KCSE MAPPING ON REACTION RATES AND REVERSIBLE REACTIONS CHEMISTRY PP 1 2 & 3 FROM 1995-2022

YEAR	QUESTION
1995	PP1 Q. 2
1996	PP1 Q.4, PP2 Q.1
1997	PP2 Q.5
1998	PP1 Q.8
1999	PP1 Q.16, PP3 Q2
2000	PP1 Q19
2001	PP1 Q.2, PP2 Q.1, PP3 Q.1
2002	PP1 Q.19, PP3 Q. 1
2003	PP1 Q.19, PP2 Q.4
2005	PP1 Q.10
2006	PP1 Q.9, PP2 Q.4
2007	PP2 Q.4
2008	PP1 Q.23, PP2 Q.4
2009	PP1 Q.27
2010	PP1 Q. 22 & 23, PP2 Q.7
2011	PP1 Q16, PP2 Q.3 & 4
2012	PP1 Q.13 &17, PP2 Q.4, PP3 Q.1
2013	PP1 Q.16&27
2014	PP1 Q.17, PP2 Q.4, PP3 Q.1
2015	PP1 Q.12, PP2 Q.6
2016	PP2 Q.3, PP3 Q.1
2017	PP1 Q.8
2019	PP1 Q.2, PP2 Q.7
2020	PP1 Q.13, PP2 Q.2
2021	PP1 Q10, PP2 Q.3
2022	PP1 Q.6 &24, PP2 Q.4, PP3 Q.1
2023	?

92.59%
TESTED

Chemical Equilibrium

- Reversible Reactions. Not all chemical reactions proceed to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus **A** and **B** may react to form **C** and **D** which react together to reform **A** and **B**.

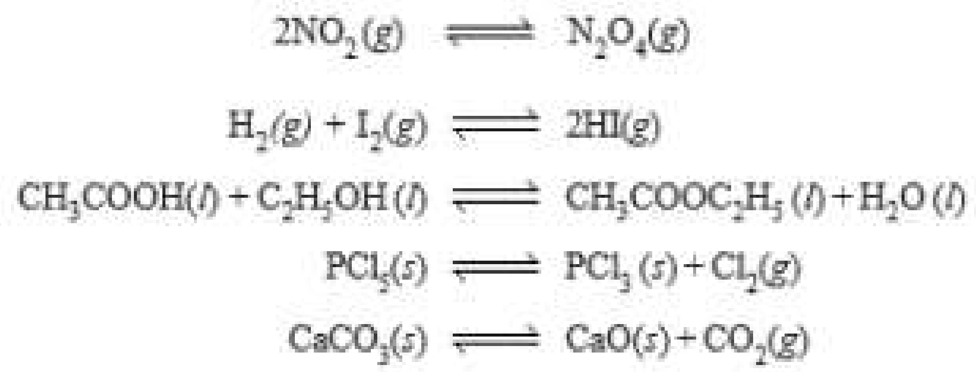
$$A + B \longrightarrow C + D \text{ (Forward reaction)}$$

$$A + B \longleftarrow C + D \text{ (Reverse reaction)}$$

- A reaction which can go in the forward and backward direction simultaneously is called **a Reversible reaction**. Such a reaction is represented by writing a pair of arrows between the reactants and products.

$$A + B \rightleftharpoons C + D$$

- The arrow pointing right indicates the forward reaction, while that pointing left shows the reverse reaction.
- A few common examples of reversible reactions are listed below:



$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

$$PCl_5(s) \rightleftharpoons PCl_3(s) + Cl_2(g)$$

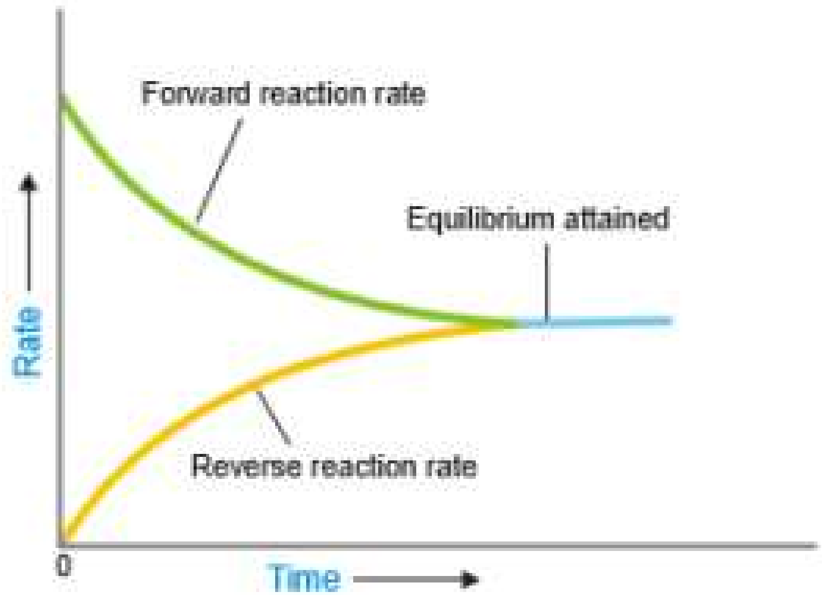
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Nature Of Chemical Equilibrium: It’s Definition.

- Let us consider the reaction;

$$A + B \rightleftharpoons C + D$$

- If we start with **A** and **B** in a closed vessel, the forward reaction proceeds to form **C** and **D**. The concentrations of **A** and **B** decrease and those of **C** and **D** increase continuously. As a result the rate of forward reaction also decreases and the rate of the reverse reaction increases. Eventually, the rate of the two opposing reactions equals and the system attains a state of equilibrium.
- Thus Chemical equilibrium may be defined as: the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.
- Furthermore, the true equilibrium of a reaction can be attained from both sides. Thus the equilibrium concentrations of the reactants and products are the same whether we start with A and B, or C and D.



- Areaction in which the rate of forward reaction is equal to the rate of backward reaction is called a **dynamic equilibrium**. A dynamic equilibrium is therefore a balance of the rate of formation of products and reactants. This balance continues until the reactants or products are disturbed/changed/ altered.
- Dynamic equilibrium can also be defined as a reaction where the rates of forward and backward reactions are the same or equal.

Le chatelier's principle:

- The Le Chatelier's principle may be stated as : **when a stress is applied on a system in equilibrium, the system tends to adjust itself so as to reduce the stress.**
- There are three ways in which the stress can be caused on a chemical equilibrium (Factors Affecting Equilibrium):

  (1)Changing the concentration of a reactant or product.

  (2)Changing the pressure (or volume) of the system.

  (3)Changing the temperature.

- ☐ Thus when applied to a chemical reaction in equilibrium, Le Chatelier's principle can be stated as: **if a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimize the change.**

Effect Of A Change In Concentration on Equilibrium.

- We can restate Le Chatelier’s principle for the special case of concentration changes: **when concentration of any of the reactants or products is changed, the equilibrium shifts in a direction so as to reduce the change in concentration that was made**.

Effect of change of concentration on Ammonia Synthesis reaction.

- Let us illustrate the effect of change of concentration on a system at equilibrium by taking example of the ammonia synthesis reaction:

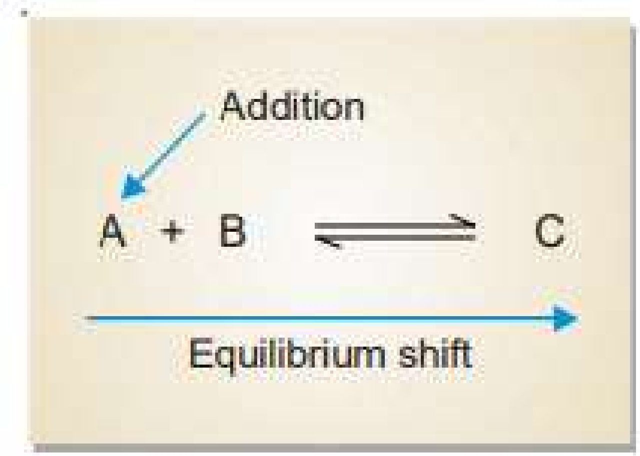
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

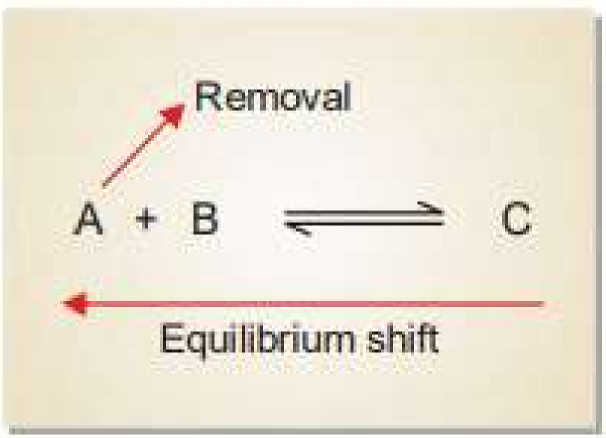
- When N2 (or H2) is added to the equilibrium already in existence (equilibrium I), the equilibrium will shift to the right so as to reduce the concentration of N2 (Le Chatelier’s principle). The concentration of NH3 at the equilibrium II is more than at equilibrium I.

- The addition of N_2 (a reactant) increases the concentration of NH_3, while the concentration of H_2 decreases. Thus to have a better yield of NH_3, one of the reactants should be added in excess.
- A change in the concentration of a reactant or product can be effected by the addition or removal of that species. Let us consider a general reaction

$$A + B \rightleftharpoons C$$

- When a reactant, say, A is added at equilibrium, its concentration is increased. The forward reaction alone occurs momentarily. According to Le Chatelier’s principle, a new equilibrium will be established so as to reduce the concentration of A. Thus the addition of A causes the equilibrium to shift to right. This increases the concentration (yield) of the product C.





- A decrease in the concentration of A by its removal from the equilibrium mixture, will be undone by shift to the equilibrium position to the left. This reduces the concentration (yield) of the product C.

Examples of influence of concentration on dynamic equilibrium

i. When sodium hydroxide is added to bromine water, it provides hydroxide ions which react with hydrogen ions in the solution to form water.

$$\underbrace{Br_2(aq) + H_2O(l)}_{\textit{Yellow-orange}} \rightleftharpoons \underbrace{OBr^-(aq) + Br^-(aq) + 2H^+(aq)}_{\textit{Colourless}}$$

- The removal of hydrogen ions from the equilibrium mixture makes the reaction to shift more to the right. This leads to fading of the yellow-orange colour, hence the changes in colour from yellow-orange to colourless.

- Addition of hydrochloric acid to bromine water introduces hydrogen ions which react with the colourless bromide and hypobromite ions to form yellow-orange aqueous bromine**. This causes the reaction to shift more to the left hence the increase in intensity of the yellow-orange colour.**
- **NOTE:** Decreasing the concentration of the hydrogen ions increases the rate of the forward reactions, hence the equilibrium shifts to the right, while increasing the concentration of hydrogen ions shifts the equilibrium to the left.

(ii) Chromate(VI)/CrO_4^{2-} ions in solution are **yellow**. Dichromate(VI)/$Cr_2O_7^{2-}$ ions in solution are orange. The two solutions exist in equilibrium as in the equation:

$$2H^{+}(aq) + \underset{\text{(Yellow)}}{2CrO_4^{2-}(aq)} \rightleftharpoons \underset{\text{(Orange)}}{Cr_2O_7^{2-}(aq)} + H_2O(l)$$

I. If an acid is/**H^+** (aq) is added to the equilibrium mixture a stress is created on the reactant side where there is already H^+ ions. The equilibrium shift forward to the right to remove/reduce the excess H^+ ions added. Solution mixture becomes More $Cr_2O_7^{2-}$ ions formed in the solution mixture hence the increase in intensity of the orange colour.

II. If a base/**OH^-** (aq) is added to the equilibrium mixture a stress is created on the reactant side on the H^+ ions. H^+ ions react with OH^- (aq) to form water.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The equilibrium shift backward to the left to replace the H^+ ions that have reacted with the OH^- (aq) ions . More of the CrO_4^{2-} ions formed in the solution mixture hence intensifies the **yellow** in colour.

III

$$2OH^-(aq) + \underset{\text{(Orange)}}{2Cr_2O_7^{2-}(aq)} \rightleftharpoons \underset{\text{(Yellow)}}{CrO_4^{2-}(aq)} + H_2O(l)$$

I. If an acid/ H^+ (aq) is added to the equilibrium mixture a stress is created on the reactant side on the OH^- (aq). H+ ions react with OH^- (aq) to form water.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The equilibrium shift backward to the left to add/replace the $2OH^-$ (aq) that have reacted with the H^+ (aq) ions . More $Cr_2O_7^{2-}$(aq) ions formed in the solution mixture makes it to be more Orange in colour.

II. If a base /OH^- (aq) is added to the equilibrium mixture a stress is created on the reactant side where there is already OH^- (aq) ions. The equilibrium shift forward to the right to remove/reduce the excess OH- (aq) ions added. More of the Cr_2O_7 $^{2-}$ ions are formed in the solution mixture making it to be more orange in colour.

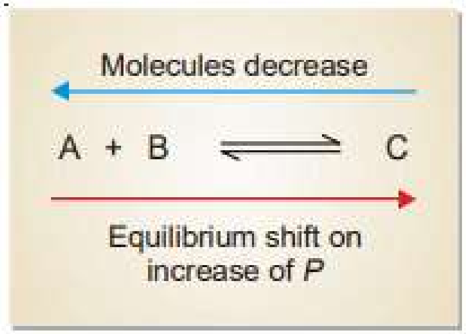
Effect of a Change In Pressure on dynamic equilibrium.

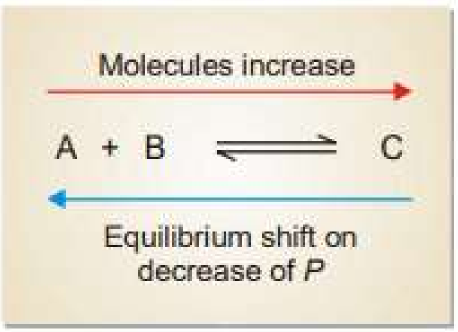
- To predict the effect of a change of pressure, Le Chatelier's principle may be stated as : **when pressure is increased on a gaseous equilibrium reaction, the equilibrium will shift in a direction which tends to decrease the pressure**.t
- The pressure of a gaseous reaction at equilibrium is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will be accompanied by a decrease of pressure of the system and *vice versa.OF*

Let us consider a reaction,

$$A + B \rightleftharpoons C$$

- The combination of **A** and **B** produces a decrease of number of molecules while the decomposition of **C** into **A** and **B** results in the increase of molecules. Therefore, by the increase of pressure on the equilibrium it will shift to right and give more **C**. A decrease in pressure will cause the opposite effect. The equilibrium will shift to the left when **C** will decompose to form more of **A** and **B**.





- The reactions in which the number of product molecules is equal to the number of reactant molecules,

e.g., $$H_2(g) + I_2(g) \rightleftharpoons 2HI$$

are unaffected by pressure changes. In such a case the system is unable to undo the increase or decrease of pressure.

NOTE:**The increase of pressure on a chemical equilibrium shifts it in that direction in which the number of molecules decreases and vice-versa.** This rule is illustrated by the examples listed in Table below.

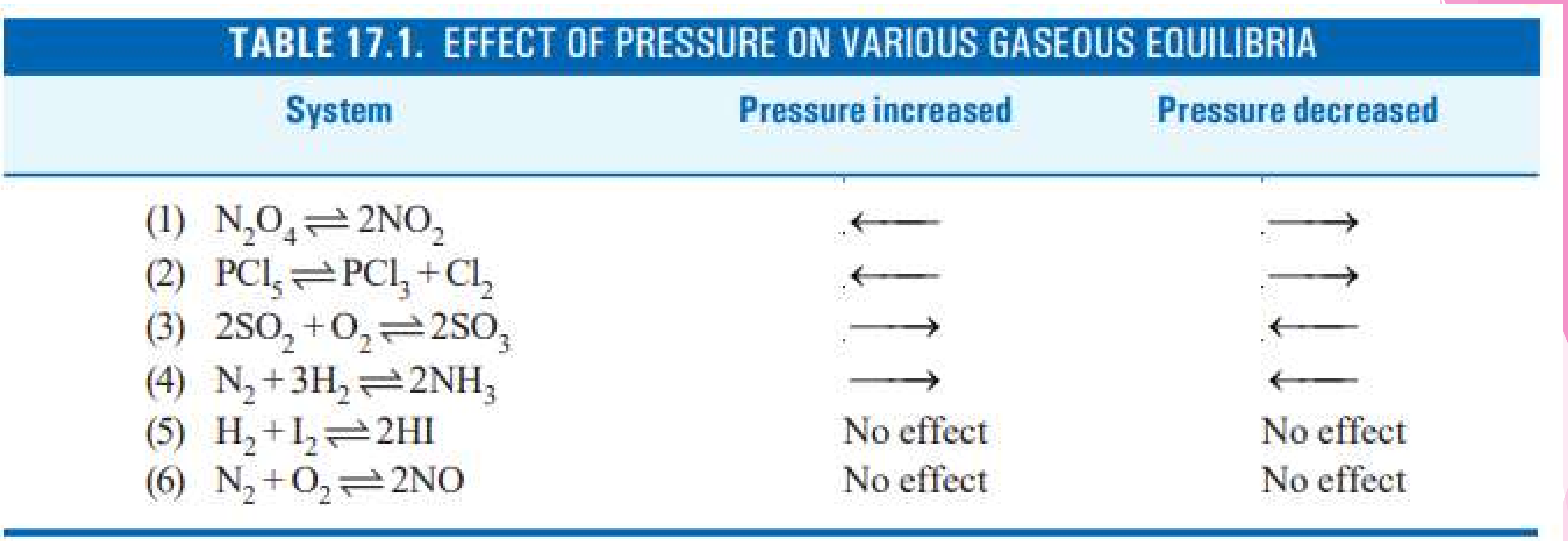


TABLE 17.1. EFFECT OF PRESSURE ON VARIOUS GASEOUS EQUILIBRIA

System	Pressure increased	Pressure decreased
(1) $N_2O_4 \rightleftharpoons 2NO_2$	←	→
(2) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$	←	→
(3) $2SO_2 + O_2 \rightleftharpoons 2SO_3$	→	←
(4) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	→	←
(5) $H_2 + I_2 \rightleftharpoons 2HI$	No effect	No effect
(6) $N_2 + O_2 \rightleftharpoons 2NO$	No effect	No effect

Effect Of Change Of Temperature on dynamic equilibrium

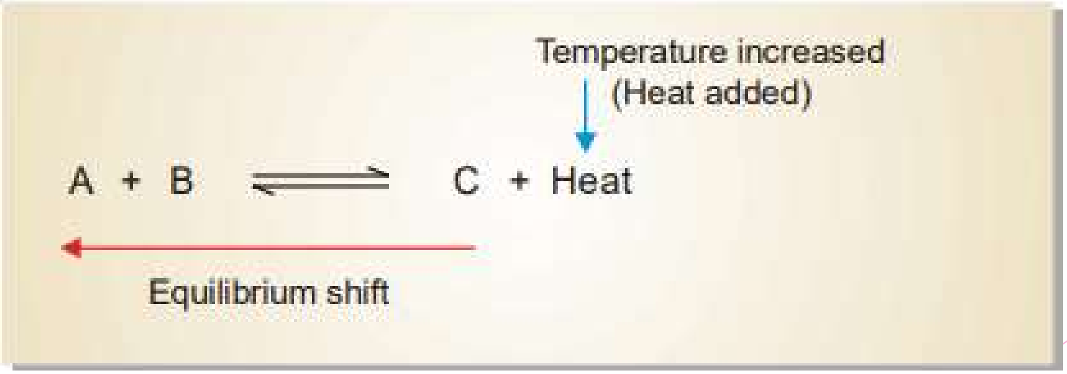
- Chemical reactions consist of two opposing reactions. If the forward reaction proceeds by the evolution of heat (exothermic), the reverse reaction occurs by the absorption of heat (endothermic). Both these reactions take place at the same time and equilibrium exists between the two.

- If temperature of a reaction is raised, heat is added to the system. The equilibrium shifts in a direction in which heat is absorbed in an attempt to lower the temperature. Thus the effect of temperature on an equilibrium reaction can be easily predicted by the following version of the Le Chatelier’s principle. **When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.**

Let us consider an exothermic reaction,

$$A + B \rightleftharpoons C + \text{heat}$$

- When the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier’s principle, the equilibrium will shift to the left which involves the absorption of heat. This would result in the increase of the concentration of the reactants A and B.

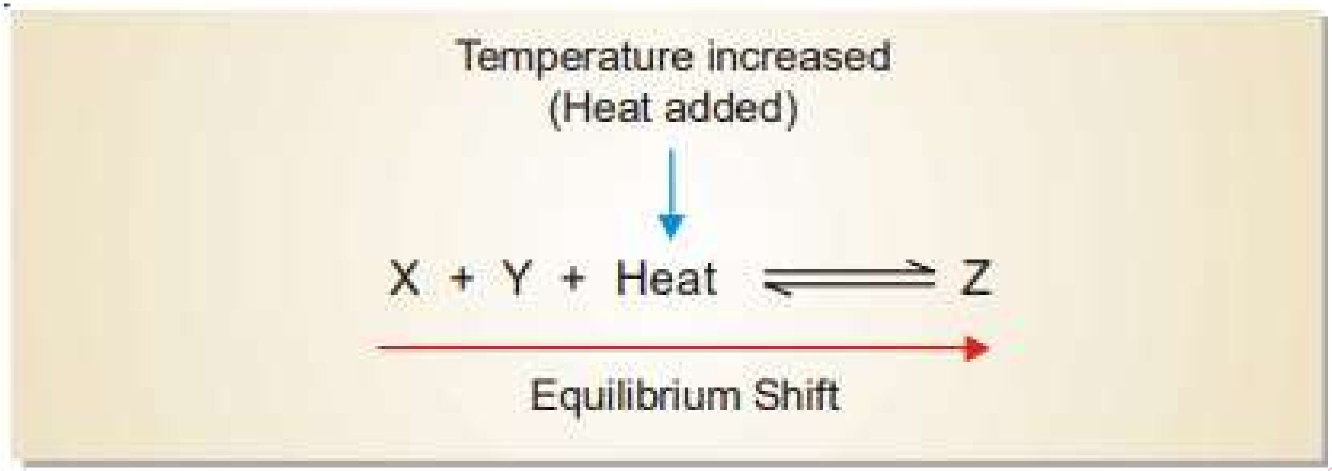


- In an endothermic reaction

$$X + Y + \text{heat} \rightleftharpoons Z$$

the increase of temperature will shift the equilibrium to the right as it involves the absorption of heat. This increases the concentration of the product Z.

In general, we can say that **the increase of temperature favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.**


Temperature increased
(Heat added)

$$X + Y + \text{Heat} \rightleftharpoons Z$$

Equilibrium Shift

Formation of Ammonia from N_2 and H_2

- The synthesis of ammonia from nitrogen and hydrogen is an exothermic reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 92.2\,\text{kJ/mol}$$

- When the temperature of the system is raised, the equilibrium will shift from right-to-left which absorbs heat (Le Chatelier’s principle). This results in the lower yield of ammonia. On the other hand, by lowering the temperature of the system, the equilibrium will shift to the right which evolves heat in an attempt to raise the temperature. This would increase the yield of ammonia.
- But with decreasing temperature, the rate of reaction is slowed down considerably and the equilibrium is reached slowly. Thus in the commercial production of ammonia, it is not feasible to use temperature much lower than 500°C. At lower temperature, even in the presence of a catalyst, the reaction proceeds too slowly to be practical.

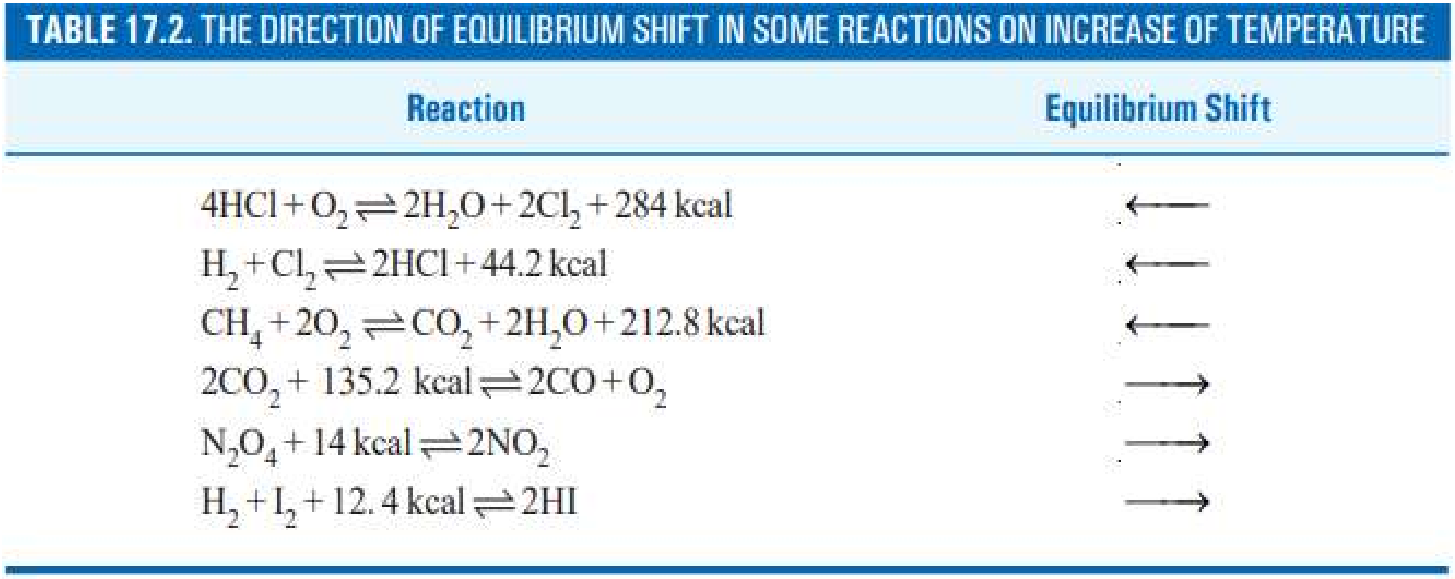


TABLE 17.2. THE DIRECTION OF EQUILIBRIUM SHIFT IN SOME REACTIONS ON INCREASE OF TEMPERATURE

Reaction	Equilibrium Shift
$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2 + 284\ \text{kcal}$	⟵
$H_2 + Cl_2 \rightleftharpoons 2HCl + 44.2\ \text{kcal}$	⟵
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O + 212.8\ \text{kcal}$	⟵
$2CO_2 + 135.2\ \text{kcal} \rightleftharpoons 2CO + O_2$	⟶
$N_2O_4 + 14\ \text{kcal} \rightleftharpoons 2NO_2$	⟶
$H_2 + I_2 + 12.4\ \text{kcal} \rightleftharpoons 2HI$	⟶

Note: kcal is the short form for kilocalories.
1kcal = 4.184kJ

CONDITIONS FOR MAXIMUM YIELD IN INDUSTRIAL PROCESSES

- With the help of Le Chatelier’s principle we can work out the optimum conditions for securing the maximum yield of products in industrial processes.

Synthesis of Ammonia (Haber Process)

- The manufacture of ammonia by Haber process is represented by the equation

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 92.2 kJ/mol$$

- A look at the equation provides the following information:

(a) the reaction is exothermic

(b) the reaction proceeds with a decrease in the number of moles.

i. **Low temperature**. By applying Le Chatelier’s principle, low temperature will shift the equilibrium to the right. This gives greater yield of ammonia. In actual practice a temperature of about 450°C is used when the percentage of ammonia in the equilibrium mixture is 15.

ii. **High pressure**. High pressure on the reaction at equilibrium favours the shift of the equilibrium to the right. This is so because the forward reaction proceeds with a decrease in the number of moles. A pressure of about 200 atmospheres is applied in practice

iii. **Catalyst.** As already stated, low temperature is necessary for higher yield of ammonia. But at relatively low temperatures, the rate of reaction is slow and the equilibrium is attained in a long time. To increase the rate of reaction and thus quicken the attainment of equilibrium, a catalyst is used. **Finely divided iron** containing **molybdenum** is employed in actual practice. **Molybdenum** acts as a promoter that increases the life and efficiency of the catalyst.

Note: Pure N_2 and H_2 gases are used in the process. Any impurities in the gases would poison the catalyst and decrease its efficiency.

Manufacture of Sulphuric acid (Contact Process)

- The chief reaction used in the process is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 175.7\text{kJ/mol}$$

Following information is revealed by the above equation:

(a) the reaction is exothermic.

(b) the reaction proceeds with a decrease in number of moles.

On the basis of Le Chatelier's principle, the conditions for the maximum yield can be worked out as below:

i. **Low temperature**. Since the forward reaction is exothermic, the equilibrium will shift on the right at low temperature. An optimum temperature between 400-450°C is required for the maximum yield of sulphur (VI) oxide.

ii. **High pressure**. Since the number of moles are decreased in the forward reaction, increase of pressure will shift the equilibrium to the right. Thus for maximum yield of SO_3, 2 to 3 atmosphere pressure is used.

iii. **Catalyst.** At the low temperature used in the reaction, the rate of reaction is slow and the equilibrium is attained slowly. A catalyst is, therefore, used to speed up the establishment of the equilibrium. Vanadium (V) oxide, V_2O_5, is commonly used and it has replaced the earlier catalyst *platinum asbestos* which was easily poisoned by the impurities present in the reacting gases. All the same, SO_2 and O_2 used for the manufacture of sulphuric acid must be pure and dry.

Manufacture of Nitric acid (Birkeland-Eyde process)

Nitric acid is prepared on a large scale by making use of the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \text{ - 180.75kJ/mol}$$

The equation tells us that:

(a) the reaction proceeds with no change in the number of moles.

(b) the reaction is endothermic and proceeds by absorption of heat.

The favourable conditions for the maximum yield of NO are:

i. **High temperature**. Since the forward reaction is endothermic, increase of temperature will favour it (Le Chatelier's principle). Thus a high temperature of the order of 3000°C is employed to get high yield of nitric acid.

ii. **No effect of pressure**. Since the forward reaction involves no change in the number of moles, a change in pressure has no effect on the equilibrium.

iii. **High concentration**. The formation of nitric oxide is favoured by using high concentrations of the reactants i.e. N_2 and O_2.

END

It was a nice journey, now read and revise this entire topic 3 times for it will not miss in your chemistry exams.

ORGANIC CHEMISTRY II (ALKANOLS AND AKANOIC ACIDS)

ALKANOLS (ALCOHOLS)

- **Alkanols** are alkane-derived organic compounds that have an alcohol (-OH) functional group bonded to them. That is one hydrogen atoms from an alkane is replaced with hydroxyl (-OH) group.
- Alkanols have a hydroxyl (-OH) which is the functional group of the series. The functional group determines the chemical properties of the alkanols.
- They are saturated organic compounds.

General formula and nomenclature of alkanols

- The genera formula of alkanols is **ROH**, where R is an alkyl group. Alkyl group is the name given to the group of atoms remaining when one of the hydrogen atom of an alkane is removed. Eg

Methane (CH_4) ⟶ Methyl (CH_3) group.

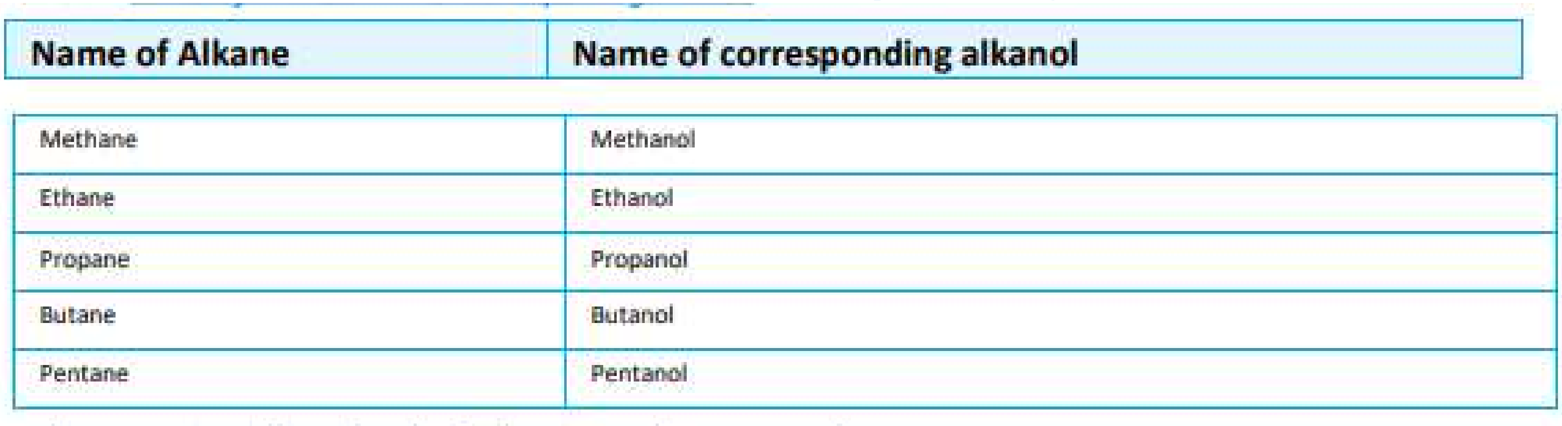
Ethane (CH_3CH_3) ⟶ ethyl (CH_3CH_2-) group

- Methyl and ethyl are examples of alkyl groups and can be represented by letter **R**.
- To get the number of carbon and hydrogen atoms, represented by **R** in the general formula, we use another formula $C_nH_{2n+1}OH$, where n is the number of carbon atoms which can be 1, 2, 3, 4………..

Nomenclature

- Alkanols are named by replacing the ‘e’ of the corresponding alkene with the suffix –ol.

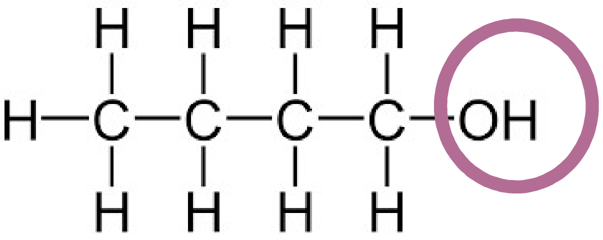
Names of Alkanes and their corresponding Alkanols



Name of Alkane	Name of corresponding alkanol
Methane	Methanol
Ethane	Ethanol
Propane	Propanol
Butane	Butanol
Pentane	Pentanol

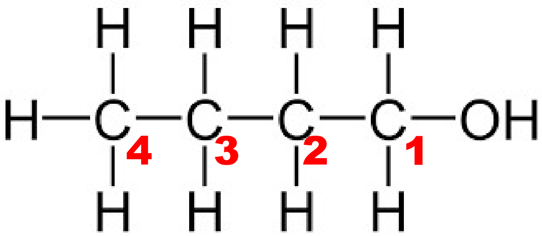
Rules for naming alkanols

I. Identify the longest carbon chain containing the hydroxyl group (-OH) which gives the parent name:

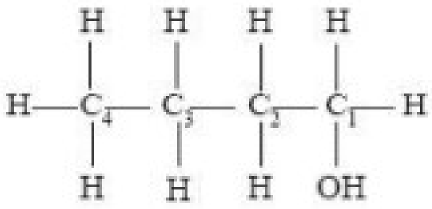


Butan-

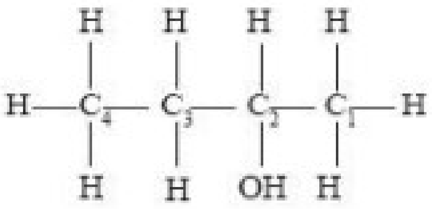
II. Number the longest carbon chain such that the carbon to which the hydroxyl group is attached has the lowest number possible.



III. Indicate the position of the hydroxyl group in the name, e.g

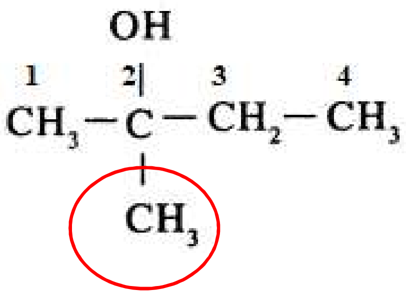


Butan -1- ol



Butan - 2- ol

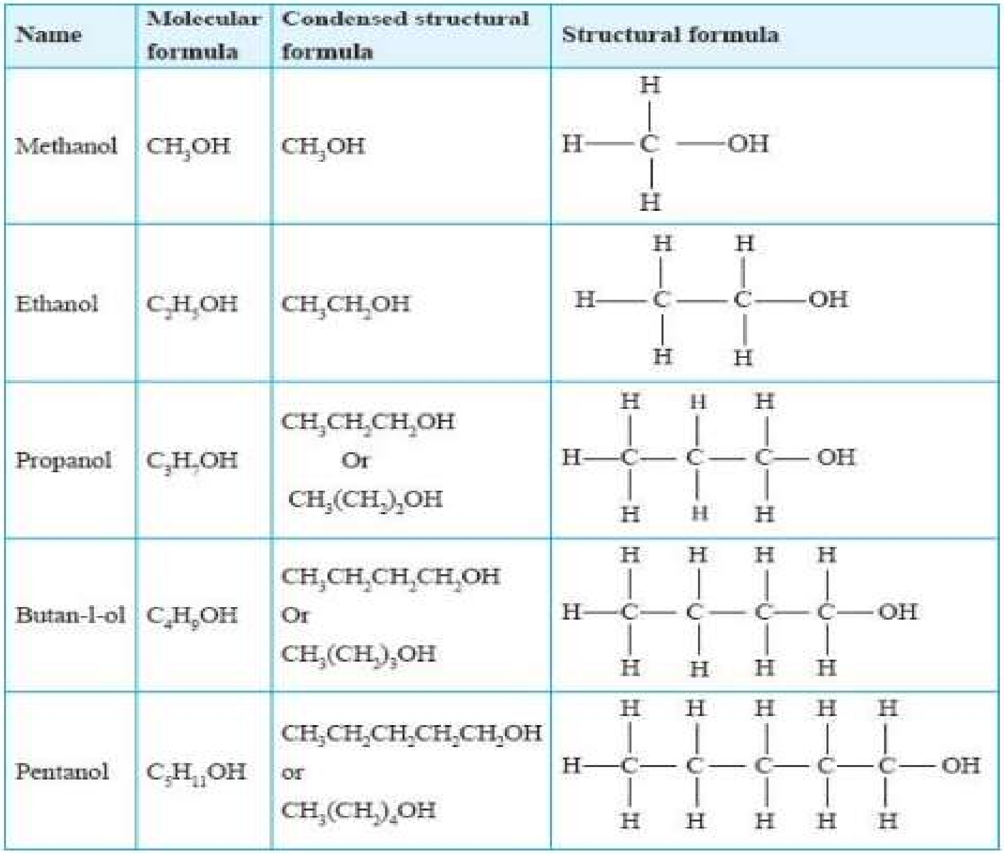
IV. Locate the position of the other substituent groups using numbers that correspond to their position along the carbon chain.



$$\overset{1}{CH_3}-\overset{OH}{\overset{2}{\underset{CH_3}{C}}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

2-Methylbutan-1-ol

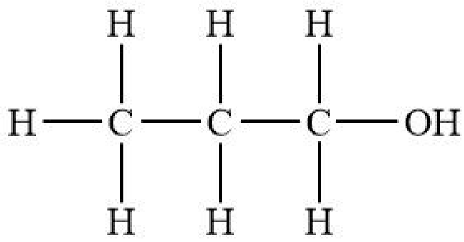
Names, molecular formula and structures of some alkanols



Name	Molecular formula	Condensed structural formula	Structural formula
Methanol	CH_3OH	CH_3OH	$H-\overset{H}{\underset{H}{C}}-OH$
Ethanol	C_2H_5OH	CH_3CH_2OH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$
Propanol	C_3H_7OH	$CH_3CH_2CH_2OH$ Or $CH_3(CH_2)_2OH$	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$
Butan-1-ol	C_4H_9OH	$CH_3CH_2CH_2CH_2OH$ Or $CH_3(CH_2)_3OH$	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$
Pentanol	$C_5H_{11}OH$	$CH_3CH_2CH_2CH_2CH_2OH$ or $CH_3(CH_2)_4OH$	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$

Isomerism

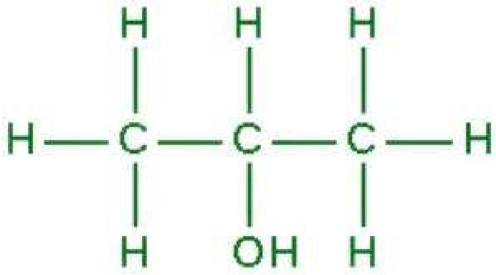
- Alkanols exhibit two types of isomerism, positional and branching isomerism. In positional isomerism the position of the functional group (-OH) varies within the carbon chain. For example: When the -OH group is attached to the first carbon atoms, the molecular structure can be represented as:



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & \mid & & \mid & & \mid & & \\ H & - & C & - & C & - & C & - & OH \\ & & \mid & & \mid & & \mid & & \\ & & H & & H & & H & & \end{array}$$

Propan-1-ol

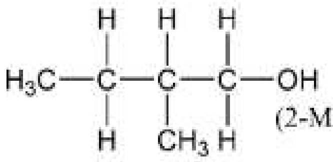
- When the OH group is attached to the second carbon atom the molecular structure will be:



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & \mid & & \mid & & \mid & & \\ H & - & C & - & C & - & C & - & H \\ & & \mid & & \mid & & \mid & & \\ & & H & & OH & & H & & \end{array}$$

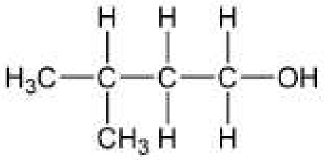
Propan-2-ol

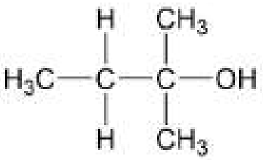
- In branching isomerism, the molecular formula of the compound remains the same. However, there is rearrangement of carbon atoms such that one or more carbon atoms from the molecule form alkyl groups attached to the longest carbon chain. For example:



(2-Methylbutan-1-ol)

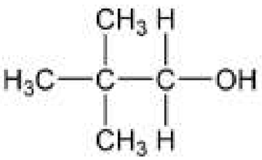
(3-Methylbutan-1-ol)



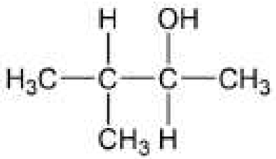


(2-Methylbutan-2-ol)

(2,2 dimethylpropan-1-ol)



(3-Methylbutan-2-ol)



Preparation of Alkanols

- Alkanols can be prepared in two ways;

I. **Hydrolysis of alkenes.**

II. **Fermentation of carbohydrates** e.g. starch and sugars such as glucose, etc

Preparation of ethanol by hydrolysis of ethane

- Ethanol is produced in large quantities, from hydrolysis of ethene.
- Ethene to be used in this process is produced by **cracking long chain alkanes** which are broken down into an alkene and shorter alkane.
- The ethene produced is mixed with steam and passed over **a phosphoric acid catalyst** at a **temperature of about 300˚C** and **60 atmospheres pressure** to produce ethanol.

$$C_2H_4(g) + H_2O(g) \underset{\text{Phosphoric acid catalyst}}{\overset{300^{\circ}C,\ 60atm}{\rightleftharpoons}} C_2H_5OH(g)$$

General formula;

$$C_nH_{2n} + H_2O(g) \xrightleftharpoons[\text{Phosphoric acid catalyst}]{300^\circ C,\ 60atm} C_nH_{2n+1}OH$$

- Ethene can be also hydrolysed using concentrated sulphuric(VI) acid.

$$CH_2H_4(g) + H_2SO_4(aq) \longrightarrow C_2H_5OSO_3H(l)$$

- When water is added to the mixture, the ethylhydrogen sulphate is hydrolysed to ethanol.

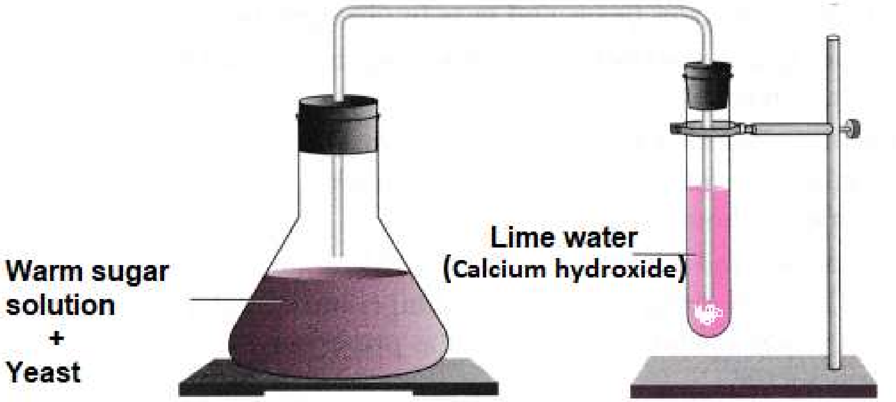
$$CH_3CH_2OSO_3H(g) + H_2O(l) \longrightarrow CH_3CH_2OH(l) + H_2SO_4(aq)$$

- The mixture of ethanol and the acid is separated by distillation because of the difference in **boiling points.**

Preparation of ethanol by fermentation of glucose in the laboratory

Experiment;

- Add 10g of ordinary sugar to 100 cm3 of warm water in a conical flask. Add a spatulaful of yeast to the solution. Set up the apparatus as shown below.
- Leave the mixture undisturbed for about 2-3 days at a temperature of about 30oC. Record all the observations that are made. After about 2 days, remove the cork and smell.



- **Fermentation** is the decomposition of an organic substance by micro-organisms to produce alcohol, carbon(IV) oxide and heat.
- Ethanol is a colourless liquid with a distinct characteristic smell. Ethanol can be prepared by the decomposition of glucose molecules in the presence of enzymes. The sugar ($C_6H_{12}O_6$) molecules are broken down into ethanol and carbon(IV) oxide by the enzymes in the yeast. Calcium hydroxide is used to **test the presence of carbon(II) oxide**, this is confirmed by the formation of the white precipitate.
- Yeast in this case is used as a catalyst.

$$\text{Glucose} + \xrightarrow{\text{yeast}} \text{Ethanol} + \text{carbon(IV) oxide}$$

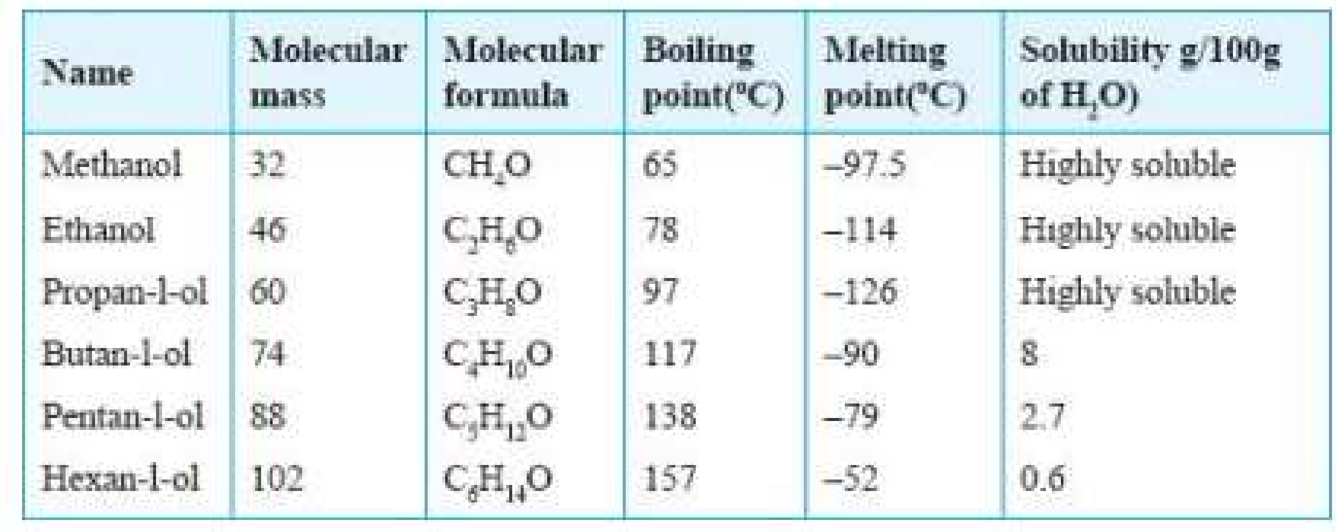
$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2C_2H_5OH(aq) + 2CO_2(aq)$$

- However, a very small amount of alcohol is usually produced by fermentation (about 10% ethanol by volume). The alcohol content can be **increased by fractional distillation** of the crude solution. The ethanol obtained contains 5% water. **The water can be removed by using a suitable drying agent such as calcium oxide**, to obtain absolute ethanol.

Physical properties of alkanols (alcohols)

- Alcohols are colourless.
- They generally give a sweet smell except for glycerol and a few lower alcohols.
- They are flammable and produce a blue flame; because they are saturated
- They don't produce any smoke while burning. Because they are saturated
- They are generally liquid at room temperature. Although glycerol is a viscous liquid
- Boiling Point of Alcohol - They generally have higher boiling points if we compare them with other hydrocarbons. For example, ethanol shows a boiling point of 78.29°C while hexane shows a boiling point of 69°C. **This is because of the presence of intermolecular hydrogen bonding between hydroxyl groups of alcohols.** The boiling point of alcohol. **increases with an increasing number of carbon atoms in organic alcoholic compounds.**
- **Alcohols are acidic in nature**. They react with metals such as sodium, potassium etc. It is due to the polarity of the bond between a hydrogen atom and the oxygen atom of the hydroxyl group.

- Alcohols are soluble in water since they are polar molecules. Solubility decreases with increase in molecular weight.



Name	**Molecular mass**	**Molecular formula**	**Boiling point(°C)**	**Melting point(°C)**	**Solubility g/100g of H_2O)**
Methanol	32	CH_4O	65	–97.5	Highly soluble
Ethanol	46	C_2H_6O	78	–114	Highly soluble
Propan-l-ol	60	C_3H_8O	97	–126	Highly soluble
Butan-l-ol	74	$C_4H_{10}O$	117	–90	8
Pentan-l-ol	88	$C_5H_{12}O$	138	–79	2.7
Hexan-l-ol	102	$C_6H_{14}O$	157	–52	0.6

Chemical properties of Alkanols (alcohols)

I. Combustion of alcohols.

- Alcohols burns readily in air with a pale blue flame to produced carbon (IV) oxide and water only. This is because alcohols are saturated and undergoes complete combustion. For example ethanol burns in air to produce carbon (IV) oxide and water.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

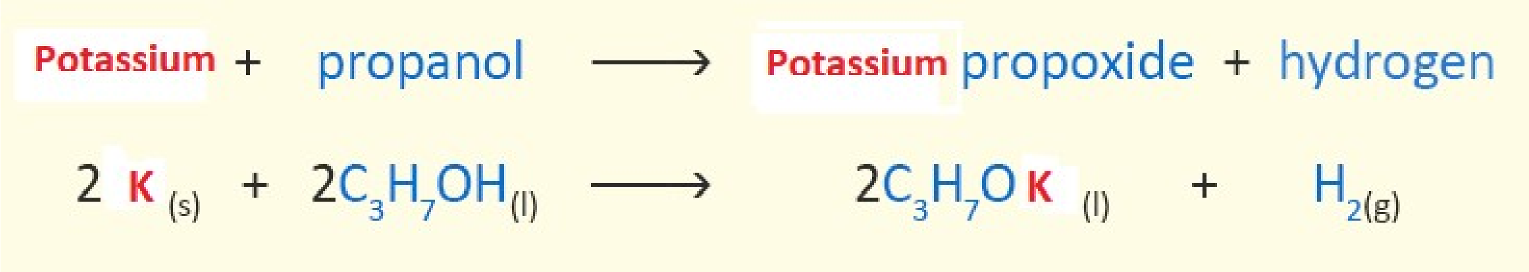
II. Reaction of alkanols with sodium or potassium

- Since the solutions of alkanols have a pH slightly below 7 (week base) they react with metals such as sodium and potassium to liberate hydrogen gas and salt, (metal alkyloxide)
- For example sodium reacts with ethanol to liberate hydrogen gas and sodium ethoxide.

$$\text{Ethanol} + \text{sodium} \longrightarrow \text{sodium ethoxide} + \text{hydrogen}$$

$$2C_2H_5OH(l) + 2Na(s) \longrightarrow 2C_2H_5ONa(aq) + H_2(g)$$

- Sodium ethoxide hydrolyses in water to generate –OH which makes the solution alkaline.
- Potassium also reacts with propanol to produce hydrogen gas and potassium propoxide, as shown below.



Potassium + propanol ⟶ Potassium propoxide + hydrogen

$$2\,K_{(s)} + 2C_3H_7OH_{(l)} \longrightarrow 2C_3H_7OK_{(l)} + H_{2(g)}$$

☐ Metals reacts with any other alkanol to liberate a salt and hydrogen gas

☐ **Note:** The general equation of the reaction is:

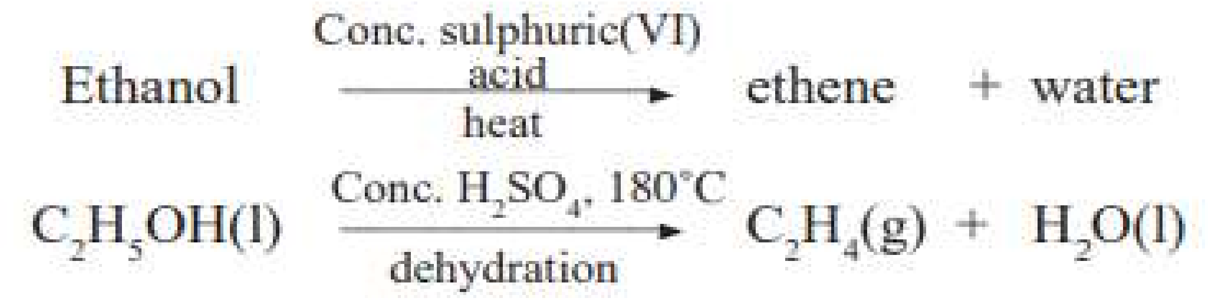
$$\mathbf{2R–OH(aq) + 2M(s) \longrightarrow 2ROM(aq) + H_2\ (g)}$$

Where, R – alkyl group of the reacting alkanol.

M – metal reacting with the alkanol e.g. potassium or sodium

III. Reaction of ethanol with concentrated sulphuric (VI) acid

- Concentrated (VI) sulphuric acid reacts with ethanol at 180˚C to form ethene and water. This is a **dehydration** reaction. This is the reverse of the reaction used to produce ethanol from ethene.



$$\text{Ethanol} \xrightarrow[\text{heat}]{\text{Conc. sulphuric(VI) acid}} \text{ethene} + \text{water}$$

$$C_2H_5OH(l) \xrightarrow[\text{dehydration}]{\text{Conc. } H_2SO_4,\ 180^\circ C} C_2H_4(g) + H_2O(l)$$

Note: At 140˚C another organic compound known as ether is formed.

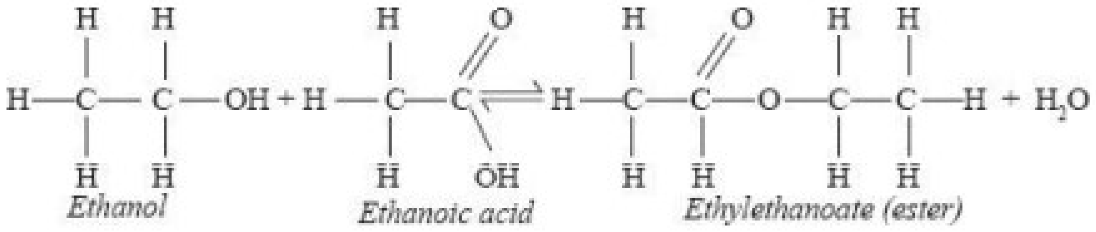
IV. Ester formation

- 4. Ester formation Alkanols react with alkanoic acids presence of a few drops of concentrated sulphuric(VI) acid to form compounds with a **pleasant smell** called **esters**. For example, ethanol reacts with ethanoic acid in the presence of a few drops of concentrated sulphuric(VI) acid(**catalyst**) to form a substance with characteristic pleasant smell called **ethyl ethanoate**. This substance is an ester. The process of ester formation is known as **esterification**.

$$\text{Ethanol} + \text{ethanoic acid} \underset{H_2SO_4}{\overset{\text{Conc.}}{\rightleftharpoons}} \text{ethyl ethanoate} + \text{water}$$

$$CH_3CH_2OH(l) + CH_3COOH(aq) \underset{H_2SO_4}{\overset{\text{Conc.}}{\rightleftharpoons}} \underset{\text{(Ester)}}{CH_3COOCH_2CH_3} + H_2O$$

- Below is the equation showing the structural formulae of the reactants and products.

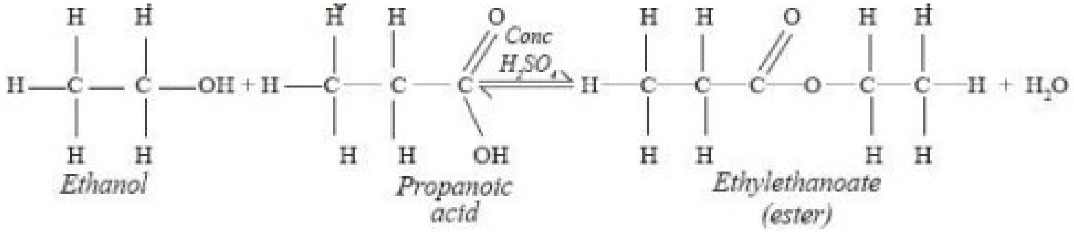


- The **alkyl** part of the ester is derived from the alkanol, while the **alkanoate** part is derived from the acid. The **alkyl group from the alkanol attaches itself to the carboxylic acid thereby displacing a hydrogen atom**.
- Ethanol also reacts with propanoic acid to form an ester known as ethylpropanaote

$$C_2H_5OH + CH_3CH_2COOH(aq) \underset{}{\overset{\text{Conc } H_2SO_4}{\rightleftharpoons}} CH_3CH_2COOC_2H_5(l) + H_2O(l)$$

Ethanol *Propanoic acid* *Ethyl propanoate (ester)*

- ❑ Below is the equation showing the structural formulae of the reactants and products.



- ❑ Under ordinary conditions the reaction takes place slowly. Therefore, concentrated sulphuric(VI) acid is added **to catalyse the reaction**.

V. Oxidation of ethanol

- When acidified potassium dichromate(VI) is added to ethanol, its colour changes from orange to green.
- When acidified potassium manganate(VII) is added to ethanol, the purple colour changes to colourless.
- Potassium dichromate(VI) and potassium manganate(VII) are oxidising agents. They oxidise ethanol to ethanoic acid. The oxidation of ethanol is a two step process.

Ethanol is first converted to **ethanal.** This is a slow process.

$$\text{Ethanol} + \text{oxygen} \longrightarrow \text{ethanal} + \text{water}$$

$$C_2H_5OH(l) + \underset{\substack{\uparrow \\ \text{from oxidizing} \\ \text{agent}}}{[O]} \xrightarrow[H^+(aq)]{Cr_2O_7^{2-}(aq)} CH_3CHO(l) + H_2O(g)$$

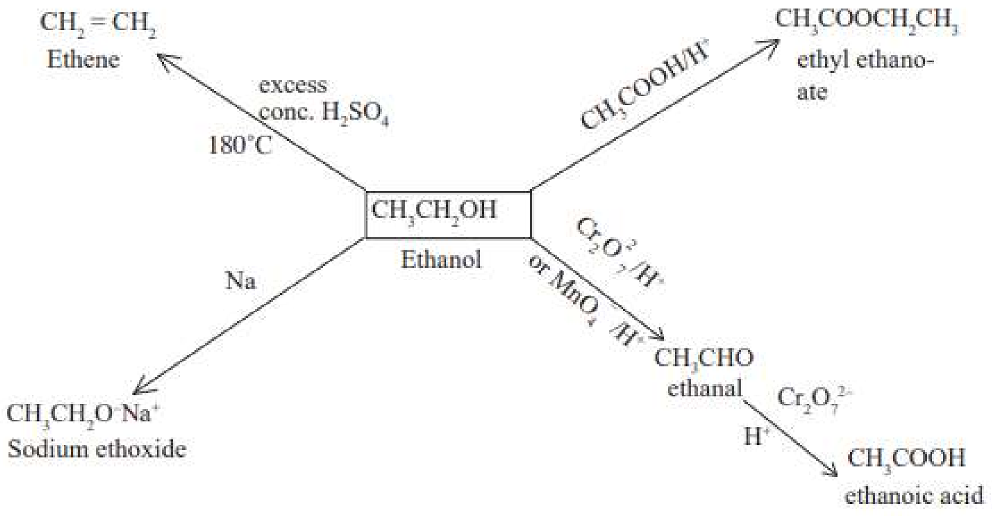
Then rapid conversion of ethanal to ethanoic acid.

$$\text{Ethanal} + \text{oxygen} \xrightarrow[\text{H}^+(aq)]{\text{Cr}_2\text{O}_7^{2-}(aq)} \text{ethanoic acid}$$

$$\text{CH}_3\text{CHO}(aq) + [\text{O}] \xrightarrow[\text{H}^+(aq)]{\text{Cr}_2\text{O}_7^{2-}} \text{CH}_3\text{COOH}(aq)$$

- The oxidising property of the chromate(VI) is used in some breathalysers to indicate the level of alcohol (alkanol) content in the breath of motorists.

Summary of some reactions of ethanol



Uses of Akanols

i. As solvents, i.e., in the preparation of drugs.
ii. As fuels when blended with gasoline to form gasohol.
iii. In the manufacture of synthetic fibres, e.g., polyvinylchloride and polythene.
iv. As an antiseptic when used under specified concentrations.
v. Ethanol is used as an alcoholic drink only in low concentrations.

Exercise

1. Draw the structures and name the alkanols with the following number of carbon atoms: (a) Six (b) Seven (c) Ten
2. Draw the structural formula for each of the following compounds. (a) Pentan -1-ol (b) Butan-2-ol (c) 2-methylpropan -1-ol (d) 2, 3-dichlorobutan -1-ol (e) 2, 3-dimethyl pentan -2-ol
3. Name the following compounds:

(i) CH3CH(CH3)CH(OH)CH3

(ii) CH3C(CH3)(OH)CH3

(iii) CH2(Br)CH2CH2CH(OH)CH3

(iv) CH3CH(Cl)CH2OH

4. An organic compound with a molecular formula of C2H12O shows six different isomers.

(i) Draw the structural formula for each of the isomers.

(ii) Name each of the isomers.

(iii) Classify each isomer as a primary, secondary or a tertiary alkanol.

5. Esters can be made by the reaction of many different types of alkanols (alcohols) and alkanoic (carboxylic) acids.

(a) Write an equation for the reaction between:

(i) Methanol and ethanoic acid.

(ii) (ii) Ethanol and butanoic acid.

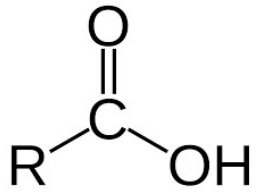
(b) Draw the structural formula of the products represented in the equations 5(a) (i) and (ii)

6. Methanol, $\mathrm{CH3\ OH}$ and ethane $\mathrm{CH3\ CH3}$, have almost the same molecular mass. Explain why the b.p of methanol is 65˚C while that of ethane is –88.6˚C.

7. Yeast must be added to glucose solution in order for fermentation to occur. Explain why yeast is needed.

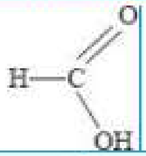
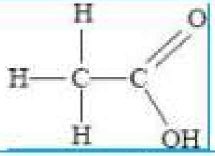
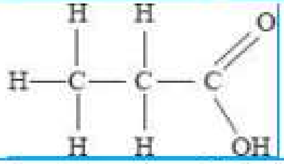
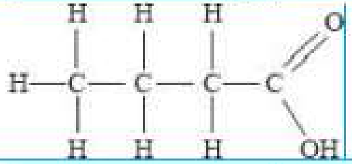
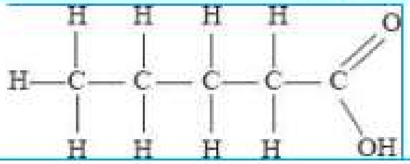
Alkanoic acids

- Alkanoic acids are organic acids which are sometimes called **carboxylic acids**. They are so called because they have a carboxyl group (-COOH) as their functional group. A carboxyl group has the structural



- They may be regarded as being derived from alkanes by replacing one of the hydrogen atoms with a–COOH group.
- Alkanoic acids form homologous series with a general formula R–COOH where R is an alkyl group or H in case of the first one.
- We use the general formula $C_n H_{2n+1}COOH$ to calculate their molecular formula.
- Alkanoic acids are naturally found in fruits such as oranges, lemon and pepper.
- Methanoic acid is present in nettle leaves and insect stings such as bees and wasps.
- Ethanoic acid is commonly know as vinegar
- Butanoic acid is found in beef fat (Butter). Hexandioic acid is found in palm oil and olive oil.

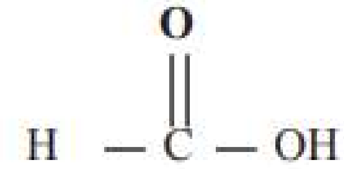
Structural formulae of the first five alkanoic acids.

Alkanoic acid	Structural formula
Methanoic	
Ethanoic	
Propanoic	
Butanoic	
Pentanoic	

Nomenclature

- Alkanoic acids are named by replacing the “e” ending of the corresponding alkane by the suffix – oic;.
- The carbon atom to which the functional group is attached is given position one.
- The first member of the series is methanoic acid with the formula **HCOOH**. In methanoic acid, **R** is represented by **H** while for the rest of the members, **R** is represented by an alkyl group.

The structure of methanoic acid is therefore,



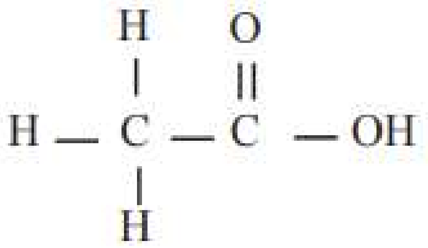
$$\mathrm{H - \overset{\overset{\Large O}{\|}}{C} - OH}$$

- The second member of the alkanoic acid is ethanoic acid, which has two carbon atoms. Since one of the carbon atoms is already attached to the functional group, the value of n in the general formula $C_nH_{2n+1}COOH$ is 1. When we substitute, we get the molecular formula for ethanoic acid as follows.

$$C_1H_{(2\times 1)+1}COOH$$

$$CH_3COOH$$

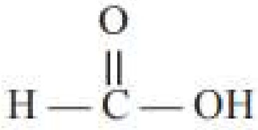
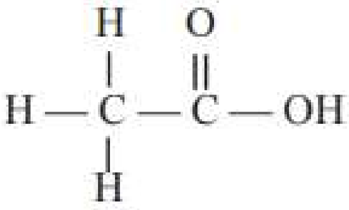
The structural formula is represented as



$$\begin{array}{ccccccc} & & H & & O & & \\ & & | & & \| & & \\ H & - & C & - & C & - & OH \\ & & | & & & & \\ & & H & & & & \end{array}$$

Ethanoic acid

The first 10 alkanoic acids

Name	**Molecular formula**	**Structural formula**
Methanoic acid	HCOOH	 $H-\overset{\overset{O}{\parallel}}{C}-OH$ or HCOOH
Ethanoic acid	CH_3COOH	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{O}{\parallel}}{C}-OH$ or CH_3COOH

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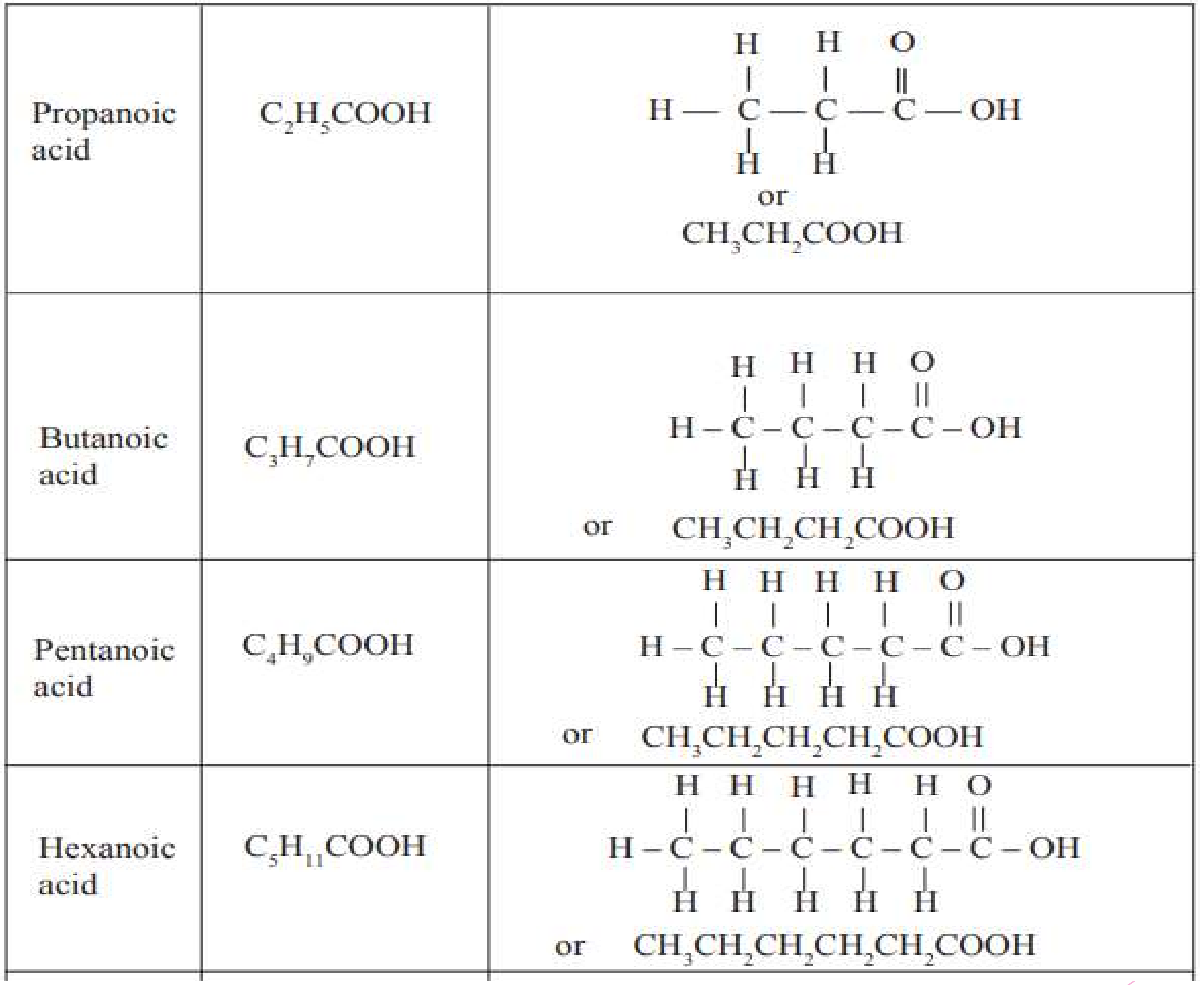
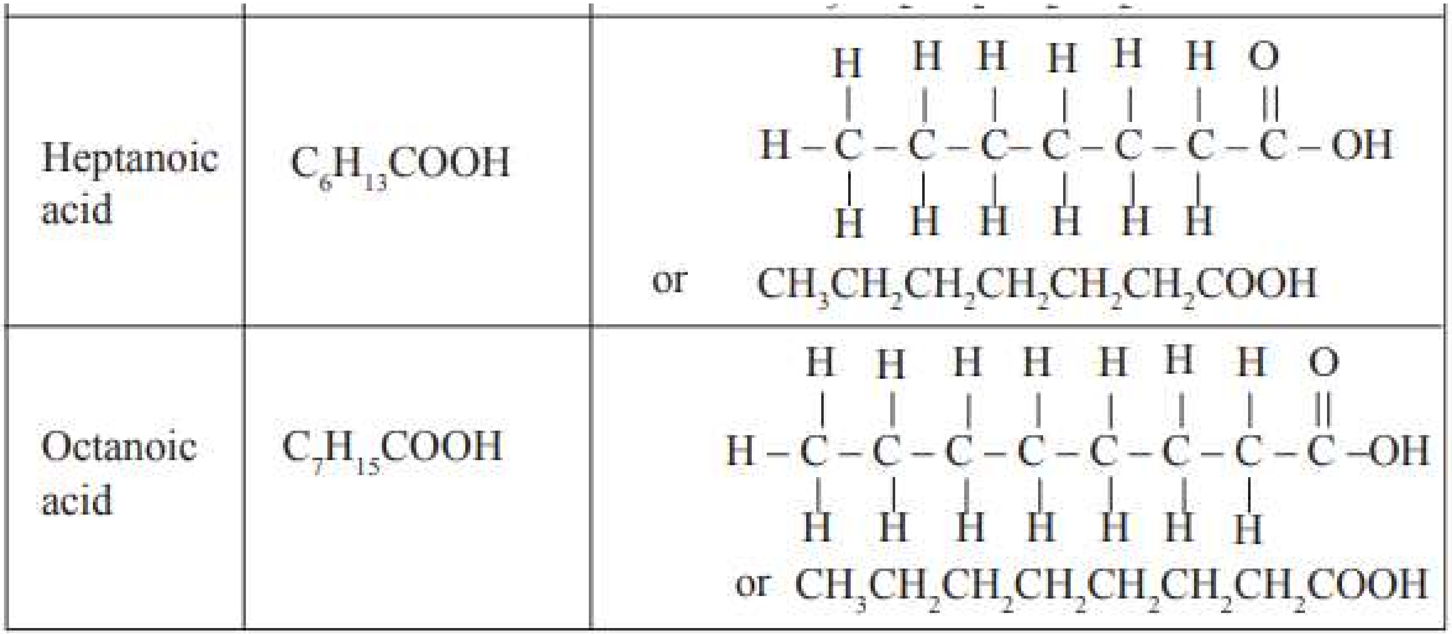


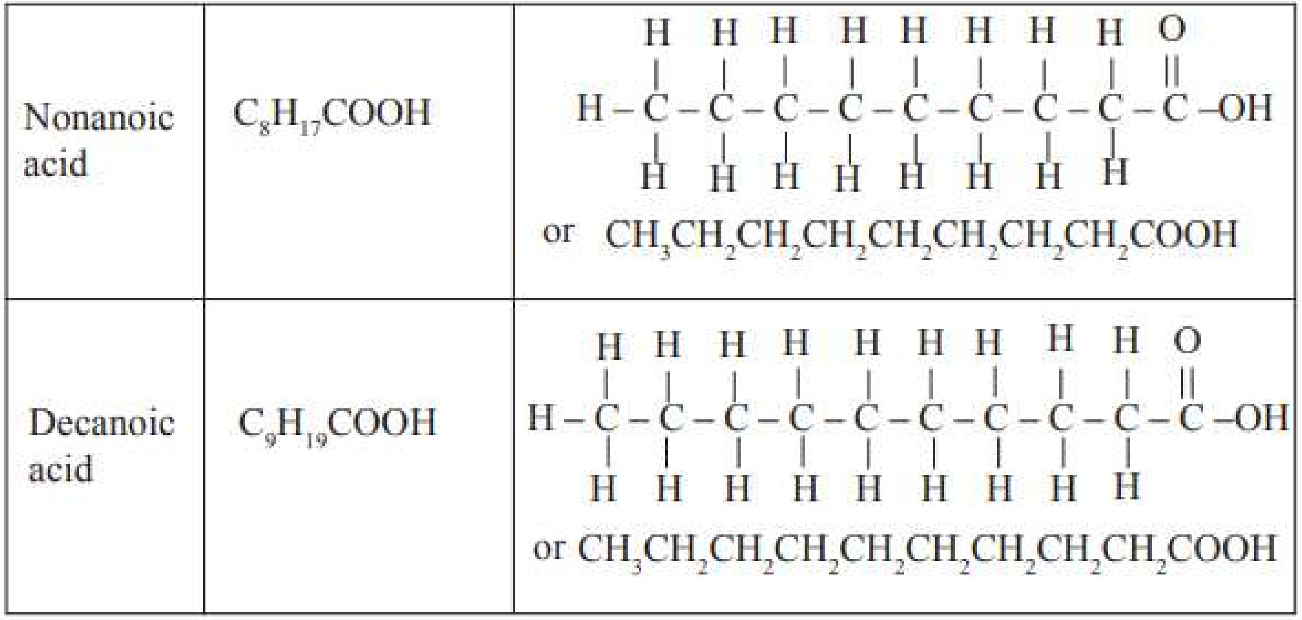
Propanoic acid	C_2H_5COOH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or CH_3CH_2COOH
Butanoic acid	C_3H_7COOH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2COOH$
Pentanoic acid	C_4H_9COOH	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2CH_2COOH$
Hexanoic acid	$C_5H_{11}COOH$	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2CH_2CH_2COOH$

Cont....



Heptanoic acid	$C_6H_{13}COOH$	$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2CH_2CH_2CH_2COOH$
Octanoic acid	$C_7H_{15}COOH$	$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$

Conti….



Nonanoic acid	$C_8H_{17}COOH$	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$
Decanoic acid	$C_9H_{19}COOH$	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$ or $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$

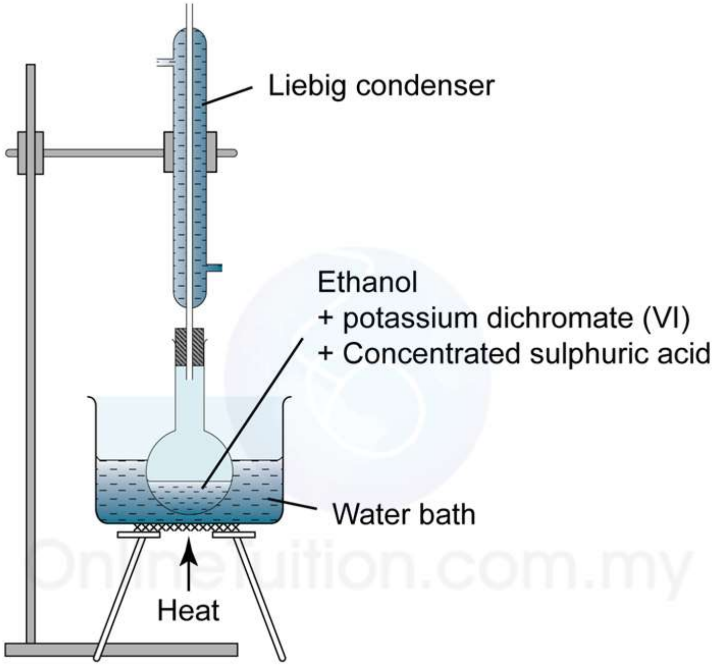
The alkanoic acids as a homologous series

The alkanoic acids are another homologous series of organic compounds with the following characteristics

- They have the functional group -COOH attached to the hydrocarbon chain
- The members have a general formula $C_nH_{2n+1}COOH$ or RCOOH, where n = 0, 1, 2, ……
- Members of the series differ from the next by a $-CH_2-$group.
- They have similar chemical properties.
- They show a gradual increase in physical properties such as melting points, boiling points and density.

Laboratory Preparation of Ethanoic Acids

- Ethanoic acid is prepared by warming a mixture of ethanol and excess acidified potassium dichromate(VI) or excess acidified potassium manganate(VII).



- On heating, acidified potassium manganate(VII) oxidises ethanol to ethanoic acid.

$$CH_3CH_2OH \xrightarrow[2H^+]{MnO_4} CH_3COOH(aq) + H_2O(l)$$

- Ethanol vapour will condense into liquid in the Liebig condenser and flow back into the flask to complete the reaction.

Observations made in the flask

i. **colourless solution**: During the reaction the purple solution turns colourless. The colour of the solution is colourless because the purple manganate(VII) (MnO^{-4}) ions are reduced to colourles manganese(II) (Mn^{2+}) ions.

ii. Green solution when acidified potassium chromate(VI) in place of acidified potassium manganate(VII); the orange colour of potassium dichromate (VI) turns green as the oxidation progresses when the mixture is heated.

- To ensure complete oxidation, excess oxidising agent is used. The condenser ensures any vapour escaping is condensed back into the flask for further reaction.
- The solution in the flask contains the oxidising agent, water and ethanoic acid. In order to obtain pure ethanoic acid the mixture is distilled. The distillate collected at about 118 °C is ethanoic acid which is a colourles liquid with a sharp smell.

- The mixture is heated by using a water bath;

I. to keep the temperature constant

II. to ensure a uniform heating (heat is evenly supplied)

METALS

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CHEMISTRY PP2
KCSE MAPPING ON METALS 1995-2022

YEAR	METALS	QUESTION	YEAR	METALS	QUESTION
1995	COPPER	Q.4	2014	ALUMINIUM	Q.6
1996	ALUMINIUM	Q.3	2016	ALUMINIUM	Q.5
1999	SODIUM	Q.4	2017	LEAD	Q.6
2000	LEAD	Q.2	2019	ZINC	Q.2
2002	COPPER	Q.6	2020	IRON	Q.3
2003	ALUMINIUM	Q.5	2021	-	-
2005	SODIUM	Q.7	2022	-	-
2006	IRON	Q.6	2023	?	?
2009	IRON	Q.7			
2010	ZINC	Q.6			

EXTRACTION OF METALS

General method of extracting metals

- Metals can be extracted from rocks called Ores. Extraction of metals from their ores involves the following general processes.
- Very few metal ores are concentrated enough for the metal to be extracted without first purifying the ore to concentrate it. The process of concentrating an ore may include:

(i) Removing any magnetic materials with a magnet.

(ii) Dissolving the mineral in a suitable solvent.

(iii) Washing with water to remove earthy matter.

(iv) Froth flotation. This is one of the methods used in purifying metal ores. The ore is ground into a fine powder. It is then mixed with water containing special oils such as pine oil as frothing agents and air blown into the mixture. Separation is possible because of the different densities of the materials. This imparts an oil coat in every grain of the ore making it hydrophobic ('water hating'). This creates two layers. A froth forms on top with most of the minerals and the waste materials or impurities at the bottom. The top layer with the metal of interest is removed and dried in readiness for further processing. Copper pyrites, zinc blende and galena one concentrated this way.

- ❑The method of extraction of a metal depends on the metal’s reactivity. The most reactive metals such as sodium are obtained by electrolysis. The less reactive metals such as iron are extracted by reduction of their oxides using suitable reducing agents.

SODIUM

Occurrence

❑Sodium naturally occurs as:

(i) Brine-a concentrated solution of sodium chloride(NaCl(aq)) in salty seas and oceans.

(ii) Rock salt (solid sodium chloride)-NaCl(s)

(iii) Trona sodium (sesquicarbonat)-($NaHCO_3.Na_2CO_3.2H_2O$) especially in lake Magadi in Kenya.

(iv) Chile saltpeter (sodium nitrate)-($NaNO_3$)

❑The ores from which sodium can be extracted are sodium chloride (NaCl) and Rock salt.

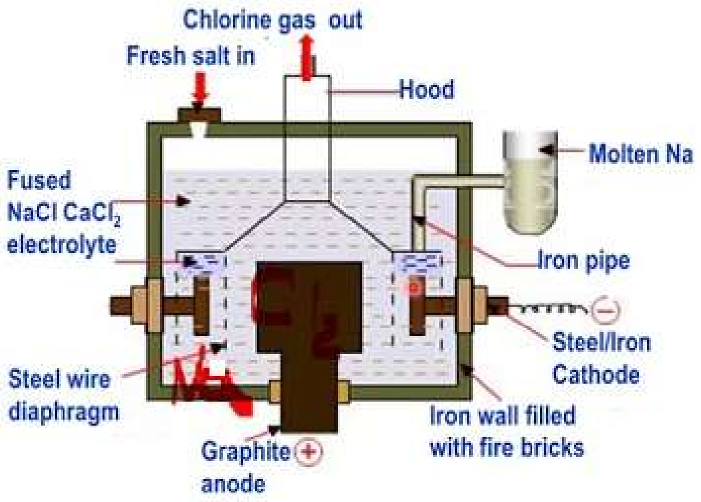
❑The chief ore from which sodium is extracted is rock salt because it is the most abundant and also requires very little purification.

Extraction

- Sodium is very reactive therefore can only be extracted by electrolysis. It is extracted by electrolysis of molten sodium chloride in a **Down's cel**l; hence the process is commonly referred to as the **Down's process**.

Down's process.

- This process takes place in a Down's cell as shown in the figure below.



- The Down’s cell consists of:
    - I. An iron shell lined with heat bricks forming heat resistant wall, **its purpose is to maintain the high temperature so that the electrolyte does not crystallize**. It also contains the mixture of salts to be electrolyzed.
    - II. A carbon (graphite) anode: This is where chloride ions are discharged to form the chlorine gas which escapes through the hood.
    - III. A circular steel/Iron cathode: This is where sodium ions are discharged to form molten sodium.
    - IV. steel diaphragm/gauze: is suspended between the electrodes to **prevent recombination** of sodium at the cathode and chlorine gas at the anode back to sodium chloride.
- Calcium chloride is added to the sodium chloride **to lower the melting point of sodium chloride from about 800°C to 600°C.**
- The advantage of lowering the melting point of sodium chloride is save the cost of electricity used in heating since is economical.

- During electrolysis, sodium metal forms at the cathode whereas chlorine gas forms at the anode.

At the Anode: chloride ions are discharged to form chlorine gas.

$$2Cl^{-}(l) \rightarrow Cl_2(g) + 2e^{-}$$

- Anode is made of graphite because. graphite is inert and **does not react with chlorine gas even at high temperature**

At the cathode: Sodium ions are discharged to form molten sodium.

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

- Molten sodium is less dense than molten sodium chloride, hence it rises to the top of the cathode from where it is periodically removed.
- The hood is used to collect the chlorine gas and channel it out, where it is tapped to prevent it from being released to the atmosphere as it is poisonous and hazardous to environment.
- Liquid Calcium can also be discharged at the cathode, the calcium is separated from molten sodium because:
  i. Calcium has a higher melting point compared to sodium so on cooling it crystallises first leaving liquid sodium which is trapped.
  ii. calcium liquid is more dense than molten sodium

- Sodium ion is preferably discharged instead of calcium ion at the cathode because:

i. Sodium ions are lower in electrochemical series than calcium ions.
ii. Sodium ions have higher concentration in the electrolyte than calcium ions.

Advantages of Downs cell.

Sodium metal obtained has high degree of purity (99.5%).

The starting material, sodium chloride is very cheap.

Chlorine is obtained as a useful by-product.

NB: The industry that can be built next to a sodium extraction plants is industrial manufacture of hydrochloric acid since choline which a by-product in the extraction of sodium used as a raw material in the manufacture of hydrochloric acid.

- A high current of about 35,000 amperes is passed through the electrolyte which is molten sodium chloride to:
  1. To decompose the ore.
  2. Maintain the ore in liquid state due to resistance.

Environmental effects of Downs cell.

I. Chlorine gas produced is poisonous when inhaled.
II. Formation of gullies
III. Noise pollution

Uses of Sodium

I. Used in sodium vapour lamps to give a yellow light in street lighting.

II. An alloy of potassium and sodium is used as **coolant** in nuclear reactors because it has a low melting point and is a good conductor of heat.

III. Used in the manufacture of sodium peroxide which is used as a bleaching agent and sodium cyanide which is used in the extraction of gold.

IV. Molten sodium is used as a reducing agent in the extraction of titanium from its chloride.

ALLUMINIUM METAL

Occurrence

- Aluminium is also a very reactive metal and therefore does not occur freely. It is found in compounds with other elements.
- Aluminium is the most common naturally occurring metal. It makes 7% of the earths crust.
- These are some examples of aluminium ores.

Ores	Chemical name	Formula
Bauxite	Hydrated aluminium oxide	$Al_2 O_3 .2H_2 O$
Mica	Potassium aluminium silicate	$K_2 Al_2 Si_6 O_6$
Corundum	Anhydrous aluminium oxide	Al_2O_3
China clay	Aluminium silicate	**Al_2SiO_5**

Extraction of Aluminium

- The chief ore from which aluminium is extracted is ($Al_2O_3.2H_2O$).
- Aluminum is extracted by the electrolytic method because it is a reactive metal. The ore is concentrated before it is electrolysed.

Concentration of the ore.

- Mining of bauxite is done through open cast method. The bauxite has a lot of impurities which include mud and other major impurities such as iron(III) oxide and silicon(IV) oxide (sand).
- The impurities are removed during the process of concentration through the following steps.

StepI: Removal of iron(III) oxide:

- Bauxite is ground into a fine powder to increase the surface area of ore and then heated to remove water of crystallization, then dissolved in **hot concentrated sodium hydroxide or potassium hydroxide solution under pressure of about 4 atmosphere**.
- The aluminium oxide dissolve in concentrated sodium hydroxide to form sodium tetrahydroxoaluminate because it is amphoteric oxide.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)$$

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(s) \longrightarrow 2[Al(OH)_4]^-(aq)$$

- Silicon(IV) oxide also dissolves in concentrated sodium hydroxide because it is an acidic in nature to form sodium silicate and water.

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

$$SiO_2(s) + 2OH^-(aq) \longrightarrow SiO_3^{2-}(aq) + H_2O(g)$$

- Iron(III)oxide being insoluble in the base is filtered off as a residue (red mud) to obtain a filtrate containing aluminate and silicate ions. The filtrated is then cooled.

Step II: Formation of Aluminium Hydroxide

- Aluminium hydroxide can be obtained in two ways

  i. Treating the filtrate (sodium tetrahydroxoaluminate) with **carbon(IV) oxide gas** which precipitates aluminium hydroxide leaving the silicate in solution.

$$\mathbf{2Na[Al(OH)_4]\ (aq)\ +\ CO_2(g) \rightarrow 2Al(OH)_3\ (s)\ +\ NaCO_3\ (aq)\ +\ H_2O(l)}$$

$$2[Al(OH)_4]^-(aq) + CO_2(g) \longrightarrow 2Al(OH)_3(s) + CO_3^{2-}(aq) + H_2O(l)$$

  i. The filtrate can be diluted with water, then agitated in air to enhance hydrolysis of the aluminate ions and finally **seeded** with freshly prepared aluminium hydroxide.

$$Al(OH)_4^-(aq) \xrightarrow[Seed]{Al(OH)_3(s)} Al(OH)_3(s) + OH^-(aq)$$

- The aluminium (III) hydroxide ($Al(OH)_3$) residue is filtered off. Silicon (IV)oxide remain in the solution as filtrate.

Step III: Roasting of Aluminium Hydroxide

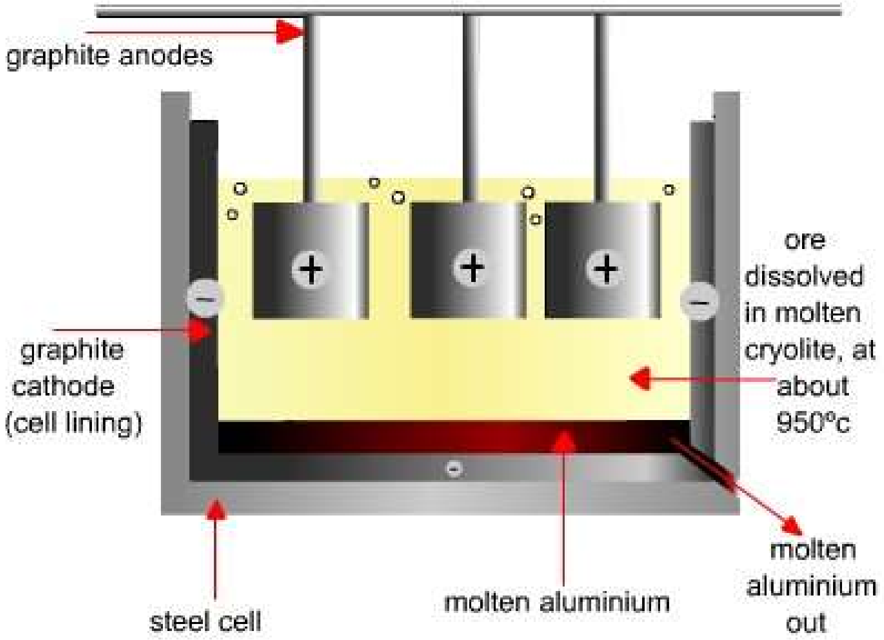
- Aluminium hydroxide is then heated at temperatures of about 1000˚C to give aluminium oxide and water.

$$2Al(OH)_3\,(s) \xrightarrow{1000^{\circ}C} Al_2O_3\,(s) + 3H_2O(l)$$

Step IV: Electrolysis of Aluminium oxide.

- The aluminium oxide is first melted to allow the ions to move freely towards the electrodes within the moltenl electrolyte and then electrolysed. Aluminium oxide is composed of aluminium ions, $\mathbf{Al^{3+}}$ and oxide ions, $\mathbf{O^{2-}}$.
- Pure aluminium (III)oxide (Al_2O_3) has a very high melting point of 2015ºC. Alot of energy is required to melt the oxide. It is therefore dissolved first in **molten cryolite** /sodium hexafluoroaluminate (III)(Na_3AlF_6) **to lower the melting point to about 800ºC. - 1000˚C**.

- ☐ Advantage of lowering of melting point is to minimize the cost of electricity hence economical.
- ☐ The molten electrolyte is put in the Hall cell made up of a steel tank lined with carbon graphite and an anode suspended into the electrolyte.



- During electrolysis, aluminium is deposited at the cathode and oxygen is liberated at the anode.
- The reactions taking place at the electrodes are as follows:

At the cathode

$$Al^{3+}(l) + 3e \longrightarrow Al(l)$$

At the anode

$$2O^{2-}(l) \longrightarrow O_2(g) + 4e^-$$

- Multiply 1st equation by 4 and 2nd by 3 to balance the number of electrons at the cathode and anode:

$$4Al^{3+}(l) + 12e^- \longrightarrow 4Al(l)$$

$$6O^{2-}(l) \longrightarrow 3O_2(g) + 12e^-$$

- Therefore, the final equations at the cathode and anode are:

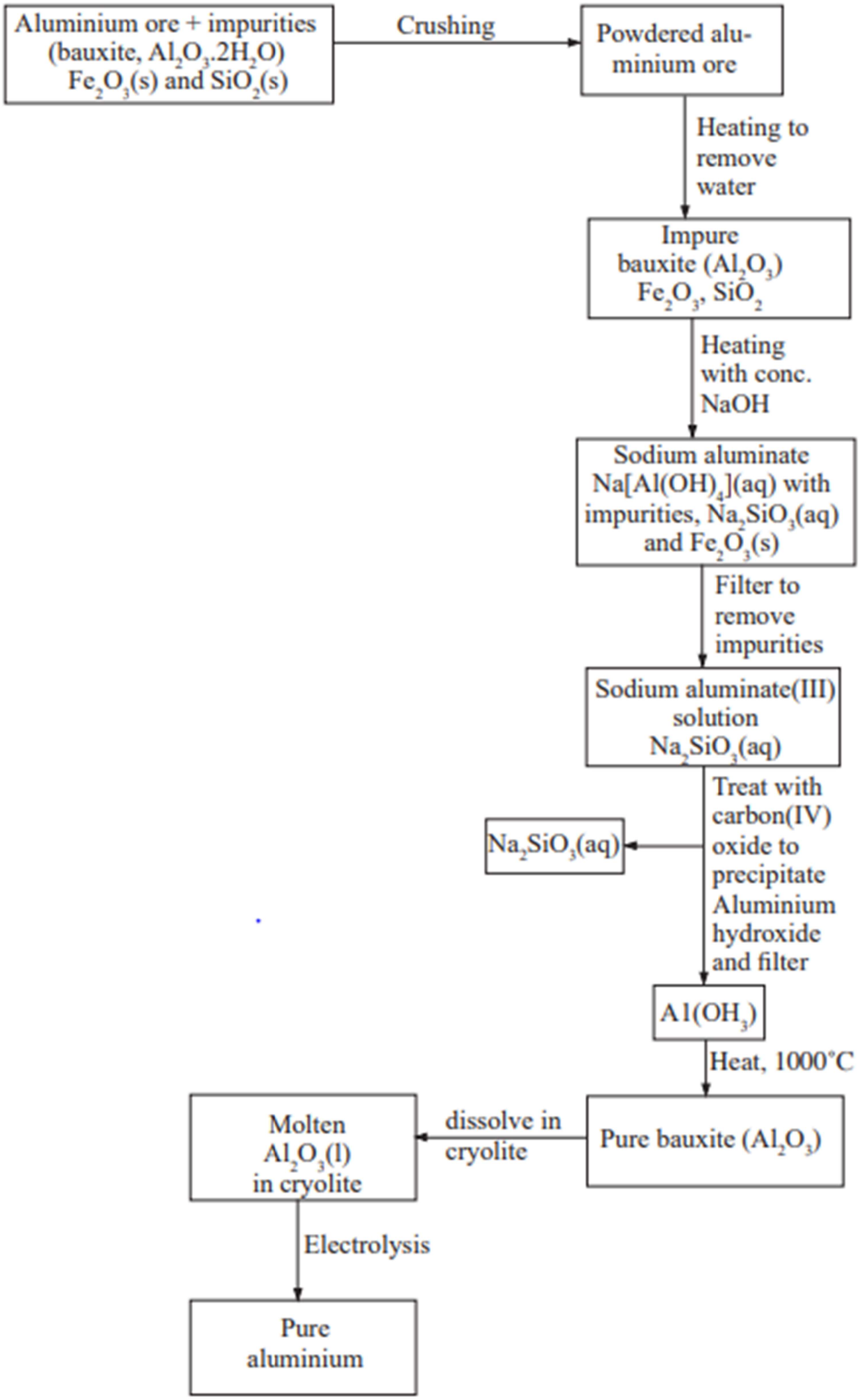
(i) At the cathode;

$$4Al^{3+}(\mathbf{l}) + 12e \longrightarrow 4Al(\mathbf{l})$$

(ii) At the anode;

$$6O^{2-}(l) \longrightarrow 3O_2(g) + 12e$$

- ❑Aluminium is denser than the electrolyte therefore sink to the bottom of the Hall cell and it is tapped off at intervals.
- ❑At the high temperature of about 800°C, the oxygen evolved reacts with the carbon electrode to form carbon(IV) oxide. This corrodes the carbon anode which should be replaced from time to time.



Aluminium ore + impurities (bauxite, $Al_2O_3.2H_2O$) $Fe_2O_3(s)$ and $SiO_2(s)$

Crushing

Powdered aluminium ore

Heating to remove water

Impure bauxite (Al_2O_3) Fe_2O_3, SiO_2

Heating with conc. NaOH

Sodium aluminate $Na[Al(OH)_4](aq)$ with impurities, $Na_2SiO_3(aq)$ and $Fe_2O_3(s)$

Filter to remove impurities

Sodium aluminate(III) solution $Na_2SiO_3(aq)$

Treat with carbon(IV) oxide to precipitate Aluminium hydroxide and filter

$Na_2SiO_3(aq)$

$Al(OH_3)$

Heat, 1000°C

Pure bauxite (Al_2O_3)

dissolve in cryolite

Molten $Al_2O_3(l)$ in cryolite

Electrolysis

Pure aluminium

Uses of Aluminium

I. Used in making aeroplane parts, buses, tankers, furniture because aluminium is very light.

II. Used making duralumin-an alloy which is harder and has a higher tensile strength. Duralumin is used in the construction of aircraft and car window frames.

III. Used making utensils, sauce pans, spoons because it is light, good conductor of electricity and Malleable.

- **Malleability** means metal can be hammered into a thin sheet

IV. Used making overhead electric cables because it is light, ductile and good conductor of electricity and is light.

- **Ductile** means that the metal can be made into thin wires.

V. Used in the thermite process as a reducing agent for production of Manganese, Chromium and Titanium.

VI. Some aluminium compounds are used in sewage treatment.

VII. Manufacture of aluminium paint. This is used in coating radiators, storage tanks and other metal works.

VIII. In the manufacture of explosives e.g. a mixture of ammonium nitrate and aluminium powder is explosive.

Environmental effects of extracting Aluminium from Bauxite.

- ❑Carbon(IV)oxide gas that escape to the atmosphere is a green house gas that causes global warming.
- ❑Bauxite is extracted by open caste mining that causes land degradation.

Test for presence of Al^{3+}

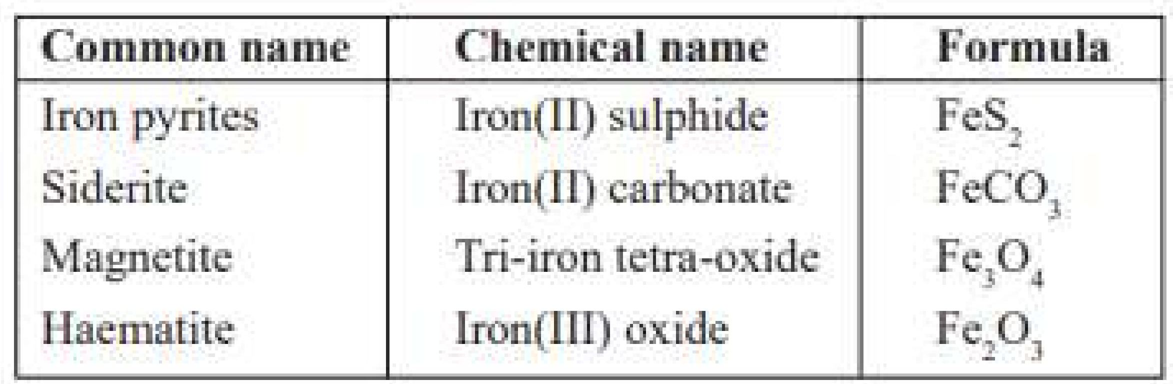
- ❑If an ore is suspected to contain Al3+ it is;
  i. Crushed and added hot Nitric (V) acid to free the ions present.
  ii. the free ions are then added a precipitating reagent like 2M sodium hydroxide or 2M aqueous ammonia.

Observation	**Inference**
White precipitate in excess 2M NaOH(aq)	Pb^{2+} , Al^{3+}, Zn^{2+}
White precipitate in excess 2M NH^3(aq)	Pb^{2+} , Al^{3+}
No black precipitate on adding Na_2S(aq)	Al^{3+}
No white precipitate on adding either NaCl(aq),HCl(aq),H_2SO_4(aq),Na_2SO_4(aq)	Al^{3+}

IRON

Occurrence

- Iron is the second most common naturally occurring metal. It makes 4% of the earths crust. Below are the ores when iron can be extracted.



Common name	Chemical name	Formula
Iron pyrites	Iron(II) sulphide	FeS_2
Siderite	Iron(II) carbonate	$FeCO_3$
Magnetite	Tri-iron tetra-oxide	Fe_3O_4
Haematite	Iron(III) oxide	Fe_2O_3

- The most abundant ores which are normally used for extracting iron are **magnetite** and **haematite**. With the chief ore being **haematite**.
- The ores of iron contain **silica** (SiO_2) and **aluminium (II) oxide** as impurities.

Extraction

- Iron is usually extracted from its oxides or siderite. The following are the raw materials:

(i) Haematite(Fe_2O_3)
(ii) Coke/charcoal/ carbon
(iii) Limestone

- Iron extraction involves the following steps.

Step I: Preparation of the Ore

- The chief ore can be prepared by heating either iron pyrites (FeS_2) or siderite ($FeCO_3$) in air.
- The iron pyrites (FeS_2) or siderite ($FeCO_3$) is first crushed after which it is heated in air. The process of heating removes water and other impurities with low melting points. This gives iron ore with about 30 – 95% of iron(III) oxide depending on the quality of the ore. The other remaining percentage are impurities such as **silica (SiO_2**) and **alumina (Al_2O_3**). These are the main impurities.

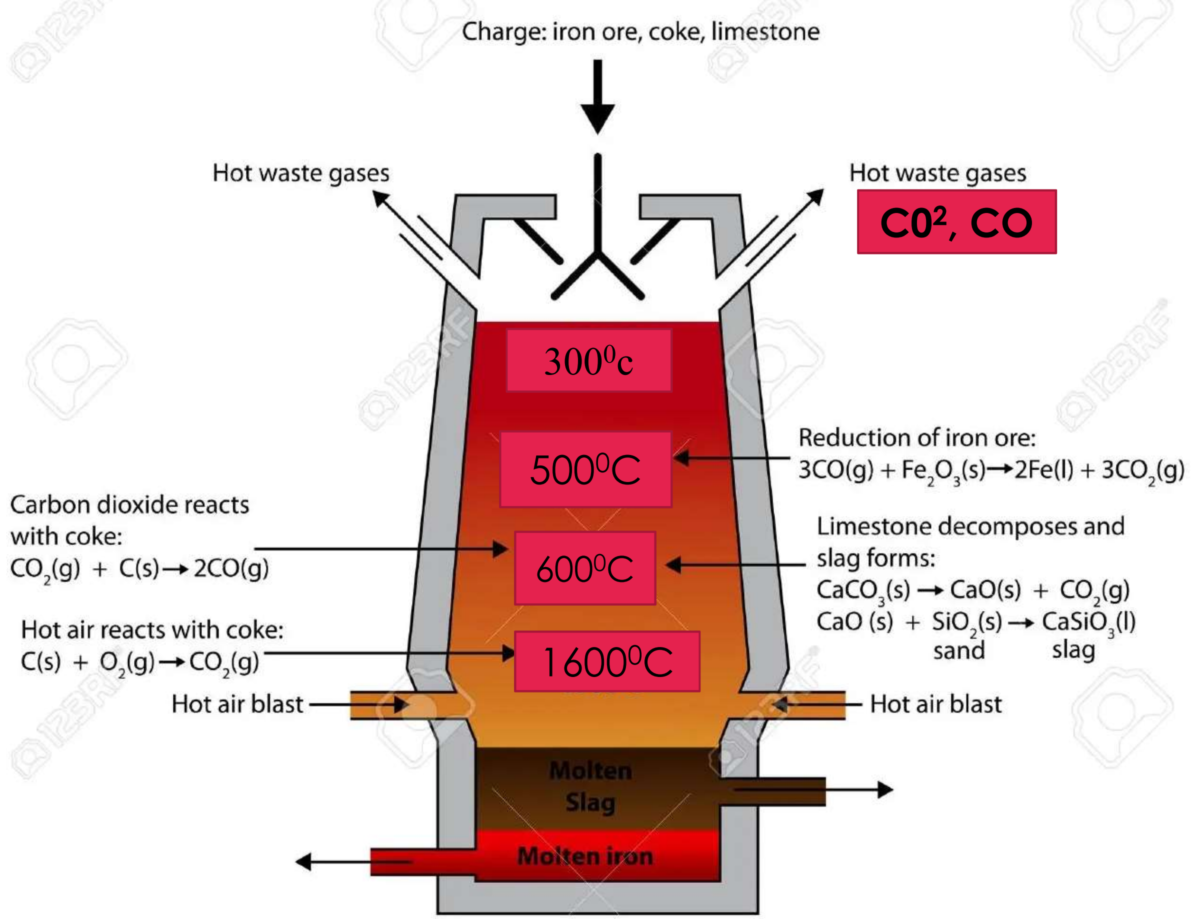
- Sulphide and carbonate ores are converted to chief ore (haematite) by roasting in air as follows:

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

$$4FeCO_3(s) + O_2(g) \longrightarrow 2Fe_2O_3(s) + 4CO_2(g)$$

Step II: Preparation of the Ore

- This is carried out in the blast furnace as shown in figure below.


Charge: iron ore, coke, limestone
Hot waste gases
Hot waste gases
$C0^2$, CO
300^0c
500^0C
600^0C
1600^0C
Reduction of iron ore:
$3CO(g) + Fe_2O_3(s) \rightarrow 2Fe(l) + 3CO_2(g)$
Carbon dioxide reacts with coke:
$CO_2(g) + C(s) \rightarrow 2CO(g)$
Limestone decomposes and slag forms:
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$CaO(s) + \underset{\text{sand}}{SiO_2(s)} \rightarrow \underset{\text{slag}}{CaSiO_3(l)}$
Hot air reacts with coke:
$C(s) + O_2(g) \rightarrow CO_2(g)$
Hot air blast
Hot air blast
Molten Slag
Molten iron

- The raw materials are fed into the blast furnace. This is done through hoppers at the top of the furnace. The raw materials are:
  - **iron ore** –(mainly haematite, iron(III) oxide).
  - **coke** –which is a cheap form of carbon made from coal.
  - **limestone** –which is used to remove wastes.
- The furnace is covered with **inverted** double cap to reduce amount of any gases escaping .
- Near the base, blast of hot air at about 827°C is driven into the furnace through small holes called **Tuyeres**. As the air enters ,it reacts with coke to form carbon(IV)oxide gas. This reaction is highly **exothermic**, hence raises the temperature of the furnace to 1600°C.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -394\text{kJ/mol}$$

- As the carbon(IV) oxide rises up the middle of the furnace, it reacts with more coke reducing it to carbon(II) oxide gas. This reaction is **endothermic** and hence the temperature drops to about 1000°C.

$$CO_2\,(g) + C(s) \longrightarrow 2CO\,(g) \quad \Delta H = +173kJ$$

- The carbon(II) oxide gas formed then reduces the chief ore (Iron(III) oxide) to iron metal and it being oxidized to carbon(IV) oxide . This reaction takes place at the upper part of the furnace at temperatures of about $500^{0} – 700^{o}$C. Both carbon and carbon (II) oxide ac as reducing agents.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe\,(s) + CO_2(g)$$

- Carbon(II) oxide is the main reducing agent because of the **large surface that is in contact with the iron(III) oxide**.
- The carbon (II) oxide gas produced is recycled.

- The iron produced denser than iron ore hence falls to the lower part of the furnace where the temperatures are high enough to keep it molten. The temperature at this region is about 1535^0C – 3000^0C.
- The limestone fed into the furnace alongside coke and iron(II) oxide is decomposed by heat in the furnace to form calcium oxide and carbon(IV) oxide.

$$\mathbf{CaCO_3(s) \xrightarrow{Heat} CaO(s) + CO_2(s)}$$

- The limestone helps in the removal of the sandy impurities which include acidic impurities in the ore to form a liquid slag.
- Calcium oxide (Quicklime)being basic reacts with the amphoteric oxide impurities silicon(IV)oxide(SiO_2) and aluminium(III)oxide(Al_2O_3) in the ore to form slag which are calcium silicate and calcium aluminate.

$$\mathbf{CaO(s) + SiO_2(s) \rightarrow CaSiO_3(l)}$$

$$\mathbf{CaO(s) + Al_2O_3(s) \rightarrow CaAl_2O_3(l)}$$

- Note: The main component of the slag is calcium silicate.
- The role of the slag is to prevent Iron from being oxidized by hot air.
- The slag formed is tapped off at a higher level of the furnace because of **its lower density and also it is immiscible with molten iron**. The iron obtained from the blast furnace is 90–95% pure and it is called “pig Iron”. The main impurity in pig iron is carbon. Other impurities are silicon, manganese, sulphur and phosphorus, depending on the composition of the original ore.
- The 5% of carbon can be reduced by blowing oxygen into molten iron which converts carbon into carbon (iv) Oxide.

Effect of the impurities on the Iron

i. Impurities make iron less hard and brittle.

ii. Impurities lowers the melting point of iron.

USES OF THE SLAG

☐The slag tapped can be used in;

(i) tarmacking roads

(ii)cement manufacture

(iii)As building construction material

USES OF IRON

- ❑Iron is mainly used to make:

i. Gates ,pipes, engine blocks, rails, charcoal iron boxes, lamp posts because it is cheap

ii. Nails, cutlery, scissors, sinks, vats, spanners, steel rods, and railway points from steel.

Environmental effects of extracting iron from blast furnace.

i. Carbon(IV)oxide(CO_2) gas is a green house gas that causes global warming if allowed to escape from the furnace.

ii. Carbon(II)oxide(CO)gas is a highly poisonous odourless gas that can kill on leakage. It is **preferentially** absorbed by the haemoglobin in mammals instead of Oxygen to form a stable compound that reduce free hemoglobin in the blood.

iii. Haematite (Fe_2O_3), Magnetite(Fe_3O_4) and Siderite ($FeCO_3$) are extracted through open cast mining that cause soil degradation.

TEST FOR THE PRESENCE OF IRON

- ❑Iron naturally exist in its compound as Fe^{2+} /Fe^{3+} .

The ore is first ground into fine powder then hot concentrated sulphuric (VI)or Nitric(V)acid is added to free the ions present. The free ions are then added a precipitating reagents such as 2M sodium hydroxide or 2M aqueous ammonia which forms;

i. an insoluble **green** precipitate in excess of 2M sodium hydroxide or 2M aqueous ammonia if Fe^{2+} ions are present.

ii. an insoluble **brown** precipitate in excess of 2M sodium hydroxide or 2M aqueous ammonia if Fe^{3+} ions are present.

Observation	Inference
green precipitate in excess 2M NaOH(aq)	Fe^{2+}
green precipitate in excess 2M NH3(aq)	Fe^{2+}
brown precipitate in excess 2M NaOH(aq)	Fe^{3+}
brown precipitate in excess 2M NH3(aq)	Fe^{3+}

PRACTICE QUESTIONS

KCSE CHEMISTRY PAPER 2
2006 Q.6, 2009 Q.7 and 2020 Q.3

ELECTROCHEMISTRY

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KCSE MAPPING ON ELECTROCHEMISTRY FROM 1995-2022 CHEMISTRY PAPER 2

YEAR	QUESTION	YEAR	QUESTION
1995	WAS NOT TESTED	2008	6
1996	2	2009	3
1997	1	2010	1
1999	2	2011	2
2000	1	2012	5
2001	3	2013	4
2002	4	2015	4
2003	2	2016	4
2004	7	2017	2
2005	3	2018	3
2006	1	2019	6

YEAR	QUESTION
2020	4
2021	7
2022	3
2023	?

85.52% tested

ELECTROCHEMISTRY

- It is a branch of physical chemistry which deals with interconversion of chemical energy to electrical energy or electrical energy to chemical energy.
- It can also be defined as the study of electron movement in an oxidation or reduction reaction at a polarized electrode surface.
- Electrochemistry therefore deals mainly with:

i) Reduction and oxidation

ii) Electrochemical (voltaic) cell

iii) Electrolysis (electrolytic) cell

Redox reactions

The term **redox** is an abbreviation of reduction and oxidation. The first three letters are taken from the word reduction and the other two from the word oxidation respectively, to form redox. Redox reactions therefore involve **oxidation** and **reduction**.

- **A redox reaction** is one in which reduction and oxidation processes occur simultaneously.

Other definitions

I. In teams of oxygen transfer:

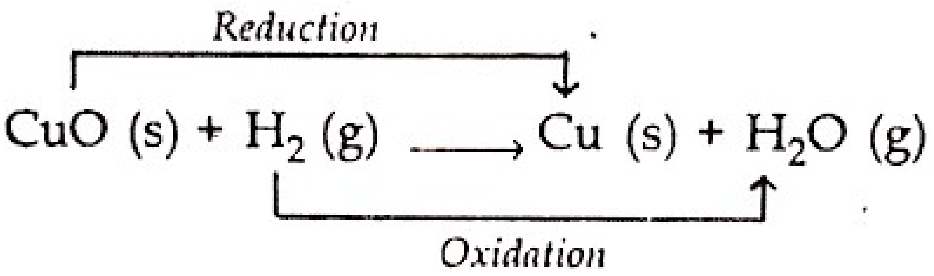
i) Reduction is **removal** of oxygen.

ii) Oxidation is **addition** of oxygen.

iii) Redox is simultaneous addition and removal of oxygen.

iv) Reducing agent is the species that undergoes oxidation, therefore gains oxygen.

v) Oxidizing agent is the species that undergoes **reduction**, therefore **looses/donates** oxygen. E.g When hydrogen is passed through heated copper (II) oxide, it is oxidized to water and copper (II) oxide is reduced to copper metal as in the equation below:



$$CuO\ (s) + H_2\ (g) \longrightarrow Cu\ (s) + H_2O\ (g)$$

II. In terms of hydrogen transfer:

- Oxidation is the **removal** of hydrogen while the Reduction is the **addition** of hydrogen.
- Redox is is simultaneous addition and removal of hydrogen atom.
- Reducing agent is the species that undergoes **oxidation**, therefore looses/ donates hydrogen.
- Oxidizing agent is the species that undergoes **reduction**, therefore gains hydrogen.

For example, When hydrogen sulphide gas is bubbled into a gas jar containing chlorine gas it is oxidized (loose the hydrogen) to sulphur (yellow solid). The chlorine is reduced (gain hydrogen) to hydrogen chlorine gas.

$$\underset{\text{(Oxidizing agent)}}{C_2(g)} + \underset{\text{(Reducing agent)}}{H_2S(g)} \longrightarrow S(s) + 2HCl(s)$$

III. In terms of electron transfer

- Oxidation is **loss** of electrons while reduction is **gain** of electrons. Therefore, redox is simultaneous gain and loss of electrons.
- Reducing agent is the species that undergoes **oxidation**, therefore **looses** electrons while oxidizing agent is the species that undergoes **reduction**, therefore **gains** electrons.

Experimental example.

Displacement of metals from their solutions.

Procedure:

Place 5cm^3 each of Iron (II) sulphate (VI) solution into three different test tubes. Add about 1g of copper tunings into one test tube then zinc and magnesium powders separately into the other test tubes. Shake thoroughly for 2 minutes each. Record any colour changes in the table below.

Metal added to Iron (II) sulphate (VI) solution	Colour Changes
Copper	
Zinc	
Magnesium	

- When a more reactive metal is added to a solution of less reactive metal, it displaces it from its solution.
- When a less reactive metal is added to a solution of a more reactive metal, it does not displace it from its solution.
- Copper is less reactive than iron therefore does not displace iron from its solution and therefore, the solution remains green.

$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ (oxidation or donation of electrons)

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$(reduction or gain of electrons

---

$Cu^{2+}(aq) + Fe(s) \longrightarrow Fe^{2+}(aq) + Cu(s)$

- Zinc and Magnesium are more reactive than iron therefore displaces iron from its solution and hence the green colour of the solution fades.

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+(}aq) + 2e^{-}} \quad \text{(oxidation or donation of electrons)}$$

$$\mathrm{Fe^{2+(}aq) + 2e^{-}} \longrightarrow \mathrm{Fe(s)} \text{(reduction or gain of electrons}$$

$$\mathbf{Fe^{2+(}aq) + Zn(s) \longrightarrow Zn^{2+(}aq) + Fe(s)}$$

Note: The more reactive metals undergoes oxidation by donating or loosing electrons to form ions while the less reactive metals undergoes reduction by its ions in solution gaining the electrons to form the metal.

- displacement of metals involves therefore electron transfer from a more reactive metal to ions of another less reactive metal.

Note:

(i) The number of electrons donated/lost MUST be equal to the number of electrons gained/acquired.

(ii) During displacement reaction, the colour of ions /salts fades but does not if displacement does not take place.

Oxidation Numbers

- An oxidation number is the apparent charge that an element has in a compound or the charge on an ion.

Rules of Assigning Oxidation Numbers

1. The oxidation number of an uncombined element is zero (0), e.g., in molecules, O_2, Cl_2, H_2, **the oxidation number of all the atoms is zero**.
2. The charge on an ion containing one element is equal to the oxidation number of that element. Oxidation number is written with the plus(+) or minus(–) sign in front.

Ion	**Mg^{2+}**	**N^{3-}**	**O^{2-}**	**H^+**
Oxidation number	+2	-3	-2	+1

3. Oxidation number of hydrogen in all compounds that contain it is + 1 except in metal hydrides where it is –1.

Compound	HCl	H_2O	HF	NaH	MgH_2
Oxidation number	+1	+1	+1	-1	-1

4. Oxidation number of oxygen in all compounds that contain it is –2, except in peroxides where it is –1 and OF_2 where it is +2.

Compound	H_2O	CuO	H_2O_2	OF_2
Oxidation number	-2	-2	-1	+2

5. In compounds, the sum of the oxidation numbers of all constituent atoms is equal to zero, e.g.,

Compound	H_2O	Na_2O_2	NaCl
Oxidation number	$2(+1)=0$	$2(+1) + 2(-1)=0$	$(+1)+(-1)=0$

6. In ions containing more than one element, the overall charge is equal to the sum of the oxidation numbers of the constituent elements.

Compound	NH_4^+	OH^-	SO_4^{2-}
Oxidation number	$-3+4(+1)=+1$	$-2+(+1)= -1$	$+6+4(-2)= -2$

Note: When the oxidation number of an element in a compound or ion is not known, it is calculated from those of others by using rule 5 and 6 respectively.

worked example

Determine the oxidation number of;

(a) Nitrogen, NO_2^{-1}

$$\Rightarrow x + (-2 \times 2) = -1$$

$$x = -1 - (-4) = +3$$

b) Sulphur in, $SO_3{}^{2-}$

=> $x + (-2 \times 3) = -2$

$x = -2 - (-6) = +4$

c) Chromium in $Cr_2O_7{}^{2-}$

=> $2x + (-2 \times 7) = -2$

$2x = -2 - +2 + -14 = +12$

$x = 12/2 = +6$

d) Sulphur in H_2SO_4

$\Rightarrow 2(+1)+x+4(-2)=0$

$\Rightarrow +2+x-8=0$

$\Rightarrow X=+6$

Determine the oxidation numbers of the atoms in the brackets.

(a) SO3 $^{2-}$ (S)

(b) NH_3 (N)

(c) PbO2 (Pb)

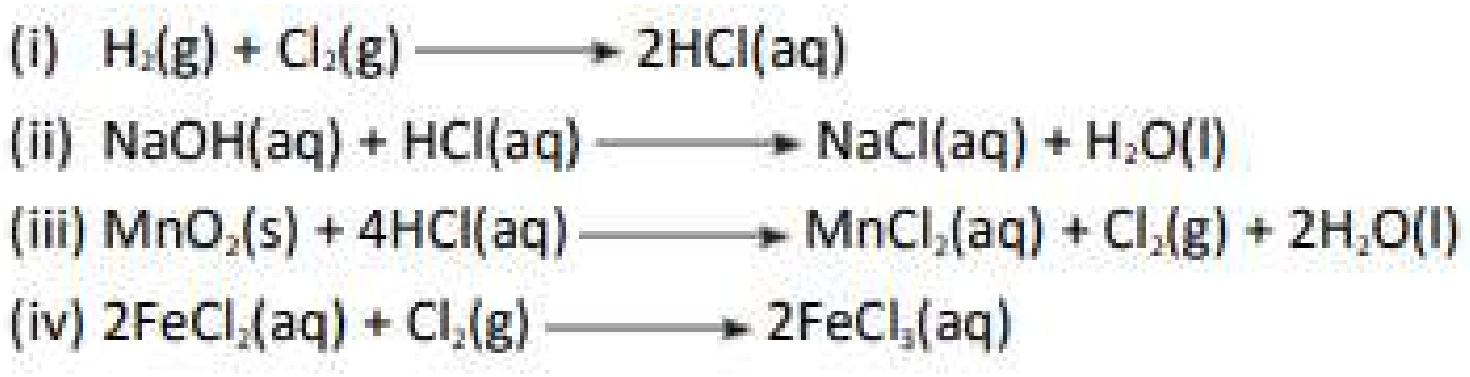
(d) CO_2 (C)

(e) HCO^{3-} (C)

2. Which of the species in the following equations undergoes:

(a) oxidation?

(b) (b) reduction?



(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(aq)$

(ii) $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

(iii) $MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$

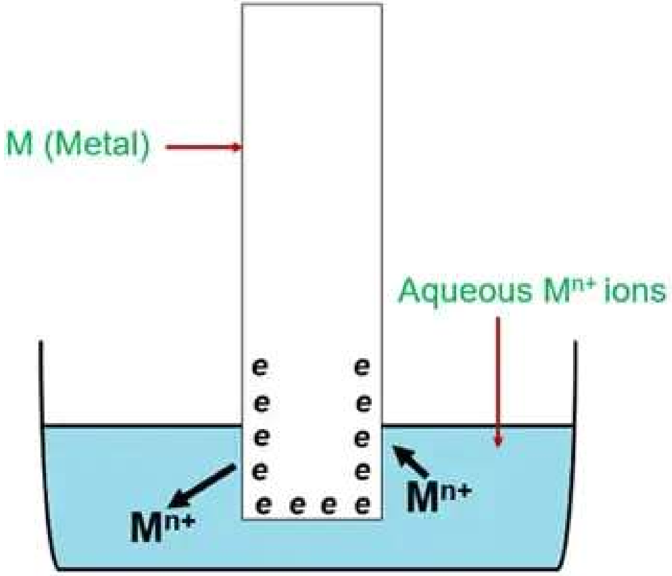
(iv) $2FeCl_2(aq) + Cl_2(g) \longrightarrow 2FeCl_3(aq)$

Electrochemical Cell

- An electrochemical cell is a device that can generate electrical energy from the chemical reactions occurring in it, or use the electrical energy supplied to it to facilitate chemical reactions in it.

The Tendency of Metals to Form Ions

- When a metal rod is dipped in an aqueous, solution of its ions, some of its surface atoms lose electrons and go into solution as ions. The lost electrons remain on the metal surface as illustrated.



- When a metal rod/plate is put in a solution of its own salt, some of the metal ionizes and dissolve into the solution i.e.

$$\textbf{Metal atoms solution} \longrightarrow \textbf{Metal ions in solution}$$

$$M(s) \longrightarrow M^{+}(aq) + e^{-} \quad \textbf{(Monovalent metal)}$$

$$M(s) \longrightarrow M^{2+}(aq) + 2e^{-} \quad \textbf{(divalent metal)}$$

$$M(s) \longrightarrow M^{3+}(aq) + 3e^{-} \quad \textbf{(trivalent metal)}$$

The ions move into the solution leaving electrons on the surface of the metal rod/plate.

- The **metal** rod becomes therefore **negatively** charged while its own **solution** positively charged. As the positive charges of the solution increase, some of them recombine with the electrons to form back the metal atoms.

$$M^{+}(aq) + e^{-} \longrightarrow M(s) \quad \textbf{(Monovalent metal)}$$

$$M^{2+}(aq) + 2e^{-} \longrightarrow M(s) \quad \textbf{(divalent metal)}$$

$$M^{3+}(aq) + 3e^{-} \longrightarrow M(s) \quad \textbf{(trivalent metal)}$$

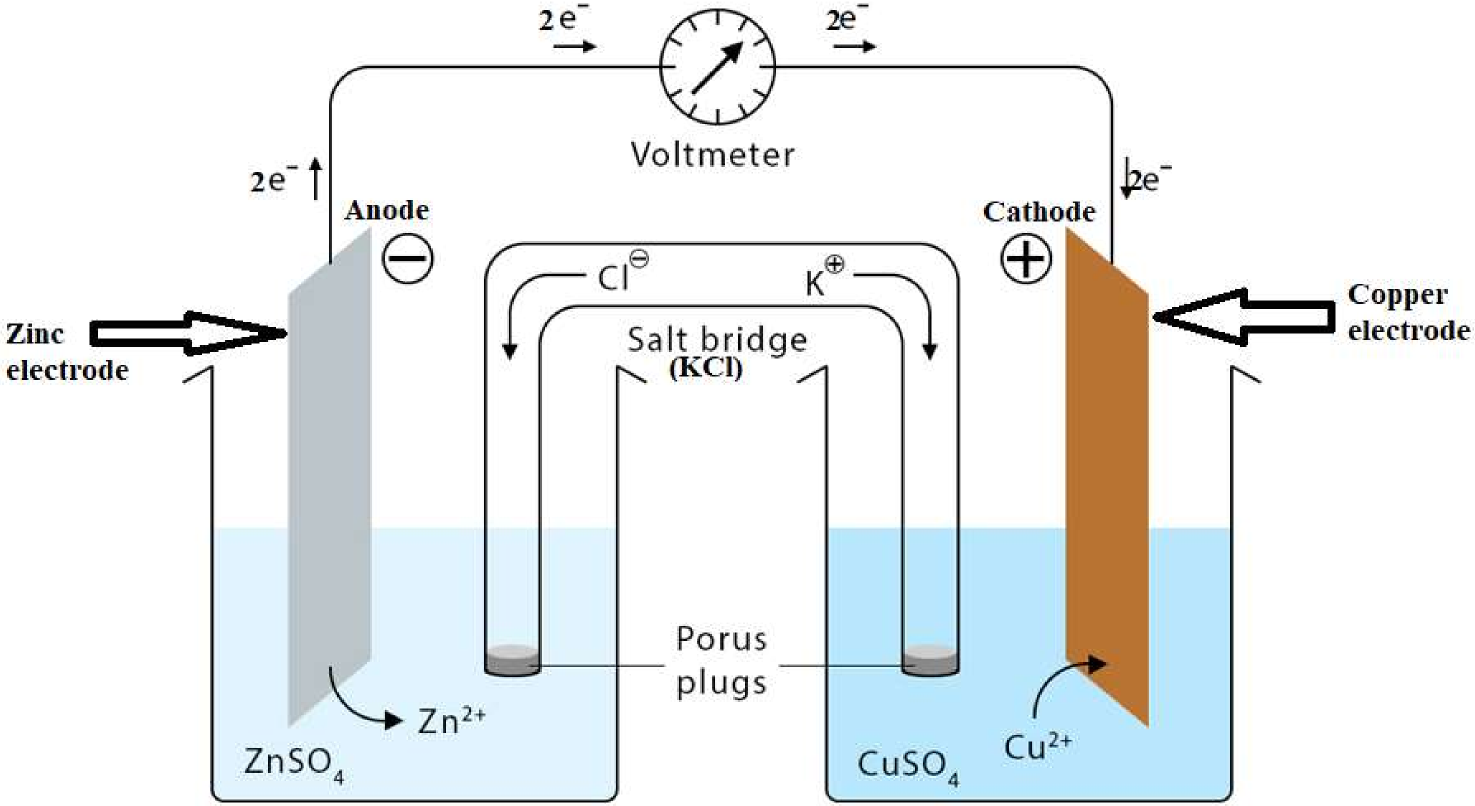
- When a metal rod is put in a solution of its own salt, it forms a half-cell. The tendency of metals to ionize differ from one metal to the other. The difference can be measured by connecting two half cells to form an electrochemical cell.

- The half cell can be represented as: metal | metal ion. **The vertical line represents the phase boundary where a potential difference develops**. For example, a zinc half-cell is represented as;

$$Zn(s) \mid Zn^{2+}(aq)$$

- The concentration of electrons on the metal rod is measured by a quantity called the **electrode potential**.
- Things to note when drawing an electrochemical or voltaic cell:
  - i. The half-cell of the more receive metal is placed on the left hand side.
  - ii. The electrons move from anode to cathode and the movement is showed by an arrow. This is because the oxidation always take place at the anode and the reduction at the cathode.
  - iii. The two half-cells are connected with a salt bridge. The salt bridge can be a U-tube filled with electrolyte e.g.KNO_3 , $NaNO_3$ or a filter paper soaked in the electrolyte.
  - iv. The two electrodes that is anode and cathode are connected using a copper wire.
  - v. Each electrode is dipped in 1M of its solution.

- Below is an example of zinc-copper metal electrochemical cell:



- When a copper-copper ions half-cell, Cu(s) | Cu^{2+} (aq) is connected to a zinc-zinc ions half-cell, Zn(s) | Zn^{2+}(aq), the following observations are made:
    1. The zinc rod in the zinc-zinc ions half-cell wears out.
    2. The intensity of the blue colour of copper(II) sulphate solution decreases and red-brown deposits appear on the copper rod in the copper-copper ions half-cell.
    3. A voltage of 1.10V is registered by the voltmeter as a measure of the electromotive force (e.m.f) of the cell. Practically the voltage reading is lowered because the connecting wires have some resistance to be overcome.
- In the left-hand side beaker (anode), the zinc rod dissolves by losing two electrons to form zinc ions, Zn^{2+}(aq).

$$\mathbf{Zn\ (s) \longrightarrow Zn^{2+}(aq) + 2e^-}$$

- The electrons then flow through the external wire to the right-hand side beaker (Cathode). The copper(II) ions, Cu^{2+}(aq), take these electrons and copper metal is deposited.

$$\mathbf{Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)}$$

- The overall reaction is as follows:

$$\mathbf{Zn\ (s)\ +\ Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq)\ +\ Cu(s)}$$

- The overall reaction is an oxidation-reduction reaction. Oxidation always occurs at the **anode** and reduction always occurs at the **cathode** The $Zn(s)|Zn^{2+}(aq)$ half-cell is therefore the anode, and the $Cu^{2+}(aq)\ |Cu(s)$ half-cell is the cathode.
- For the negative half cell (anode) the Cl^- from salt bridge **neutralize** the increased **positive** (Zn^{2+}) ion, while for the positive half cell (cathode) the K^+ from salt bridge increase the decreased positive(Cu^{2+}) ion.
- The purpose of the salt bridge therefore is to:
  1. complete the circuit by making contact between the two solutions
  2. Maintains balance of charges in electrolytes by providing ions to replace those ions that are used up or those that are formed.
- The ionic equation and the e.m.f. of the electrochemical cell can be summed up in what is called **a cell notation**. A cell diagram is a shorthand for writing down the cell formed by connecting two half-cells.

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu(s)$ $E = +1.10\ V$

Note:

- | – A single vertical line represents a change in state or a phase between the metals and their ions
- || – A double vertical line indicates the salt bridge connecting the half-cells.
- Within a half- cell, the reactants are written before the products e.g. zinc metal (reactant) dissolves to form zinc ions (product), in the other half-cell, copper(II) ions, Cu^{2+}, (reactant) gain, electrons to form copper metal, Cu(s), (product).
- By convention, the more electropositive electrode (one that does not ionise easily) is put on the right-hand side.

The e.m.f. of the cell is given by:

$$E_{\text{cell}} = E\ (\text{right-hand side electrode}) - E\ (\text{left-hand side electrode})$$

$$\mathbf{E_{cell} = E_{RHS} - E_{LHS}}.$$

Standard Electrode Potentials

- ☐ The standard electrode potential is denoted by E^{θ} .
- ☐ The standard electrode potential is obtained if the **hydrogen** half cell is used as **reference** and is therefore referred to as the standard hydrogen half cell. Being the reference electrode, it is assigned an electrode potential 0.00 V.

standard conditions for measuring electrode potential

i. Temperature of 25°C.

ii. All solutions have a concentration of 1 mole per litre (1 M).

iii. Pressure of 1 atmosphere.

- ☐ Platinised platinum electrode is used as the electrode when the half-cell does not include a metal, e.g., $H_2(g) \mid H^+(aq)$.

Functions of the platinized platinum electrode

i. It acts as an inert metal connection to the $H \mid H^+(aq)$ system.

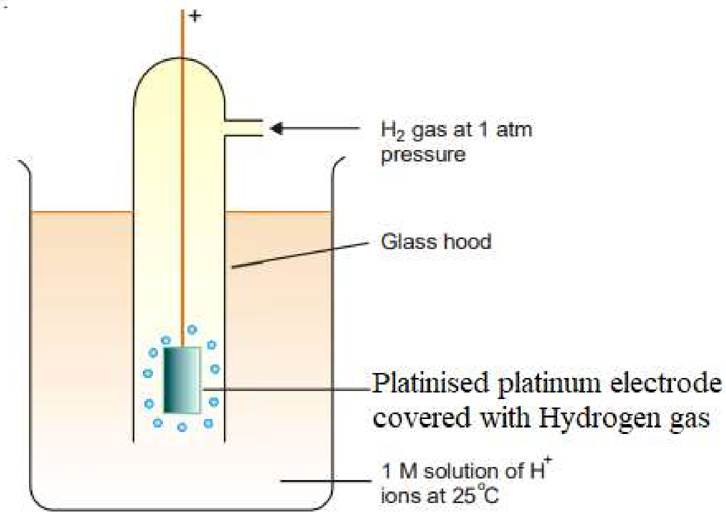
ii. It provides a surface area on which dissociation of hydrogen molecules can take place.

iii. It serves as an electrical conductor to the external circuit.

- The standard electrode potential consist of inert platinum electrode immersed in 1M solution of (sulphuric(VI) acid) hydrogen ions. H^+. Hydrogen gas is bubbled on the platinum electrode which is dipped in a solution containing 1 M hydrogen ions.

$$1/2\ H_2\ (g) \rightleftharpoons H^+\ (aq)\ +\ e^-$$

- The standard hydrogen half-cell is presented as:



$$\mathbf{Pt(s),\ H_2(g)\ |\ H^+(aq).}$$

- ☐ standard electrode potential, E for this reference half-cell which is zero can be represented as:

$$\frac{1}{2} H_2(g) \longrightarrow H^+(aq) + e^- \quad E = 0.00\ V$$

- ☐ The emf of the unknown half-cell, E° , can then be calculated from the expression

$$E_{measured} = E_R - E_L$$

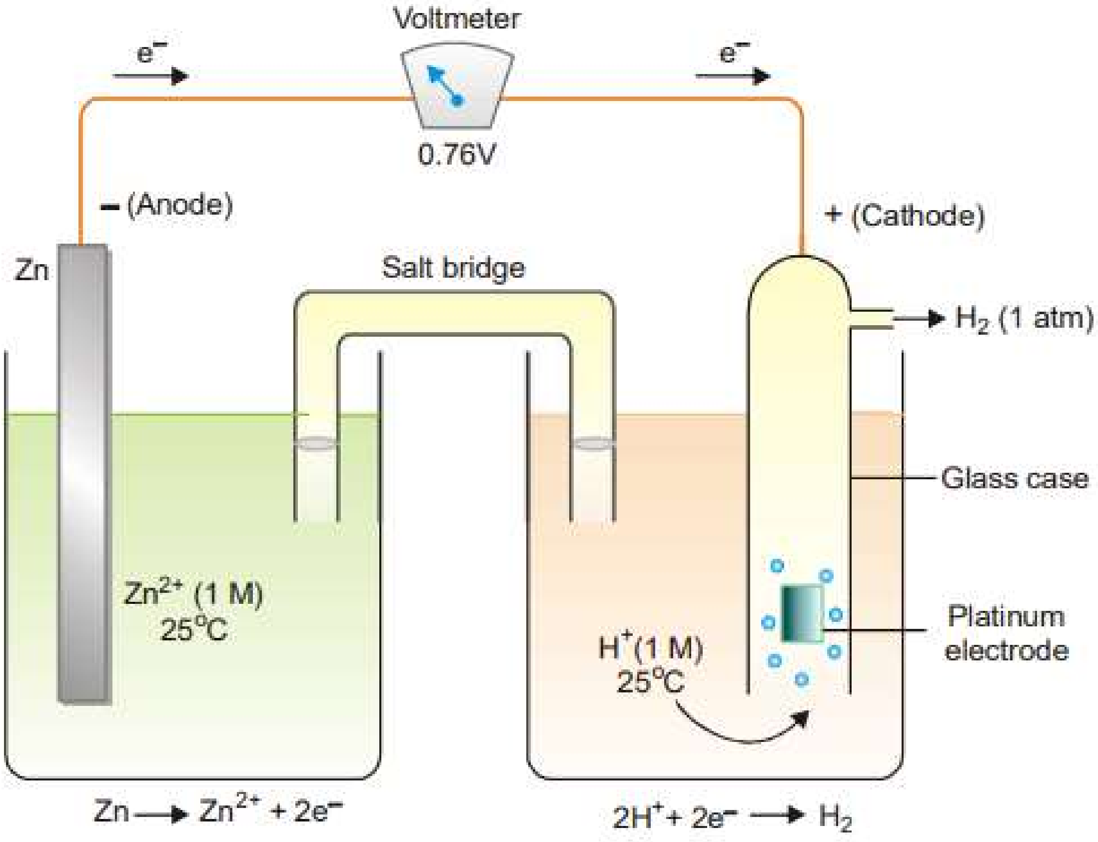
If the standard half-cell acts as anode, the equation becomes.

$$E_R = E_{measured} \qquad (E_L = 0)$$

On the other hand, if standard half-cell is cathode, the equation takes the form

$$E_L = -E_{measured} \qquad (E_R = 0)$$

For example, it is desired to determine the emf of the zinc electrode, Zn | Zn^{2+}. It is connected with the standard hydrogen electrode as shown in figure. The complete electrochemical cell may be represented as :



$E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L}$

$= 0.00V - 0.76V$

$= -0.76V$

The overall ionic equation is:

$Zn(s) + 2H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \quad E\theta = -0.76\ V$

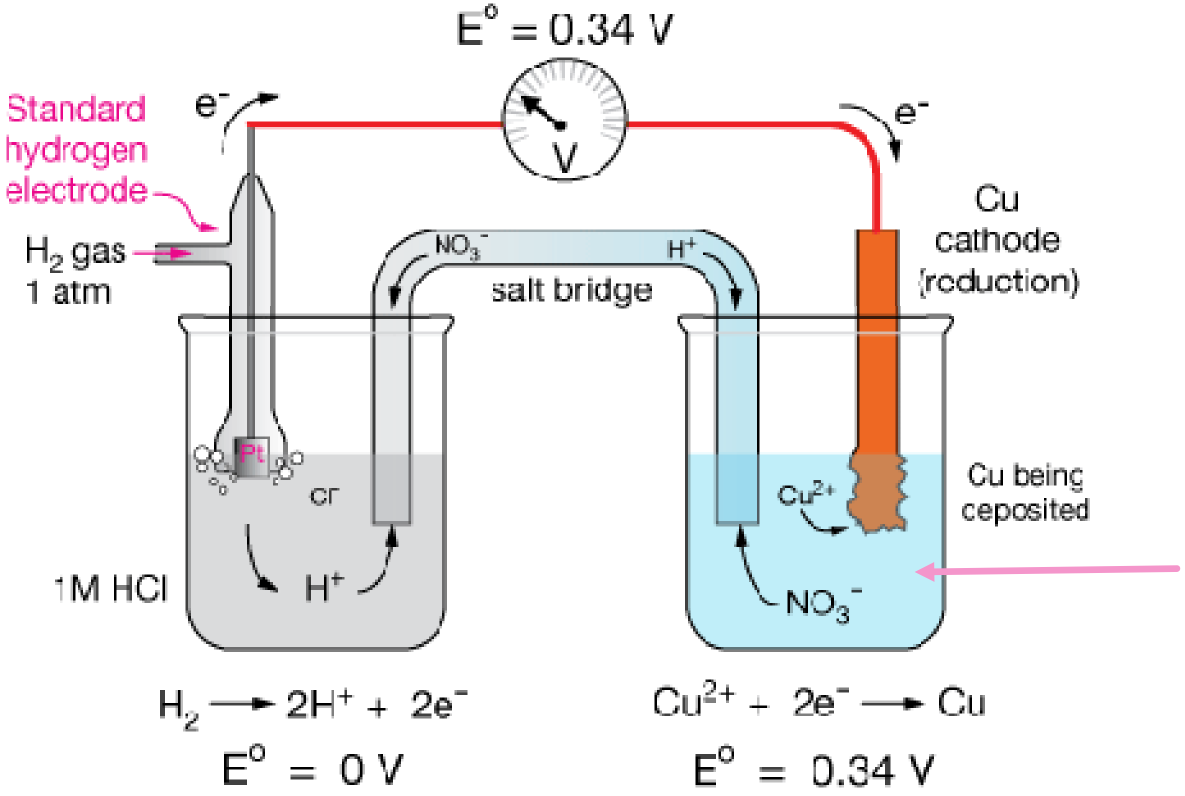
Cell notation,

$Zn(s) | Zn^{2+}(aq) \| H^{+}(aq) | H_2(g), Pt(s) \quad E^{\theta} = -0.76V$

- ❑ Similarly, the emf of the copper electrode, Cu^{2+} | Cu can be determined by pairing it with the Standard hydrogen electrode when the electrochemical cell can be represented as :

$Pt(s)\ H_2(g) | H^{+}(aq) \| Cu^{2+}(aq) | Cu(s)\ E\theta = +0.34V$

Measuring the standard electrode potential for Cu(s) | Cu^{2+} (aq) half cell



1 M Cu^{2+}

$E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L}$

$= 0.34V - 0.00V$

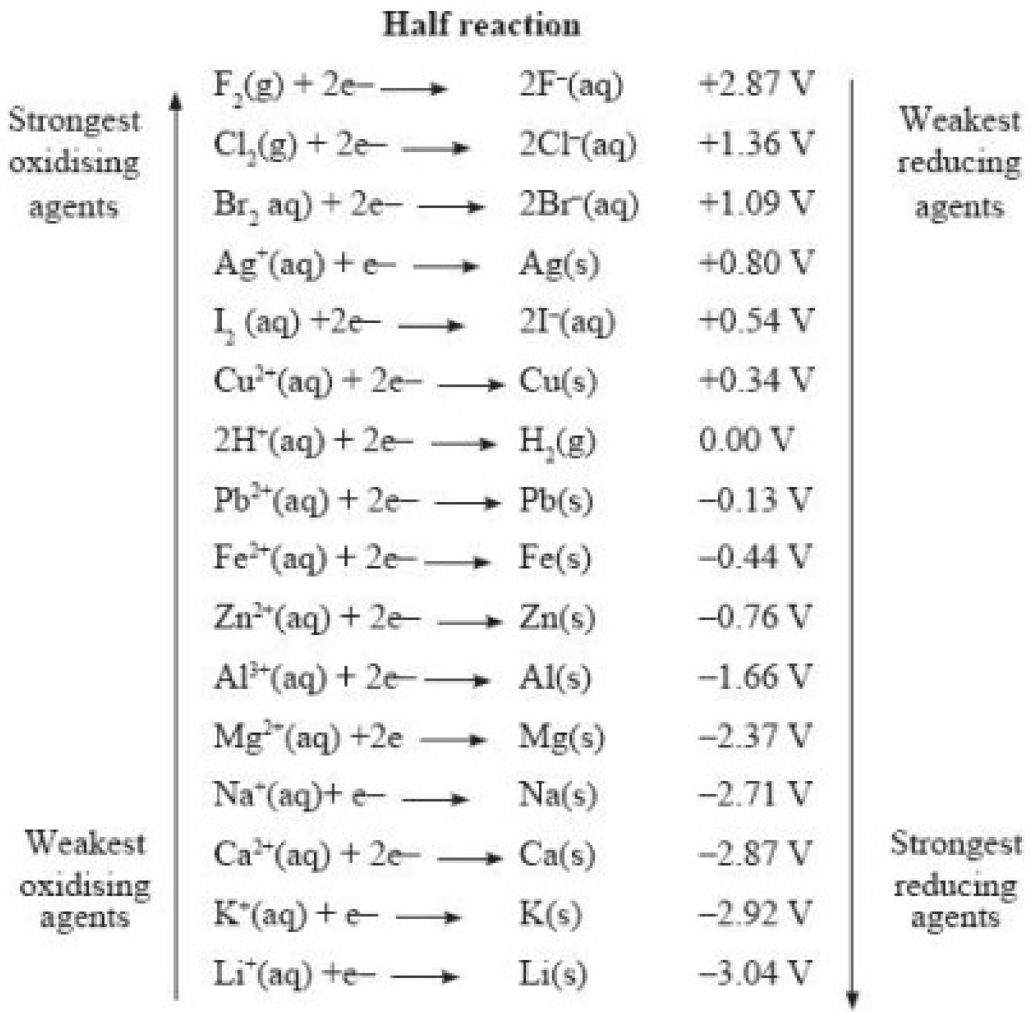
$=+0.34V$

Overall equation;

$H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^{+}(aq) + Cu(s) \quad E^{\theta} = +0.34\ V$

- ☐ The standard electrode potential difference **is the potential difference for a cell comprising a particular element in contact with one molar solution of its ions and the standard hydrogen electrode.**
- ☐ Standard electrode potentials are sometimes referred to as **standard reduction potential** because they relate to the reduction reactions.

Standard electrode potential



	Half reaction		
Strongest oxidising agents	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87 V	Weakest reducing agents
	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36 V	
	Br_2 aq) + $2e^- \longrightarrow 2Br^-(aq)$	+1.09 V	
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80 V	
	$I_2\,(aq) + 2e^- \longrightarrow 2I^-(aq)$	+0.54 V	
	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34 V	
	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00 V	
	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13 V	
	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44 V	
	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76 V	
	$Al^{3+}(aq) + 2e^- \longrightarrow Al(s)$	−1.66 V	
	$Mg^{2+}(aq) + 2e \longrightarrow Mg(s)$	−2.37 V	
	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71 V	
Weakest oxidising agents	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87 V	Strongest reducing agents
	$K^+(aq) + e^- \longrightarrow K(s)$	−2.92 V	
	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.04 V	

Uses of Standard Electrode Potentials

- Standard electrode potentials are used in:
  - (i) Comparing the oxidising and reducing powers of substances.
  - (ii) Determining the e.m.f. of a cell.
  - (iii) Predicting whether or not a reaction will take place.

Comparing Oxidising and Reducing Power

- ☐ Lithium with **$E^{\theta} = -3.04$ V** has the **highest tendency to lose electrons** and therefore it is the **strongest reducing agent**. The **more negative the E^{θ} value the greater the reducing power**. Lithium has the least tendency to accept electrons hence it is the weakest oxidising agent.
- ☐ Fluorine with **E^{θ} of + 2.87 V has the highest tendency to accept electrons and therefore the strongest oxidising agent. The more positive the E^{θ} value, the greater the oxidising power**. Conversely, fluorine is the weakest reducing agent since it has the least tendency to lose electrons.

Predicting Feasibility of Reaction.

- The feasibility of a redox reaction can be predicted with the help of the electrochemical series.
- The net emf of the reaction, E_{cell}, can be calculated from the expression

$$E^{\theta}_{cell} = E^{\theta}_{R\,(Cathode)} - E^{\theta}_{L\,(anode)}$$

E^{θ}_{cell} = **+ ve, the reaction is feasible**

E^{θ}_{cell} = **-ve, the reaction is not feasible**

Solved problem 1.

Predict whether the reaction $2Ag(s) + Zn^{2+}(aq) \longrightarrow Ag^{+}(aq) + Zn(s)$ is feasible or not hence write the cell notation for the reaction given the cell half reactions as:

$2Ag^{+}(aq) + 2e^{-} \xrightarrow{\qquad\qquad} 2Ag(s) \qquad E^{\theta} = +0.80V$

$Zn^{2+}(aq) + 2e^{-} \xrightarrow{\qquad\qquad} Zn(s) \qquad E^{\theta} = -0.76\ V$

Solution

Anode: $2Ag(s) \longrightarrow 2Ag^{+}(aq) + 2e^{-}$ $E^{\theta} = +0.80V$

Cathode: $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$ $E^{\theta} = -0.76\ V$

$$E^{\theta}_{cell} = E^{\theta}_{Cathode} - E^{\theta}_{anode}$$

$$= -0.763\ V - 0.80$$

$$= -1.563$$

Since E^{θ}_{cell} is negative, the given reaction is **not feasible**.

Cell notation:

$$Ag(s)|\ Ag^{+}(s)\ ||\ Zn^{2+}(aq)\ |\ Zn(s)\quad E^{\theta} = -1.56V$$

Solved problem 2

The reduction potentials of $Mg(s) \mid Mg^{2+}(aq)$ and $Zn(s) \mid Zn^{2+}(aq)$ half-cells are:

$$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s) \quad E^\theta = -2.37V$$

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \quad E^\theta = -0.76\ V$$

Using the electrode potentials, answer the following questions.

(i) Write an ionic equation for a cell made by combining the two half cells.

(ii) Calculate the e.m.f. of the cell formed in part (i).

(iii) Write the cell notation for the cell.

Solution:

(i) Since the electrode potential of magnesium is more negative, magnesium is the stronger reducing agent. Zinc undergoes reduction while magnesium is oxidised. The sign of the E^θ value of Mg changes from negative to positive.

Anode: $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$ $E^{\theta} = -2.37V$

Cathode: $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$ $E^{\theta} = -0.76\ V$

$E^{\theta}_{cell} = E^{\theta}_{R\ (Cathode)} - E^{\theta}_{L\ (anode)}$

$= -0.76V-(-2.37V)$

$=-0.76+2.37$

$=+1.61$

$Mg(s) + Zn^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Zn(s)$ $E^{\theta} = +1.61V$

(iii) **$Mg(s) \mid Mg^{2+}(aq) \mid\mid Zn^{2+}(aq) \mid Zn(s)$ E^{θ} cell = + 1.61V**

Solved problem 3

Calculate the e.m.f. for the electrochemical cell represented below: $Al(s) \mid Al^{3+}(aq) \mid\mid Zn^{2+}(aq) \mid Zn(s)$.

Give that:

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s) \quad E° = -1.66\ V$$

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \quad E° = -0.76\ V$$

Solution

Note: to combine the two half equations, the number of electrons should be equal. To do this, multiply the first equation by 2 and the second by 3.

$$2Al(s) \longrightarrow 2Al^{3+}(aq) + 6e^- \quad E° = -1.66\ V$$

$$3Zn^{2+}(aq) + 6e^- \longrightarrow 3Zn(s) \quad E° = -0.76\ V$$

$$E^{\theta}_{cell} = E^{\theta}_{R\ (Cathode)} - E^{\theta}_{L\ (anode)}$$

$$= -0.76V-(-1.66V)$$

$$= -0.76+1.66v$$

$$= +0.90V$$

$$2Al(s) + 3Zn^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Zn(s) \quad E° = +0.90V$$

Solved problem 4

Use the cell representation below to answer the question that follows

$Cu(s) \mid Cu^{2+}(aq) \mid\mid Ag^{+}(aq) \mid\mid Ag(s)$ E^{θ} cell = + 0.46 V

Given that the E value for $Ag^{+}(aq) \mid Ag(s)$ is + 0.80 V, calculate the E^{θ} value for Cu(s) | Cu2+(aq).

Solution

$$E^{\theta}_{cell} = E^{\theta}_{R\ (Cathode)} - E^{\theta}_{L\ (anode)}$$

$$+0.46V = +0.80V - E^{\theta}_{L\ (anode)}$$

$$= -+0.80V - 0.4$$

$$E^{\theta}_{L\ (anode)} = +0.34V$$

Solved problem 5

Use the standard electrode potentials for elements A, B, C, D and E given below to answer the questions that follow. The letters do not represent actual symbols of elements.

	E^θ (volts)
$A^{2+}(aq) + 2e^- \longrightarrow A(s)$	−2.37
$B^{2+}(aq) + 2e^- \longrightarrow B(s)$	−0.76
$C^+(aq) + e^- \longrightarrow \frac{1}{2} C_2(g)$	0.00
$D^{2+}(aq) + 2e \longrightarrow D_2(s)$	+0.34
$\frac{1}{2} E_2(g) + e^- \longrightarrow E^-(aq)$	+ 1.36

(i) What is the Eθ value of the strongest oxidising agent? Explain.

- **+ 1.36 most positive**

(ii) Which two of the above elements would produce the largest e.m.f or potential difference in an electrochemical cell Explain.

- **A and E, the elements with the most positive Eθ and the most negative E^θ .**

(iii) What would be the initial potential difference of the cell chosen in(ii) above?

$$E^{\theta}_{cell} = E^{\theta}_{R\ (Cathode)} - E^{\theta}_{L\ (anode)}$$

$$= +1.36V - (-2.37V)$$

$$= +1.36V + 2.37V$$

$$= +3.73V$$

(vi) Write the cell representation for the electrochemical cell formed.

$A(s)\,|\,A^{2+}(aq)\,||\,E_2(g)\,|\,E^{-}(aq), Pt\ (s)$ $\quad E^{\theta} = +3.73\ V$

Note: Pt presents platinum electrode, any gas half cell MUST be attached to the platinum electrode.

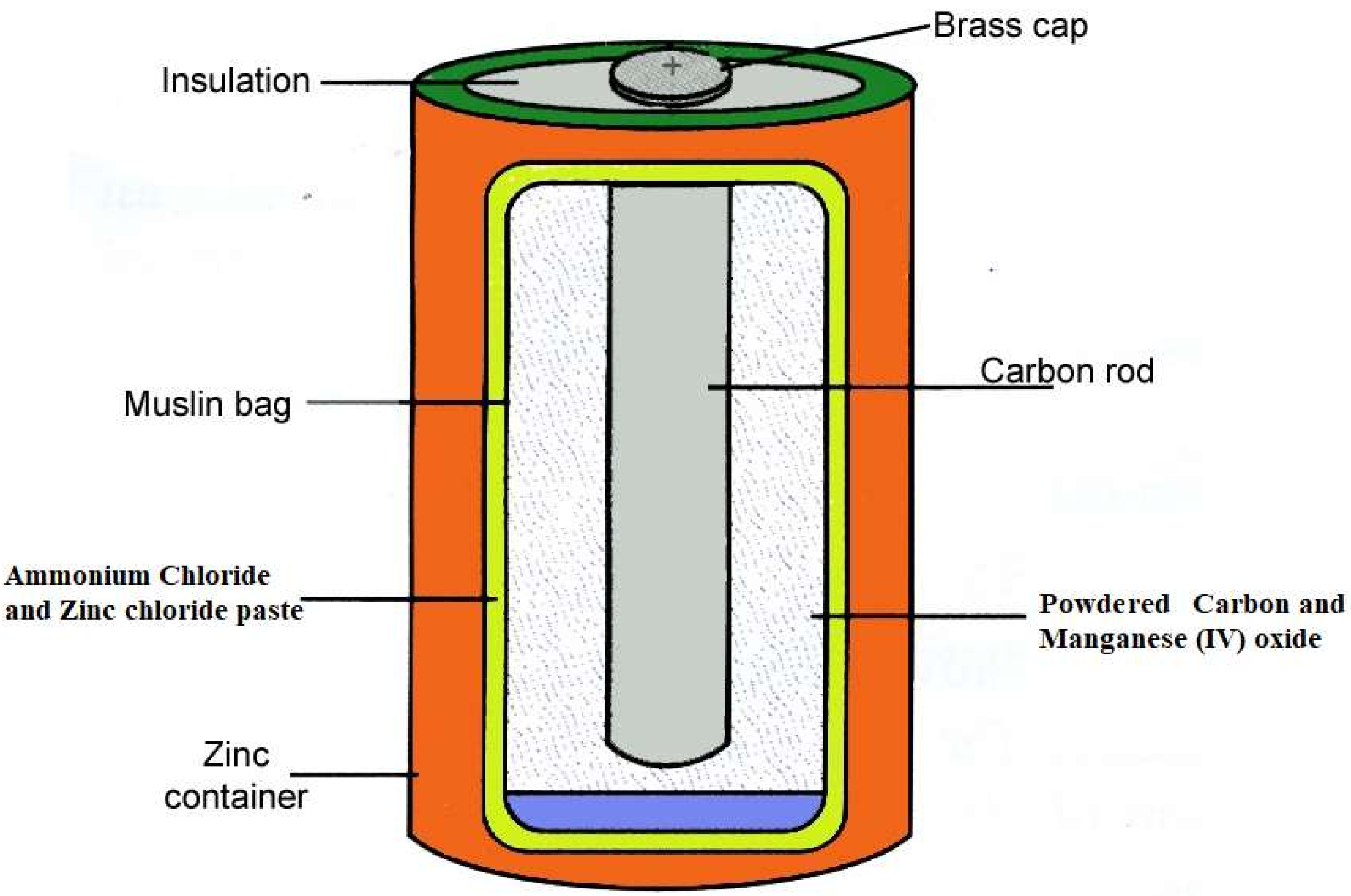
Key notes

- When the half cells given are having positive and negative $\mathbf{E^{\theta}}$ then:
    1. Positive $\mathbf{E^{\theta}}$ is a an oxidizing agent positive means addition. The oxidizing agent undergoes reduction hence makes the Cathode electrode and is placed on the right hand side of the electrochemical cell.
    2. Negative E^{θ} is a reducing agent, negative meaning substraction. The reducing agent undergoes oxidation hence makes the anode electrode and placed at the left-hand side.
- If given half cells are both have positive $\mathbf{E^{\theta}}$ then;
    1. The one with the most positive is the strongest oxidizing agent hence have higher tendency of accepting electron (s) therefore, it undergoes reduction hence make the cathode and placed on the right-hand side.
    2. The one with the least positive have high tendency of losing electrons hence oxidized therefore, makes the anode and placed on the left-hand side.
- When both half-cell have negative $\mathbf{E^{\theta}}$ then the one with the highest negative $\mathbf{E^{\theta}}$ is the strongest reducing agent therefore, undergoes oxidation hence make the anode electrode thus placed on the left-hand side. The one with the least negative $\mathbf{E^{\theta}}$ undergoes reduction therefore, make the cathode electrode and placed on the right-hand side.

- The redox reactions in an electrochemical or voltaic is commercially applied to make the:
  - (a) Dry /primary/Laclanche cell.
  - (b) Wet /secondary /accumulators.
  - (c) Fuel cell

Dry cell or Le Clanche cell

- ☐ It consists of a zinc can which forms the negative terminal (anode) and a graphite or carbon rod which is the positive terminal (cathode).
- ☐ The graphite/carbon rod is surrounded by a paste of ammonium chloride.
- ☐ Zinc chloride and powdered manganese(IV) oxide mixed with carbon. Carbon is added to increase conductivity and retain moisture.
- ☐ The powder increases the surface area of the positive terminal.
- ☐ The function of manganese(IV) oxide is to **oxidise the hydrogen produced at the electrode to water** thus preventing any bubbles from coating the carbon terminal which would reduce its efficiency. It also increases the surface area for the electrolyte.


Brass cap
Insulation
Carbon rod
Muslin bag
Ammonium Chloride and Zinc chloride paste
Powdered Carbon and Manganese (IV) oxide
Zinc container

At the negative terminal (anode):

$$Zn(s) \xrightarrow{\hspace{3cm}} Zn^{2+}(aq) + 2e^{-}$$

At the positive, terminal (cathode) ammonium ions are converted to ammonia and hydrogen gases.

$$2NH_4(aq) + 2e^{-} \xrightarrow{\hspace{3cm}} 2NH_3(g) + H_2(g)$$

- ☐ The gases produced do not escape but are immediately used up in other reactions. The hydrogen is oxidised to water by the manganese(IV) oxide.
- ☐ Ammonia forms a complex ion with the zinc chloride in the paste.
- ☐ A simple dry cell can produce a potential of 1.5 V. Dry ammonium chloride **does not conduct an electric current**. This explains why a paste, which is an electrolyteis sued.

Accumulators

- The main features of a lead-acid accumulator are the lead plate which is the negative terminal and the lead (VI) oxide plate which is the positive terminal.
- At the negative terminal, lead atoms lose electrons to form lead(II) ions.

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e–$$

- At the positive terminal, lead(IV) oxide reacts with hydrogen ions in sulphuric (VI) acid forming lead(II) Ions:

$$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$$

- The lead (II) ions formed react instantly with the sulphate ions to form lead(II) sulphate which is insoluble and adheres to the electrodes.

$$Pb^{2+}(aq) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s)$$

- The net reaction that takes place is:

$$Pb\,(s) + PbO(s) + 4H^+(aq) + SO_4{}^{2-}(aq) \xrightarrow{Discharging} 2PbSO_4(s) + 2H_2O(l)$$

Fuel Cells

- Fuel cells are electrochemical cells which convert the chemical energy of a fuel directly to electrical energy. One of the most important fuel cells is the hydrogen oxygen cell.
- At the negative terminal, hydrogen reacts with hydroxide ions to form water and electrons are released.

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

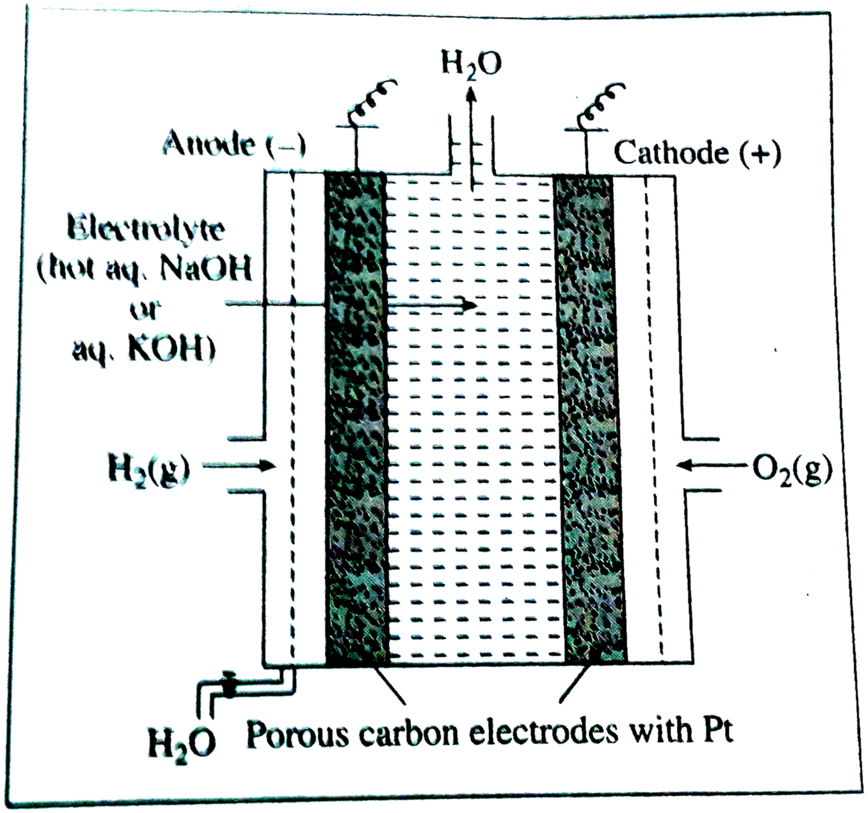
- At the positive terminal, oxygen and water acquire electrons to form hydroxide ions.

$$O_2(g) + H_2O(l) + 4\ e^-(aq) \longrightarrow 4OH(aq)$$

- The overall reaction in the hydrogen | oxygen cell is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

- The electrode other than completing the circuit also catalyses the reactions which increase the output of the cell.



Hydrogen–oxygen (H_2–O_2) fuel cell

Electrolysis

- Electrolysis **is the decomposition of an electrolyte by passing electric current through its solution**.
- Electrolytes **are electrovalent substances that form ions in solution which conduct an electric current.** Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes**.**

MECHANISM OF ELECTROLYSIS

- ❑ The cations **migrate to the cathode and form a neutral atom by accepting electrons from it**. The anions **migrate to the anode and yield a neutral particle by transfer of electrons to it**. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes chemical reaction takes place.

Example. Let us consider the electrolysis of hydrochloric acid as an example. In solution, HCl is ionised,

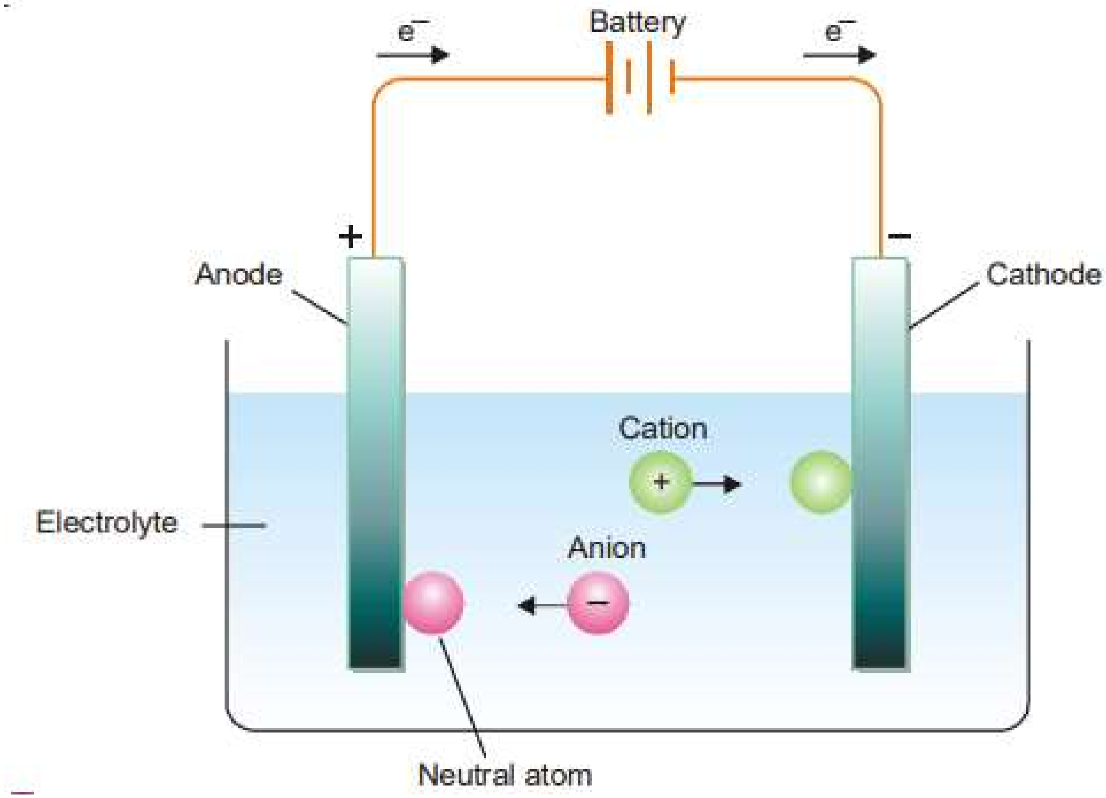
$$HCl \longrightarrow H^{+} + Cl^{-}$$

- In the electrolytic cell Cl^- ions will move toward the anode and H^+ ions will move toward the cathode. At the electrodes, the following reactions will take place.

At cathode :

$$\mathrm{H}^+ + e^- \longrightarrow \mathrm{H} \qquad (\textit{Reduction})$$

As you see, each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Pairs of hydrogen atoms then unite to form molecules of hydrogen gas, H_2.



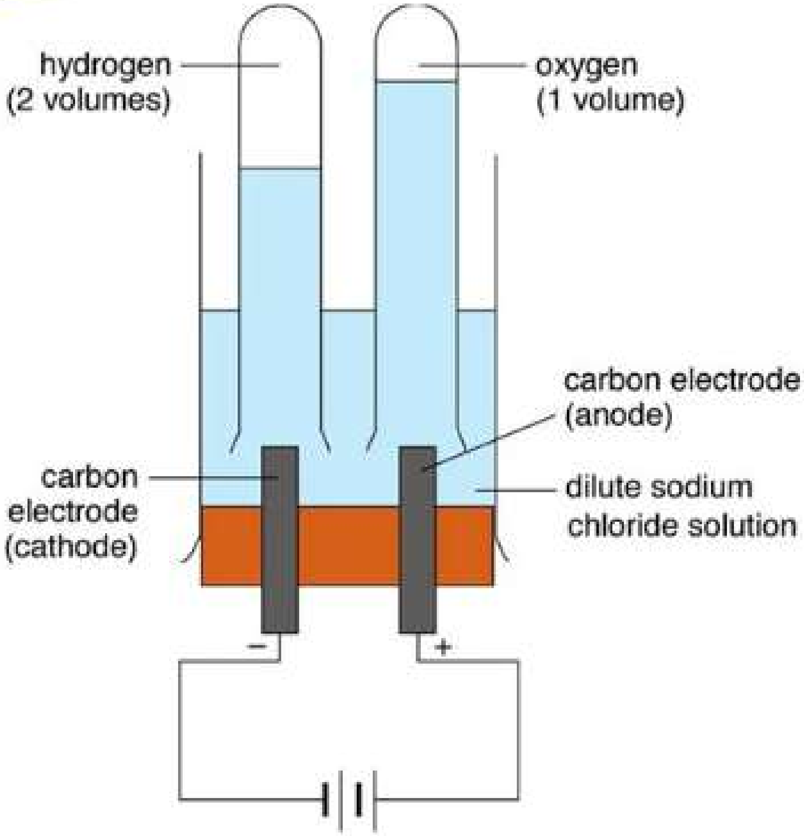
At Anode :

$$\mathrm{Cl^-} \longrightarrow \mathrm{Cl} + e^- \qquad \textit{(Oxidation)}$$

- After the chloride ion loses its electron to the anode, pair of chlorine atoms unite to form chlorine gas, Cl_2.
- The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction is :

$$2HCl \longrightarrow H_2 + Cl_2 \qquad (\textit{Decomposition})$$

Electrolysis of dilute sodium chloride



Cation	Anion
H^+(aq)	OH^-(aq)
Na^+(aq)	Cl^-(aq)

- Sodium chloride solution contains sodium ions (Na^+) and chloride ions (Cl^-) from sodium chloride, hydrogen ions (H^+) and hydroxide ions (OH^-) from water.
- Chloride ions (Cl^-) and hydroxide ions (OH^-) migrate to the anode on passing electric current through the solution. Hydroxide ions (E^θ= + 0.04 V) have a greater tendency to lose electrons compared to the chloride ions. (E^θ= +1.36 V). The anion with a low E^θ value is preferentially discharged.
- Sodium ions (Na^+) and hydrogen ions (H^+) migrate to the cathode but hydrogen ions (E^θ= 0.00 volts) are preferentially discharged because they have a greater tendency to gain electrons than sodium ions (E^θ = – 2.71 volts). Note the cations with a higher E^θ has a higher tendency to gain electrons.

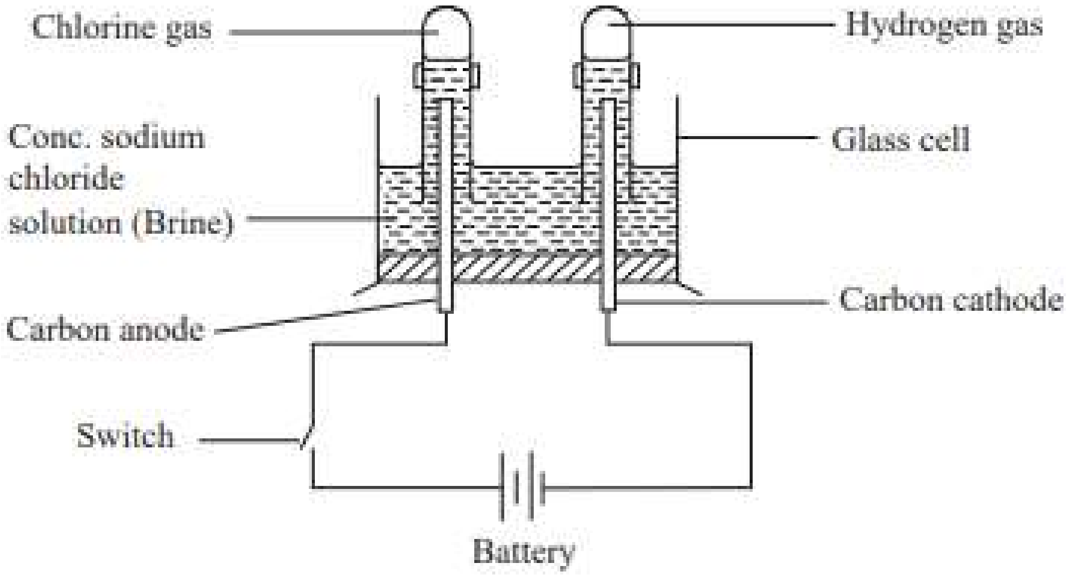
At the anode	At the cathode
Ions present Cl^- (aq), OH^- (aq) Both ions move to the anode. OH^- ion is discharged because it is lower in electrochemical series. OH^- is discharged by losing an electron $OH^-(aq) \rightarrow OH(g) + e-$ Four OH^- ions are discharged, the OH groups interact to form one mole of oxygen and two moles of water as shown below, releasing 4 electrons which move to the cathode. **Overall reaction** **$4OH^- (aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$**	Ions present Na+ (aq), H+ (aq) Both ions move to the cathode. H+ ion is discharged in preference to Na+ ion because it is lower than Na+ ion in the electrochemical series. It gains an electron to form H atom. $H^+ (aq) + e^- \rightarrow H (g)$ The hydrogen atoms combine to form H2 (g) molecules. $H(g) + H(g) \rightarrow H_2 (g)$ Therefore; $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$ But the $4e^-$ produced at the anode must react hence overall equation is **$4H^+ (aq) + 4e^- \rightarrow 2H_2 (g)$**

Note: The 4e^- released at the anode must be taken up by H^+ ions. So, we must multiply the last equation under cathode by 2 to get the overall equation.

Finally, Na^+ and Cl^- ions remain in solution forming sodium chloride; solution of higher concentration.

Electrolysis of dilute sodium chloride evolves oxygen gas at the anode and hydrogen gas at the cathode in the ratio of 1:2. This is essentially the electrolysis of water since oxygen and hydrogen are the constituents of water.

Electrolysis of concentrated sodium chloride solution (Brine)



Ions present

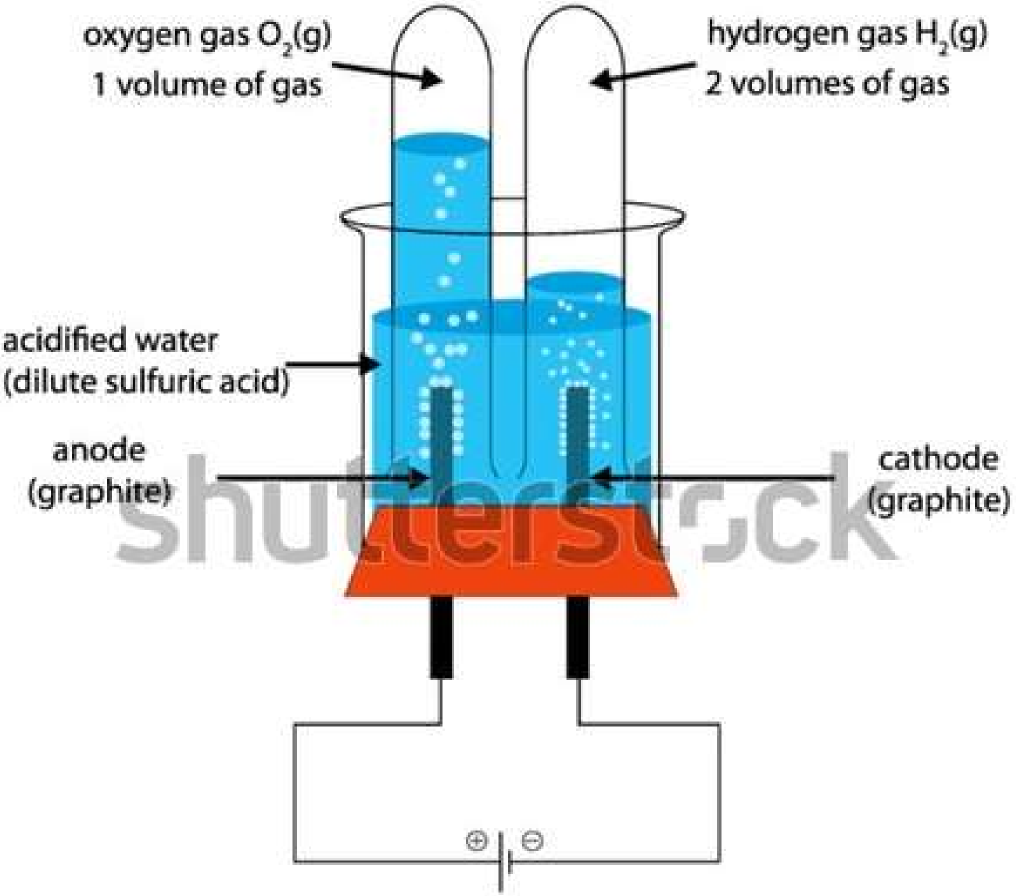
From sodium chloride Na^+ (aq), Cl^- (aq)

From water H^+ (aq), OH^-(aq)

At the anode	At the cathode
Cl^- (aq), OH^- (aq) Although OH^- ion is lower in the electrochemical series than Cl^- , the concentration of Cl^- ions at the cathode is greater than the OH^- ions. Therefore, Cl^- ions are discharged in preference to OH^- ions $2Cl^- (aq) \rightarrow Cl_2 (g) + 2e^-$	Na^+ (aq), H^+ H^+ ions are discharged in preference to Na^+ ions because H^+ ion is lower in electrochemical series than Na^+ ion. $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

- ☐ The discharge of hydrogen ions leads to an increase in hydroxide (OH^-) ions concentration and the solution becomes alkaline. As the electrolysis process continues, the concentration of chloride ions decreases and eventually hydroxide ions are oxidised to water and oxygen gas.

Electrolysis of the dilute sulphuric (VI) acid



Ions present

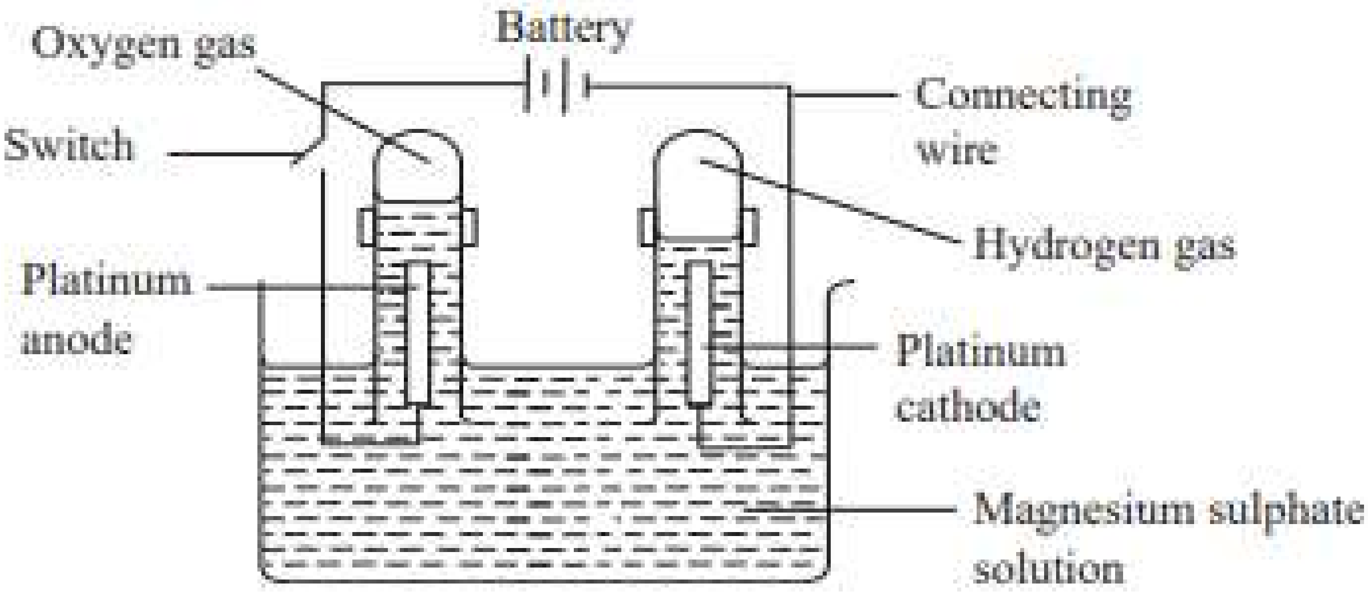
From sulphuric(VI) acid, H^+ (aq), SO_4^{2-} (aq)

From water H^+ (aq), OH^- (aq)

At the anode	At the cathode
Ions SO_4^{2-} (aq), OH^- (aq) Both ions move to the anode. OH- ion is lower in the electrochemical series and is therefore discharged preferentially to SO_4^{2-} ion by loss of one electron. **OH^- (aq) → OH (g) + e-** The OH(g) ions interract to form 1 mole of O_2 and 2 moles of water **Overall ionic equation**. $4OH^- (aq) \rightarrow 2H_2O(l) + O_2 (g) + 4e^-$	Ions H^+ (aq) H^+ ions moves to the cathode and gain an electron to form H atom. **H^+ (aq) + e- → H (g)** Since hydrogen is a diatomic gas, the atoms combine to form a hydrogen molecule. **H (g) + H (g) → H_2 (g)** The 4e– from the anode are taken up by H+ ions giving 2 moles of hydrogen gas. **Overall ionic equation** $4H^+ (aq) + 4e^- \rightarrow 2H_2 (g)$

- The four electrons lost by hydroxide ions to form one mole of oxygen molecules are gained by the four hydrogen ions to form two moles of hydrogen molecules. For every mole of oxygen gas produced at the anode two moles of hydrogen are formed at the cathode. The volume of hydrogen is therefore twice that of oxygen.
- The amount of water in the electrolyte decreases as the electrolysis process continues. This causes an increase in the concentration of the acid.

Electrolysis of aqueous magnesium sulphate



- The ions present in magnesium sulphate solution are magnesium (Mg^{2+}), sulphate (SO_4^{2-}), hydrogen (H^+) and hydroxide (OH^-). When an electric current is passed through the solution, hydroxide ions ($E^\theta = +0.40$ volts) and sulphate ions ($E^\theta = +2.01$ volts) migrate to the anode. Hydroxide ions are preferentially discharged because of their greater tendency to lose electrons.

Reaction at Anode;

$$4OH^-(aq) \rightarrow 4OH(aq) + 4e^-$$

$$4OH(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Overall;

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e-$$

- Both magnesium ($E^\theta = -2.38$ volts) and hydrogen ions ($E^\theta = 0.00$ volts) migrate to the cathode. Hydrogen ions are preferentially discharged because of their greater tendency to gain electrons.

Reactions at Cathode

$$4H^+(aq) + 4e^- \rightarrow 4H(g)$$

$$4H(g) \rightarrow 2H_2(g)$$

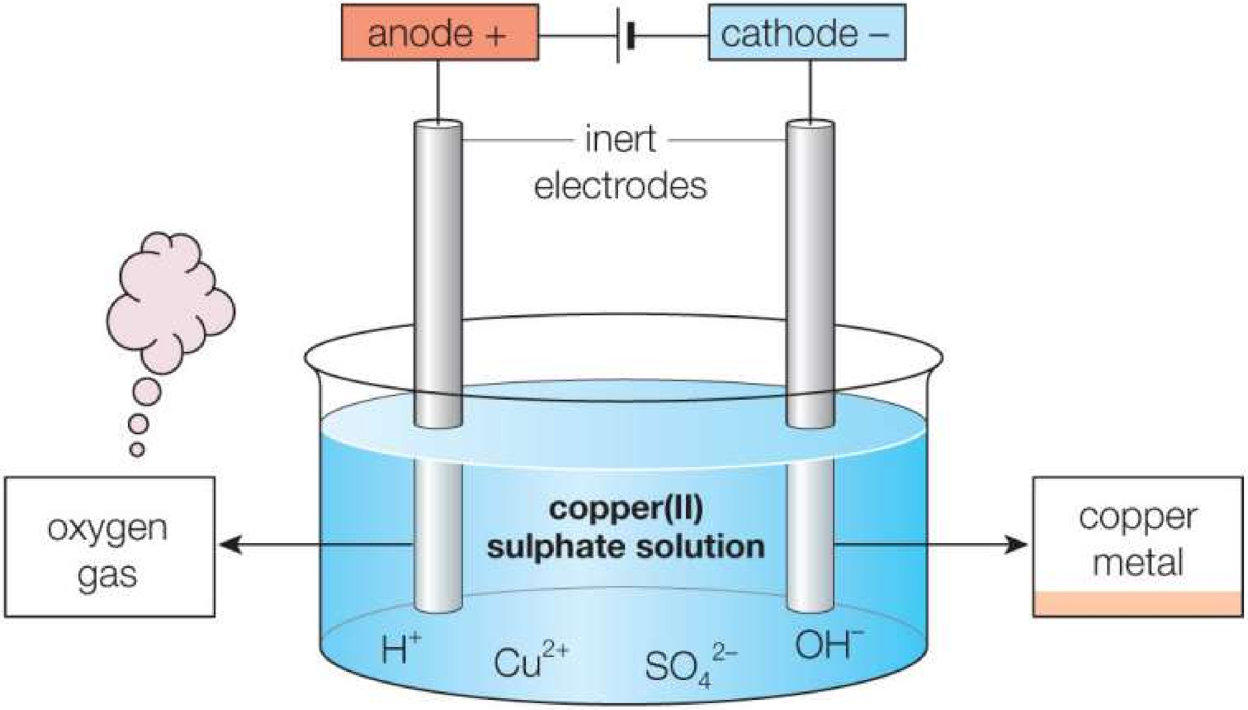
Overall;

$$4H^+(aq) + 4e^- \rightarrow 2H_2(g)$$

- ❑ It is observed that the volume of oxygen gas produced at the anode and hydrogen gas at the cathode are in the ratios of 1:2 respectively.

Electrolysis of copper(II) sulphate solution using inert electrodes.

- Inert electrodes are substances like carbon (graphite) or platinum. They take no part in electrolysis except to carry electrons to and from the electrolyte.



Ions present

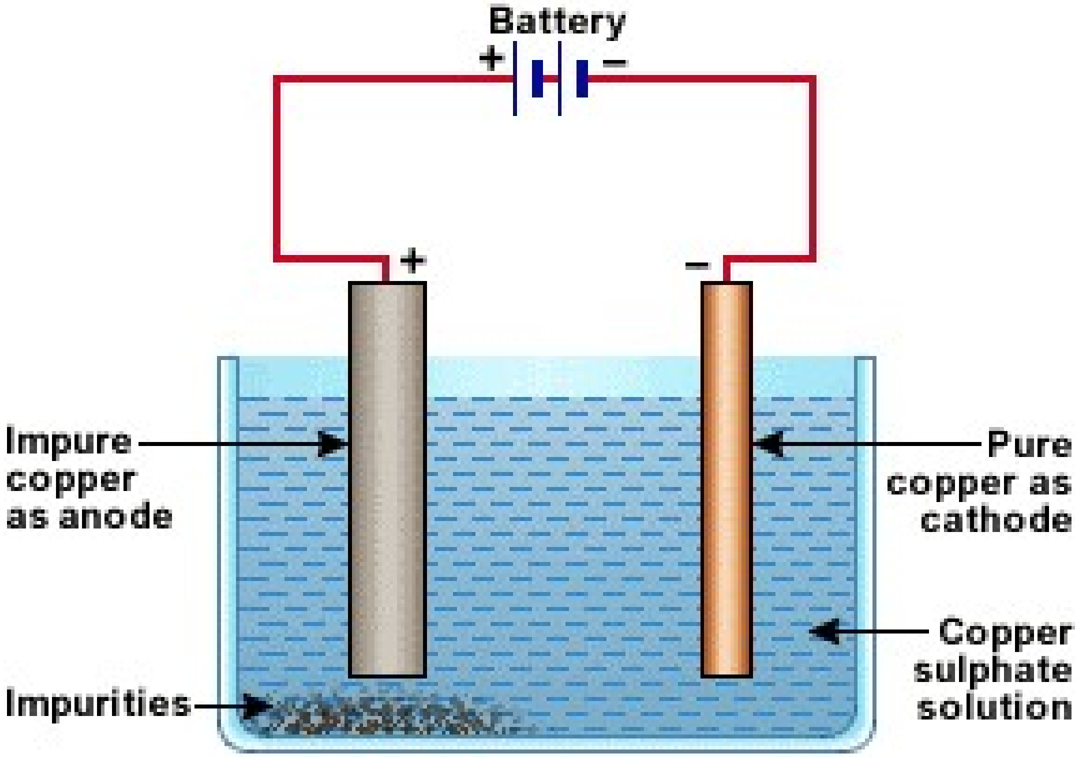
From copper (II) sulphate, $Cu^{2+}(aq)$, $SO_4^{2-}(aq)$

From water H^+ (aq), OH^- (aq)

At the anode	At the cathode
▪ SO_4^{2-}– (aq), OH^- (aq) both move to the anode, ▪ OH^- ions preferentially lose electrons being lower in the electrochemical series. They combine to form water and oxygen Ionic equation. **$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$** Bubbles of oxygen gas are observed at the anode. ▪ The mass anode remains the same.	▪ Cu^{2+} (aq), H^+ (aq) both move to the cathode. ▪ Cu^{2+} ions gain electrons, to form copper which appears as a brown deposit, at the cathode i.e Cu2+ ions are preferentially discharged. Ionic equation: **$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$** ▪ Mass of the cathode increases due to the red-brown coating.

- The concentration of copper(II) ions in solution decreases and the blue colour of the copper(II) sulphate solution becomes pale and finally colourless. Hydrogen ions accumulate in the solutions and therefore the solution becomes acidic.

Electrolysis of copper(II) sulphate solution using copper electrodes.



Ions present

From copper (II) sulphate, $Cu^{2+}(aq)$, $SO_4^{2-}(aq)$

From water $H^+(aq)$, $OH^-(aq)$

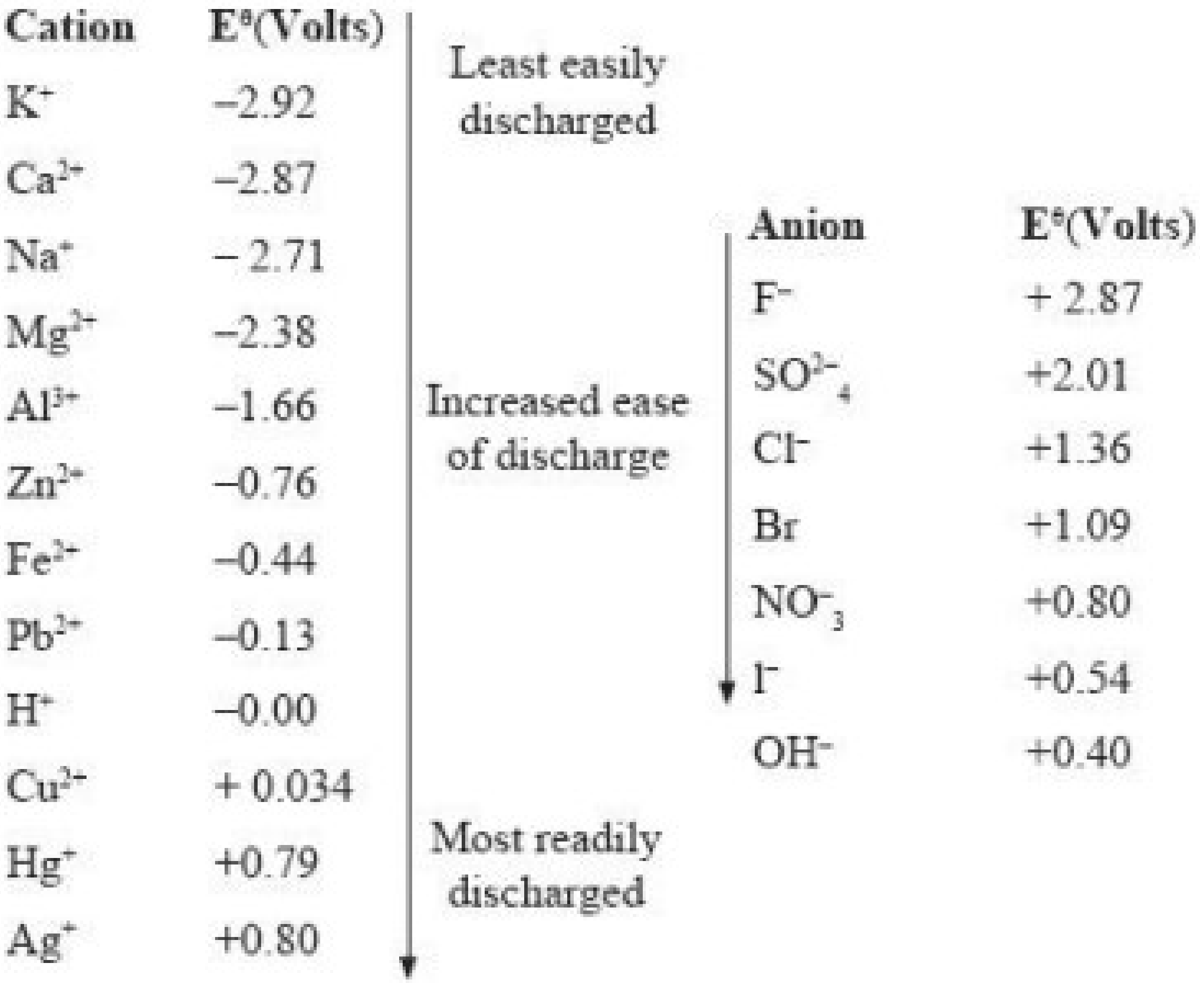
At the anode	At the cathode
$SO_4^{2-}(aq)$, $OH^-(aq)$ ❑ These ions move to the anode. We would expect OH^- ions to be oxidised. But because of the nature (type) of electrodes used i.e copper; **none** of the Instead,copper electrode dissolves i.e. $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ ❑ Copper is an active electrode and it therefore gets dissolved. This process is called **electrode ionisation** and it causes a decrease in mass.	$Cu^{2+}(aq)$, $H^+(aq)$ ❑ These ions move to the cathode. Cu^{2+} ions are lower in electrochemical series and are preferentially discharged by gaining electrons to form a brown solid which is copper. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ ❑ Copper is deposited on the cathode and it causes an increase in mass of cathode.

- The amount of copper oxidised at the anode is equal to the amount of copper deposited on the cathode and therefore the concentration of copper(II) ions in the solution remains the same. The colour of the blue solution does not fade.

Factors Affecting Preferential Discharge During Electrolysis

I. Position in the Electrochemical Series

- The ease of reduction of cations and oxidation anions depends on their position in the electrochemical series. The cations high in the series require more energy to be reduced. Anions high in the series require more energy to be oxidised.



Cation	E^0(Volts)
K^+	–2.92
Ca^{2+}	–2.87
Na^+	– 2.71
Mg^{2+}	–2.38
Al^{3+}	–1.66
Zn^{2+}	–0.76
Fe^{2+}	–0.44
Pb^{2+}	–0.13
H^+	–0.00
Cu^{2+}	+ 0.034
Hg^+	+0.79
Ag^+	+0.80

Least easily discharged

Increased ease of discharge

Most readily discharged

Anion	E^0(Volts)
F^-	+ 2.87
$SO^{2-}{}_4$	+2.01
Cl^-	+1.36
Br	+1.09
$NO^-{}_3$	+0.80
I^-	+0.54
OH^-	+0.40

II. The concentration of the electrolyte

- A cation or anion whose concentration is high is preferentially discharged if the ions are close in the electrochemical series.

III. **The product obtained at the electrode depends on the nature of electrode used.**

Applications of Electrolysis

i. **Extraction of Reactive Elements**

- Electrolysis is used in the extraction of reactive elements such as sodium, magnesium, aluminum and chlorine.

ii. **Electroplating**

- This is the process of using electricity to coat one metal with another.

Importance of electroplating

a) protecting some metals from corrosion.

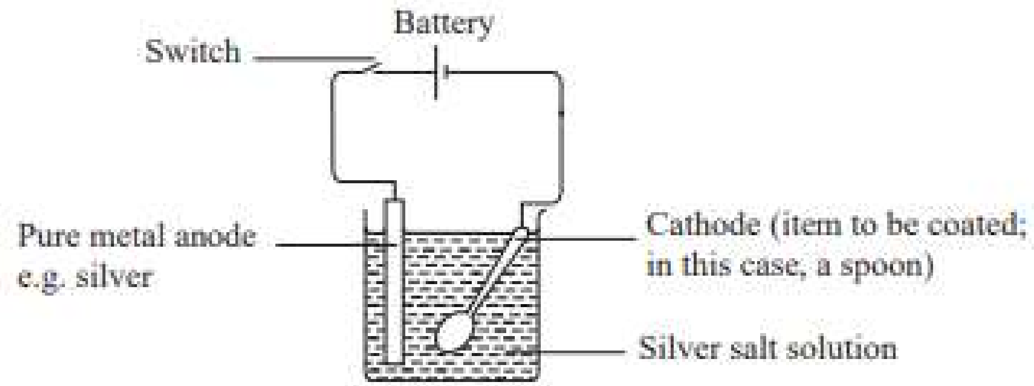
b) making an article look attractive e.g Gold plated watches, silver utensils.

Examples

(i) Most metal objects are made of iron or steel. To prevent rusting, they are nickel–chromium plated e.g. bicycle handlebars, car rims, among others.

(ii) Silver or gold plating is done e.g, on spoons, plates and jewellery items to improve their appearance.

(iii) 'Tin cans'—Cans made of steel are electroplated using a thin layer of tin to prevent them from rusting.



Conventional electrolytic cell that can be used for electroplating

iii. Sacrificial metal (cathodic protection)

- ☐ Iron or steel structures are protected from corrosion through sacrificial protection either by galvanising or cathodic protection.

iv. **Cathodic protection**

- ☐ Corrosion involves loss of electrons by an element to form ions. If it is a less reactive metal it is connected to a more reactive metal by a conductor when the conditions for causing corrosion are present, the more reactive metal ionises at the expenses of the less reactive. The more reactive metal is sacrificed and the method is sacrificial protection.

v. **Galvanising**

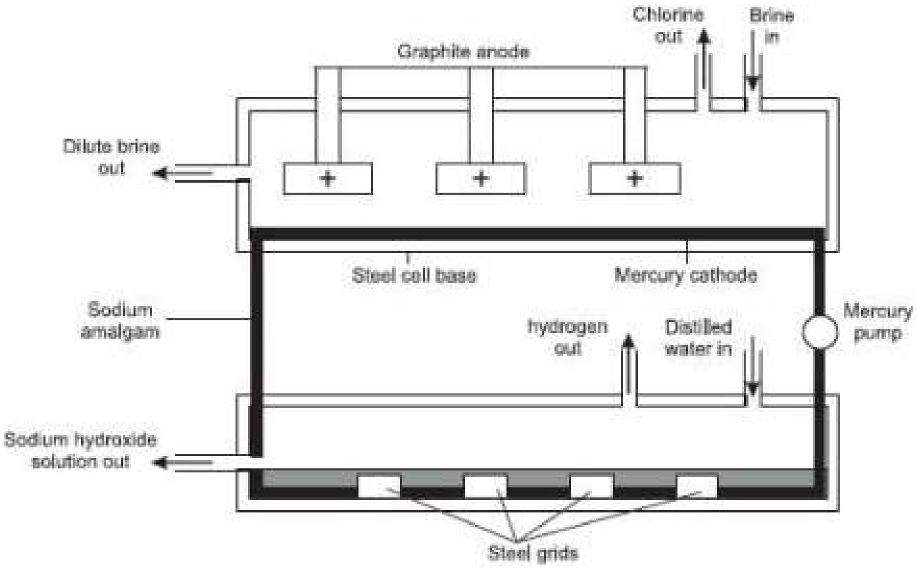
- ☐ When the galvanised surface is scratched and iron is exposed, zinc passes into solution as zinc ions rather than Fe^{2+} ions. This is possible because zinc is easily oxidised than iron.

vi. **Purification of Metals**

- ☐ Copper and other less reactive metals are purified by electrolysis. The impure metal is made the anode and pure metal the cathode. The electrolyte contains the cation of the metals being purified.

Manufacture of sodium hydroxide, chlorine and hydrogen

- The main raw material is concentrated sodium chloride (brine).
- Electrolysis of brine yields sodium hydroxide, chlorine and hydrogen.
- The cells that are used to eletrolyse concentrated sodium chloride are Mercury cell and diaphragm cell/ membrane cell. Below is a mercury cell.



- This mercury acts as the cathode from where sodium is discharged.

$$2Na^+\ (aq) + 2e- \rightarrow Na(l)$$

Note: when **graphite** electrodes are used, the potential between **Na**$^+$ and **H**$^+$ is too high to be overcome, hence **H**$^+$ ***is preferentially discharged***. **Mercury electrode** is used to overcome the potential between Na$^+$ and H$^+$ ***because it has very low resistance*** and thus discharge **Na**$^+$ at the cathode.

- Graphite is made the anode because it is an inert electrode hence resists corrosion by chlorine which is discharged and collected at the anode i.e**.**

$$2Cl^-\ (aq) \rightarrow Cl_2\ (g) + 2e^-$$

- Sodium formed at the cathode dissolves in mercury forming sodium-mercury amalgam (NaHg). The amalgam is reacted with water to form sodium hydroxide solution and hydrogen gas.

$$\underset{\text{sodium-mercury amalgam}}{2NaHg\ (l)} + 2H_2O\ (l) \longrightarrow 2NaOH(aq) + H_2\ (g) + 2Hg(l)$$

- The mercury produced is recycled. Chlorine, sodium hydroxide and hydrogen are packaged in readiness for use.

- The sodium hydroxide obtained this way is about fifty per cent pure. Pure sodium hydroxide is obtained by evaporating the water in the aqueous sodium hydroxide solution to get pellets or flakes.
- The process is expensive due to the high cost of mercury and the safety measures applied since **mercury is poisonous**.

Quantity of electricity

The coulomb

- The coulomb is **the practical unit used to measure the quantity of electricity or charge**. An electric current is produced in the opposite direction to the flow of electrons in a circuit.
- Its denoted by C.

Q(charge in Coulombs)= I (current in Amperes) X t(time in soconds)

$$Q=It$$

Solved example

Calculate the quantity of electricity passed when a current of 0.6 ampere flow for 50 minutes.

Solution

$$Q = It$$

$$= 0.6 \times (50 \times 60)$$

$$= 1800\ C$$

Faraday’s Law of electrolysis

It state that: ***The mass of a substance produced during electrolysis is directly proportional to the quantity of electricity passed***.

Solved example 1.

A student set up an experiment for the electrolysis of copper(II) sulphate solution. A current of 0.5A was passed through the circuit for 3860 seconds. A mass of 0.64 g of copper was deposited.

(i) Which electrode gained mass?

(ii) How many coulombs are needed to deposit one mole of copper? (R.A.M of Cu = 64)

Solution

(i) The cathode gained mass

(ii) Q=It

=0.5x 3860

=1930C

This means 1930C of electricity deposited 0.64 of copper

1 mole of copper has a mass of 64 g. From the relative atomic mass (RAM) given we then say:

If 1930 C can deposit 0.64g of copper

x C would deposit 64g of copper.

$$x = \frac{1930C \; x \; 64g}{0.64}$$

$$= 193{,}000C$$

Note: that 96,500 coulombs is called the Faraday's constant. It's symbol is F.

1F = 1 mole of electrons = 96500C.

Solved problem

During electrolysis of copper(II) sulphate solution, a current of 0.5A was passed for a period 3860s.The amount of metal deposited was 0.64g.

(i) Calculate the charge carried by the metal ion.

(ii) Write an ionic equation for the reaction. (R.A.M of Cu = 64, 1F = 96500C)

Solution

$$\text{Mass}=\frac{RAM\ x\ Q}{Charge\ \ x\ Faraday}$$

$$0.64=\frac{64\ X\ 0.5\ X\ 3860}{e\ X\ 96500}$$

$$e=\frac{64\ X\ 0.5\ X\ 3860}{0.64\ X\ 96500}$$

$$=2$$

Charge =+2

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

Solved problems

During electrolysis of an aqueous solution of a salt of metal M, a current of 2.0A was passed for 32 minutes 10 seconds. The mass of metal M deposited was 2.24g.

(i) On which electrode was the metal deposited?

(ii) Calculate the quantity of charge needed to deposit 1 mole.

(iii) Calculate the charge carried on the ion.

(iv) Write an ionic equation to show how the ions of M are discharged at the electrode. (R.A.M of metal M is 112)

solution

(i) At the negative electrode (cathode)

(ii) Q=2.0A X (32X60+10)

= 2.0 X 1930

=3860C

3860C deposited 2.24g

X C would deposit 112g

$$=\frac{3860C \ x \ 112g}{2.24g}$$

$=19300C$

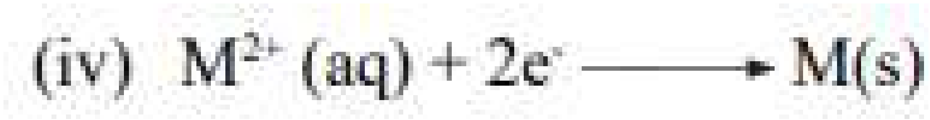
(iii) $1F=96500C$

$yF=193000C$

$$y=\frac{193000 \ C}{96500C}$$

$=2F$

Since 1F = 1 mole of electrons, 2F means 2 moles of electrons were required. Therefore, the charge on the ion is +2.



(iv) $M^{2+}(aq) + 2e^{-} \longrightarrow M(s)$