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, 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.

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 Electrons & $\frac{1}{\text{Oxidation State}}$

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

think in terms of oxidation state and then reverse effect on electrons.

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

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

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

Loss or gain of oxygen

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

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

- 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.

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO$$

$$C_2H_{4(g)} + H_{2(g)} \xrightarrow[150^\circ C]{Ni} C_2H_{6(g)}$$

- Ethanol (CH_3CH_2OH) 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	Gain	Loss
Definition of reduction	Gain	Loss	Gain

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.

$$Cu_{(s)}\ Fe_{(s)}\ Br_{2(l)}\ Cl_{2(g)}\ O_{2(g)}$$

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

$$CO_2\ \ C\ +4\ O\ -2$$

$$H_2O\ \ H\ +1\ O\ -2$$

$$H_2O_2\ \ H\ +1\ O\ -1$$

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

$$NaH\ \ Na\ +1\ H\ -1$$

- 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.

$$NaCl\ \ Na^+\ Cl^-$$

$$Na\ +1\ Cl\ -1$$

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

$$CCl_4$$
$$C\ +4\ Cl\ -1$$

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

$$CH_4\ \ C\ -4\ H\ +1$$
$$NH_3\ \ N\ -3\ H\ +1$$

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

$$SO_4^{2-}$$
$$O\ -2\ (4 \times -2 = -8)$$
$$S\ +6$$

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_2O_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.

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:

Cu_2O copper(I) oxide	CuO copper(II) oxide
$FeCl_2$ Iron(II) chloride	$FeCl_3$ Iron(III) chloride

Exercises:

1) Deduce the oxidation states of the following:

$O_{2(g)}$ 0	$S_{8(s)}$ 0	$F_{2(g)}$ 0
$N_{2(g)}$ 0	$Al_{(s)}$ 0	$Fe_{(s)}$ 0
$Cu_{(s)}$ 0	$Mn_{(s)}$ 0	$Na_{(s)}$ 0

2) Deduce the oxidation states of the following ions:

$F^-_{(aq)}$ −1	$Cl^-_{(aq)}$ −1	$Na^+_{(aq)}$ +1
$Mg^{2+}_{(aq)}$ +2	$Al^{3+}_{(aq)}$ +3	$Fe^{2+}_{(aq)}$ +2
$Cu^+_{(aq)}$ +1	$Mn^{2+}_{(aq)}$ +2	$O^{2-}_{(aq)}$ −2

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

$\mathbf{C}O_{2(g)}$ $x-2(2)=0$ $x=+4$	$\mathbf{N}H_{3(g)}$ $x+1(3)=0$ $x=-3$	$H_2\mathbf{S}O_{3(aq)}$ $1(2)+x-2(3)=0$ $x=+4$
$\mathbf{Fe}_2O_{3(s)}$ $2x-2(3)=0$ $x=+3$	$\mathbf{Si}F_{4(g)}$ $x-1(4)=0$ $x=+4$	$K\mathbf{I}O_{3(aq)}$ $1+x-2(3)=0$ $x=+5$
$Na_2\mathbf{S}O_{4(s)}$ $2(1)+x-2(4)=0$ $x=+6$	$H_2\mathbf{O}_{2(l)}$ $1(2)+2x=0$ $x=-1$ Peroxide	$Na_2\mathbf{Cr}_2O_{7(s)}$ $1(2)+2x-2(7)=0$ $x=+6$

Charge = oxidation state
in metallic ions or ionic compounds

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

CO_3^{2-} $x-2(3)=-2$ $x=+4$	**N**O_3^{-} $x-2(3)=-1$ $x=+5$	**S**O_4^{2-} $x-2(4)=-2$ $x=+6$
PO_4^{3-} $x-2(4)=-3$ $x=+5$	**N**O_2^{-} $x-2(2)=-1$ $x=+3$	**S**O_3^{2-} $x-2(3)=-2$ $x=+4$

5) Deduce the oxidation state of the metal ion in the following
Assume positive with roman numerals ig?

iron(II) oxide +2	manganese(IV) oxide +4	manganate(VII) ion +7
chromium(III) oxide +3	copper(I) chloride +1	copper(II) chloride +2

Oxidizing and reducing agents

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

$$Mg_{(s)} + CuSO_{4(aq)} \rightarrow MgSO_{4(aq)} + Cu_{(s)}$$

$$Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$$

$$0 \qquad +2 \qquad\qquad +2 \qquad\qquad 0$$

$Mg_{(s)}$ $0 \rightarrow +2$ (oxidation - reducing agent)

$Cu^{2+}_{(aq)}$ $+2 \rightarrow 0$ (reduction - oxidizing agent)

Exercises:

Identify the oxidizing and reducing agents in the following reactions:

1) $Cl_{2(aq)} + 2Br^{-}_{(aq)} \rightarrow 2Cl^{-}_{(aq)} + Br_{2(aq)}$
   $Cl_{2(aq)}$ $0 \rightarrow -1$ (Oxidized, Reducing Agent)
   $Br^{-}_{(aq)}$ $-1 \rightarrow 0$ (Reduced, Oxidizing Agent)
2) $Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

3) $2Fe_{(s)} + 3V_2O_{3(aq)} \rightarrow Fe_2O_{3(aq)} + 6VO_{(aq)}$

Balancing redox equations in acidic solutions

Example: Balance the following equation in acidic solution

$$Fe^{2+}_{(aq)} + MnO_4^{-}{}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$$

(i) Balance for atoms other than H or O

(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.

Exercises:

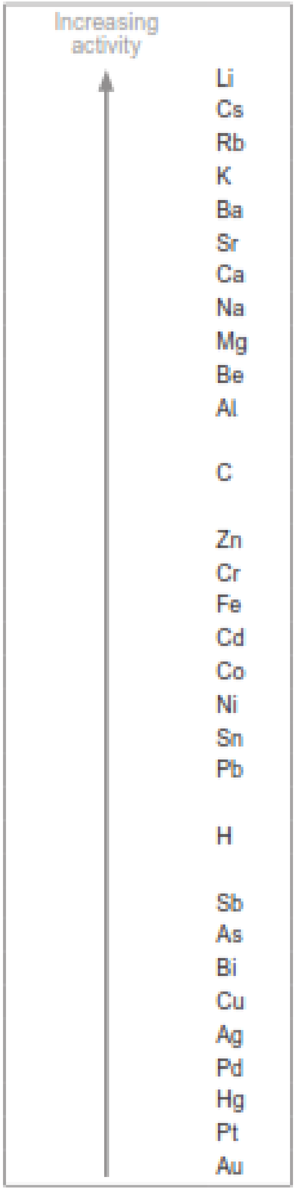
Balance the following redox equations in acidic solution:

1) $Ag_{(s)}$ + $NO_3^-{}_{(aq)} \rightarrow Ag^+{}_{(aq)} + NO_{(aq)}$

2) $I^-{}_{(aq)} + ClO_3^-{}_{(aq)} \rightarrow I_{2(aq)} + Cl_{2(aq)}$

The activity series

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



- 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:

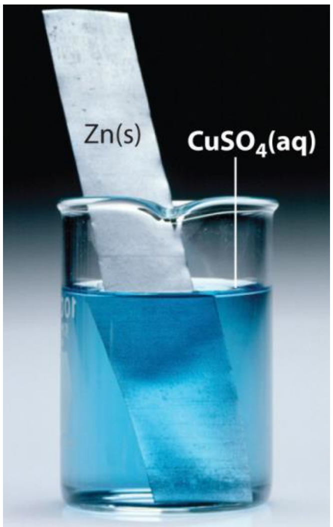
$$Mg_{(s)} + CuSO_{4(aq)} \rightarrow MgSO_{4(aq)} + Cu_{(s)}$$

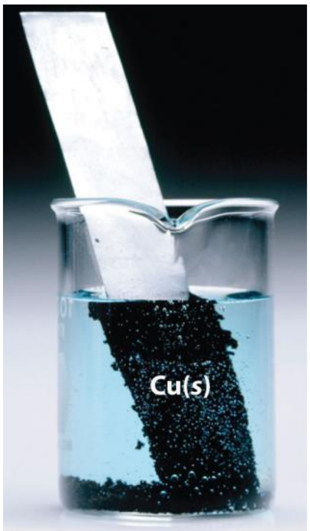
$$\underset{0}{Mg_{(s)}} + \underset{+2}{Cu^{2+}_{(aq)}} \rightarrow \underset{+2}{Mg^{2+}_{(aq)}} + \underset{0}{Cu_{(s)}}$$

- 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.





$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

- 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.

1) $K_{(s)} + Pb(NO_3)_{2(aq)} \rightarrow$

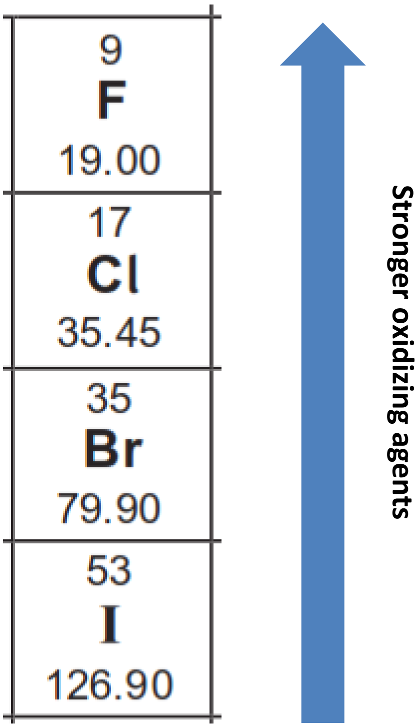
2) $Mg_{(s)} + Cs_2(SO_4)_{(aq)} \rightarrow$

3) $Fe_{(s)} + Al(NO_3)_{3(aq)} \rightarrow$

4) $Cu_{(s)} + ZnSO_{4(aq)} \rightarrow$

5) $Cu_{(s)} + AgNO_{3(aq)} \rightarrow$

Group 17 redox reactions



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.

$$Cl_{2(g)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$$

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.

1. $Cl_{2(aq)} + 2I^-_{(aq)} \rightarrow I_{2(aq)} + 2Cl^-_{(aq)}$

2. $I_{2(aq)} + 2Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2I^-_{(aq)}$

3. $Br_{2(aq)} + 2Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2Br^-_{(aq)}$

4. $Br_{2(aq)} + 2I^-_{(aq)} \rightarrow I_{2(aq)} + 2Br^-_{(aq)}$

5. $F_{2(aq)} + 2Cl^-_{(aq)} \rightarrow 2F^-_{(aq)} + Cl_{2(aq)}$

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.

$$\text{Step 1}\quad 2Mn^{2+}_{(aq)} + 4OH^{-}_{(aq)} + O_{2(aq)} \rightarrow 2MnO_{2(s)} + 2H_2O_{(l)}$$

$$\text{Step 2}\quad MnO_{2(s)} + 2I^{-}_{(aq)} + 4H^{+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$$

$$\text{Step 3}\quad 2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^{-}_{(aq)}$$

- The ratio of O_2 in step 1 to $S_2O_3^{2-}$ 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 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.

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

$$\text{Step 1}\quad 2Mn^{2+}_{(aq)} + 4OH^{-}_{(aq)} + O_{2(aq)} \rightarrow 2MnO_{2(s)} + 2H_2O_{(l)}$$

$$\text{Step 2}\quad MnO_{2(s)} + 2I^{-}_{(aq)} + 4H^{+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$$

$$\text{Step 3}\quad 2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^{-}_{(aq)}$$

a) State what happened to the O_2 in step 1 in terms of electrons.

b) State the change in oxidation number for manganese in step 2.

c) 0.0002 moles of I^- were formed in step 3. Calculate the amount, in moles, of oxygen, O_2, dissolved in water.

d) Calculate the concentration of dissolved oxygen in mol dm^{-3}, gdm^{-3} and 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:

$$\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^-}$$

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

$$\mathbf{MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}}$$

$$\mathbf{Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}}$$

- Balanced equation in acidic solution:

$$\mathbf{5Fe^{2+}{}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+} + 4H_2O_{(l)}}$$

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:

$$\mathbf{5Fe^{2+}{}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+} + 4H_2O_{(l)}}$$

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:

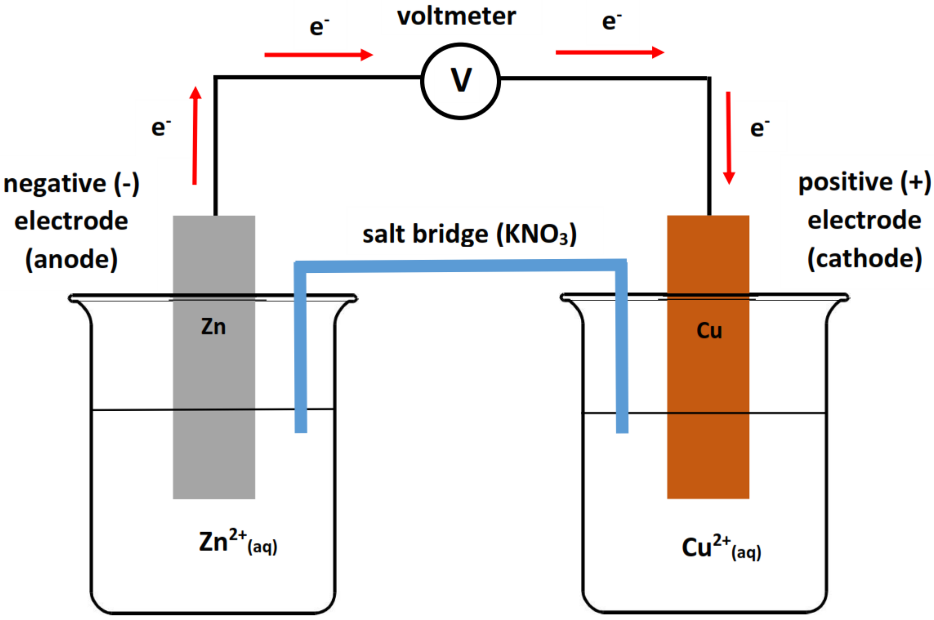
- For voltaic cells, a cell diagram convention should be covered.

Syllabus objectives

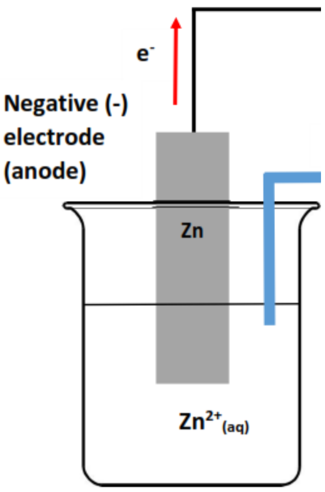
Objective	I am confident with this	I need to review this	I need help with this
Construct and annotate diagrams of voltaic and electrolytic cells			
Explain how a voltaic cell produces an electric current			
Distinguish between electron flow and ion flow in both electrochemical cells			
Deduce the products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

Voltaic cells

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



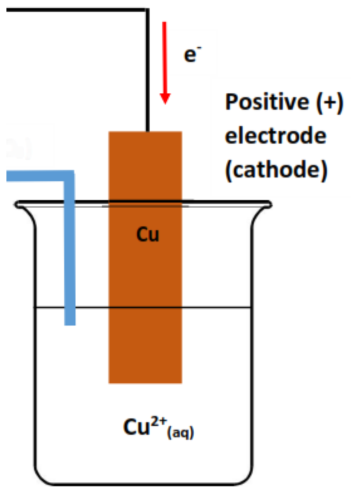
At the anode (oxidation)



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

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

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.

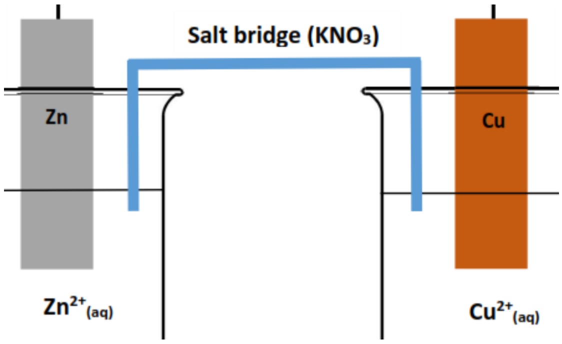
$$Cu^{2+}{}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$$

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

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

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 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 bride.

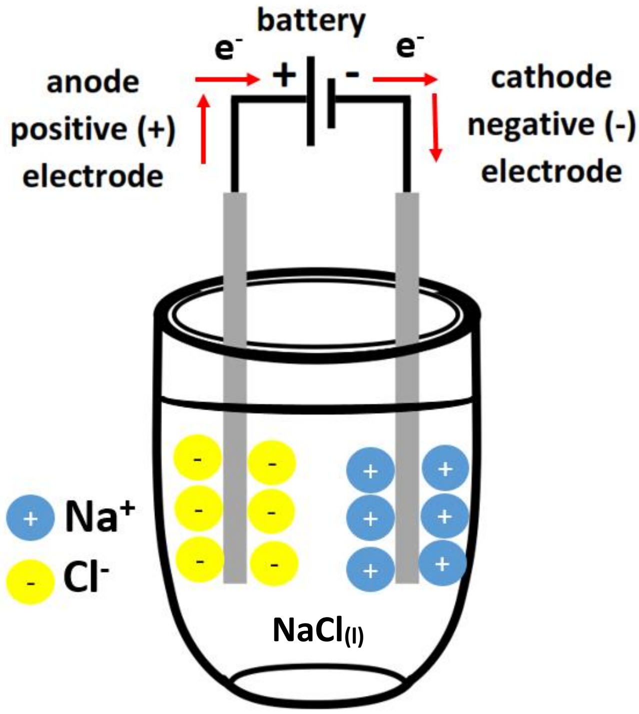
$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

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)

$$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$$

$$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$$

Overall equation:

$$2NaCl_{(s)} \rightarrow 2Na_{(l)} + Cl_{2(g)}$$

- 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.

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

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

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