

Redox SL

Answers

IB CHEMISTRY SL

<div>25</div> <div>Mn</div> <div>Manganese 54.938045</div>	<div>16</div> <div>S</div> <div>Sulfur 32.065</div>	<div></div> <div>J</div> <div></div>	<div>6</div> <div>C</div> <div>Carbon 12.0107</div>	<div>2</div> <div>He</div> <div>Helium 4.002602</div>	<div>25</div> <div>Mn</div> <div>Manganese 54.938045</div>
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9.1 Oxidation and reduction

Understandings:

- Oxidation and reduction can be considered in terms of oxygen gain/hydrogen loss, electron transfer or change in oxidation number.
- An oxidizing agent is reduced and a reducing agent is oxidized.
- Variable oxidation numbers exist for transition metals and for most main-group non-metals.
- The activity series ranks metals according to the ease with which they undergo oxidation.
- The Winkler Method can be used to measure biochemical oxygen demand (BOD), used as a measure of the degree of pollution in a water sample.

Applications and skills:

- Deduction of the oxidation states of an atom in an ion or a compound.
- Deduction of the name of a transition metal compound from a given formula, applying oxidation numbers represented by Roman numerals.
- Identification of the species oxidized and reduced and the oxidizing and reducing agents, in redox reactions.
- Deduction of redox reactions using half-equations in acidic or neutral solutions.
- Deduction of the feasibility of a redox reaction from the activity series or reaction data.
- Solution of a range of redox titration problems.
- Application of the Winkler Method to calculate BOD.

Guidance:

- Oxidation number and oxidation state are often used interchangeably, though IUPAC does formally distinguish between the two terms. Oxidation numbers are represented by Roman numerals according to IUPAC.
- Oxidation states should be represented with the sign given before the number, eg +2 not 2+.
- The oxidation state of hydrogen in metal hydrides (-1) and oxygen in peroxides (-1) should be covered.
- A simple activity series is given in the data booklet in section 25.

9.2 Electrochemical cells

Understandings:

- Voltaic (Galvanic) cells:
- Voltaic cells convert energy from spontaneous, exothermic chemical processes to electrical energy.
- Oxidation occurs at the anode (negative electrode) and reduction occurs at the cathode (positive electrode) in a voltaic cell.
- Electrolytic cells:
- Electrolytic cells convert electrical energy to chemical energy, by bringing about non-spontaneous processes.
- Oxidation occurs at the anode (positive electrode) and reduction occurs at the cathode (negative electrode) in an electrolytic cell.

Applications and skills:

- Construction and annotation of both types of electrochemical cells.
- Explanation of how a redox reaction is used to produce electricity in a voltaic cell and how current is conducted in an electrolytic cell.
- Distinction between electron and ion flow in both electrochemical cells.
- Performance of laboratory experiments involving a typical voltaic cell using two metal/metal-ion half-cells.
- Deduction of the products of the electrolysis of a molten salt.

Guidance:

- For voltaic cells, a cell diagram convention should be covered.

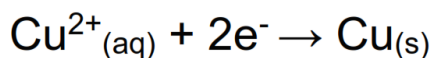
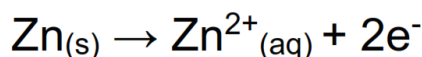
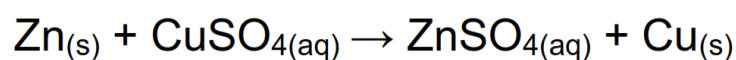
Definitions of oxidation and reduction

Oxidation and reduction can be defined in terms of:

- Loss or gain of electrons (electron transfer).
- Loss or gain of oxygen.
- Loss or gain of hydrogen.

Electron transfer

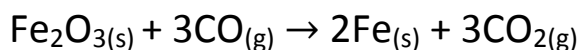
- Oxidation is the loss of electrons.
- Reduction is the gain of electrons.



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- In the above reaction, $\text{Zn}_{(\text{s})}$ has been oxidized and $\text{Cu}^{2+}_{(\text{aq})}$ has been reduced.

Loss or gain of oxygen

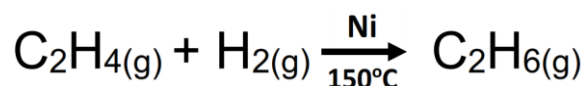
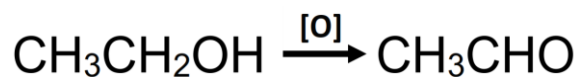
- Oxidation is the gain of oxygen.
- Reduction is the loss of oxygen.



- In the above reaction, Fe_2O_3 has been reduced (loss of oxygen) and CO has been oxidized (gain of oxygen).

Loss or gain of hydrogen

- Oxidation is the loss of hydrogen.
- Reduction is the gain of hydrogen.



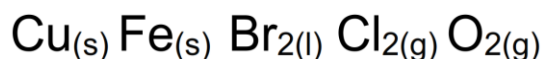
- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) has been oxidised (loss of hydrogen) and ethene (C_2H_4) has been reduced (gain of hydrogen).

Exercise: Complete the following table.

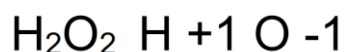
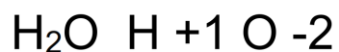
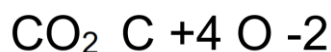
	Electron transfer	Loss or gain of oxygen	Loss or gain of hydrogen
Definition of oxidation	Loss of electrons	Gain of oxygen	Loss of hydrogen
Definition of reduction	Gain of electrons	Loss of oxygen	Gain of hydrogen

Assigning oxidation states

- Oxidation states are written with the + or – first followed by the number (+2, not 2+).
- Elements have an oxidation state of zero.



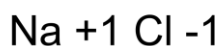
- Oxygen in a compound has an oxidation state of -2, except in peroxides when it is -1.



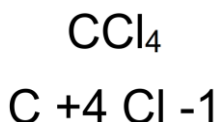
- Hydrogen in a compound has an oxidation state of +1, except in metal hydrides when it is -1.



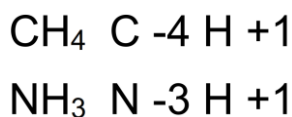
- Group 1 and 2 elements in compounds have oxidation states of +1 and +2 respectively.
- Fluorine in compounds always has an oxidation state of -1.
- In metals, the charge on the ion is the same as the oxidation state, for example in Cu^{2+} the oxidation state of the copper ion is +2
- In an ionic compound, the oxidation state of each species is the same as the charge on the ion.



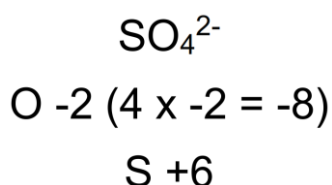
- For covalent compounds, assume that the more electronegative atom has a negative oxidation state and the less electronegative atom has a positive oxidation state.



- The sum of the oxidation states in a neutral compound is equal to zero.



- The sum of the oxidation states in a polyatomic ion is equal to the charge on the ion.



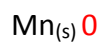
Summary:

Rules for determining oxidation states	
1.	Free elements are assigned an oxidation state of zero.
2.	The sum of the oxidation states of all the atoms in a compound must be equal to the net charge on the compound.
3.	The alkali metals (Li, Na, K, Rb, and Cs) in compounds are always assigned an oxidation state of +1.
4.	Fluorine in compounds is always assigned an oxidation state of -1.
5.	The alkaline earth metals (Be, Mg, Ca, Sr, Ba, and Ra) and Zn in compounds are always assigned an oxidation state of +2.
6.	Hydrogen in compounds is assigned an oxidation state of +1 except in certain metal hydrides (e.g. NaH) which is -1.
7.	Oxygen in compounds is assigned an oxidation state of -2 except in peroxides (e.g. H ₂ O ₂) which is -1.
8.	Halogens in compounds are assigned an oxidation state of -1.
9.	The charge on a metal ion is the same as its oxidation state, e.g. Zn ²⁺ has an oxidation state of +2.

Exercises:

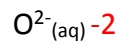
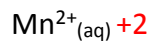
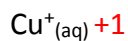
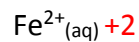
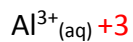
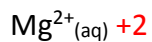
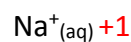
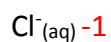
1) Deduce the oxidation states of the following:

All are elements, therefore the oxidation state is zero



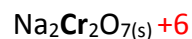
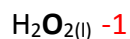
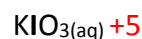
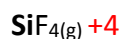
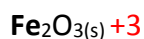
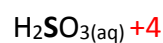
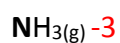
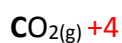
2) Deduce the oxidation states of the following ions:

For monoatomic ions, the oxidation state is the same as the charge on the ion



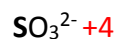
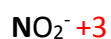
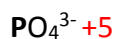
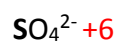
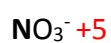
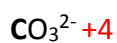
3) Deduce the oxidation states of the species in bold in the following compounds:

All are neutral compounds so the sum of the oxidations states is zero.



4) Deduce the oxidation state of the species in bold in the following polyatomic ions:

The sum of the oxidation states is equal to the charge on the ion.



5) Deduce the oxidation state of the metal ion in the following

The Roman numerals are oxidation numbers (same as oxidation states).

iron(II) oxide +2

manganese(IV) oxide +4

manganate(VII) ion +7

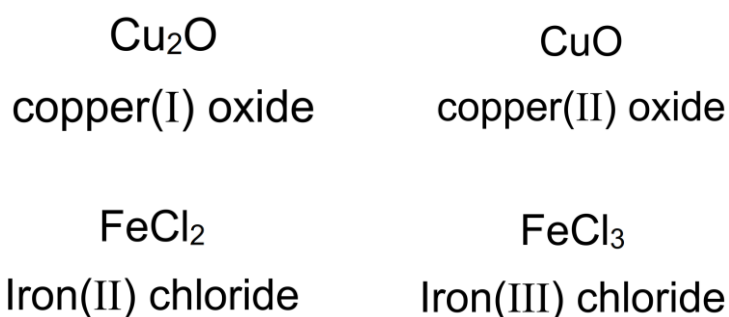
chromium(III) oxide +3

copper(I) chloride +1

copper(II) chloride +2

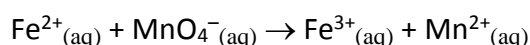
Oxidation states can be represented by a Roman numeral (note that these are actually called oxidation numbers, but are used interchangeably with oxidation state).

Examples:

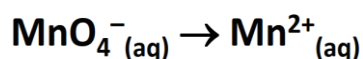


Balancing redox equations in acidic solutions

Example: Balance the following equation in acidic solution



(i) Balance for atoms other than H or O

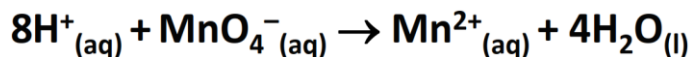


Same number of Mn atoms on both sides

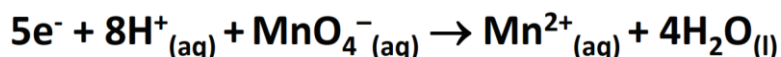
(ii) Balance for O by adding water (H_2O) to the side with fewer number of O atoms



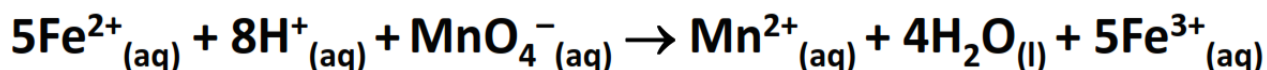
(iii) Balance for H by adding H^+ ions to the side with the fewer number of H atoms



(iv) Balance for charge by adding electrons to make the charge the same on both sides of the arrow.

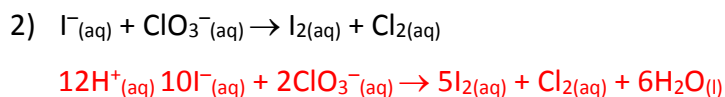
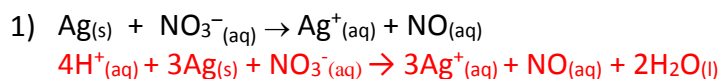


(v) Combine both equations with same number of electrons on both sides.



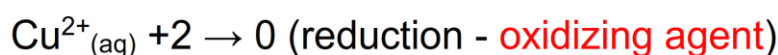
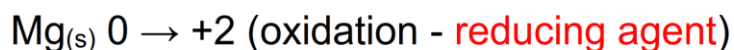
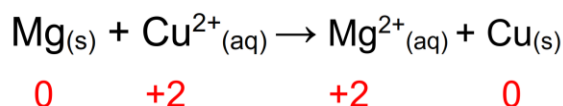
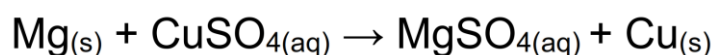
Exercises:

Balance the following redox equations in acidic solution:



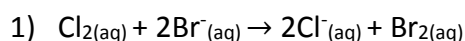
Oxidizing and reducing agents

- An oxidizing agent is reduced – it oxidizes another species.
- A reducing agent is oxidized – reduces another species.



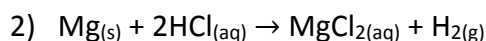
Exercises:

Identify the oxidizing and reducing agents in the following reactions:



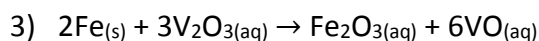
Oxidizing agent: Cl_2

Reducing agent: Br^-



Oxidizing agent: HCl

Reducing agent: Mg



Oxidizing agent: V_2O_3

Reducing agent: Fe

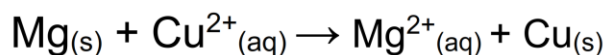
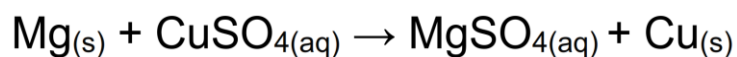
The activity series

- The activity series lists metals in order of their strength as reducing agents.

↑ Increasing activity	Li
	Cs
	Rb
	K
	Ba
	Sr
	Ca
	Na
	Mg
	Be
	Al
	C
	Zn
	Cr
	Fe
	Cd
	Co
	Ni
	Sn
	Pb
	H
	Sb
	As
	Bi
	Cu
	Ag
	Pd
	Hg
	Pt
	Au

- Metals at the top of the activity series are stronger reducing agents (more readily oxidized)
- Metals at the bottom of the activity series are weaker reducing agents (less readily oxidized).
- A metal at the top of the activity series can reduce the ions of a metals lower in the activity series.

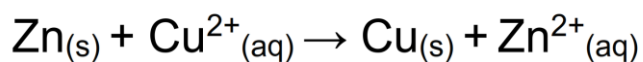
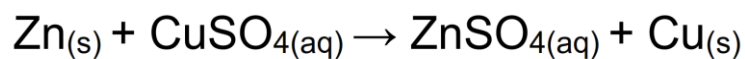
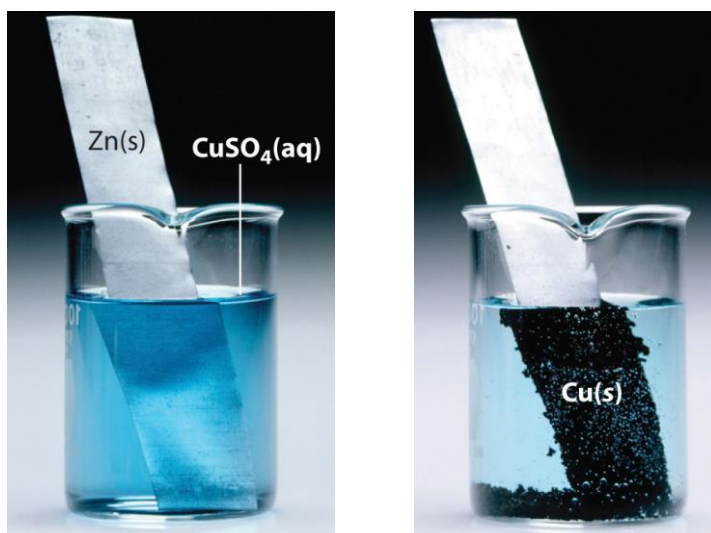
Example:



- Mg has reduced the Cu^{2+} ions (Mg is a stronger reducing agent).

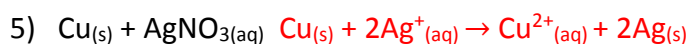
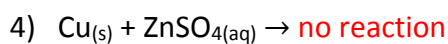
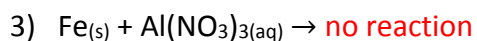
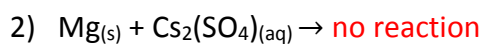
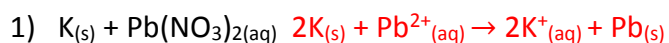
Displacement reactions

In the reaction below, a piece of zinc is added at an aqueous solution of copper(II) sulfate.




- The Zn has displaced the Cu^{2+} ions in solution.
- Zn has reduced the Cu^{2+} ions because Zn is a stronger reducing agent (higher in the activity series).

Exercise: use the activity series to predict if the following reactions will take place or not. If the reaction takes place, write the net ionic equation for the reaction.



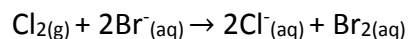
Group 17 redox reactions

9 F 19.00	 Stronger oxidizing agents
17 Cl 35.45	
35 Br 79.90	
53 I 126.90	

Elements at the top of the group 17 are stronger oxidizing agents.

Elements at the bottom of group 17 are weaker oxidizing agents.

For example, if chlorine gas (Cl_2) is bubbled through a solution of bromide ions (Br^-), the Cl_2 will displace the Br^- ions from solution.



The solution changes from colourless to brown.

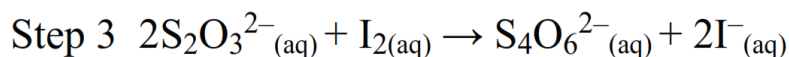
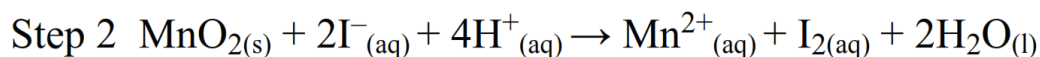
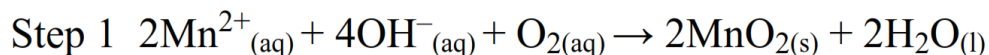
Cl_2 is a stronger oxidizing agent than Br_2 therefore the Cl_2 is reduced and Br^- ions are oxidized.

Exercise: Predict if the following reactions will occur. Explain your answer for each.



The Winkler method

- The Winkler method uses redox reactions to find the concentration of oxygen in water.
- It can be used to measure the biochemical oxygen demand (BOD) of a water sample.



- The ratio of O_2 in step 1 to $\text{S}_2\text{O}_3^{2-}$ in step 3 is 1:4

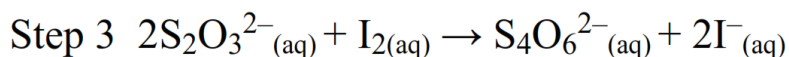
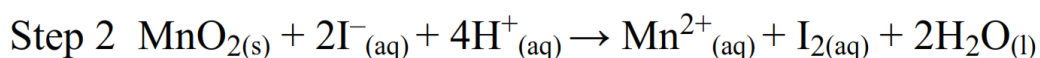
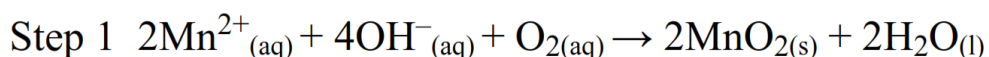
Example:

A 500 cm^3 sample of water was reacted with MnSO_4 in a basic solution, followed by the addition of acidified KI. 12.50 cm^3 of $0.0500 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3_{(\text{aq})}$ was required to react with the I_2 produced. Calculate the dissolved oxygen content of the water.

[See video for solution.](#)

Exercise:

The Winkler method uses redox reactions to find the concentration of oxygen in water. 100 cm^3 of water was taken from a river and analysed using this method. The reactions taking place are



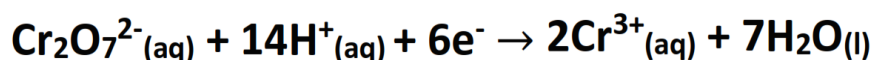
- State what happened to the O_2 in step 1 in terms of electrons. **It has been reduced (gain of electrons, decrease in oxidation number).**
- State the change in oxidation number for manganese in step 2. **+4 to +2**
- 0.0002 moles of I^{-} were formed in step 3. Calculate the amount, in moles, of oxygen, O_2 , dissolved in water. **$0.0002 \div 4 = 5 \times 10^{-5} \text{ mol O}_2$**
- Calculate the concentration of dissolved oxygen in mol dm^{-3} , g dm^{-3} and ppm.
 $\text{C (mol dm}^{-3}\text{)} = 5 \times 10^{-5} \text{ mol} \div (100 \div 1000) = 5 \times 10^{-4} \text{ mol dm}^{-3}$
 $\text{C (g dm}^{-3}\text{)} = 5 \times 10^{-5} \times 32.00 = 1.6 \times 10^{-3} \text{ g} \div (100 \div 1000) = 0.016 \text{ g dm}^{-3}$
 $\text{C (ppm)} = (1.6 \times 10^{-3} \text{ g} \div 100) \times 10^6 = 16 \text{ ppm}$

Redox titrations

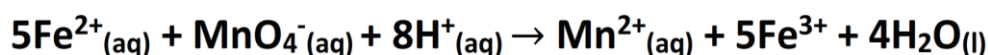
- Redox titration is used to determine the concentration of an analyte containing either an oxidizing or a reducing agent.
- Redox titration can be used to find the amount of iron in a sample. In these titrations Fe^{2+} is oxidised to Fe^{3+} by an oxidising agent:



- The oxidising agent is usually acidified potassium manganate(VII) or potassium dichromate(VI).



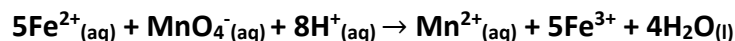
- Balanced equation in acidic solution:



Example:

All the iron in a 1.500 g tablet was dissolved in an acidic solution and converted to Fe^{2+} , which was then titrated with KMnO_4 . The titration required 35.60 cm^3 of 0.100 mol dm^{-3} KMnO_4 . Calculate the total mass of iron in the tablet and its percentage by mass.

The overall equation for the reaction is shown below:



Solution:

- Calculate the amount (in mol) of KMnO_4 required to react with the Fe^{2+} , using the equation $n = CV$

$$n(\text{KMnO}_4) = 0.100 \times (35.60 \div 1000) = 3.56 \times 10^{-3} \text{ mol}$$

- Use the molar ratio to determine the amount (in mol) of Fe^{2+} ions in the solution.

Molar ratio is 1 mol MnO_4^{-} to 5 mol Fe^{2+}

$$3.56 \times 10^{-3} \times 5 = 0.0178 \text{ mol Fe}^{2+}$$

- Calculate the mass of iron in the tablet using the equation $m=nM$ (molar mass of Fe is 55.85 g mol^{-1})

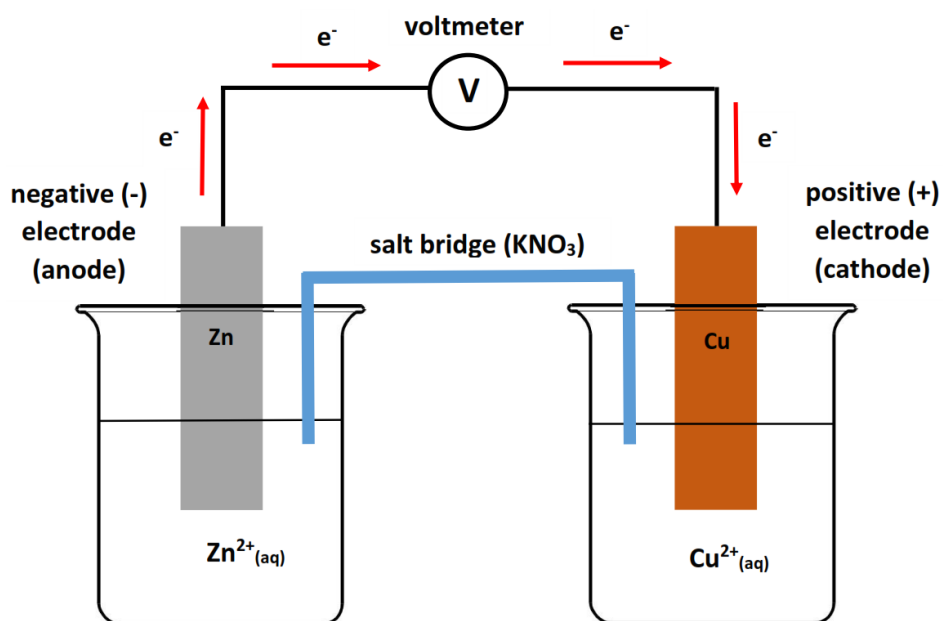
$$0.0178 \times 55.85 = 0.994 \text{ g}$$

- Calculate the percentage by mass of iron in the tablet.

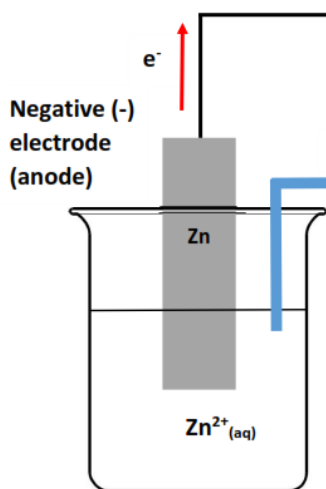
$$(0.994 \div 1.500) = 66.2 \%$$

Voltaic cells

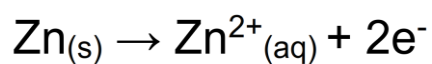
- Voltaic cells are also known as galvanic cells or batteries.



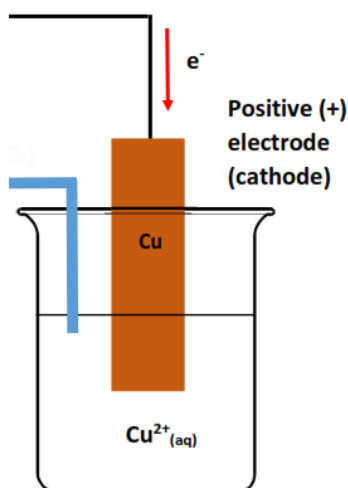
At the anode (oxidation)



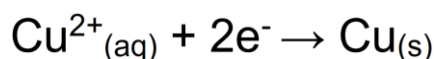
- The zinc atoms lose electrons (oxidation).
- The electrons flow in the wire to the copper half-cell.
- The mass of the zinc electrode decreases.



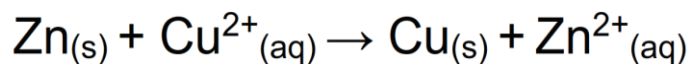
At the cathode (reduction)



- The electrons flow to the copper electrode from the zinc electrode.
- The copper ions in solution gain electrons (reduction).
- The mass of the copper electrode increases.

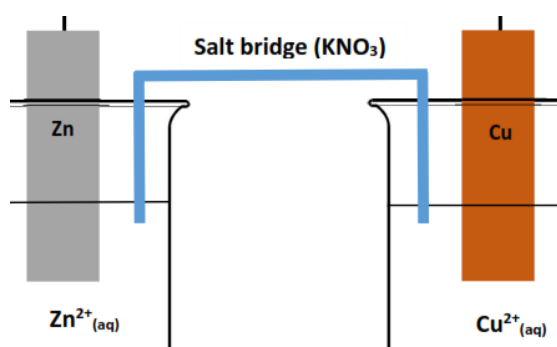


- The metal higher in the activity series is oxidised and the metal lower in the activity series is reduced.



Salt bridge

- The salt bridge allows ions to move between the two half-cells, thereby completing the circuit.
- Positive ions flow into the cathode and negative ions flow into the anode.



Voltaic cells summary

- Oxidation occurs at the anode (negative electrode)
- Reduction occurs at the cathode (positive electrode)
- The electrons flow from the anode to cathode in the wires producing an electric current.
- Cations (positive ions) move in the salt bridge from anode to cathode.
- Anions (negative ions) move in the salt bridge from cathode to anode.

Cell diagram convention

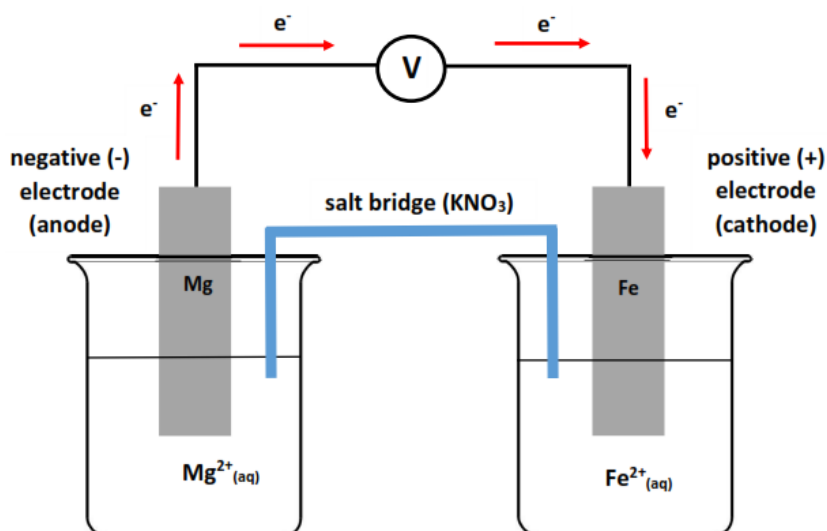
- The species on the left is oxidised (Zn) and the species on the right is reduced (Cu^{2+}).
- The double vertical line represents the salt bridge.



Exercises:

Magnesium is higher in the activity series than iron. Draw an annotated diagram of a voltaic cell made from a magnesium half-cell and an iron half-cell. Write half equations for the reactions that occur in each half-cell and describe how the current is conducted.

Mg is higher in the activity series than Fe, therefore Mg is oxidized at the anode and Fe is reduced at the cathode



At the anode (oxidation): $\text{Mg}_{(\text{s})} \rightarrow \text{Mg}^{2+}_{(\text{aq})} + 2\text{e}^{-}$

At the cathode (reduction): $\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Fe}_{(\text{s})}$

Overall reaction: $\text{Mg}_{(\text{s})} + \text{Fe}^{2+}_{(\text{aq})} \rightarrow \text{Mg}^{2+}_{(\text{aq})} + \text{Fe}_{(\text{s})}$

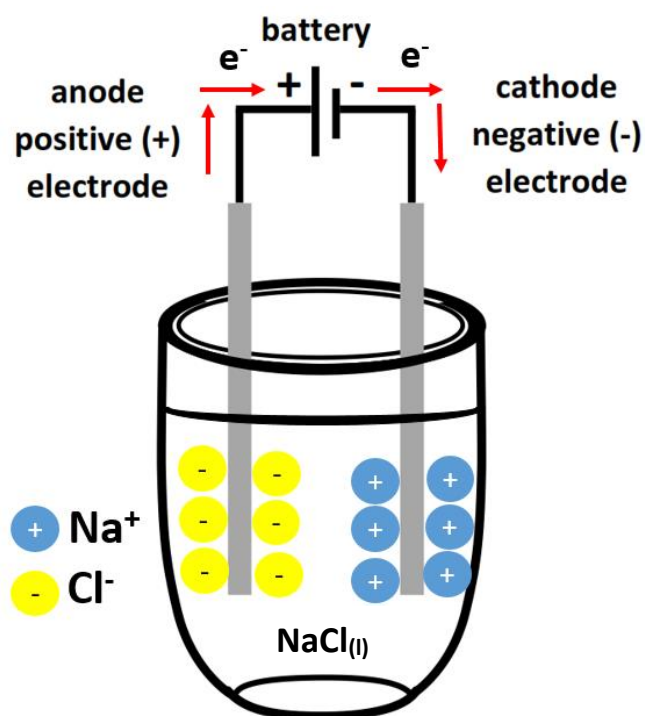
Anions move in the salt bridge from cathode to anode.

Cations move in the salt bridge from anode to cathode.

Electrons flow in the wires from anode to cathode.

Electrolytic cells

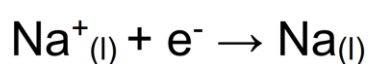
- An electrolytic cell uses a single container in which an ionic compound is heated until it melts (becomes molten).
- An electric current is supplied from a battery and the oppositely charged ions are attracted to the anode or cathode where they are oxidized or reduced.
- The electrons move in the wires and the ions move in the electrolyte.



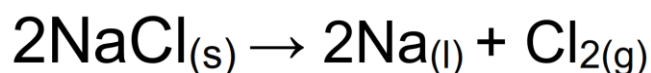
At the anode (oxidation)



At the cathode (reduction)



Overall equation:

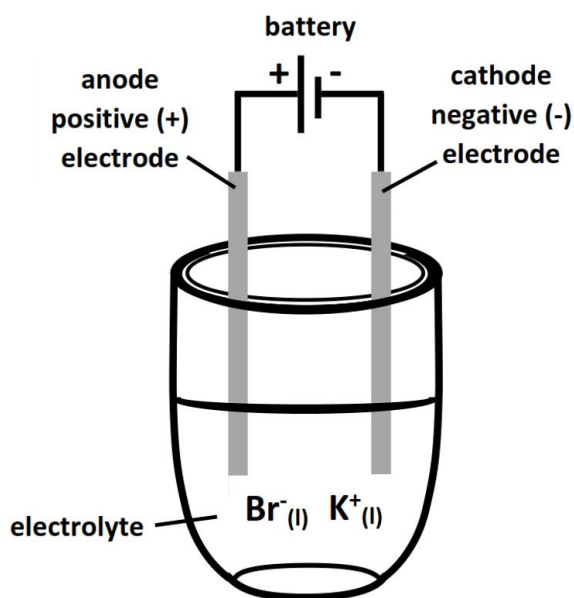


- The ratio of Na to Cl_2 is 2:1

Exercise

- 1) a) Draw a diagram of apparatus that could be used to electrolyse molten potassium bromide. Label the diagram to show the polarity of each electrode and the product formed.

(i)

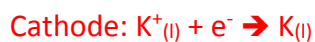
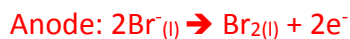


- b) Describe the two different ways in which electricity is conducted in the apparatus.

Electrons flow through connecting wires.

Ions move through the electrolyte to the electrodes and are oxidized or reduced.

- c) Write an equation to show the formation of the product at each electrode.
Determine the mole ratio in which the substances are formed.



mol ratio K : Br₂ 2:1

Electrochemical cells comparison

Voltaic cell	Electrolytic cells
A spontaneous reaction produces an electric current.	An electric current drives a non-spontaneous reaction.
Current is conducted by electron flow in wires and movement of ions in salt bridge	Current is conducted by electron flow in wires and movement of ions in electrolyte
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Chemical energy is converted to electrical energy	Electrical energy is converted to chemical energy
Reaction is exothermic	Reaction is endothermic
Oxidation occurs at the anode and reduction at the cathode	Oxidation occurs at the anode and reduction at the cathode