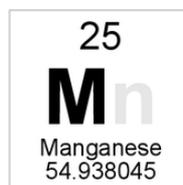
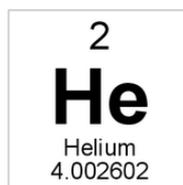
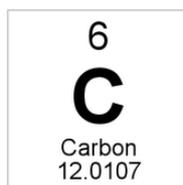
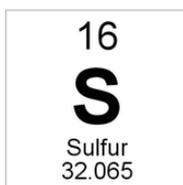
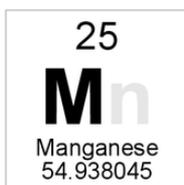


Redox SL

IB CHEMISTRY SL



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, e.g. +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.

Syllabus objectives

Objective	I am confident with this	I need to review this	I need help with this
Define oxidation and reduction in terms of loss or gain of electrons, loss or gain of oxygen and loss or gain of hydrogen			
Determine the oxidation state of an atom in a compound or ion			
Identify which species is oxidised or reduced based on change in oxidation state			
Identify the oxidising and reducing agents in a chemical reaction			
Balance redox equations in acidic solutions			
Use the activity series to predict if a reaction will take place			
Solve problems involving redox titrations			
Calculate the BOD of a water sample using the Winkler method			

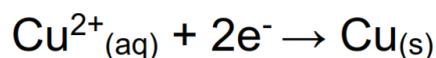
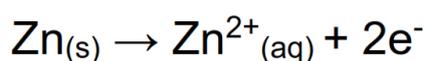
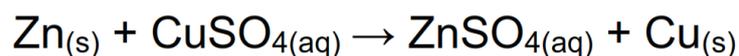
Definitions of oxidation and reduction

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

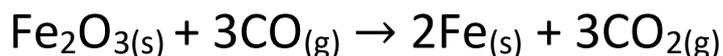
- Oxidation is the loss of electrons and an increase in oxidation state.
- Reduction is the gain of electrons and a decrease in oxidation state.



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

Loss or gain of oxygen

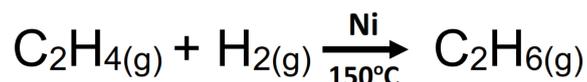
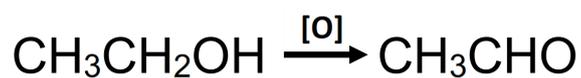
- Oxidation is the gain of oxygen.
- Reduction is the loss of oxygen.



- 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.



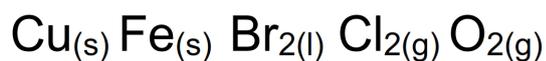
- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) has been oxidised (loss of hydrogen) and ethene (C_2H_4) has been reduced (gain of hydrogen).

Exercise: Complete the following table.

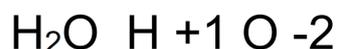
	Electron transfer	Loss or gain of oxygen	Loss or gain of hydrogen
Definition of oxidation			
Definition of reduction			

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.



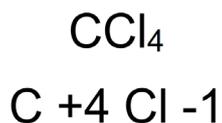
- Hydrogen in a compound has an oxidation state of +1, except in metal hydrides when it is -1.



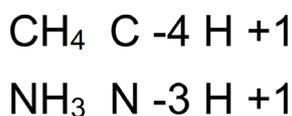
- Group 1 and 2 elements in compounds have oxidation states of +1 and +2 respectively.
- Fluorine in compounds always has an oxidation state of -1.
- In metals, the charge on the ion is the same as the oxidation state, for example in Cu^{2+} the oxidation state of the copper ion is +2
- In an ionic compound,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



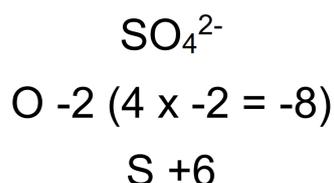
- For covalent compounds, assume that the more electronegative atom has a negative oxidation state and the less electronegative atom has a positive oxidation state.



- 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.



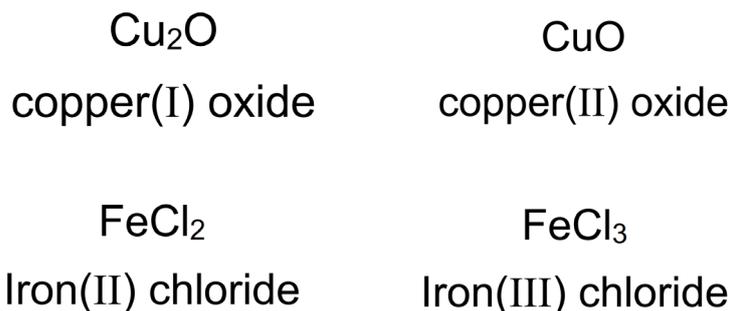
Summary:

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 (zero).
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 unless it is combined with fluorine or in peroxides (e.g. H ₂ O ₂) which is -1.
8.	Chlorine is assigned an oxidation state of -1 unless it is combined with oxygen or fluorine.
9.	The charge on a metal ion is the same as its oxidation state, e.g. Zn ²⁺ has an oxidation state of +2.

Oxidation numbers

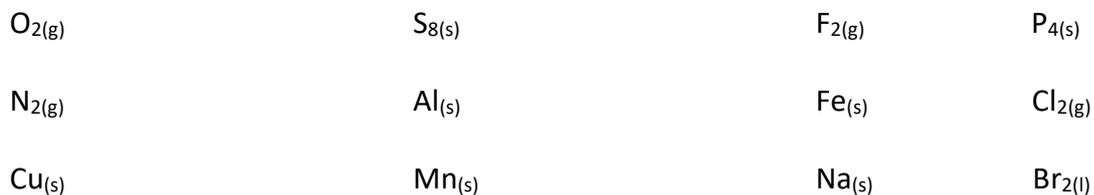
- Oxidation states can be represented by a Roman numeral (note that these are actually called oxidation numbers but are used interchangeably with oxidation state).

Examples:

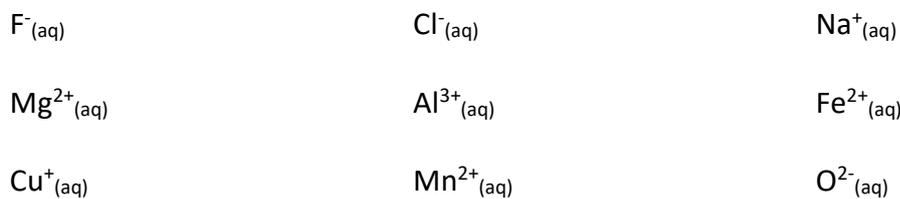


Exercises:

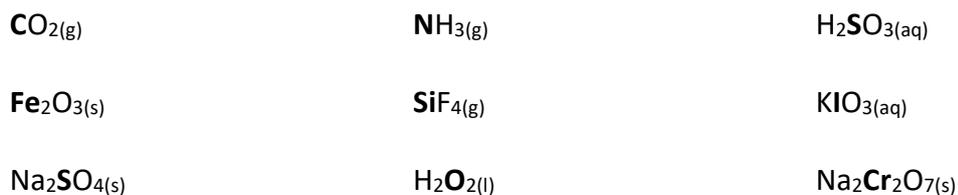
1. Deduce the oxidation states of the following:



2. Deduce the oxidation states of the following ions:



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



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



5. Deduce the oxidation number of the metal ion in the following:

iron(II) oxide

manganese(IV) oxide

manganate(VII) ion

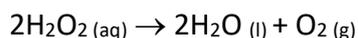
chromium(III) oxide

copper(I) chloride

copper(II) chloride

Disproportionation reactions

- A disproportionation reaction is a redox reaction in which one species is simultaneously oxidised and reduced (one species acts as both the oxidising and reducing agent).



- In the reaction, oxygen has both been both oxidised (increase in oxidation state) and reduced (decrease in oxidation state).

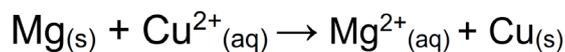
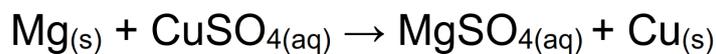
Exercise: Copper chloride in solution reacts as follows:



Determine the oxidation states of the species in the reaction and explain why this is a disproportionation reaction.

Oxidising and reducing agents

- An oxidising agent is reduced – it oxidises another species.
- A reducing agent is oxidised – it reduces another species.



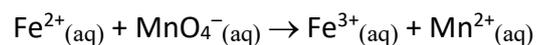
Exercises:

Identify the oxidising and reducing agents in the following reactions:

1. $\text{Cl}_{2(aq)} + 2\text{Br}^{-}_{(aq)} \rightarrow 2\text{Cl}^{-}_{(aq)} + \text{Br}_{2(aq)}$
2. $\text{Mg}_{(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{MgCl}_{2(aq)} + \text{H}_{2(g)}$
3. $2\text{Fe}_{(s)} + 3\text{V}_2\text{O}_{3(aq)} \rightarrow \text{Fe}_2\text{O}_{3(aq)} + 6\text{VO}_{(aq)}$
4. $2\text{KMnO}_{4(aq)} + 5\text{KNO}_{2(aq)} + 3\text{H}_2\text{SO}_{4(aq)} \rightarrow 2\text{MnSO}_{4(aq)} + 3\text{H}_2\text{O}_{(l)} + 5\text{KNO}_{3(aq)} + \text{K}_2\text{SO}_{4(aq)}$
5. $\text{K}_2\text{Cr}_2\text{O}_{7(aq)} + 3\text{SnCl}_{2(aq)} + 14\text{HCl}_{(aq)} \rightarrow 2\text{CrCl}_{3(aq)} + 3\text{SnCl}_{4(aq)} + 2\text{KCl}_{(aq)} + 7\text{H}_2\text{O}_{(l)}$

Balancing redox equations in acidic solutions

Example: Balance the following equation in acidic solution.



1. Balance for atoms other than H or O.
2. Balance for O by adding water (H₂O) to the side with fewer number of O atoms.
3. Balance for H by adding H⁺ ions to the side with the fewer number of H atoms.
4. Balance for charge by adding electrons to make the charge the same on both sides of the arrow.

Exercises:

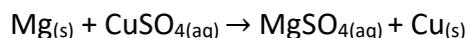
Balance the following redox equations in acidic solution:

1. $\text{Ag}(\text{s}) + \text{NO}_3^{-}(\text{aq}) \rightarrow \text{Ag}^{+}(\text{aq}) + \text{NO}(\text{aq})$
2. $\text{I}^{-}(\text{aq}) + \text{ClO}_3^{-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + \text{Cl}_2(\text{aq})$

Writing net-ionic equations

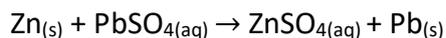
- A net-ionic equation is an equation for a redox reaction that includes only those species that participate in the reaction.
- Steps to writing a net-ionic equation:
 1. Write the molecular equation for the reaction.
 2. Write the complete ionic equation that shows all aqueous species broken down into their constituent ions.
 3. Cancel out the spectator ions (ions that appear unchanged on both sides of the equation).
 4. Write the net-ionic equation.

Example: Magnesium reacts with copper(II) sulfate as follows. Write the net-ionic equation for the reaction.

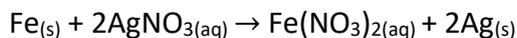


Exercises: Write the net-ionic equations for the following reactions:

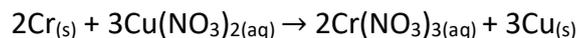
1. Zinc reacts with lead sulfate to produce zinc sulfate and lead.



2. Iron reacts with silver nitrate to produce iron(II) nitrate and silver.



3. Chromium reacts with copper(II) nitrate to produce chromium(III) nitrate and copper.



The activity series

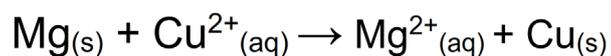
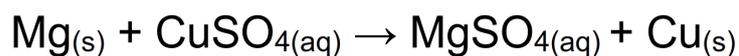
- The activity series lists metals in order of their strength as reducing agents.

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 metal lower in the activity series.

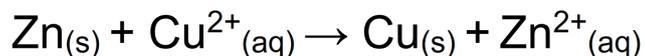
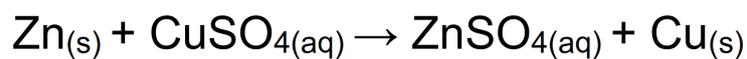
Example:



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

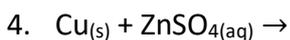
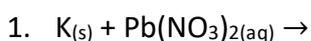
Displacement reactions

- 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 (it is 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 equations for the reaction.



Group 17 redox reactions

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

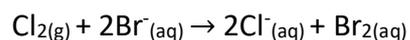


Stronger oxidizing agents

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

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

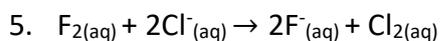
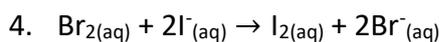
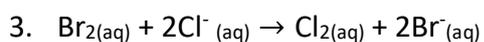
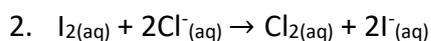
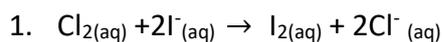
For example, if chlorine gas (Cl_2) is bubbled through a solution of bromide ions (Br^-), the Cl_2 will displace the Br^- ions from solution.



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.

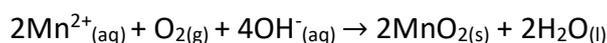


The Winkler method

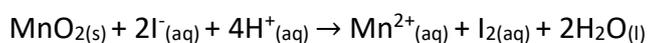
- The Winkler method uses redox reactions to find the concentration of oxygen in water.
- It can be used to measure the biochemical oxygen demand (BOD) of a water sample.
- Two samples of water are collected.
- One sample is immediately tested for $[O_2]$.
- The second sample is stored in the dark for 5 days at a constant temperature.
- After 5 days the $[O_2]$ is determined.
- To calculate the BOD, subtract the final $[O_2]$ from initial $[O_2]$.
- The BOD is usually given in $mg\ dm^{-3}$ or ppm.

There are three steps in the Winkler method:

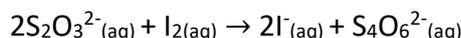
- An excess of $MnSO_4(aq)$ is added to the water sample.



- Iodide ions, $I^-(aq)$, are oxidised to form I_2



- The I_2 is titrated with $Na_2S_2O_3(aq)$



- The ratio of O_2 in step 1 to $S_2O_3^{2-}$ in step 3 is 1:4

Example:

Two $300.0\ cm^3$ samples of river water were collected. One sample was tested for the concentration of dissolved O_2 immediately and the other was stored in a dark place to be tested after 5 days.

At day 0, $15.20\ cm^3$ of $0.0200\ mol\ dm^{-3}\ Na_2S_2O_3(aq)$ was required to react with the I_2 produced. Calculate the dissolved oxygen content of the water.

After 5 days, the concentration of dissolved oxygen was determined. The second sample required $8.75\ cm^3$ of $0.0200\ mol\ dm^{-3}\ Na_2S_2O_3(aq)$ to react with the I_2 produced. Calculate the BOD of the water sample.

Exercise:

A 500 cm³ sample of water was reacted with MnSO₄ in a basic solution, followed by the addition of acidified KI. 12.50 cm³ of 0.0500 mol dm⁻³ Na₂S₂O_{3(aq)} was required to react with the I₂ produced. Calculate the dissolved oxygen content of the water.

Redox titrations

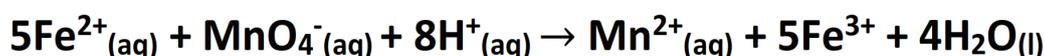
- Redox titration is used to determine the concentration of an analyte containing either an oxidizing or a reducing agent.
- Redox titration can be used to find the amount of iron in a sample. In these titrations Fe²⁺ is oxidised to Fe³⁺ by an oxidising agent:



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



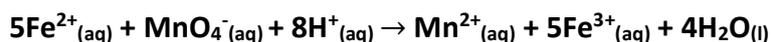
- Balanced equation in acidic solution:



Example:

All the iron in a 1.500 g tablet was dissolved in an acidic solution and converted to Fe²⁺, which was then titrated with KMnO₄. The titration required 35.60 cm³ of 0.100 mol dm⁻³ KMnO₄. Calculate the total mass of iron in the tablet and its percentage by mass.

The overall equation for the reaction is shown below:



Solution:

1. Calculate the amount (in mol) of KMnO_4 required to react with the Fe^{2+} , using the equation $n = CV$
2. Use the molar ratio to determine the amount (in mol) of Fe^{2+} ions in the solution.
3. Calculate the mass of iron in the tablet using the equation $m=nM$ (molar mass of Fe is 55.85 g mol^{-1})
4. Calculate the percentage by mass of iron in the tablet.

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:

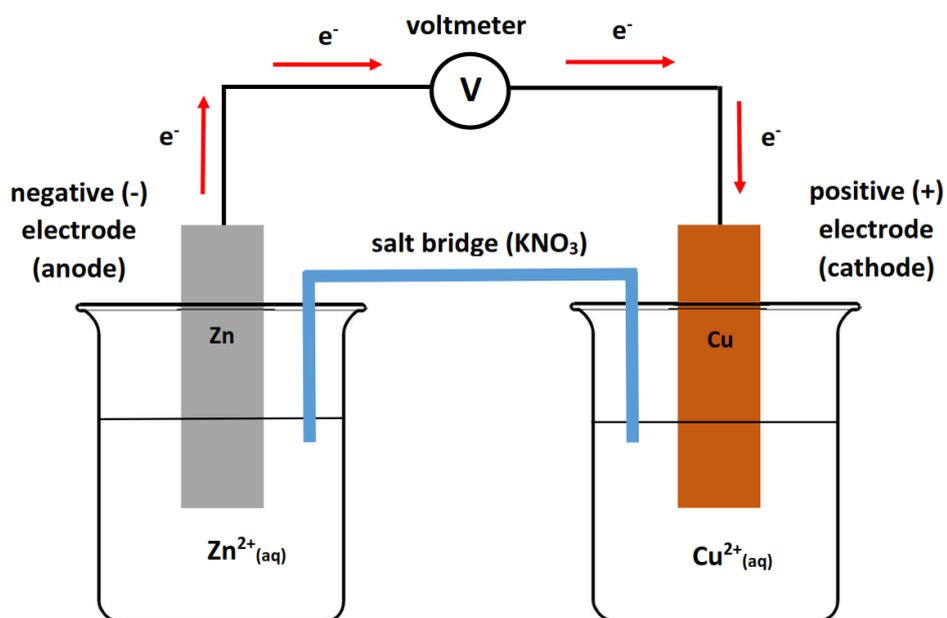
- For voltaic cells, a cell diagram convention should be covered.

Syllabus objectives

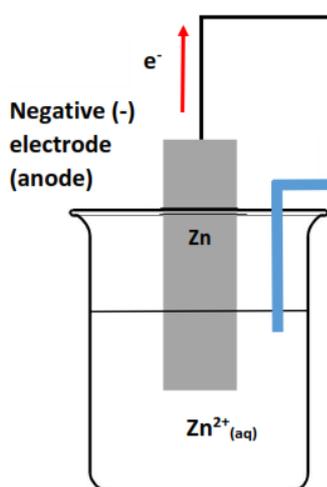
Objective	I am confident with this	I need to review this	I need help with this
Construct and annotate diagrams of voltaic and electrolytic cells			
Explain how a voltaic cell produces an electric current			
Distinguish between electron flow and ion flow in both electrochemical cells			
Deduce the products of the electrolysis of molten salts			

Voltaic cells

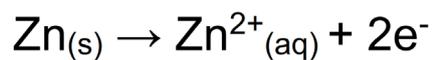
- Voltaic cells are also known as galvanic cells or batteries.



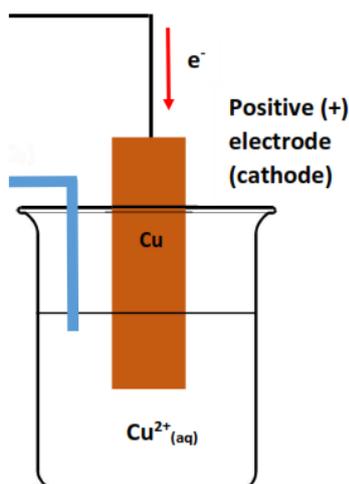
At the anode (oxidation)



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



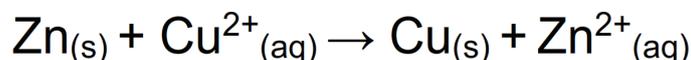
At the cathode (reduction)



- 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.

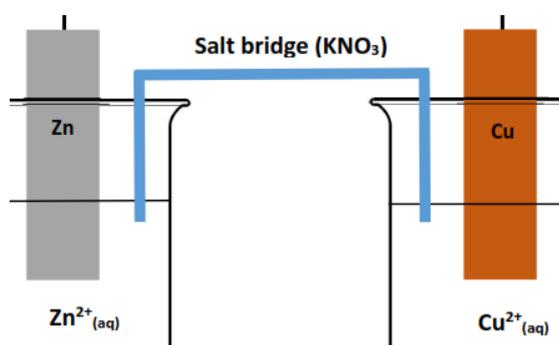


- The metal higher in the activity series is oxidised and the metal lower in the activity series is reduced.



Salt bridge

- The salt bridge allows ions to move between the two half-cells, thereby completing the circuit and keeping the half-cell electrically neutral.
- 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).
- Current is conducted by electron flow in the external circuit (from the anode to cathode) and movement of ions in the salt bridge.
- Cations (positive ions) move in the salt bridge to the cathode.
- Anions (negative ions) move in the salt bridge to the 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.

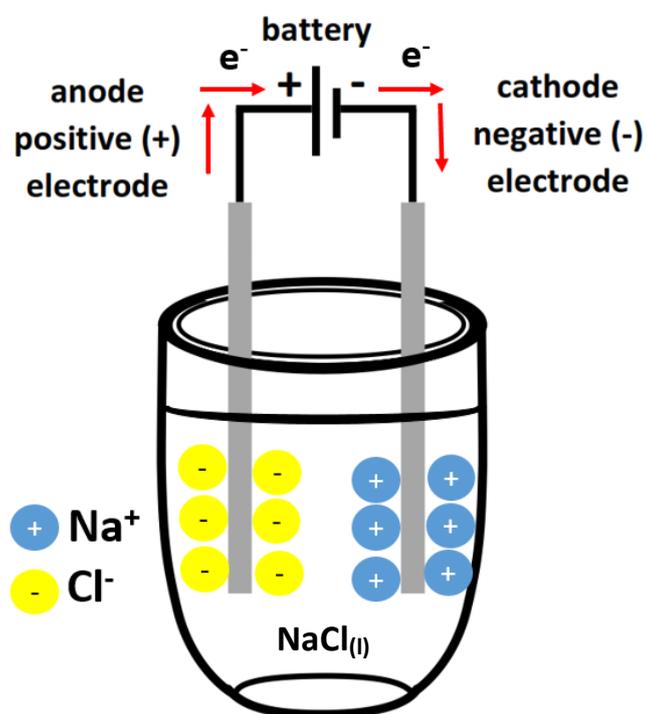


Exercises:

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.

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.



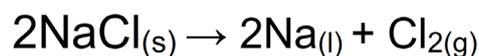
At the anode (oxidation)



At the cathode (reduction)



Overall equation:



- The ratio of Na to Cl₂ is 2:1

