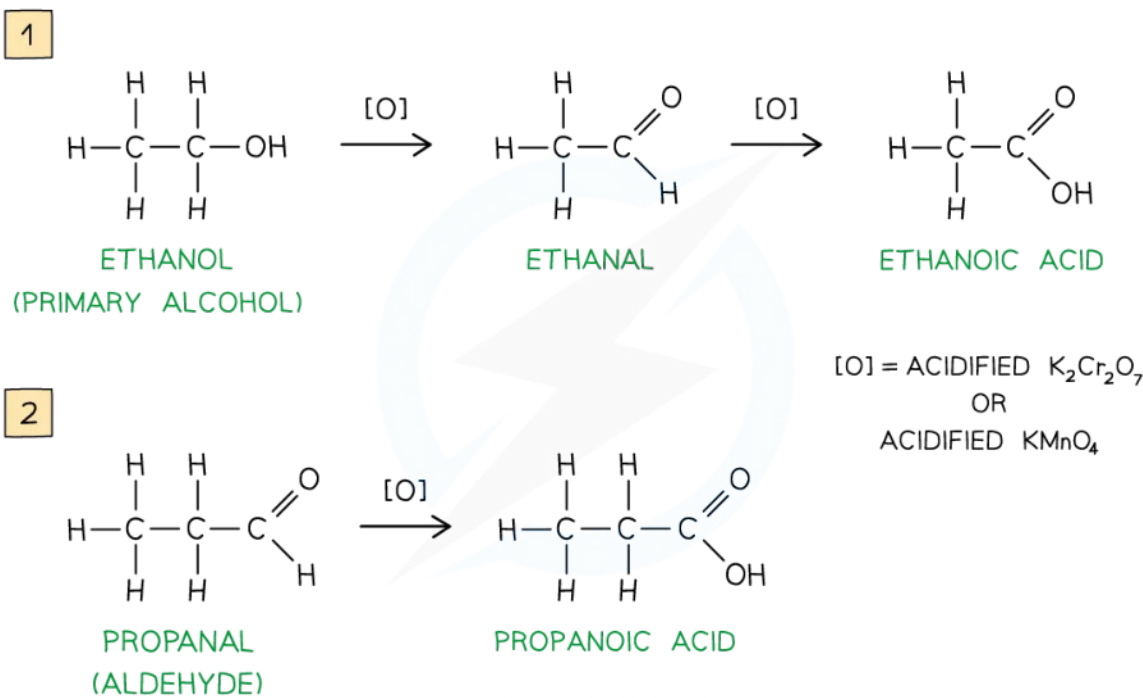
- Primary alcohols** can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- The oxidising agents of alcohols include **acidified  $K_2Cr_2O_7$**  or **acidified  $KMnO_4$**
- Acidified potassium dichromate(VI)**,  $K_2Cr_2O_7$ , is an orange oxidising agent



Your notes

- Acidified means that the potassium dichromate(VI) is in a solution of **dilute acid** (such as dilute sulfuric acid)
- For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
  - When alcohols are **oxidised** the orange dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) are reduced to green  $\text{Cr}^{3+}$  ions
- Acidified potassium manganate(VII)**,  $\text{KMnO}_4$ , is a purple oxidising agent
  - As with acidified  $\text{KMnO}_4$ , the potassium manganate(VII) is in an acidic medium to allow the reduction of potassium manganate(VII) to take place
    - When alcohols are **oxidised**, the purple manganate ions ( $\text{MnO}_4^-$ ) are reduced to colourless  $\text{Mn}^{2+}$  ions

### Diagram to show the oxidation of of primary alcohols



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*A primary alcohol can be oxidised to an aldehyde and then carboxylic acid*

### Further Oxidation

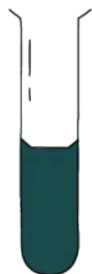
- If the **aldehyde** is not distilled off, further oxidation with **excess** oxidising agent will oxidise it to a **carboxylic acid**
- The reaction takes some time to complete and requires sustained heating

### Test for alcohols

- The oxidation using **acidified potassium dichromate(VI)** provides the basis for the test for **alcohols** as the reaction gives a strong colour change from **orange to green**

- Unfortunately, it does not work for tertiary alcohols, which cannot be oxidised

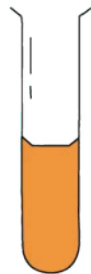
### The test for primary and secondary alcohols



PROPAN-1-OL  
(PRIMARY ALCOHOL)



PROPAN-2-OL  
(SECONDARY ALCOHOL)



2-METHYL-PROPAN-2-OL  
(TERTIARY ALCOHOL)

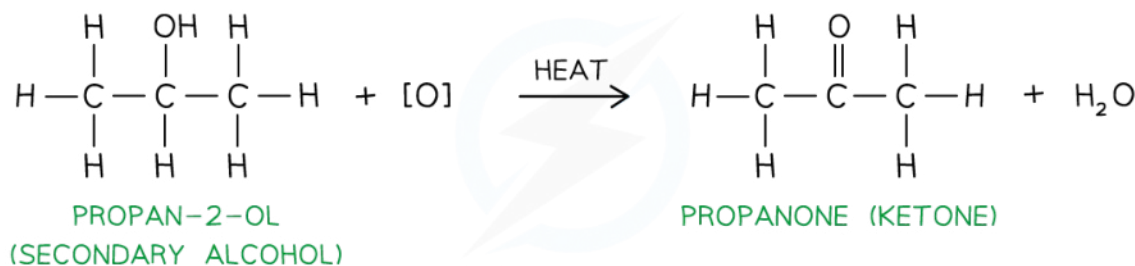
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**When primary, secondary and tertiary alcohols are reacted with acidified potassium dichromate(VI), primary and secondary alcohols cause a colour change from orange to green. There is no reaction with tertiary alcohols so the colour remains orange**

### Oxidation of Secondary Alcohols

- Secondary alcohols can be oxidised to form ketones only
- To get a good yield of the ketone the reaction requires some sustained heating

#### Oxidation of secondary alcohols



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#### Secondary alcohols oxidise to form ketones

- Tertiary alcohols do not undergo oxidation
  - This is because there must be a hydrogen on the functional group carbon, which breaks off to form water
  - There are only C-C bonds on the functional group carbon in a tertiary alcohol

### Distillation & Reflux

#### Distillation



Your notes

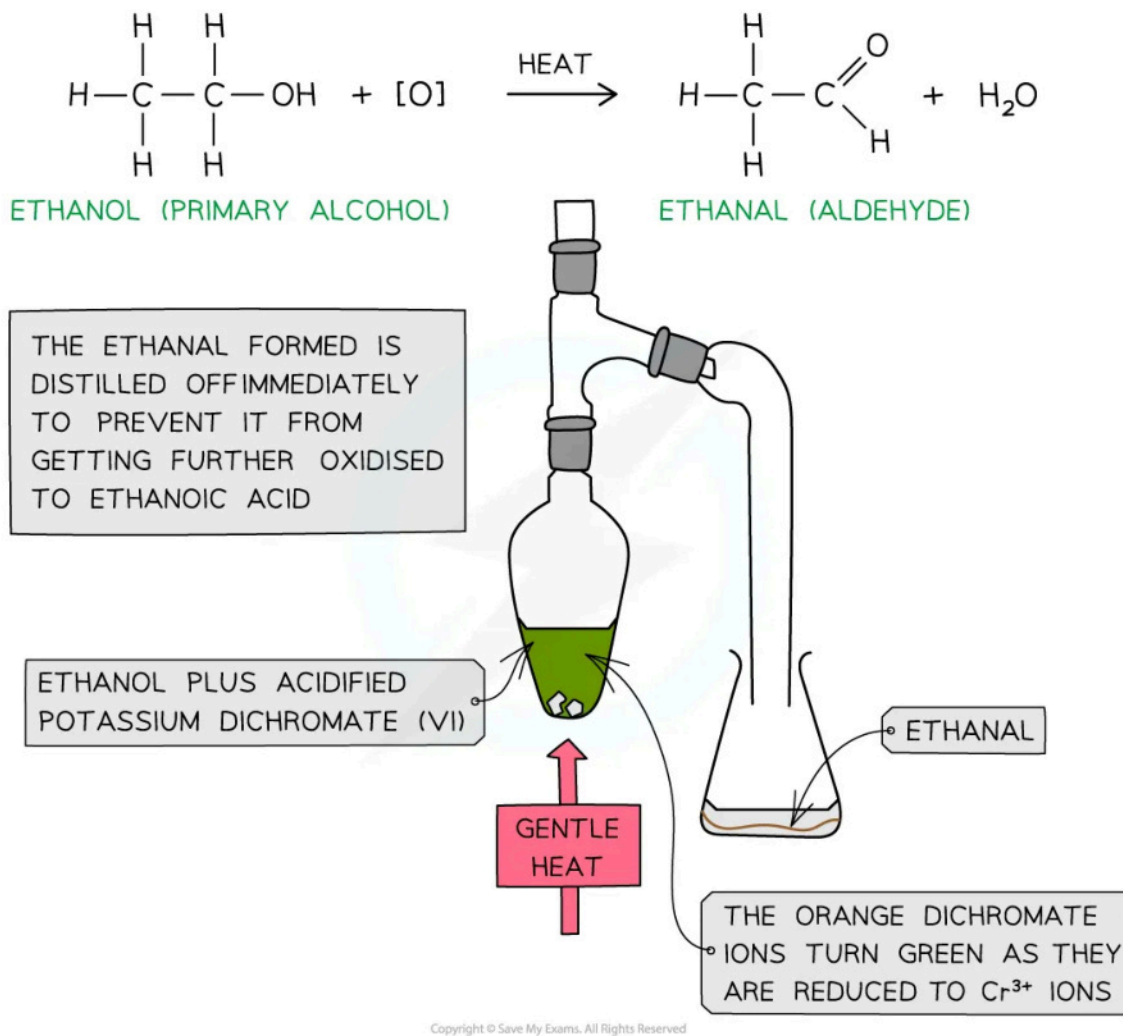




Your notes

- To produce an aldehyde from a primary alcohol the reaction mixture must be heated
- The **aldehyde** product has a lower boiling point than the **alcohol** (since it has lost the **H-bonding**) so it can be **distilled off** as soon as it forms
- **Distillation** can be carried out using a simple side arm arrangement which acts as an air condenser or the vapours can be made to pass through a condenser

### Diagram of distillation apparatus



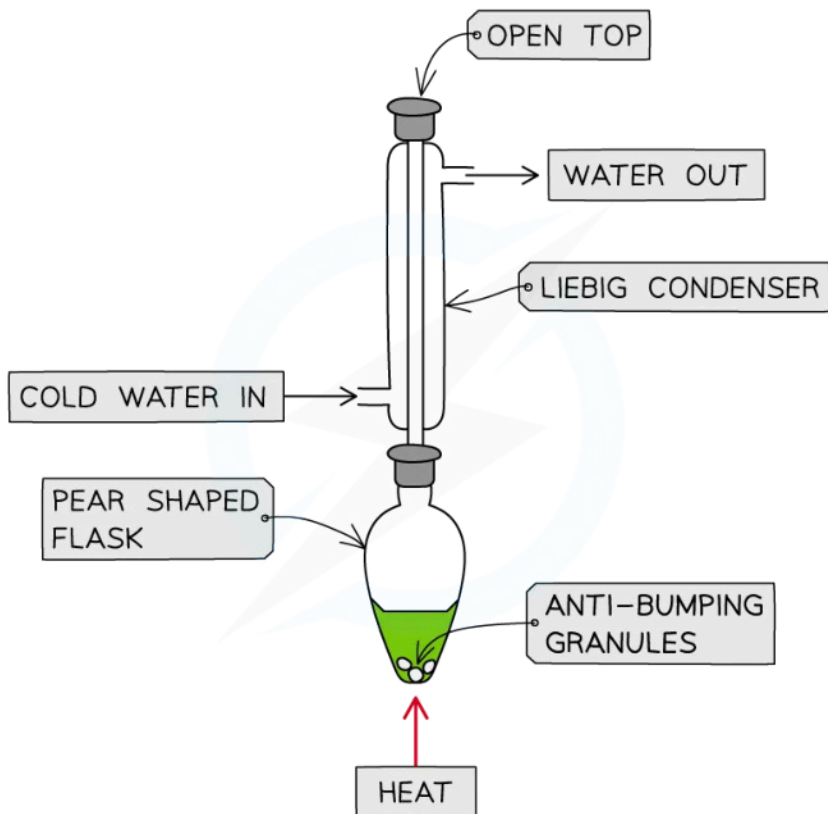
### Oxidation of ethanol by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form an aldehyde by distillation

#### Heating under reflux

- For reactions that require sustained heating the apparatus has to be modified

- To prevent loss of volatile reactants the apparatus includes a condenser in the vertical position which returns components back into the reaction flask
- This is known as **heating under reflux** (reflux means re-boiling)

**Diagram of reflux apparatus**



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*Heating under reflux requires the condenser to be set up vertically*



Your notes



Your notes

## Reduction of Carboxylic Acids, Aldehydes & Ketones

### Reduction of Carboxylic Acids, Aldehydes & Ketones

#### Carbonyl compounds

- Alcohols can be oxidised to carbonyl compounds in the presence of a suitable oxidising agent
  - Primary alcohol → aldehyde → carboxylic acid
  - Secondary alcohol → ketone
  - Tertiary alcohol - no reaction
- These reactions can be reversed in the presence of a suitable reducing agent
  - Carboxylic acid → aldehyde → primary alcohol
  - Ketone → secondary alcohol
- The two most common reducing agents for carbonyl compounds are:
  - Lithium aluminium hydride,  $\text{LiAlH}_4$ , in anhydrous conditions, commonly dry ether, followed by the addition of aqueous acid
    - This is the stronger of these reducing agents and can reduce carboxylic acids
  - Sodium borohydride,  $\text{NaBH}_4$ , in aqueous or alcoholic solutions
    - This is the less hazardous of these reducing agents but it cannot reduce carboxylic acids
  - Both of these reagents produce the nucleophilic hydride ion,  $\text{H}^-$

#### Examiner Tip

- You can be expected to know typical conditions and reagents of all reactions, e.g. catalysts, reducing agents, reflux, etc
- However, you do not need to know more precise details such as specific temperatures

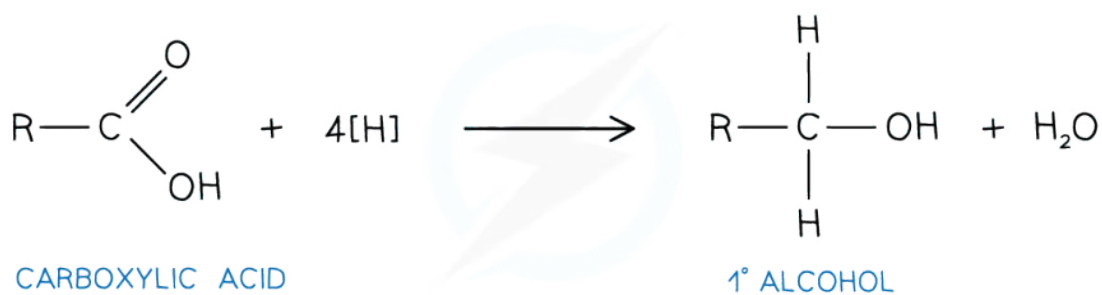
#### Reduction Reactions

- Equations for reduction reactions can be written using  $[\text{H}]$  to represent the reducing agent

#### Carboxylic acids

- Carboxylic acids are reduced to primary alcohols
  - This requires heating with  $\text{LiAlH}_4$  under reflux in dry ether followed by dilute acid
  - Remember that  $\text{NaBH}_4$  cannot reduce carboxylic acids

#### Reduction of a carboxylic acid



*Carboxylic acids are reduced to primary alcohols with  $\text{LiAlH}_4$*

## Aldehydes

- Aldehydes are reduced to primary alcohols
  - This can be with  $\text{LiAlH}_4$  or  $\text{NaBH}_4$

### Reduction of an aldehyde



*Aldehydes are reduced to primary alcohols with  $\text{LiAlH}_4$  or  $\text{NaBH}_4$*

## Ketones

- Ketones are reduced to secondary alcohols
  - This can be with  $\text{LiAlH}_4$  or  $\text{NaBH}_4$

### Reduction of a ketone



*Ketones are reduced to secondary alcohols with  $\text{LiAlH}_4$  or  $\text{NaBH}_4$*

 **Examiner Tip**

- Take care if you are asked about the formation of an aldehyde from a carboxylic acid
  - You have to use  $\text{LiAlH}_4$  refluxed in dry ether, followed by dilute acid
  - This reaction cannot be stopped at the aldehyde because the  $\text{LiAlH}_4$  is too powerful
- To form an aldehyde from a carboxylic acid, you have to reduce the carboxylic acid down to a primary alcohol and then oxidise it back up to the aldehyde



Your notes



Your notes

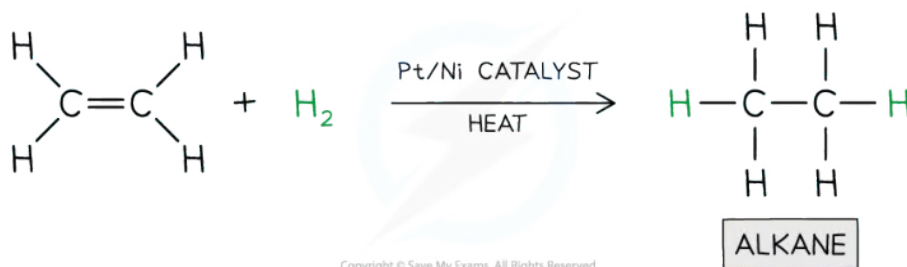
## Reduction of Unsaturated Compounds

### Reduction of Unsaturated Compounds

#### Reduction of alkenes

- Alkenes are very useful compounds as they can undergo many types of reactions
- They can therefore be used as starting molecules when making new compounds
- The reaction between an **alkene** and hydrogen is known as **hydrogenation** or **reduction**
- As well as a **nickel catalyst**, this requires a temperature of 200 °C and a pressure of 1000 kPa

#### The reduction of ethene to ethane

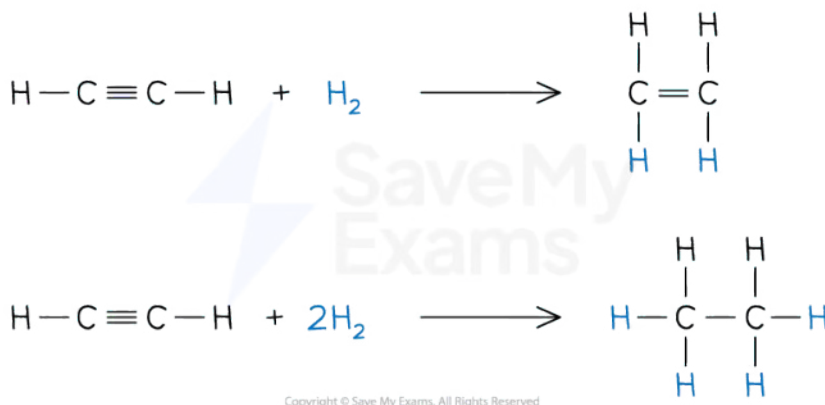


*Catalytic hydrogenation converts alkenes into useful alkanes*

#### Reduction of alkynes

- Similarly, alkynes,  $\text{C}_n\text{H}_{2n-2}$ , can be reduced to alkenes,  $\text{C}_n\text{H}_{2n}$ , and alkanes,  $\text{C}_n\text{H}_{2n+2}$
- The number of molecules of hydrogen needed to convert the organic molecule to the corresponding saturated molecule is related to the number of multiple bonds in the molecule.

#### Reduction of alkynes to alkenes and alkanes



*Alkenes require one molecule of hydrogen to be converted to an alkane. Alkynes require two molecules of hydrogen to be converted to an alkane*

- One important application of this reaction is in the production of margarine from vegetable oils
- Vegetable oils are **unsaturated** and may be **hydrogenated** to make margarine, which has a higher melting point due to stronger **London Dispersion Forces**
- By controlling the conditions it is possible to restrict how many of the C=C bonds are broken and produce **partially hydrogenated vegetable oils** which have the desired properties and textures for margarine manufacture



Your notes