

CHAPTER 7: Redox Reactions and Electrolysis

7.1 Oxidation and Reduction

7.2 Electrolysis

Learning outcomes:

- (a)
 - (i) *calculate oxidation numbers of elements in compounds and ions.*
 - (ii) *describe and explain redox processes in terms of electron transfer and/or changes in oxidation number (oxidation state).*
 - (iii) *use changes in oxidation numbers to help balance chemical equations.*
- (b) *explain, including the electrode reactions, the industrial processes of:*
 - (i) *the electrolysis of brine, using a diaphragm cell.*
 - (ii) *the extraction of aluminium from molten aluminium oxide/cryolite.*
 - (iii) *the electrolytic purification of copper.*

7.1 Oxidation and Reduction

Redox reactions

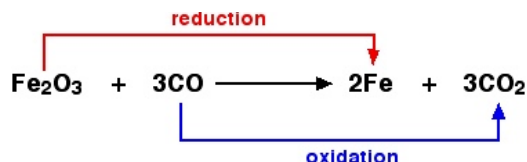
1) *Oxidation* is:

- i. gain of oxygen
- ii. loss of hydrogen
- iii. loss of electrons
- iv. increase in oxidation number

2) *Reduction* is:

- i. gain of hydrogen
- ii. loss of oxygen
- iii. gain of electrons
- iv. decrease in oxidation number

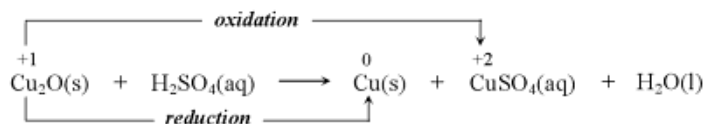
3) Oxidation and reduction always occur simultaneously in a chemical reaction. Such reaction is called a **redox reaction**. In a redox reaction, one substance must be oxidised and another must be reduced.



4) i. An *oxidising agent* is a substance which oxidises another substance and **itself is reduced**.
ii. A *reducing agent* is a substance which reduces another substance and **itself is oxidised**.

5) In short, an oxidising agent undergoes reduction while a reducing agent undergoes oxidation.

6) **Disproportionation** is a redox reaction in which both oxidation and reduction occurs on the same atom. The atom is simultaneously oxidised and reduced.



Oxidation state (oxidation number) of a substance

- 1) Oxidation state shows that total number of electrons which have been removed from or added to **an element** to get to its present state.
- 2) i. When electrons have been removed, the oxidation number increases.(positive)
ii. When electrons have been added, the oxidation number decreases.(negative)
- 3) i. Since removing electrons is an oxidation process, therefore oxidation is the increase in oxidation number
ii. Since adding electrons is a reduction process, therefore reduction is the decrease in oxidation number.
- 3) For example, from V to V^{2+} , two electrons have been removed, therefore the oxidation state of is +2. From V to V^{3+} , three electrons have been removed, therefore the oxidation state is +3. Removing another electron gives:



Four electrons have been removed starting from V, therefore the oxidation state is +4. In all cases, V has been oxidised.

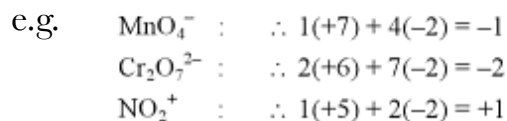
- 4) Another example, from S to S^{2-} , two electrons have been added, therefore the oxidation state is -2. S is said to have been reduced.

Rules to determine oxidation numbers of a substance

- 1) All atoms in an atom, molecule or ion can be given an oxidation number.
- 2) The rules to determine the oxidation number of a substance:
 - i. All **free atoms** in elements have an oxidation number of **zero**.
e.g.

$\overset{0}{\text{Mg}}$	$\overset{0}{\text{Fe}}$	$\overset{0}{\text{O}_2}$	$\overset{0}{\text{H}_2}$	$\overset{0}{\text{P}_4}$	$\overset{0}{\text{Cl}_2}$
--------------------------	--------------------------	---------------------------	---------------------------	---------------------------	----------------------------
 - ii. For **simple ions**, the oxidation number is the same as the **charge** on the ion.
e.g.

$\overset{+1}{\text{Na}^+}$	$\overset{+3}{\text{Al}^{3+}}$	$\overset{+2}{\text{Mg}^{2+}}$	$\overset{-2}{\text{O}^{2-}}$	$\overset{-2}{\text{S}^{2-}}$	$\overset{-1}{\text{Cl}^-}$
-----------------------------	--------------------------------	--------------------------------	-------------------------------	-------------------------------	-----------------------------
 - iii. For **polyatomic ion**, the **sum** of all the oxidation numbers of the atoms in the ion is equal to the **charge** of the ion.



iv. For a **neutral covalent molecule**, the sum of all the oxidation numbers of the atoms in the molecule is equal to **zero**.



Also, the more electronegative atom is always given a negative oxidation number while the less electronegative atom is given a positive one.

v. For **Group I and Group II elements**, their oxidation number are always +1 and +2 respectively. For aluminium, it is always +3.

vi. For **hydrogen**, its oxidation number is always +1 except in metal hydrides. For example, NaH, where its oxidation number is -1.

vii. For **oxygen**, its oxidation number is always -2 except in peroxides and fluorine compounds. For example, BaO₂, where its oxidation number is -1.

viii. For **fluorine**, its oxidation number is always -1, with no exceptions.

3) A summary:

<i>Element</i>	<i>Oxidation No.</i>	<i>Exceptions</i>
Group I	+1	–
Group II	+2	–
Aluminium	+3	–
Fluorine	-1	–
Oxygen	-2	-1 in <i>peroxides</i> (e.g. H ₂ O ₂) and +2 in OF ₂
Hydrogen	+1	-1 in <i>metal hydrides</i> (e.g. Na ⁺ H ⁻)

4) To work out the oxidation number of a particular atom in a molecule/ ion, find the sum of all the oxidation number of the atoms present and equate it to zero/ charge of the ion. An example:

To calculate the oxidation number of Mn in MnO(OH)₂, MnO₄²⁻ and Mn₂O₇.

Let the oxidation number of Mn be x .

In MnO(OH)₂ : $x + (-2) + 2(-1) = 0 \quad \Rightarrow x = +4$

In MnO₄²⁻ : $x + 4(-2) = -2 \quad \Rightarrow x = +6$

In Mn₂O₇ : $2x + 7(-2) = 0 \quad \Rightarrow x = +7$

Balancing redox equations

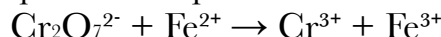
1) There are two methods to balance complicated redox equations:

- Using electron half-equations.
- Using changes in oxidation number.

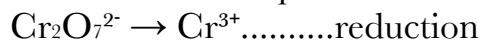
2) **Using electron half-equations:**

- In this method, the redox equation is divided into two half-equations. One for oxidation and another for reduction.
- Steps(**in acidic condition**):
 - Divide the equation or information given into two half-equations.
 - Balance all other elements other than oxygen and hydrogen.
 - Balance the oxygen by adding H_2O to the appropriate side of the equation.
 - Balance the hydrogen by adding H^+ to the appropriate side of the equation.
 - Balance the charge by adding electrons to the appropriate side of the equation.
 - Combine two half-equations such that the electrons cancel out each other.
- An example:

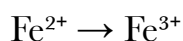
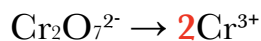
Q: Balance and complete this equation:



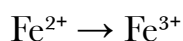
A: 1) Divide into two equations:



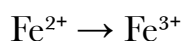
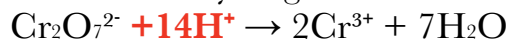
2) Balance the atoms:



3) Balance the oxygen:



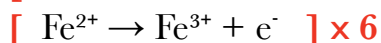
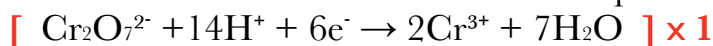
4) Balance the hydrogen:



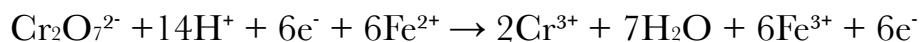
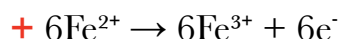
5) Balance the charge:



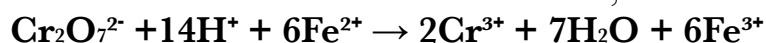
6) Cancel the electrons and combine the equations:



the combine....



same number of electrons on both sides, cancel it....



is the final answer.

iv. Steps(**in alkaline condition**):

- Balance the equation as if it happens in an acidic condition first.
- Add OH^- to both sides of the equation to react with all the H^+ to form H_2O .
- Cancel the excess H_2O on either side of the equation.

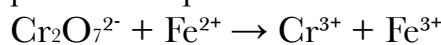
Note: If it is obvious enough that OH^- must be added in order to balance the equation, then add OH^- instead.

3) **Using changes in oxidation number:**

- i. This method utilises the fact that an increase in certain amount of oxidation number in a substance must be accompanied by a decrease in same amount of oxidation number in another substance.

ii. An example:

Q: Balance and complete this equation:



A: 1) Calculate the changes in oxidation number:

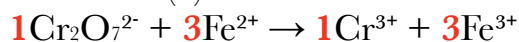
For Cr: +6 to +3, change is -3

For Fe: +2 to +3, change is +1

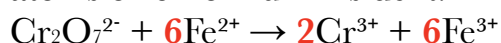
2) Balance the changes:

For Cr: -3(**1**) = -3

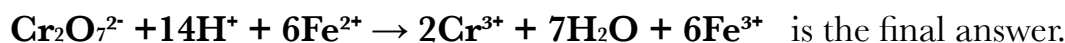
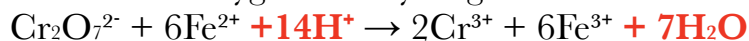
For Fe: +1(**3**) = +3



3) Multiply everything by 2 except $\text{Cr}_2\text{O}_7^{2-}$ because there are already two atoms of chromium inside it.



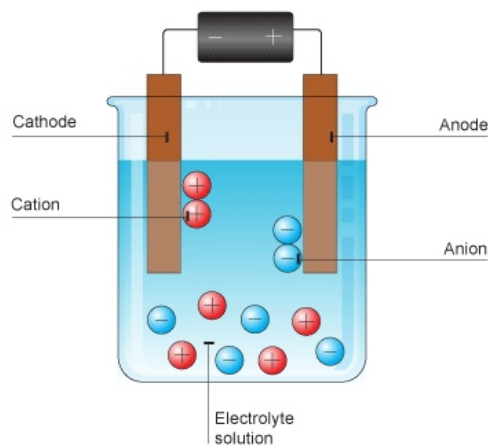
4) Balance the oxygen and hydrogen:



7.2 Electrolysis

Electrolytic cells

- 1) *Electrolysis* is the decomposition of a compound into its elements by an electric current.
- 2) Uses of electrolysis:
 - to extract useful metals from their ores.
 - to produce useful by-products such as chlorine gas.
 - to purify metals.
- 3) Electrolysis is carried out in an electrolytic cell. An electrolytic cell consists of:
 - i. the *electrolyte* which is the compound being decomposed. It is either a **molten** ionic compound or a concentrated **aqueous solution** of ions. Solid ionic compounds and covalent compounds cannot be used because they do not conduct electricity.
 - ii. the *electrodes* which are rods made from graphite or a metal which conducts electricity to and from the electrolyte.
 - *anode* is the positive electrode.
 - *cathode* is the negative electrode.
 - iii. external power supply of direct current and a complete d.c. circuit.



Redox reactions in electrolysis

- 1) During electrolysis, the **cations are attracted to the cathode** while the **anions are attracted to the anode**.

- 2) i. At the cathode, cations gain electrons and are reduced. **Reduction occurs at the cathode.**
 ii. At the anode, anions lose electrons and are oxidised. **Oxidation occurs at the anode.**
- 3) A simple example is the electrolysis of molten sodium chloride:
 i. At the cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$gain electrons, reduction.
 ii. At the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$lose electrons, oxidation.
 iii. Sodium metal and chlorine gas are produced.
- 4) For electrolysis of aqueous sodium chloride:
 i. In an aqueous solution of sodium chloride, four types of ions are present (Na^+ , Cl^- , H^+ and OH^-).
 ii. However, only one type of ion can be discharged at each electrode.
- 5) Factors that determine the selective discharge of ions in an electrolytic cell:
 i. **Position of the ion in the electrochemical series**
 - the lower it is in the electrochemical series, the higher the possibility for it to be discharged.
 ii. **Concentration of the ions**
 - the higher the concentration of the ion, the higher the possibility for it to be discharged.

The Electrochemical Series

K^+		F^-
Na^+		SO_4^{2-}
Ca^{2+}		NO_3^-
Mg^{2+}		Cl^-
Al^{3+}		Br^-
Zn^{2+}		I^-
Fe^{2+}		OH^-
Sn^{2+}		
Pb^{2+}		
H^+		
Cu^{2+}		
Ag^+		

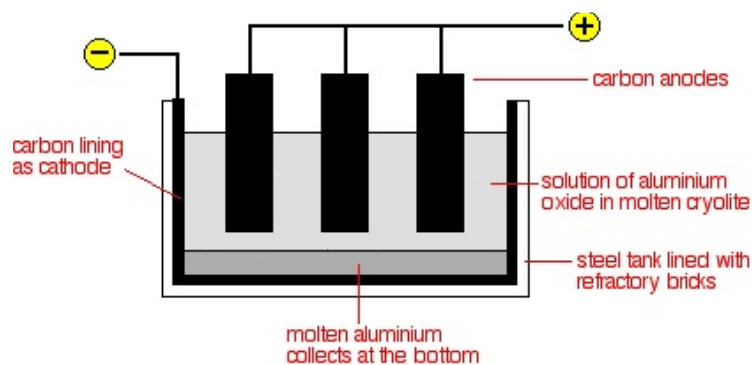


Ease of discharge
increases

- 6) For electrolysis of aqueous sodium chloride:
 i. At the cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$because H^+ is lower in the electrochemical series.
 ii. At the anode: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$because OH^- is lower in the electrochemical series.

Extraction of aluminium from bauxite ore

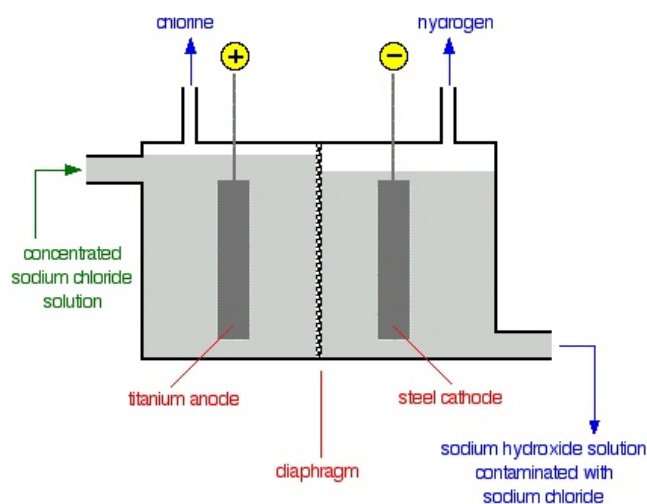
- 1) Bauxite is **impure aluminium oxide**, Al_2O_3 . The impurities are iron oxides, silicon dioxide and titanium dioxide. Bauxite is the major aluminium ore.
- 2) The first step is to purify the bauxite to get pure aluminium oxide, Al_2O_3 .
- 3) Molten aluminium oxide is electrolysed in a solution of cryolite, Na_3AlF_6 to give out the required aluminium metal.
- 4) The function of dissolving aluminium oxide in large amount of cryolite is to:
 - i. **lower the melting point** of the electrolyte from about 2140°C to 970°C .
 - ii. improve the electrical conductivity of the electrolyte.
- 5) Electrolysis of aluminium oxide is carried out in long narrow cells using carbon (graphite) electrodes.



- 6) At the cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$reduction
At the anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$oxidation
Overall equation: $4\text{Al}^{3+} + 6\text{O}^{2-} \rightarrow 4\text{Al} + 3\text{O}_2$ or $2\text{Al}_2\text{O}_3 \rightarrow 4\text{Al} + 3\text{O}_2$
- 7) Aluminium is denser than the electrolyte. It drops to the bottom of the electrolytic cell and is removed using a suction tube or through a tap hole.
- 8) The oxygen gas released will oxidise the hot carbon electrodes to carbon dioxide and carbon monoxide. So the electrodes have to be replaced from time to time.
- 9) Some environmental issues related:
 - i. The carbon monoxide gas produced is poisonous.
 - ii. Large amount of energy is needed because the current needed to electrolyse the electrolyte is very high.

Electrolysis of brine

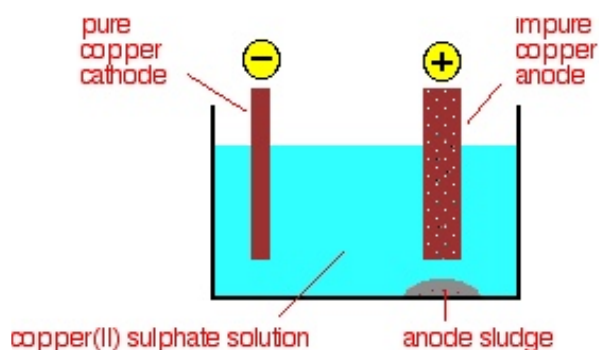
- 1) Brine is **concentrated aqueous solution of sodium chloride**. It is obtained from sea water or by dissolving rock salt in water.
- 2) Electrolysis of brine is used **to produce chlorine, hydrogen and sodium hydroxide**. A diaphragm cell is used to carry out this reaction.



- 3) The electrolyte level in the anode compartment is kept higher than in the cathode compartment. This ensures the flow of the solution is always towards the cathode compartment. This reduces the possibility of sodium hydroxide solution formed moving back as they are to be collected.
- 4) The ions present in the aqueous solution of sodium chloride are Na^+ , Cl^- , H^+ and OH^- . H^+ and OH^- comes from the slight ionisation of water.
$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$
- 5) At the cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$because H^+ is lower in the electrochemical series.
At the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$because Cl^- is in a far more greater concentration than OH^- .
Overall: **$2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 + \text{Cl}_2$**
- 6) As more and more H^+ are removed, more are formed from the ionisation of water because the position of equilibrium shifts to the right. The H^+ formed are being removed again until none is left.
- 7) At the same time, more and more OH^- are being produced. When all the H^+ are removed, only OH^- and Na^+ are left in the electrolyte and NaOH is formed.

Electrolytic purification of copper

- 1) Copper is purified to be used for electrical wiring because 99.99% of purity is required for efficient transmission of electrical energy. Even small amounts of impurity reduces its conductivity greatly.
- 2) Electrolytic purification of copper is carried out in cells using:
 - i. an electrolyte of **copper(II) sulfate solution** acidified with sulfuric acid.
 - ii. an anode of **impure copper**.
 - iii. a cathode of **pure copper**.



- 3) At the anode: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
At the cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- 4) The result is the transfer of copper from the anode to the cathode. As a result, **the cathode gets thicker and the anode get thinner**. The impurities in the anode settle down as anode 'sludge'.
- 5) The concentration of copper(II) sulfate solution **does not change** because the number of moles of Cu^{2+} ions formed at the anode is exactly the same as the number of moles of Cu^{2+} ions discharged at the cathode.