CHEMISTRY

E – LEARNING NOTE

SECOND TERM

CLASS: SS2

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SECOND TERM E-LEARNING NOTES

SUBJECT: CHEMISTRY **CLASS: SSS2**

SCHEME OF WORK

WEEKS **TOPICS/CONTENTS**

1. Revision/Chemical reaction basic concepts of reactions and products. (i) Rates of chemical reaction – meaning of chemical reaction, (ii) Rates of reaction (iii) Rate curve (iv) Collision theory (v) Factors affecting rates of chemical reaction.

2. Types of chemical reaction – exothermic and endothermic reactions (i) Relationship between endothermic and exothermic reaction (graphical representations only). (ii) List other types of chemical reactions e.g displacement, decomposition, combination, catalytic, reversible and thermal dissociation. (iii) First and second laws of thermodynamics.

3. Chemical Equilibrium- Introduction using simple equations (i) Le – Chaterlier's principle (ii) Factors affecting equilibrium of chemical reactions: Concentration, pressure and temperature.

4. Non –metals: (i) Hydrogen – configuration and oxidation number (ii) Isotopes of hydrogen (iii) unique position of hydrogen in the periodic table (iv) Preparation, properties and uses of hydrogen. (v) test of hydrogen.

5. Oxygen: General properties of oxygen family, group (VI) elements (ii) Electronic structure and bonding of oxygen (iii) Preparation, properties, uses and test of oxygen.

6. Halogen: (i) Electronic configuration of halogen (ii)Physical and chemical properties of halogens (iii) Laboratory and industrial preparation of chlorine (iv) Compounds of halogens and their uses (v) Reactions of chlorides and test for chloride.

7. Nitrogen: (i) General properties of Nitrogen family (group VII) elements. (ii) Laboratory and industrial preparation of Nitrogen. (iii) Properties and uses of Nitrogen (iv) Nitrogen cycle.

8. Compounds of Nitrogen: (i) Oxides of Nitrogen (ii) Ammonia – Preparation, properties, test and uses of ammonia.

9. Sulphur: (i) General/Properties of sulphur family (Group VIII) elements (ii) Electronic structure of sulphur (iii) Allotropes of sulphur (iv) Uses of sulphur.

10. Compounds sulphur: (i) Oxidation number of sulphur in its major compound (ii) Tetraoxosulphate (vi) acid, H_2SO_4 – the contact process (industrial preparation of H_2SO_4) (iii) uses of H_2SO_4 (iv) Excursion of a Tyre manufacturing industry.

11. Revision

12. Examination.

13. Examination.

REFERENCE TEXTS:

1 .Comprehensive Certificate Chemistry for Senior Secondary Schools by G N C Ohia et al
2. New School Chemistry for Senior Secondary Schools by Osei Yaw Ababio
3. Chemistry for Senior Secondary Schools 1 by Magbagbeola O, et al; Melrose Books and Publishers
4. Revised edition understanding chemistry for schools and colleges by Godwin O. Ojokuku.

WEEK: ONE

TOPIC: CHEMICAL REACTIONS (RATE OF CHEMICAL REACTION)

When substances react together, they form products which may be solids, liquids or gases. Chemical reactions are usually represented by an equation. The species at the left are called the reactants while those at the right hand are called the products.

Rate of chemical reaction

The rates of chemical reaction vary greatly depending on the type of chemical reaction. Some reactions are fast, some are slow and others occur at irregular speeds. **The rate of a chemical reaction is the amount (in moles) of the reactant used up or products formed at a given time.**

$$\text{Rate of reaction} = \frac{\text{change in concentration of reactant or product}}{\text{Time taken}}$$

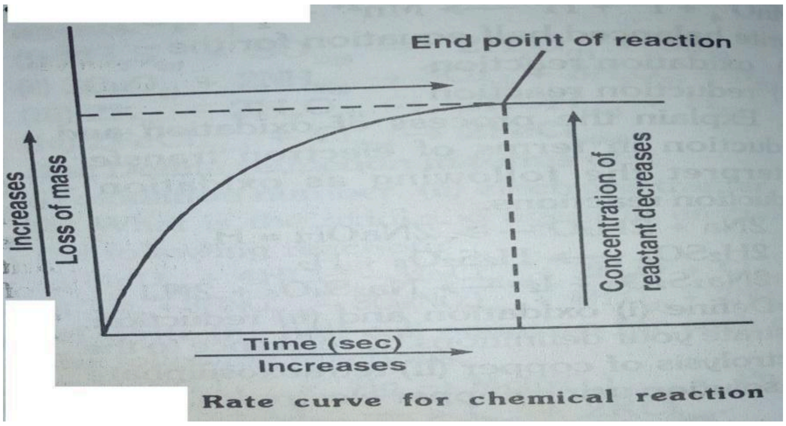
The rate of chemical reaction can also be defined as the number of moles of reactant converted or products formed per unit time.

To determine the rate of a chemical reaction, we measure the rate at which the mass or the concentration of a reactant is decreasing or a product is increasing. In case this cannot be done, we measure a property which changes proportionately with the mass of a reactant or product. Generally, we determine the rate of chemical reaction by measuring the following:

1. Decrease in the mass of the reaction system e.g. due to the escape of a gaseous product.
2. Volume of gaseous products
3. Amount of precipitate formed
4. Time taken to arrive at an easily seen stage
5. Changes in intensity of colour
6. Changes in pH
7. Changes in total gas pressure.

Rate curve: the graph which shows the rate of reaction is known as rate curve. The curve passes through the origin because there is no loss in mass right at the start of the reaction. The gradient of the curve is steep at first because the rate of reaction is fast. The gradient however becomes less steep as the rate of the reaction slows down. Finally, the curve becomes horizontal indicating the end point of the reaction. From the rate curve we can determine (a) the average rate of the reaction and (b) the rate at a particular instant during the reaction. A large gradient indicates a faster reaction rate while a small gradient indicates a slower one.

Figure: Rate curve for chemical reaction



Collision theory

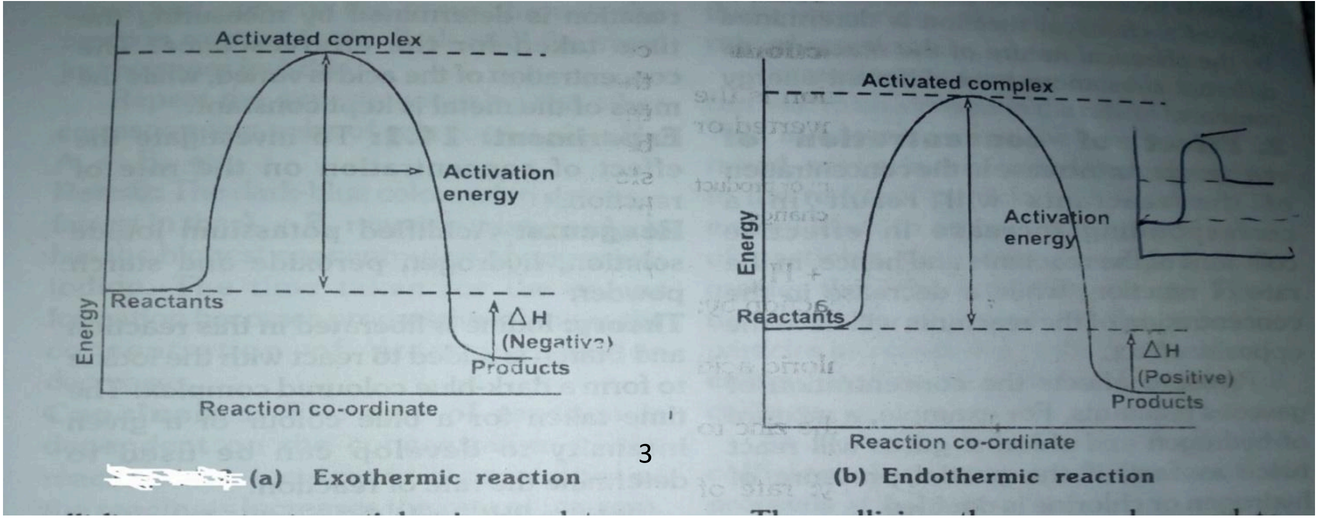
The collision theory states that for a chemical reaction to occur, the reacting particles must collide with one another. Meanwhile, not every collision between reacting particles is effective. Only small fraction of the collision results in chemical reaction. For chemical reaction to occur therefore, the reacting particles must possess a certain minimum amount of energy called

Activation energy. The activation energy is equal to the energy barrier that must be overcome before chemical reaction can take place. **Activation energy can be defined as the minimum amount of energy possessed by the reactant particles for a chemical reaction to occur.** Every reaction has its own activation energy. If it is low, the reaction will occur spontaneously at room temperature but where the activation energy is high, the reaction will not occur until more energy is supplied usually in form of heat.

Activated complex: this is the intermediate, high energy particles formed by reactant particles which have attained the activation energy. Because of their high energy content, they are unstable and readily decompose to give the products or the reactants of the reaction.

Reaction profile: this is the graphical representation of the energy change during a chemical reaction.

Energy profile for (a) exothermic and (b) endothermic reactions



Factors affecting rate of a chemical reaction

The rate of chemical reactions depend on the following factors

1. Nature of reactants
2. Concentration and pressure (for gases) of reactants
3. Temperature of the reaction mixture
4. Surface area of the reactants
5. Presence of light
6. Presence of catalyst

Nature of reactants: every substance possesses its own unique chemical nature. The rate of a chemical reaction is determined by the nature of the reactants because different substances have different energy contents. For example, when iron is placed in dilute hydrochloric acid, there is a slow evolution of hydrogen, if a piece of zinc is used, the reaction is rapid but with a piece of gold there is no evidence of reaction.

Concentration of reactants: an increase in the concentration of the reactants will result in a corresponding increase in effective collisions of the reactants and hence, in the rate of chemical reaction, while a decrease in the concentration of the reactants will have the opposite effect.

Pressure affects the concentration of gaseous reactants, hence the rate of the chemical reaction.

For example, a mixture of hydrogen and chlorine gases will react twice as fast if the partial pressure of hydrogen or chlorine is doubled. The concentration of solid and liquid reactants is unaffected by change in pressure.

Temperature: the rate of almost all chemical reactions increases with increased temperature. It is found that a temperature rise of 10^0C doubles the rate of reaction. When the temperature of a system is increased, heat energy is supplied to the reacting particles. The increase in energy results in an increase in the number of particles with activation energy or more. Thus, collision becomes more frequent and the reaction proceeds faster.

Surface area of reactants: when the surface area of a solid is increased by breaking it to smaller pieces or by grinding it to powder, there will be greater contact between the reacting species and hence, increased rate of reaction. The greater the surface area of the reactants the faster the rate of the reaction. For example, the reaction between dilute hydrochloric acid and powdered marble is faster than that of marble chip with dilute hydrochloric acid. The efficiency of solid catalyst is usually increased by increasing the surface area.

Light: some reactions known as **photochemical reactions** can be influence by the presence of light. For example, the reaction between hydrogen and chlorine takes place explosively in the presence of bright light; moderately in day light but almost negligible in the absence of light.

Other examples of photochemical reactions are:

i. Conversion of silver halide to grey metallic silver
ii. Photosynthesis in plants
iii. Reaction between methane and chlorine
iv. Decomposition of hydrogen peroxide

The reactant particles in these reactions absorb light energy and react rapidly in a series of chain reactions.

Catalyst: A catalyst is a substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction. A catalyst provides an alternative route for the reaction. Thus, a positive catalyst provides an alternative route with lower activation energy while negative catalyst provides alternative route with higher activation energy.

Characteristics of catalysts

1. It alters the rate of a chemical reaction
2. Its chemical nature remains unchanged after the reaction though its physical appearance may change
3. A catalyst is specific in action
4. It cannot start a reaction
5. It has no influence on the type of product formed
6. It has no effect on the equilibrium position of a reversible reaction
7. A catalyst will affect the rate of a reaction even though it is present in a very small amount.
8. The effect of a solid catalyst is improved by increasing the surface area.

WEEK 2

Types Of Reaction

Chemical reactions can generally be grouped as follows:

Combination reaction: this is a reaction in which two or more substances combine to form a single compound. E.g

$Fe_{(s)} + S_{(s)} \longrightarrow FeS_{(s)}$

$PbO_{2(s)} + SO_{2(g)} \longrightarrow PbSO_{4(s)}$

Polymerization of ethyne is also an example of combination reaction.

Decomposition reaction: this occurs when a single compound splits to two or more substances. When heat is applied to bring about the splitting, the reaction is called thermal decomposition. E.g.

$2Pb(NO_3)_{2(s)} \xrightarrow{heat} 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

Displacement reaction: this is a reaction in which one element or radical replaces another element or radical in a compound. More electropositive metals displace the less electropositive metals from their salts while the more electronegative non-metals displace the less electronegative ones from their salts. E.g.

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

$Cl_{2(g)} + 2KBr_{(aq)} \longrightarrow 2KCl_{(aq)} + Br_{2(l)}$

Double decomposition: this is a reaction in which the reactants decompose to form new substances by exchange of radicals. The two reactants must be soluble while only one of the products is soluble. The reaction is used to prepare an insoluble or volatile, since it can be separated from the other substance in the reaction system. E.g.

$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow \underset{\text{Precipitate}}{AgCl_{(s)}} + NaNO_{3(aq)}$

$KNO_{3(aq)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{Volatile}}{HNO_{3(g)}} + KHSO_{4(aq)}$

Catalytic reaction: this is any type of chemical reaction that uses catalyst. A **catalyst** is a substance that alters the rate of chemical reactions.

Reversible reaction: this is a chemical reaction that takes place both in forward and backward direction. The condition for the forward reaction may be (or may not be) the same as the condition for the backward reaction. E.g.

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

Thermal dissociation: in this reaction, each molecule of a substance dissociates into two or more simpler molecules or atoms on the application of heat. Unlike thermal decomposition, thermal dissociation is a reversible process e.g. $NH_4Cl_{(l)} \underset{cold}{\overset{heat}{\rightleftharpoons}} NH_{3(g)} + HCl_{(g)}$

ENERGY CHANGE IN A REACTION

Energy is defined as the ability to do work. It exists in various forms which are inter-convertible. Whenever a chemical reaction occurs, an energy change takes place because the reactants and the products possess different amount of chemical energy. The amount of chemical energy present in a reaction cannot be measured but the energy change accompanying chemical reactions can be measured in forms of:

- Heat e.g. when a strong acid and a strong base are mixed
- Light and heat e.g. when magnesium burns in air
- Sound and heat e.g. when a mixture of hydrogen and oxygen is ignited

Of the three only the heat energy can be measured easily.

Heat content and heat of reaction

Every substance possesses a characteristic internal energy which is due to its structure and physical state. The energy is known as heat content or enthalpy. It is represented by H. The energy change that accompanies a chemical reaction is known as the heat of reaction. It is denoted by ΔH.

$\Delta H = H_{\text{product}} - H_{\text{reactant}}$

EXOTHERMIC AND ENDOTHERMIC REACTION

During chemical reaction, heat can either be evolved or absorbed depending on the relative heat contents of the reactants and the product.

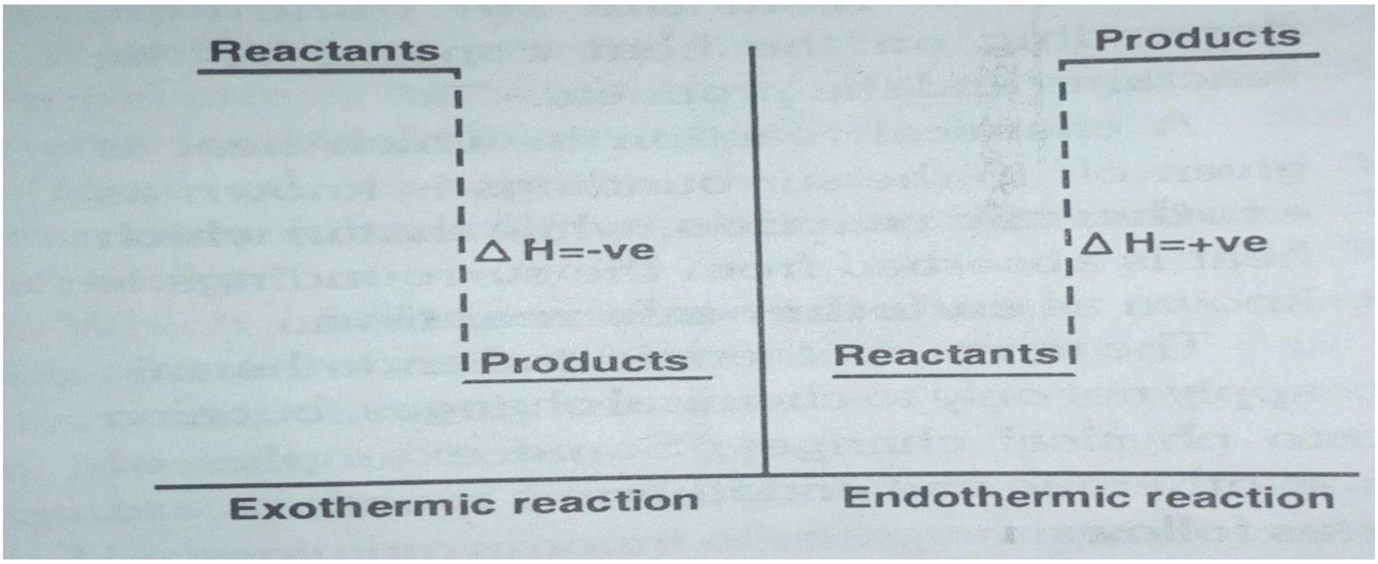
An exothermic reaction is the one during which heat is liberated to the surrounding. The total heat content of the product is less than that of the reactants.

An endothermic reaction is the one during which heat is absorbed from the surrounding. The total heat content of the product is more than that of the reactants.

In a chemical reaction, the reactant particles collide with one another. The collision results in bond-breaking and bond formation. The atoms and/or ions of the reactant particles are first broken and then regrouped to form the products. The bond-breaking process requires energy (endothermic) while the bond forming process releases energy (exothermic). The overall energy change in a chemical reaction results from the combination of the bond-breaking and bond forming energy.

For exothermic reaction: bond–breaking energy < bond-forming energy

For endothermic reaction: bond-breaking > energy bond-forming energy



Measurement of heat of reaction

If the heat of reaction is large we can detect it by feeling the temperature of the reacting vessel before and after the reaction. An exothermic reaction makes the vessel to feel warm or hot while an endothermic reaction makes the vessel to feel cool. However, for an accurate determination of ΔH, the use of calorimeter (glass calorimeter is mostly used) is adopted. The heat of reaction ΔH, depends on the following factors:

- Mass of the reactants
- Temperature and pressure of the reacting system
- Physical states of the substances involved in the reaction

The standard conditions for determining ΔH are:

- Temperature of 298K (25^{0}C)
- Pressure of $1.01 \times 10^5 Nm^{-2}$ or 1 atm or 760mmHg.
- Concentration of 1 mol/dm^3.

The ΔH obtained under these standard conditions is denoted as $\Delta H^\ominus$.

HEAT OF NEUTRALIZATION

The standard heat of neutralization $\Delta H_n^\ominus$ is the amount of heat evolved when one mole of hydrogen ion H^+, from an acid reacts with one mole of hydroxide ion OH^- from an alkali to form one mole of water under standard condition. For strong acids and strong alkalis, $\Delta H_n^\ominus$ = -57.4KJ/mol but the value is less for weak acid or weak alkalis because of the partial dissociation of the weak acids or bases/alkalis.

HEAT OF COMBUSTION

The standard heat of combustion of a substance, $\Delta H_c^\ominus$ is the heat evolved when one mole of a substance burns completely in oxygen under standard condition. It is determined by the use of bomb calorimeter.

HEAT OF SOLUTION

The standard heat of solution $\Delta H_s^\ominus$ is the amount of heat absorbed or evolved when one mole of a substance is dissolved in so much water that further dilution results in no detectable heat change. Whenever an ionic substance dissolves in water, two things happen:

- The water molecules split up the ions in the crystals into free ions. This process needs

energy known as lattice energy.
- The free ions are hydrated by water molecules. This process evolves energy known as hydration energy.

The resultant heat change of the two steps is known as heat of solution. Generally;
If lattice energy < hydration energy, the dissolution is exothermic
If lattice energy > hydration energy, the dissolution is endothermic

Bond energy: This is the average amount of energy associated with making or breaking of one mole of a particular bond in its gaseous state. It is higher in stable compounds than in reactive compounds.

The lattice energy of an ionic crystal is the heat of formation of one mole of ionic compound from widely separated gaseous ions under standard conditions.

The enthalpy change of atomization of an element is the enthalpy change when one mole of gaseous atom is formed from the element. E.g

$\frac{1}{2} H_{2(g)} \longrightarrow H_{(g)}$; $\Delta H_a = +218KJ$

Assignment

1. Define and give examples of:
- Surrounding
- Open and close system

2. Distinguish between catalyst inhibitor and catalyst promoter

Tutorial questions

1. Define rate of a chemical reaction
2. What are the factors that affect the rate of a chemical reaction?
3. State five properties of a catalyst
4. State the collision theory
5. List two factors that affect collision
6. Consider the following reaction equation:

$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

List three ways by which rate of the reaction can be increased

7. Define heat of formation

WEEK THREE

TOPIC: ENERGY CHANGE IN A REACTION

Spontaneous reaction

A spontaneous reaction is the one which has the potential to occur on its own without the assistance of any external agent. An example is the reaction of glucose with oxygen in the living tissues. By itself, a spontaneous reaction is irreversible except work is done on the system. The two factors which can affect the spontaneity of a chemical reaction are **entropy** and the **free energy** of the system undergoing the change.

ENTROPY: It is the measure of the degree of disorderliness or randomness of a system. The standard entropy change is a state function i.e. $\Delta S^\theta = S^\theta_{product} - S^\theta_{reactant}$

The S.I. unit of entropy is $JK^{-1}mol^{-1}$

The entropy increases from solid to gaseous state and vice versa. When entropy increases, ΔS^θ tends to be positive but when it decreases, ΔS^θ tends to be negative. ***Generally, an increase in temperature of a system increases the entropy of the system***. A perfectly ordered system at 0K has an entropy of zero.

ENTROPY CHANGE IN REVERSIBLE PROCESSES: the **second law of thermodynamics states that a spontaneous process occurs only if there is an increase in entropy of the system and its surrounding.** At constant temperature and pressure, the change in entropy of a reversible reaction is given as

$\Delta S = \Delta H/T$;

Where; ΔH = enthalpy change
T = absolute temperature

ΔS = entropy change

GIBB'S FREE ENERGY: The free energy of a chemical system is the energy which is available for doing work. It is the driving force that brings about a chemical change. The standard free energy change is a state function and is given as; $\Delta G = G_{\theta\ product} - G_{\theta\ reactant}$.

Free energy (G), entropy (S) and enthalpy (H) are related by the following equation;

$G = H - TS$

Hence, $\Delta G_\theta = \Delta H_\theta - T\Delta S_\theta$

ΔG_θ helps us to predict whether a chemical reaction will occur or not provided that the entropy and enthalpy change involved in the reaction are known. If;

ΔG_θ is negative, the reaction will occur (spontaneous)

ΔG_θ is positive, the reaction will not occur (non-spontaneous)

ΔG_θ is zero, the reaction is at equilibrium.

Note: An increase in the temperature of a system leads to an increase in ΔS_θ and a decrease in ΔG_θ. ***For a reaction to be thermodynamically feasible (spontaneous), ΔS_θ must be positive and ΔG_θ must be negative.***

CALCULATIONS

1. The heat of solution of NH_4NO_3 solution is 26.3KJ/mol. Calculate the quantity of heat absorbed when (a) 2 moles (b) 5g of solid NH_4NO_3 solid dissolves in a large volume of water.

2. Calculate the entropy change for the reaction;

$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$

Given that: $S_\theta H_2 = 131JK_{-1}mol_{-1}$, $S_\theta Cl_2 = 223JK_{-1}mol_{-1}$, $S_\theta HCl = 187JK_{-1}mol_{-1}$

3. Calculate the standard entropy change for the conversion of one mole of liquid water to vapour at 100_0C, given that the heat of vapourization of water is $2261Jg_{-1}$.

4. Calculate (i) the ΔH_θ (ii) ΔS_θ (iii) ΔG_θ at 30_0C and 500_0C for the reaction.

$Fe_2O_{3(s)} + 3H_{2(g)}\ 2Fe_{(s)} + 3H_2O_{(g)}$

Given:

$S_\theta Fe_2O_{3(s)} = 90JK_{-1}$; $H_\theta = -822KJmol_{-1}$

$S_\theta H_{2(g)} = 131JK-1$; $H_\theta = 0.0KJmol_{-1}$

$S_\theta Fe_{(s)} = 27JK-1$; $H_\theta = 0.0KJmol_{-1}$

$S_\theta H_2O_{(g)} = 189JK-1$; $H_\theta = -242kJmol_{-1}$

Solution

(1a).

$NH_4NO_{3(s)} + H_2O_{(l)} \longrightarrow NH_4NO_{3(aq)}$; $\Delta H_\theta = 26.3KJmol_{-1}$

From the equation;

1 mole of HN_4NO_3 produces $26.3kJmol_{-1}$

:- 2 moles of HNO_4NO_3 will produce 26.3 x 2 = $52.6kJmol_{-1}$ of heat

(1b). Molar mass of NH_4NO_3 = 80g/mol

80g produces $26.3kJmol_{-1}$

:- 5g will produce $\frac{5 \times 26.3}{80}$ = 1.64kJ/mol

(2) $H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$

$\Delta S_\theta = S_{\theta\ product} - S_{\theta\ reactant}$

$= [2S_\theta HCl - (S_\theta H_2 + S_\theta Cl_2)]$

$= (2 \times 187) - (131 + 223)$

$= 374 - 354$

$\Delta S_\theta = + 20JK_{-1}mol_{-1}$

There is an increase in randomness and disorderliness of the system since the entropy change is +ve.

(3). Mass of 1 mole of water = 18g

Heat of vapourization of H_2O = $2261Jg_{-1}$

:- Heat of vapourization of 1 mole of H_2O = 2261 x 18 $Jmol_{-1}$

= 40698 $Jmol_{-1}$

$\Delta S = T\Delta H$
$T = 100_0C = 373K$
$\Delta S = 40698$
373
$\Delta S = 109.11JK_{-1}mol_{-1}$

(4i). $\Delta H_\theta = \Delta H_\theta p - \Delta H_\theta r$
$= (2 \times H_\theta Fe + 3H_\theta H_2O) - (H_\theta Fe_2O_3 + 3H_\theta H_2)$
$= [(2 \times 0) + (3 \times -242)] - [(-822) + (3 \times 0)]$
$= 0 + (-726) - (-822) + 0$
$= - 726 + 822$
$\Delta H_\theta = 96KJmol_{-1}$

(4ii). $\Delta S_\theta = \Delta S_{\theta product} - \Delta S_{\theta reactant}$
$= [(2S_\theta Fe + 3S_\theta H_2O)] - [(S_\theta Fe_2O_3 + S_\theta H_2)]$
$= [(2 \times 27) + (3 \times 189)] - [90 + (3 \times 131)]$
$= 54 + 567 - [90 + 393]$
$= 621 - 483$
$\Delta S_\theta = + 138\ JK_{-1}mol_{-1}$
$= 0.138\ KJk_{-1}mol_{-1}$

(4iii). At 30_0C; $T = 30 + 273 = 303K$
$\Delta G_\theta = \Delta H_\theta - T\Delta S_\theta$
$= 96 - (303 \times 0.138)$
$= 96 - 41.81$
$\Delta G_\theta = +54.29\ kJmol_{-1}$
The reaction is thermodynamically not spontaneous because ΔG_θ is positive.
At 500_0C; $T = 273 + 500 = 773K$
$\Delta G_\theta = \Delta H_\theta - T\Delta S_\theta$
$= 96 - (773 \times 0.138)$
$= 96 - 106.67$
$= -10.67\ kJmol_{-1}$
The reaction is thermodynamically feasible i.e. spontaneous.

CHEMICAL EQUILIBRIUM

Chemical equilibrium is a state where there is no observable change in the properties of a system with respect to time. An equilibrium system may be static or dynamic. A static equilibrium is the one in which the system is stationary while a dynamic equilibrium is the one in which forward and backward reactions occur at the same rate, thereby producing no net change in the concentration of the reactants or products. Examples of a reaction in dynamic equilibrium are:

$3Fe_{(s)} + 4H_2O_{(g)} \;\overline{\qquad}\; Fe_3O_{4(s)} + 4H_{2(g)}$
$NH_4Cl_{(s)} \overset{heat}{\underset{cool}{\overline{\qquad}}} NH_{3(g)} + HCl_{(g)}$

LE-CHATELIER'S PRINCIPLE

The principle states that if a chemical system is in equilibrium and one of the factors involved in the equilibrium is altered, the equilibrium will shift so as to neutralize the effect of the change.

FACTORS AFFECTING EQUILIBRIUM

1. TEMPERATURE: An exothermic reaction is favoured by lowering the temperature while an endothermic reaction is favoured by raising the temperature of the system. The equilibrium position shifts to the side that if favoured. For example; $2H_{2(g)} + O_{2(g)} \;\overline{\qquad}\; 2H_2O_{(g)}$; $\Delta H = -$ ve
Lowering the temperature favours the production of steam (forward reaction), the equilibrium position will therefore shift to the right. On the other hand, raising the temperature favours the production of hydrogen and oxygen (backward reaction), hence the equilibrium position will shift to the left.

2. PRESSURE: The side of the system with higher number of moles or volumes of gas is favoured by lowering the pressure while the side with lesser number of moles or volume of gas is favoured by raising the pressure of the system e.g.
$3H_{2(g)} + N_{2(g)} \;\overline{\qquad}\; 2HN_{3(g)}$

$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$

The forward reactions in the above reactions are favoured by increasing the pressure of the system while the backward reactions are favoured by lowering the pressure.

$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$

Pressure has no effect on the reaction above because the volume of gases at both side of the reaction is the same.

3. CONCENTRATION: If the concentration of the reactant is increased, more products will be formed i.e. the forward reaction will be favoured and equilibrium position will shift to the right. The same thing happens also if part of the products formed is removed. However, if part of the reactant is removed or the concentration of the products is increased, the backward reaction will be favoured.

EQUILIBRIUM CONSTANT

Equilibrium constant is the measure of the ratio of the equilibrium concentration of the products of a reaction to the equilibrium concentration of the reactants with each concentration raised to the power corresponding to the coefficient in the balance equation of the reaction. For example

$aA + bB \longrightarrow cC + dD$

$K_c = [C]_c[D]_d$ or $K_p = PC_cPD_d$

$[A]_a[B]_b$ PA_aPB_b

[ ] means concentration

C means concentration in mol/dm_3

P means partial pressure (for gases only)

If Kc is positive, it means that the forward reaction is favoured at equilibrium but if it is negative, then the backward reaction is favoured. Generally, under the influence of temperature; whenever the equilibrium position shifts to the left (i.e. favouring the backward reaction), Kc decreases. But when the equilibrium position shifts to the right (i.e. favouring forward reaction), Kc increases. The Kc value for any reaction is constant only if the temperature remains constant.

CALCULATION

1. Calculate the equilibrium constant of the following reaction and the equilibrium constant of its backward reaction at 45_0C if the pressure of the hydrogen, iodine and hydrogen iodide gases are 0.065, 0.45 and 0.245 respectively at the equilibrium position. $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

Solution

Kc for forward reaction

$K_p = PHI_2\ (0.245)^2 = 2.05$

$PH_2PI_2\ (0.065)(0.45)$

Kp for the backward reaction

Kp = 1/Kp i.e inverse of the Kp for forward reaction

Kp = 1/2.05 = 0.49

EQUILIBRIUM CONSTANT, FREE ENERGY AND ELECTRODE POTENTIAL

Reactions with ΔG less than zero occur spontaneously. Also reaction with large Kc value goes almost to completion while those with small Kc value do not occur to reasonable extent. Hence, ΔG and Kc relationship at constant temperature is represented in the Van't Hoff Isotherm equation

$\Delta G_\theta = -RT\ln K$

Where $\ln K = -2.303\log_{10}K$

$\Delta G_\theta = -2.303RT\log_{10}K$

ΔG_θ = standard free energy

K = equilibrium constant

R = molar gas constant

T = temperature of the system in Kelvin

For an electrochemical cell

$E_\theta = RT\ln K$

nF

where; E_θ = standard electrode potential

n = number of moles of electron

F = Faraday's constant

By substitution, $\Delta G_\theta = -nFE_\theta$

INDUSTRIAL APPLICATION OF CHEMICAL EQUILIBRIUIM

1. THE HABER PROCESS

$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)}$; $\Delta H = -46.1 kJmol^{-1}$

Conditions favouring the yield of NH_3 are:

- Low temperature of about 450^{0}C
- A high pressure of about 200atm
- Catalyst – finely divided iron; it speeds up the rate of higher yield of ammonia at about 250^{0}C.

2. THE CONTACT PROCESS (Production of H_2SO_4)

The first step in the process is

$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$ $\Delta H = -395.7 kJmol^{-1}$

The conditions required for the high yield of SO_3 are:

- Low temperature of about 450 – 500^{0}C
- High pressure should be used but in practice, atmospheric pressure of 1 atm gives a high yield of SO_3.

An increase in the concentration of one of the reactants favours the production of SO_3. The SO_3 is removed from the equilibrium mixture by dissolving it in fairly conc. H_2SO_4 to form oleum which is then diluted to form H_2SO_4 of the required concentration.

- Catalyst – vanadium (V) oxide, V_2O_5.

Assignment

1. Calculate the ΔH of a chemical system when the entropy is 218.2 $JK^{-1}mol^{-1}$ and the temperature is 100^{0}C.

Tutorial questions

1. Consider the following reversible reaction which occurred at the temperature of 298K:

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$; $\Delta H = -92.37kJ$

List two factors that would increase the yield of $NH_{3(g)}$

2. Calculate the standard free energy of a reaction at 250C, when the enthalpy and the entropy of reaction are -190Jmol-1 and 20Jmol-1K-1 respectively.
3. State whether the reaction in 2 above is feasible or not. Give reason for your answer.
4. State Le Chatellier's Principle
5. Consider the equilibrium reaction represented by the equation below;

$A_{2(g)} + 3B_{2(g)} \longrightarrow 2AB_{3(g)}$; H= +xkJmol-1

Explain briefly the effects of the following changes on the equilibrium composition

- Increase in concentration of B
- Decrease in pressure of the system
- Addition of catalyst

6. The lattice energies of three sodium halides are as follows:

Compound	NaF	NaBr	NaI
Lattice Energy (kJmol-1)	890	719	670

Explain briefly the trend

WEEK 4

TOPIC: HYDROGEN

Hydrogen is the lightest element making up about 1% of the earth crust. It is widely distributed in combination with other elements in the form of water, acids, organic substances and petroleum products. It is found uncombined in very small quantity in the atmosphere.

Hydrogen is the first element in the Periodic Table. Its atom consists of one proton and one electron. It can be placed both in Group I and Group VII of the Periodic Table. In Group I because it has one electron in its valence shell and in group VII because it is only one electron short of the noble gas structure of helium. The electronic configuration is $1S^1$.

Laboratory preparation of hydrogen

Hydrogen can be prepared in the laboratory by 3 different methods

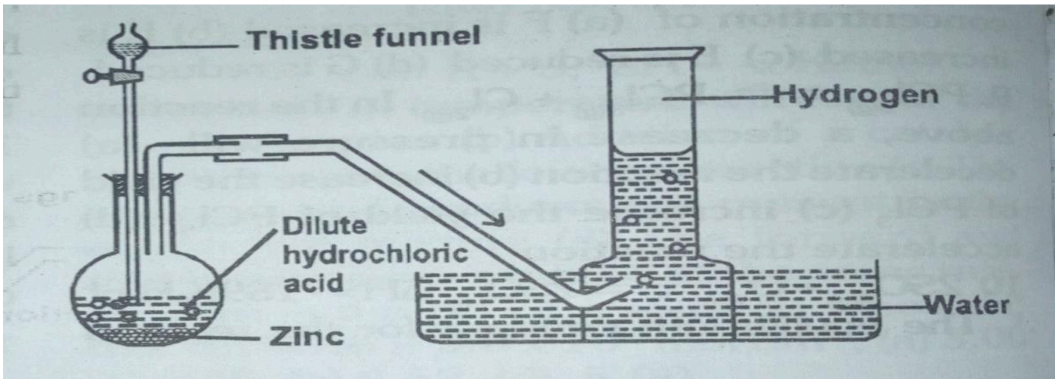
A) Action of dilute acid on zinc: dilute HCl or H_2SO_4 reacts with granulated zinc to liberate hydrogen gas.

$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$

$Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_{2(g)}$

The hydrogen gas is given off in a gas jar over water. If it is required dry, it is passed through fused calcium chloride or conc. H_2SO_4 and collected by downward displacement of air (or by upward delivery) since it is lighter than air.

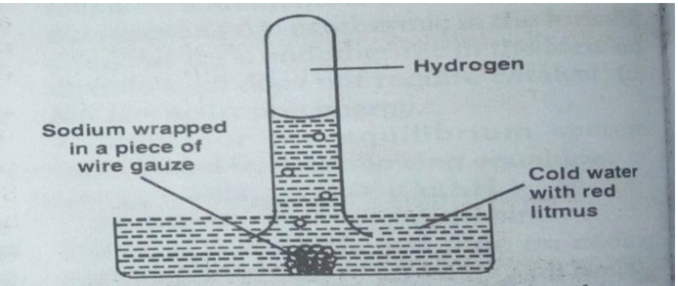
Note: dilute HNO_3 is not used for this reaction because it is a strong oxidizing agent. It will oxidize the hydrogen formed to water. It will only produce hydrogen gas with magnesium.



Preparing hydrogen by the action of a dilute acid on Zinc

(B) Action of cold water on active metal: sodium and potassium metals react vigorously with cold water to liberate hydrogen gas. Calcium undergoes the same reaction but at a slower rate.

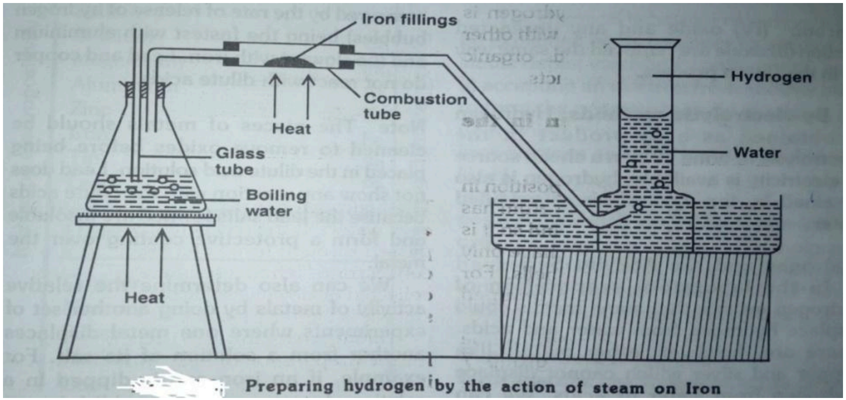
$2Na_{(s)} + 2H_2O_{(l)}\ 2NaOH_{(aq)} + H_{2(g)}$



Preparing hydrogen by the action of cold water on sodium

(C) Action of steam on iron: iron at red heat reacts with steam to produce triiron-tetraoxide (a black residue) and hydrogen gas.

$3Fe_{(s)} + 4H_2O_{(g)}\ Fe_3O_{4(s)} + 4H_{2(g)}$



Preparing hydrogen by the action of steam on Iron

INDUSTRIAL PREPARATION OF HYDROGEN

(1) FROM WATER GAS(BOSCH PROCESS): water gas is produced when steam is passed over red hot coke at about 1100_0C. When excess steam is mixed with the water gas and the mixture passed over a suitable catalyst (iron (III) oxide or chromium (III) oxide at 450_0C, the carbon (II) oxide in the water gas is converted to carbon (IV) oxide and more hydrogen is produced.

$C(s) + H_2O_{(l)} \longrightarrow CO + H_2$ endothermic reaction

$CO + H_2 + H_2O_{(g)} \longrightarrow CO_{2(g)}\ 2H_{2(g)}$ exothermic reaction

The carbon(IV) oxide is separated from the hydrogen by dissolving it in water at 30 atm pressure, or by passing the mixture through an alkali solution which absorbs carbon(IV) oxide leaving hydrogen.

$H_2O_{(l)} + CO_{2(g)} \longrightarrow H_2CO_{3(aq)}$

$NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$

Any remaining trace of carbon(II) oxide is absorbed under pressure by ammoniacal solution of copper (I) ethanoate.

(2) FROM HYDROCARBONS (METHANE): when methane is treated with steam at 800_0C and 30 atm. in the presence of nickel catalyst, a mixture of carbon(II) oxide and hydrogen gas is produced. This is known as synthesis gas

$CH_{4(g)} + H_2O_{(g)} \xrightarrow{Ni} CO + 3H_{2(g)}$

Synthesis gas;

(note the difference between water gas and synthesis gas)

The synthesis gas is mixed with more steam and passed over iron (III) oxide catalyst at 450^0C. carbon (II) oxide is converted to carbon(IV) oxide with further yielding of hydrogen. Carbon (IV) oxide and any unreacted carbon (II) oxide are removed the same way as in Bosch process.

(3) BY ELECTROLYTIC METHOD: hydrogen is obtained as a by-product in the electrolysis of brine. When a cheap source of electricity is available, hydrogen is also obtained from the electrolysis of acidified water.

PHYSICAL PROPERTIES OF HYDROGEN

1. Pure hydrogen is a colourless, odourless and tasteless gas.
2. It is neutral to litmus paper
3. It is the lighted substance known; about 14.4 times less dense than air
4. It has a very low boiling point of about -253^0C.
5. It is relatively insoluble in water.
6. It burns with a pale blue flame but does not support combustion.
7. It is not poisonous

Chemical properties

The chemical properties of hydrogen can be explained on the basis of its ability to:

- Gain an electron and form a negative hydride ion, H^-.
- Forming a covalent bond by sharing its lone electron as it is in hydrogen molecule, H – H.
- Donating its lone electron to form positive hydrogen ion, H^+ which enters into dative bonding with a molecule having lone pairs of electrons, e.g. formation of ammonium ion, NH_4^+.

The chemical properties of hydrogen are as follows:

1. Reaction with metals: hydrogen combines directly with the more reactive metals to form ionic hydrides. $2Na_{(s)} + H_{2(g)} \rightarrow 2NaH_{(s)}$
2. Reaction with oxygen: pure hydrogen burns with a pale blue flame in oxygen to form steam.
$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$
3. With halogens: hydrogen combines directly with halogens to form halides;
$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
4. Reaction with nitrogen: hydrogen combines directly with nitrogen to produce ammonia.
$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$
5. Reducing action: hydrogen is a strong reducing agent. it reduces the heated oxides of copper, lead, iron and zinc to the corresponding metals; $CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(l)}$

Uses of hydrogen

- Hydrogen is used in the synthesis of ammonia
- It is used in the hardening of vegetable and animal oil for the manufacturing of margarine, soap and candle.
- Liquid hydrogen is used as rocket fuel
- It is used in oxy-hydrogen flame to produce high temperature of over 2000^0C that is capable of melting metals.
- It is used in atomic hydrogen flame
- It is used for filling balloons
- It is a constituent of many gaseous fuels such as water gas and coal gas.
- It is used for the extraction of tungsten from its ore.

Test for hydrogen

When a lighted splinter is inserted into a test-tube containing hydrogen, it burns with a pop sound.

Isotopes of hydrogen

Hydrogen has three isotopes namely

- Protium or hydrogen – ^1_1H
- Deuterium or heavy hydrogen – ^2_1H
- Tritium – ^3_1H

The most abundant is protium, although it is less reactive. Tritium is radioactive with a half life of about 12 years.

Hydrides

When reactive metals like sodium, potassium and calcium react with hydrogen, **ionic hydrides** are

formed. The ionic hydrides share some properties with other ionic compounds e.g.
1. They are crystalline solids with high boiling and melting points
2. They conduct electricity when molten
3. They combine readily with water to form hydroxides and liberate hydrogen gas

$CaH_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + 2H_{2(g)}$

- Aluminium and boron form complex covalent hydrides which are important reducing agents especially in organic chemistry, e.g. lithium tetrahydridoaluminate(III), $LiAlH_4$ and sodium tetrahydrido borate (III), $NaBH_4$.
- Non-metals like chlorine and nitrogen form simple covalent hydrides which are gaseous at room temperature. The hydrides of fluorine and oxygen however are liquid at room temperature because of the presence of hydrogen bonds.
- The hydrides of the more electronegative elements like chlorine and sulphur form acidic solutions when dissolved in water.

Assignment

Answer question 4 on page 228 of Essential Chemistry

Tutorial questions

1. State three properties of hydrides
2. What are the isotopes of hydrogen?
3. State the property of hydrogen which makes it suitable for filing balloons
4. Why is helium preferred to hydrogen in filling balloons?
5. State three industrial methods for preparing hydrogen
6. Under what conditions will hydrogen react with (i) oxygen (ii) chlorine (iii) nitrogen (iV) calcium. Write balance equations for the reactions.
7. state the test for hydrogen

WEEK 5

TOPIC: OXYGEN

Oxygen is the most abundant element on earth. It belongs to the Group VI of the Periodic Table. The other elements in the Group are sulphur, selenium, tellurium and polonium. There is an increase in metallic properties from oxygen to polonium; hence the elements in oxygen family vary widely in their chemical properties. The following trends are seen in the Group;

- All the elements have an outer electronic configuration s^2,p^4
- The atomic radius increases down the Group
- The melting and boiling points increase from oxygen to tellurium
- Electronegativity decreases down the Group

General properties of Group VI elements

1. They are chemically reactive
2. They have high electron affinity and tend to form covalent compound with other non-metals. Only polonium which is a metal is an exception to this property.
3. The most common oxidation state is -2. However, +2, +4 and +6 oxidation states are possible for sulphur, selenium, tellurium and polonium.

The bonding capacity of oxygen

The electronic configuration of oxygen is $1s^2,2s^2,2p^4$ (2,6). It requires two more electrons to completely fill its valence shell. This is achieved by gaining or sharing electrons. When oxygen gains two electrons from metals, it form **ionic compound**s e.g. Na_2O, CaO MgO etc. When it shares electrons with other non-metal, **covalent compounds** are formed e.g. O_2, SO_2, CO_2 etc. Oxygen can also form **coordinate bonding** in molecules e.g in CO

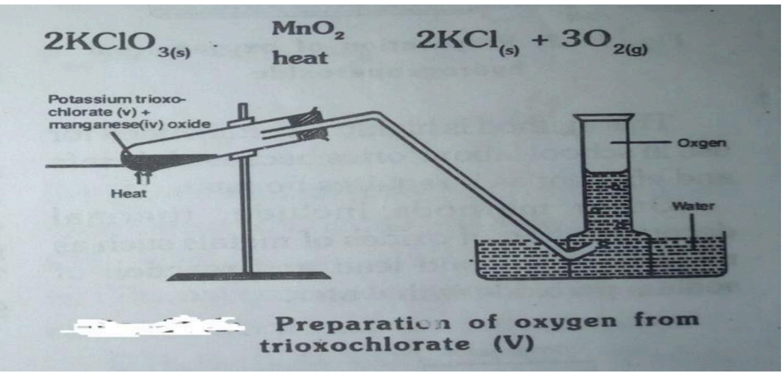
Laboratory preparation of oxygen

1. By the reaction of hydrogen peroxide with acidified potassium tetraoxomanganate (VII) in the cold. It is a redox reaction in which $KMnO_4$ is the oxidizing agent and H_2O_2 is the reducing agent.

$5H_2O_{2(aq)} + 2KMnO_{4(aq)} + 3H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$

2. By catalytic decomposition of potassium trioxochlorate (V). $KClO_3$ is heated with the catalyst MnO_2. The $KClO_3$ decomposes to oxygen and potassium chloride;

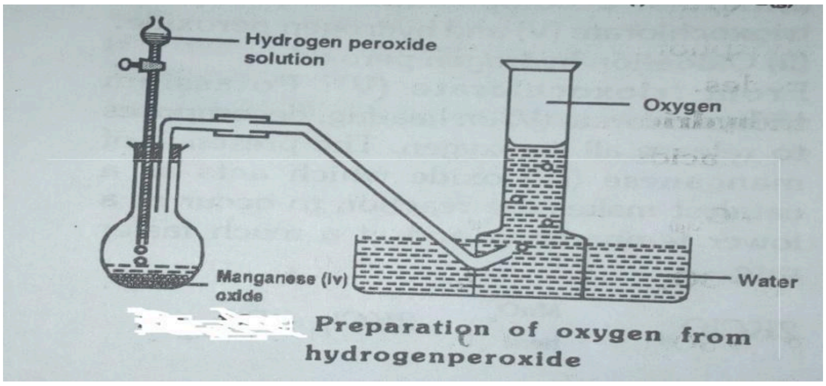
$2KClO_{3(s)heat} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$ In both cases, oxygen is collected over water.


$$2KClO_{3(s)} \xrightarrow[heat]{MnO_2} 2KCl_{(s)} + 3O_{2(g)}$$

[redacted] Preparation of oxygen from trioxochlorate (V)

3. By catalytic decomposition of hydrogen peroxide: add 10 volume or 3% hydrogen peroxide solution very slowly to a catalyst such as manganese (IV) oxide (MnO_2). Oxygen gas will be liberated;

“$H_2O_{2(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$

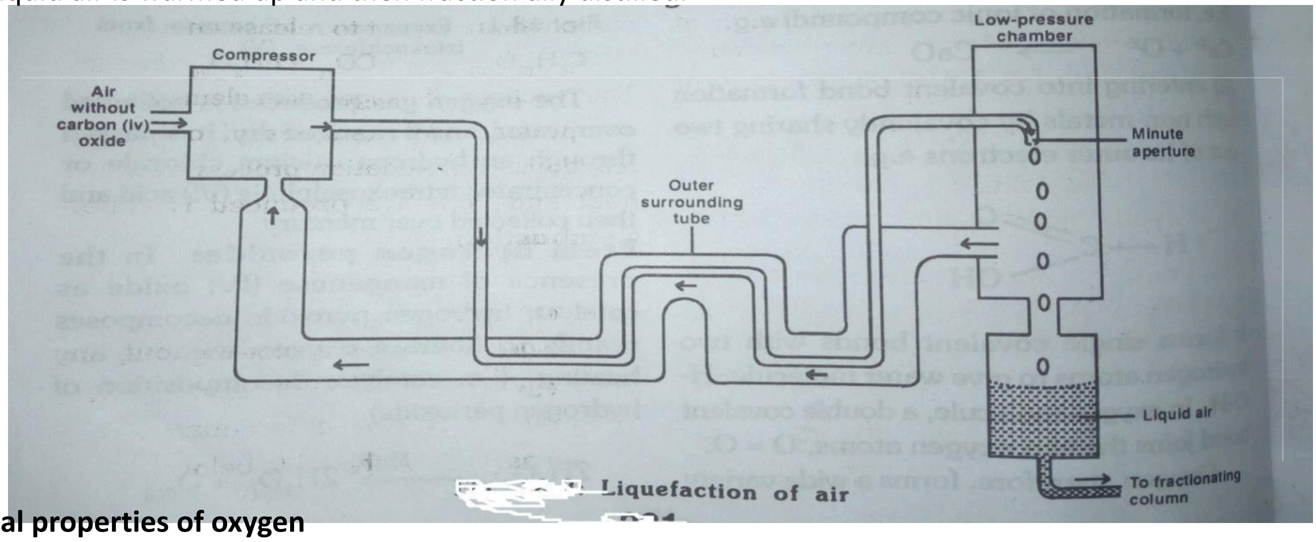


[redacted] Preparation of oxygen from hydrogenperoxide

Industrial preparation of oxygen

Oxygen is prepared industrially by the fractional distillation of air. The following are the steps involved’

- Cold air is compressed to about 150atm
- The compressed air is cooled by refrigeration to separate out CO2 and water vapour. The two gases become solids and are removed by filtration.
- Cold air is allowed to expand through a nozzle. The expansion causes air to cool rapidly.
- The compression and expansion cycles are repeated until the temperature reaches about -2000C, when liquid air is produced.
- The liquid air is warmed up and then fraction ally distilled.



[redacted] Liquefaction of air

Physical properties of oxygen

1. it is slightly denser than air
2. It is a colourless and odourless gas
3. It has no effect on moist litmus paper
4. It is sparingly soluble in water
5. It does not burn but support combustion
6. It is non-poisonous

Chemical properties of oxygen

A. Reaction with metals: the reaction of oxygen with metals depends on the reactivity of the metals.

- Alkali metals react readily with oxygen; hence they are usually kept under oil e.g. sodium

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

- Alkali earth metals like magnesium burn vigorously in oxygen to form oxides

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

- Metals such as iron and cupper react with oxygen, only when heated strongly, to form oxides e.g.

$2Fe(s) + 2O_2(g) \xrightarrow{heat} Fe_3O_4(s)$

B. Reaction with non-metals:

- Hydrogen burns in oxygen with pale blue flame to form water

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

- Carbon burns in limited supply of oxygen to produce carbon (II) oxide gas;

$2C(s) + O_2(g) \rightarrow 2CO(g)$

- In excess oxygen, carbon burns to produce carbon (IV) oxide;

$C(s) + O_2(g) \rightarrow CO_2(g)$

- Sulphur burns with a bluish flame to produce sulphur (IV) oxide;

$S(s) + O_2(g) \rightarrow SO_2(g)$

The reactions of oxygen with metals and non-metals are all oxidation reactions. Oxidation reactions include burning of fuels, rusting o iron and respiration.

Binary compounds of oxygen

An oxide is a compound of oxygen and another element. They are grouped into five;

1. Acidic oxide
2. Basic oxide
3. Amphoteric oxide
4. Neutral oxide
5. Higher oxide

Acidic oxides: these are oxides of non-metals. They dissolve in water to form acids e.g. SO2, CO2, SO3, NO2, P4O10.

$SO_2(g) + H2O(l) \rightarrow H_2SO_3(aq)$

Acidic oxides do not react with acids but react with alkalis to form a salt and water.

$SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$

Silicon (IV) oxide, SiO2 is a solid at room temperature. It is an acidic oxide. It does not dissolve in water but react with sodium hydroxide to form sodium trioxosilicate (IV) and water.

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

Properties of acidic oxides

- They are usually gases at room temperature (except P4O10 and SiO2)
- If soluble, they dissolve in water to form acidic solution
- They react with alkalis or bases to form a salt and water only.

Basic oxide: they are oxides of metals. Most of them are insoluble in water. A few of them such as Na2O and K2O dissolve readily in water. These soluble oxides are called alkalis. Calcium oxide (quick lime) dissolves moderately in water (a vigorous reaction) to form lime water.

Basic oxides are solids at room temperature. They react with acids to form salts and water only, e.g.

$CaO(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$

Amphoteric oxide: these are metallic oxides that react with both acids and bases to form salts and water only e.g. zinc oxide-ZnO, aluminium-Al_2O_3 and lead (II) oxide – PbO.

Neutral oxides: some non-metals form oxides that show neither basic nor acidic properties. They are called neutral oxides. They are insoluble in water (except water itself). Examples are water, carbon (II) oxide and nitrogen (II) oxide.

Higher oxides: Higher oxides are oxides containing a higher proportion of oxygen than the ordinary oxides. Example Perioxides (H_2O_2, K_2O_2, CaO_2, BaO_2), Dioxides (PbO_2, MnO_2) and Mixed oxides (Pb_3O_4, Fe_3O_4)

Uses of oxygen

Oxygen is used:

1. In steel making industry to burn off or oxidize impurities such as carbon, sulphur and phosphorus.
2. In the hospital to help patients with breathing difficulties
3. By mountain climbers, pilots of high-flying fighter planes and deep sea divers to help them breathe at high altitude and under water.
4. In the oxy-acetylene flame (about 35000C) to cut metals or weld them together.

5. In the manufacture of important chemical compounds like tetraoxosulphate (VI) acids, trioxonitrate (V) acid and ethanoic acid
6. Liquid oxygen and fuels are used as propellants for space rockets.

Test for oxygen

When a glowing splinter is interted into the jar containing the unkown gas, if the gas is oxygen, the splinter will be rekindled.

Assignment

Dinitrogen (I) oxide behaves like oxygen when brought close to glowing splinter. Highlight the differences between oxygen and dinitrogen (I) oxide.

Tutorial questions

1. State the steps involved in the industrial preparation of oxygen
2. Give any three uses of oxygen
3. With two examples each, briefly describe types of oxides
4. Give four physical properties of oxygen
5. with the aid of balanced equation, Show the reaction of oxygen with a metal and a non-metal
6. Describe one way by which oxygen can be produced in the laboratory

WEEK 6

TOPIC: HALOGENS

The halogens are the group VII elements. The family comprises of fluorine, chlorine, bromine, iodine and astatine. Each member of the family contains 7 electrons at the valence shell. Halogens are the most reactive non-metals; hence, they don’t occur freely in nature but combine with metals to form salts. Fluorine is the most reactive element in the family and is in many ways unique. Bromine and iodine are chemically very similar to chlorine. Astatine is a radioactive element and has been made artificially. It does not occur naturally.

Electronic configuration and properties of halogen

The electronic configuration of halogens is one electron short of the noble gas structure. Each atom of the elements in the group complete its octet structure by either:;

- Gaining one electron usually from group I and II to form a univalent negative ion, e.g. F-, Cl-, Br-.

Or

- Sharing a pair of electrons in a single covalent with another atom having a fairly similar electronegative value as in gaseous chlorine; Cl – Cl, and hydrogen chloride; H – Cl.

The electronic configurations of halogens are:

9F – 2,7
17Cl – 2,8,7
35Br – 2,8,18,7
53I – 2,8,18,18,7
85At – 2,8,18,32,18,7

General properties of halogens

1. They are all diatomic molecules; hence they have low melting and boiling points and are soluble in covalent non-polar liquids.
2. At room temperature, fluorine and chlorine are gases, bromine is liquid and iodine is solid. The boiling point increases down the group.
3. They are coloured with typical penetrating odours. The colours deepen down the group. Fluorine is pale yellow, chlorine is greenish-yellow, bromine is reddish-brown and iodine is purple balck.
4. Their reactivity decrease down the group. The reactivity series such as volatility, solubility, electronegativity, oxidizing ability and tendency to enter into chemical reaction decrease down the group. This gradation in properties is due to the increasing complexity of the atoms as their atomic numbers increase from fluorine to iodine.
5. All halogens dissolve to some extent in water. Fluorine reacts vigorously with water to produce oxygen and hydrogen fluoride.

6. They are all strong oxidizing agents. Fluorine oxidizes water to peroxide. Chlorine reacts slowly with water to give oxochlorate (I) acid, (HClO). The oxochlorate (I) acid decomposes to give hydrochloric acid and oxygen.

$2HClO(aq) \longrightarrow 2HCl(aq) + O2(g)$

7. They all combine readily with most metals (except gold, platinum and titanium) and non-metals (except oxygen, carbon and nitrogen) to form ionic and covalent compounds respectively. These compounds contain halide ion, X- in which they have oxidation state of -1. E.g.

$2Na(s) + X_2 \longrightarrow 2NaX(s)$

$2P(s) + 3X_2 \longrightarrow 2PX_3(s)$

Note: under certain conditions, the less reactive halogens react more vigorously than chlorine. For example, bromine is capable of corroding gold because it is a liquid and has more concentration than chlorine which is a gas.

1. They combine with hydrogen to form gaseous covalent compounds of formula HX. The halide ion has an oxidation state of -1.
2. They react with silver to form silver halide. Only silver fluoride is soluble. Silver chloride is white, silver bromide is pale yellow and silver iodide is bright yellow. This characteristic can be used to test for halides.
3. They all react with sodium hydroxide to give a mixture of halide salt and oxochlorate (I) salts e.g.

$Cl2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaClO(aq) + H2O(l)$

4. More reactive halogen displaces (displacement reaction) less reactive halogens from their salts. This is a typical redox reaction e.g. $Br2(aq) + 2KI(aq) \longrightarrow 2KBr(aq) + I2(aq)$

CHLORINE AND ITS COMPOUNDS

Chlorine is most important halogen. It does not occur freely in nature but in combined state as chlorides, mostly sodium chloride.

Laboratory preparation of chlorine

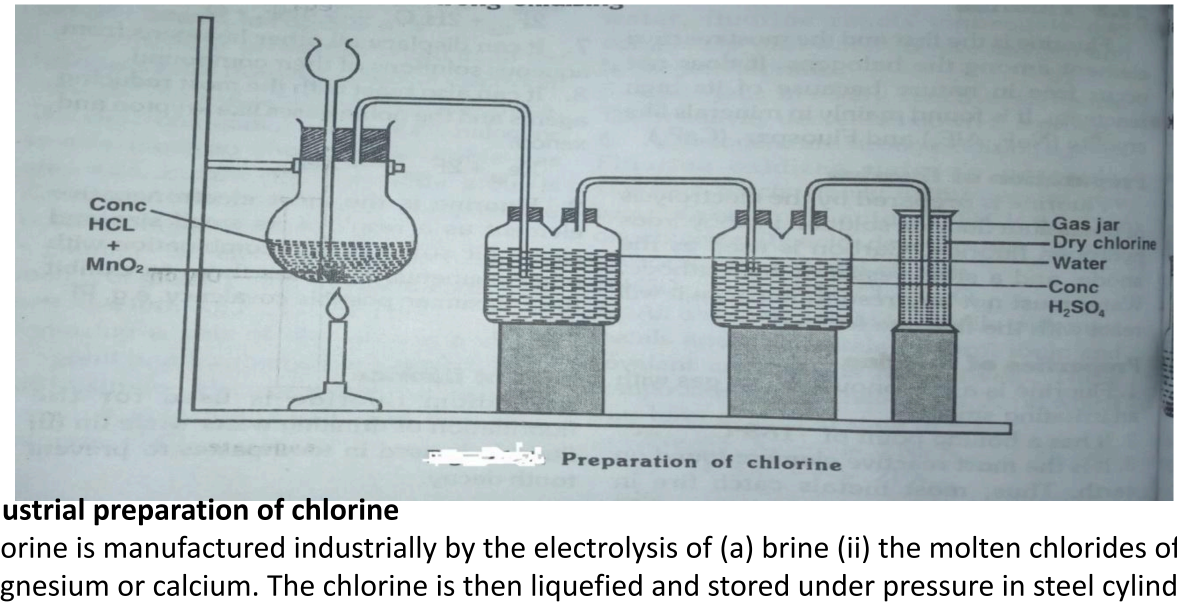
Chlorine is usually prepared by the oxidation of concentrated hydrochloric acid with a strong oxidizing agent such as manganese (IV) oxide – MnO2, potassium tetraoxomanganate (VII)-KMnO4 or lead (IV) oxide – PbO2.

- **Using MnO2:** heat a mixture of MnO2 and conc. HCl . the acid is oxidize to liberate chlorine.

$MnO2(s) + 4HCl(aq) \xrightarrow{heat} MnCl2(aq) + 2H2O(l) + Cl2(g)$

- **Using KMnO4** – heat is not required. The conc. HCl is oxidized upon addition of KMnO4.

$2KMnO4(aq) + 16HCl(aq) \longrightarrow 2MnCl_2(aq) + 2KCl(aq) + 8H_2O(l) + 5Cl_2(g)$



Preparation of chlorine

Industrial preparation of chlorine

Chlorine is manufactured industrially by the electrolysis of (a) brine (ii) the molten chlorides of sodium, magnesium or calcium. The chlorine is then liquefied and stored under pressure in steel cylinder.

Physical properties of chlorine

1. It is a greenish – yellow gas with an unpleasant choking smell.
2. It is moderately soluble in water
3. It is about 2.5 times denser than air
4. It can easily be liquefied under a pressure of about 6atm.
5. It is poisonous

Chemical properties of chlorine

- Displacement of other halogens (except fluorine) – chlorine displaces other halogens below it in the Periodic Table from their respective acids and salts e.g

$Cl2(g) + 2NaBr(aq) \longrightarrow 2NaCl(aq) + Br_2(l)$

$Cl2(g) + 2HI(aq) \longrightarrow 2HCl(aq) + I_2(s)$

- Direct combination with other elements:

(i) Metals react readily with chlorine especially when heated to form the corresponding chloride e.g.

$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$

Note: where a metals forms more than one chloride, the higher chloride is usually formed due to the oxidative nature of chlorine. For example, Iron(III) chloride and not iron (II) chloride is formed in the reaction above.

(ii) All non-metals (except the noble gases, oxygen, nitrogen and carbon) burn in chlorine to produce the corresponding chlorides e.g. hydrogen and chlorine combine explosively in bright sunlight to produce hydrogen chloride. The reaction is slower in diffuse light.

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

- Reaction with hydrogen – chlorine reacts readily with molecular hydrogen as well as compounds containing hydrogen to form hydrogen chloride e.g.

(i) with hydrocarbons – chlorine removes hydrogen from burning hydrocarbon like wax, candle, petrol or methane to form hydrogen chloride fumes and soot. Also, a filter paper saturated with turpentine ($C_{10}H_{16}$) will rapidly catch fire in a jet of chlorine to form soot and misty fumes of hydrogen chloride gas.

$C_{10}H_{16}(l) + 8Cl_2(g) \longrightarrow 10C(s) + 16HCl(g)$

Under controlled condition, substitution reaction occurs. In this reaction, chlorine reacts with saturated hydrocarbons to produce chlorinated hydrocarbons and hydrogen chloride e.g.

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$
Chloromethane

$CH_3Cl(g) + Cl_2(g) \longrightarrow CH_2Cl_2(g) + HCl(g)$
Dichloromethane

$CH_2Cl_2(g) + Cl_2(g) \longrightarrow CHCl_3(g) + HCl(g)$
Trichloromethane

$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$
Tetrachloromethane

(ii) with ammonia – chlorine reacts with ammonia to form nitrogen and hydrogen chloride. The hydrogen chloride then reacts with excess ammonia to form ammonium chloride.

$2NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6HCl(g)$

$HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

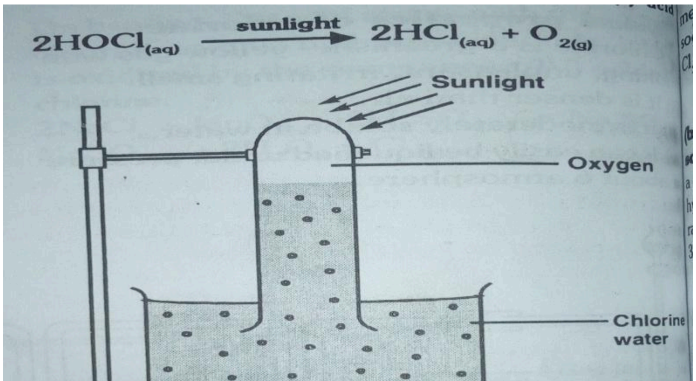
(iii) with hydrogen sulphide – when hydrogen sulphide and chlorine are mixed, a yellow deposit of sulphur is formed as a result of oxidation of sulphide by chlorine.

$H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S(l)$

(iv) with water – chlorine water (formed by bubbling chlorine through water) gives off oxygen when exposed to sunlight. This is due to the formation of oxochlorate (I) acid which decomposes slowly to yield hydrogen chloride and oxygen.

$Cl_2(g) + H_2O(l) \longrightarrow HCl(g) + HOCl(aq)$

$2HOCl(aq) \xrightarrow{sunlight} 2HCl(aq) + O_2(g)$



[redacted]: Effect of sunlight on chlorine water

- **As an oxidizing agent** – chlorine is a powerful oxidizing agent because of: (i) its ability to remove hydrogen (ii) its readiness to accept electron from reducing agents to from chloride ions e.g.

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

Green yellow

(ii) when bubbled through a freshly prepared solution of H2SO3, chlorine oxidizes the trioxosulphate (IV) ion to tetraoxosulphate (VI) ion.

$H_2SO_3(aq) + H_2O(l) + Cl_2(g) \longrightarrow H_2SO_4(aq) + 2HCl(aq)$

- **As a bleaching agent** – in the presence of water, chlorine bleaches most dyes and inks except those containing carbon like printer’s ink. The bleaching action of chlorine is due to its ability to react with water to form oxochlorate (I) acid. The oxochlorate (I) acid is unstable and decomposes to release oxygen which oxidizes the dye to form a colourless compound.

$HOCl(aq) \longrightarrow HCl(aq) + [O]$

Dye + [O] (dye + O)

Coloured colourless

- **Reaction with alkali**

(i) with dilute alkali – when chlorine is bubbled through a cold dilute solution of sodium hydroxide, a pale – yellowish mixture of the oxochlorate (I) and chloride of the metal is formed

e.g. Cl2(g) + 2NaOH(aq) NaOCl(aq) + NaCl(aq) + H2O(l)

Sodium oxochlorate (I)

Bleaching powder is prepared by bubbling chlorine through a freshly prepared solution of slaked lime; Cl2(g) + Ca(OH)2(s) CaOCl2. H2O(s)

Slaked lime bleaching powder

(ii) with conc. Alkali solution – if chlorine is bubbled through a hot conc. Solution of sodium hydroxide, a mixture of trioxochlorate (V) and chloride of the metal is formed.

3Cl2(g) + 6NaOH(aq) NaClO3(aq) + 5NaCl(aq)

Sodium trioxochlorate (V)

Test for chlorine

1. Drop a piece of damp blue litmus paper into the gas jar of the unknown gas. If the litmus paper turns pink and then becomes bleached, the gas is chlorine.
2. Drop a piece of damp starch-iodide paper into the unknown gas jar. If the paper turns dark blue, then the gas is chlorine.

Uses of chlorine

- As a powerful germicide, it is used in the sterilization of water
- It is used as a bleaching agent for cotton, linen and wood-pulp. It is too strong for bleaching animal fibre.
- It is used in the manufacture of;

Important organic solvents like CHCl3, CCl4 etc

Polyvinyl chloride (PVC) a widely used plastic

Hydrochloric acid

KClO3 used for making matches and in fireworks and NaClO3 which is a weed killer.

Bleaching powder and NaClO used in dye works and laundry.

Domestic antiseptic e.g. acidified NaClO

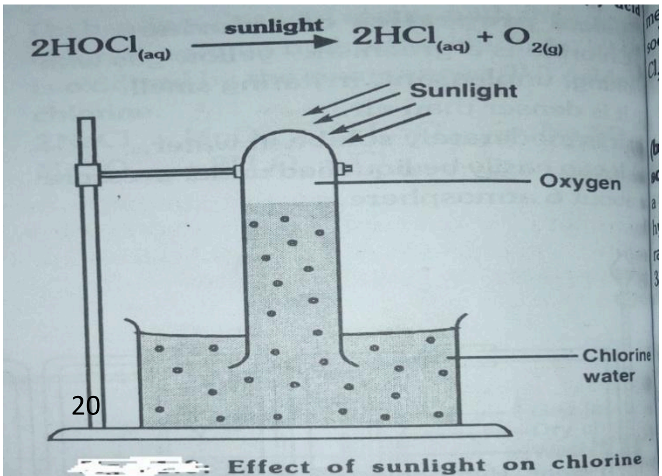
HYDROGEN CHLORIDE

Hydrogen chloride is a hydride of chlorine. It exists as a gas at s.t.p. and dissolves in water to form hydrochloric acid. It was first prepared by priestly in 1772.

Laboratory preparation of hydrogen chloride

Hydrogen chloride is prepared in the laboratory by the action of concentrated tetraoxosulphate (VI) acid on sodium chloride. The gas is dried by passing it through concentrated H_2SO_4 and is collected by downward delivery.

$2NaCl(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4 + 2HCl(g)$



Effect of sunlight on chlorine

Industrial preparation of hydrogen chloride

It is prepared industrially be the direct combination of hydrogen and chlorine gases obtained from the electrolysis of brine.

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Physical properties of hydrogen chloride

- It is colourless with a sharp irritating smell
- It is slightly denser than air
- It turns moist blue litmus paper red (property of an acidic oxide)
- It is very soluble in water forming an aqueous solution of hydrochloric acid
- It fumes strongly in moist air forming droplets of hydrochloric acid
- It does not burn or support combustion
- Dry hydrogen chloride dissolves readily in non-polar solvent like chloroform and toluene, but does not ionize as it does in polar solvent.

Chemical properties of hydrogen chloride

1. Reaction with ammonia – hydrogen chloride gas reacts with ammonia gas to form a dense white fumes of solid ammonium chloride.

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

2. Reaction with metals – hydrogen chloride gas on heating reacts with many metals, forming the corresponding chlorides and hydrogen. If the metal can form two chlorides, the lower chloride is formed.

$Zn(s) + 2HCl(g) \rightarrow ZnCl_2(s) + H_2(g)$

$Fe(s) + 2HCl(g) \rightarrow FeCl_2\ (s) + H_2(g)$

Assignment

Describe an experiment to show that hydrogen chloride gas in readily soluble in water. Name another gas which shows this property.

Tutorial question

- Name any five gases that are collected by downward delivery
- Name any three gases that are collected by upward delivery
- Draw and label the laboratory set up for the preparation of chlorine gas
- Show the reaction of chlorine with saturated hydrocarbon to produce chlorinated hydrocarbon. What condition is required for the reaction to take place? What type of reaction is it?
- With the aid of balanced equations, show the reaction of chlorine with (i) dilute alkali (ii) conc. Alkali solution
- State five physical properties of hydrogen chloride
- State what happens when chlorine reacts with iron (II) chloride
- State five general properties of halogens
- How do we test for chlorine
- State three uses of chlorine

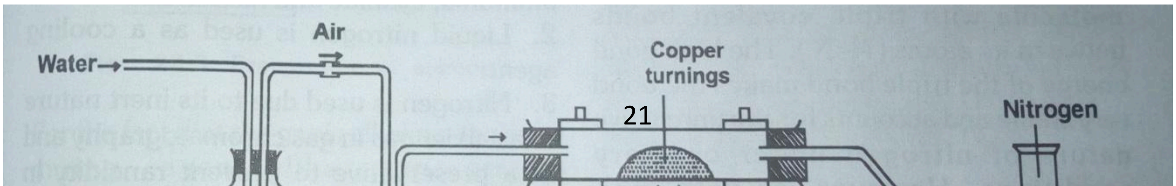
WEEK 7

TOPIC: NITROGEN AND ITS COMPOUNDS

Nitrogen forms about 78% by volume of the atmosphere. It can be found in combined form in trioxonitrate (V) of sodium and calcium. It can also be found in organic matters like proteins, urea and the vitamin B compounds.

Laboratory preparation of nitrogen

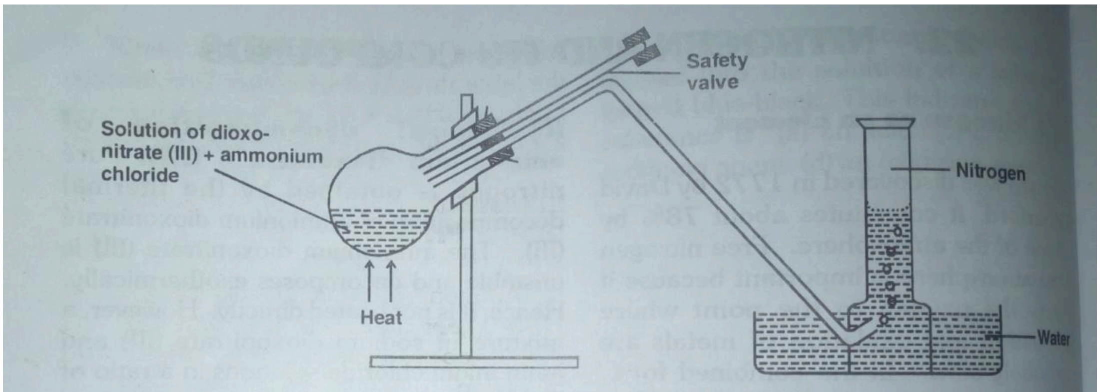
- **From air:** nitrogen can be obtained from air by removing the other constituents. The CO2 and O2 can be removed by passing the air through caustic soda and heated copper turning respectively. The nitrogen obtained by this method contains about 1% by volume of rare gases as impurities and is denser than pure nitrogen.



- **From ammonium dioxonitrate (III) – NH_4NO_2:** thermal decomposition of NH_4NO_2 yields pure nitrogen. The NH_4NO_2 should not be heated directly because it is unstable and decomposes exothermically. Hence, a mixture of $NaNO_2$ and NH4Cl in a ratio of 7:5 is heated to yield NH_4NO_2 which in turn decomposes to form nitrogen and steam.

$NaNO_2(aq) + NH_4Cl(aq) \longrightarrow NH_4NO_2(aq) + NaCl(aq)$

$NH_4NO_2(aq) \longrightarrow N_2(g) + 2H_2O(l)$



: Preparation of nitrogen by the action of heat on ammonium dioxonitrate (III)

- **From ammonium heptaoxodichromate (VI):** when (NH4)2Cr2O7 is heated, it decomposes to yield nitrogen. (NH4)2Cr2O7(s) N2(g) + Cr2O3(s) + 4H2O(l)
- **From ammonia:** when ammonia is oxidized by hot copper (II) oxide, nitrogen is liberated. 2NH3(g) + 3CuO(s) 3Cu(s) + 3H2O(g) + N2(g)
- **From dinitrogen (I) oxide:** when N2O is paased over red hot copper, the gas is reduced to nitrogen. N2O(g) + Cu(s) CuO(s) + N2(g)

Industrial preparation

In the industries, nitrogen is prepared by the fractional distillation of liquid air. Carbon (IV) oxide is first removed from air, by passing the air through caustic soda, before liquefaction. The liquid air (without CO_2) is subjected to successive compression and cooling processes. During distillation, nitrogen gas first evolves at -1960C (at s.t.p) and is separated from oxygen which distils at -1830C (at s.t.p). the nitrogen is stored in steel cylinders and sold as liquid nitrogen or as the compressed gas.

Physical properties of nitrogen

1. It is a colourless, odourless and tasteless gas
2. Pure nitrogen is slightly lighter than air
3. It is only slightly soluble in water
4. It has a boiling point of -1960C and melting point of -2100C.

Chemical properties of nitrogen

Nitrogen is a Group V element which forms covalent bonds in it compounds. It can also form ionic bonds with Group I and II elements by accepting 3 electrons to form nitride ion; N3-. The oxidation states vary from -3 to +5 in its various compounds. Nitrogen gas is unreactive under ordinary conditions because of the high bond energy of the triple bond (N≡N) in its atoms. However, at high temperature and pressure nitrogen combines directly with hydrogen, oxygen and certain metals.

1. Reaction with metals: Nitrogen combines directly with very electropositive metals to form nitrides e.g

$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

$Mg_3N_2(s) + 6H_2O(l) \xrightarrow[warm]{} 3Mg(OH)_2(aq) + 2NH_3(g)$

2. Reaction with non-metals: nitrogen combines reversibly with hydrogen to form ammonia. With oxygen, it combines directly at very high temperature of about 20000C or in the presence of a high voltage electric spark to form small amount of nitrogen (II) oxide. This reaction occurs in the atmosphere during lightning flashes.

$N_2(g) + O_2(g) \xrightarrow{} 2NO(g)$

Uses of nitrogen

- It is used in the manufacturing of ammonia, cyanide, cyanomide, and carbamide (an important fertilizer)
- Liquid nitrogen is used as cooling agent
- Because of its inert nature, it is used as a carrier gas in gas chromatography, provision of inert condition for certain industrial processes that involve easily oxidizable chemicals e.g. the manufacturing of transistors and annealing of metals.
- It is used as preservative to prevent rancidity in packaged foods

COMPOUNDS OF NITROGEN

AMMONIA

Ammonia is a very important chemical. It is a hydride of nitrogen.

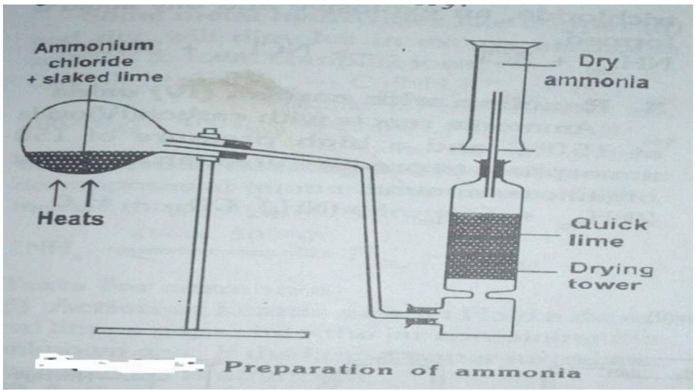
Laboratory preparation of ammonia

Ammonia is prepared in the laboratory by heating any ammonium salt with a non-volatile base. Ammonium chloride and calcium hydroxide are usually employed because calcium hydroxide is cheap and not deliquescent like sodium hydroxide and potassium hydroxide. The two reactants must be properly grounded to provide maximum surface area for the reaction.

$Ca(OH)_2(s) + 2NH_4Cl(s) \xrightarrow{} CaCl_2(s) + 2H_2O(l) + 2NH_3(g)$

The suitable drying agent for ammonia is quicklime (CaO). Silica gel may also be used.

Laboratory preparation of ammonia



Preparation of ammonia

Industrial preparation of ammonia

The industrial process for the production of ammonia is called Haber process. It involves mixing nitrogen and hydrogen in the volume ration 1:3 and passing the mixture:

- Over finely divided iron as catalyst
- At a temperature of about 4500C and
- A pressure of about 200 atm.

The yield of ammonia is about 15%. The Ammonia is liquefied by cooling while the unused gases are recirculated
for further production.

$N_2(g) + 3H_2(g) \xrightarrow{} 2NH_3(g)$

An ammonia molecule has pyramidal shape. The presence of lone pair of electron and the different electronegativity values of nitrogen and hydrogen makes ammonia molecule polar. Because of this, hydrogen bonds occur readily between ammonia molecules and between ammonia and water molecules.

Physical properties of ammonia

1. It is a colourless gas with choking smell
2. It is poisonous when in large quantity because of its effects on respiratory muscles.
3. It is an alkaline gas
4. It is about 1.7 times less dense than air
5. It is a very soluble gas. About 1200 volumes of ammonia dissolves in 1 volume of water at s.t.p.

This is due to the readiness with which it forms hydrogen bonds with water to give aqueous ammonia – $NH_3.H_2O$. The aqueous ammonia ionizes slightly to give ammonium ion and hydroxyl ion. The hydroxyl ion gives aqueous ammonia its weak alkaline property.

Chemical properties of ammonia

- Ammonia burns readily in oxygen, but not in air, with a greenish yellow flame to form water vapour and nitrogen;

$4NH_3(g) + 3O_2(g) \longrightarrow 6H_2O(g) + 2N_2(g)$

In the presence of heated platinum catalyst however, ammonia reacts with air to produce nitrogen (II) oxide;

$4NH_3(g) + 5O_2(g) \xrightarrow[\text{platinum}]{} 4NO(g) + 6H_2O(l)$

- As a reducing agent

(i) It reduces heated copper (II) oxdie to metallic copper

$2CuO(s) + 2NH_3(g) \longrightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$

(ii) It reduces chlorine to hydrogen chloride and nitrogen. The hydrogen chloride then reacts with excess ammonia to produce dense white fume of ammonium chloride.

$2NH_3(g) + 3Cl_2(g) \longrightarrow 6HCl(g) + N_2(g)$

$6NH_3(g) + 6HCl(g) \longrightarrow 6NH_4Cl(s)$

Overall reaction ; $8NH_3(g) + 3Cl_2(g) \longrightarrow 6NH_4Cl(s) + N_2(g)$

The ammonia must be supplied in excess. If however, chlorine is in excess, nitrogen (II) chloride – NCl_3 , an explosive and oily liquid will be formed.

$NH_3(g) + 3Cl_2(g) \longrightarrow NCl_3(l) + 3HCl(g)$

- Reaction with carbon(IV) oxide: at about 1500C and 150 atm, ammonia reacts with carbon (IV) oxide to produce urea, an important organic compound.

$2NH_3(g) + CO_2(g) \longrightarrow (NH_2)_2CO(s) + H_2O(l)$

- Thermal decomposition; at temperature above 5000C or during prolong sparkling, ammonia decomposes to form nitrogen and hydrogen

- As a base: ammonia is a weak base because it can accept proton to form ammonium ion. It reacts with acids to form ammonium salt.

$NH_3(g) + H^+ (aq) \longrightarrow NH_4^+(aq)$

$2NH_3(g) + H_2SO_4(aq) \longrightarrow (NH_4)_2SO_4(s)$

- As a precipitating agent: aqueous ammonia precipitates the insoluble hydroxides of metals from the solution of their salts. The following are the common insoluble hydroxides.

$Pb^{2+}(aq) + 2OH^-(aq) \longrightarrow Pb(OH)_2(s)$ – white ppt

$Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$ – white gelatinous ppt

$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$ - reddish brown ppt

$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$ – blue ppt

Some of these hydroxide like $Cu(OH)_2$ and $Zn(OH)_2$ dissolve in excess ammonia to form complex ions. The complex ion formation is used as confirmatory test for copper and zinc in qualitative analysis.

$Cu(OH)_2(s) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$

Deep blue solution

$Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow Zn(NH_3)^{2+} + 2OH^-(aq)$

Colourless solution

Test for ammonia

1. Action of litmus paper – hold a damp red litmus paper into the jar containing the unknown gas with choking smell. If the litmus paper turns blue, then the gas is ammonia.
2. Action with hydrochloric acid – dip a glass rod in con. HCl and then insert it in the gas jar containing the unknown gas, white fumes are formed if the gas is ammonia.

Uses of ammonia

- It is used for softening temporary hard water
- Aqueous ammonia is used in laundry as solvent for removing grease and oil stains
- Aqueous ammonia is used as a refrigerant, although it is being replaced by less toxic compounds
- It is used in the manufacture of HNO3 and Na2CO3.
- It is used in the manufacturing nitrogenous fertilizers like (NH4)2SO4, NH4NO3, (NH4)3PO4 and carbamide.

Assignment

Briefly discuss the nitrogen cycle

Tutorial questions

1. State the test for ammonia
2. Describe the preparation of nitrogen from air
3. State three uses of ammonia
4. Describe any three chemical properties of ammonia
5. Explain what happens when aqueous ammonia is added in excess to a solution of copper(II) salt.

WEEK 8

TOPIC: NITROGEN AND ITS COMPOUNDS

Oxides of Nitrogen

Oxides are known for every oxidation state of nitrogen from +1 to +5. These are Dinitrogen(i)oxide, N_2O, nitrogen(ii)oxide NO, nitrogen(iii)oxide, N_2O_3, nitrogen(iv)oxide, NO_2 and nitrogen(v)oxide, N_2O_5.

Assignment

Give the preparation (Laboratory and industry), properties (physical and chemical), uses and test of all the five oxides of nitrogen.

Trioxonitrate (V) acid – HNO_3

It is an important acid used in the laboratory and in the industries. It was previously known as aqua fortis; meaning strong water.

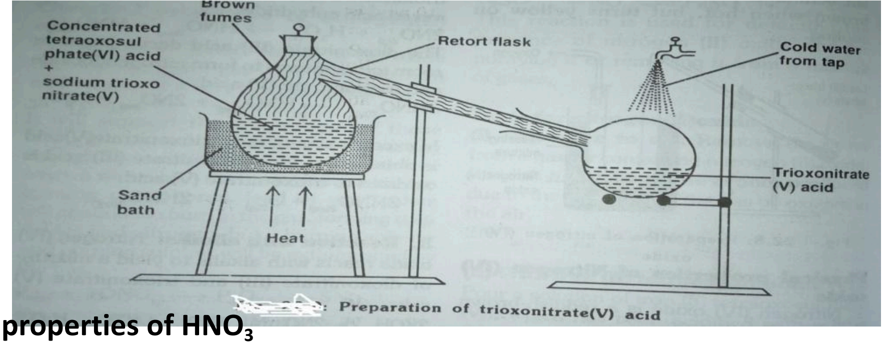
Laboratory preparation of HNO_3

HNO3 can be prepared from any trioxonitrate(V) salt. KNO3 and NaNO3 are usually used because they are cheap. When these trioxonitarte (V) salts are reacted with conc. H2SO4, HNO3(a more volatile acid) is displaced.

$KNO_3(aq) + H_2SO_4(aq) \longrightarrow KHSO_4(aq) + HNO_3(g)$

$NaNO_3(aq) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(g)$

Laboratory preparation of HNO_3



: Preparation of trioxonitrate(V) acid

Physical properties of HNO_3

- It is a fuming liquid with a sharp choking smell. The pure HNO_3 is colourless but turns yellowish after sometimes due to the decomposition of some of the acid to yield NO_2 which then dissolves in it.

- Pure HNO_3 is miscible with water in all proportions and forms a constant boiling mixture with it at 121^0C. this mixture consisting of about 68% HNO_3 is the ordinary conc. HNO_3 found in the laboratory. Pure HNO_3 containing 98% acid is known as fuming HNO_3.

- Pure and ordinary conc. HNO_3 are corrosive and must be handled with care.

Chemical properties of HNO3.

1. **As an acid**

(i) it neutralizes bases and alkalis to form metallic trioxonitrate (V) and water

$NaOH(aq) + HNO_3(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$

$CaO(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l)$

(ii) it reacts with metallic trioxocarboantes(IV) to liberate carbon(IV) oxide.

$CaCO_3(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

(iii) very dilute HNO_3 (about 1%) react with calcium, magnesium or manganese to liberate hydrogen. Conc. HNO_3 does not liberate hydrogen gas when reacted with metals, unlike other acids, because the hydrogen gas formed is immediately oxidized to water by the HNO_3.

$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2 + H_2(g)$

2. **As an oxidizing agent**:

HNO_3 is a strong oxidizing agent. it can undergo reduction in many ways to form various products like NO_2, HNO_2, NO, N_2O, N_2, N_2OH, N_2H_4 and NH_4^+, depending on the concentration of the acid, the strength of the reducing agent and the temperature.

When dilute HNO3 acts as the oxidizing agent, the trioxonitrate (V) ion, NO_3^-

- **is reduced to NO**

e.g. $NO_3^-(aq) + 4H^+(aq) + 3e- \longrightarrow NO(g) + 2H_2O(l)$

When conc. HNO_3 is the oxidizing agent, the NO_3

- **is reduced to NO_2**

$NO_3^-(aq) + 2H^+(aq) + e- \longrightarrow NO_2(g) + H_2O(l)$

With non-metals: Hot conc. HNO_3 oxidizes non-metals to their highest oxides which may then react with water to form the corresponding acids. At the same time, the acid itself is reduce to nitrogen (IV) oxide;

e.g $C(s) + 4HNO_3(aq) \xrightarrow{heat} CO_2(g) + H_2O(l) + 4NO_2(g)$

$S(s) + 6HNO_3(aq) \xrightarrow{heat} H_2SO_4(aq) + 2H_2O(l) + 6NO_2(g)$

With metals:

(i) metals which are mild reducing agents like Cu, Pb, Hg and Ag when reacted with pure HNO_3 are oxidized ton their trioxonitrates (V) while the HNO_3 itself is reduced to NO_2. However, with moderately conc. HNO_3 (about 50%) these metals still react the same way but the HNO_3 is reduced to NO e.g.

$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$

Pure

$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$

(ii) Aluminium and iron do not react with the conc. HNO_3. This may be due to the formation of a surface coating of oxide which is passive and stops any further reaction by the acid. Conc. HNO_3 is thus usually transported in containers lined with aluminium or iron.

(iii) magnesium, zinc and iron reacts with dilute HNO_3 to form the corresponding metallic trioxonitrates(V) and ammonium trioxonitrate (V) or nitrogen (I) oxide.

$4Zn(s) + 10HNO(aq) \longrightarrow 4Zn(NO_3)_2(aq) + 3H_2O(l) + NH_4NO_3(aq)$

(iv) Tin reacts with conc. HNO3 to form a hydrated oxide instead of a trioxonitrate (V)

$Sn(s) + 4HNO_3(aq) \longrightarrow SnO_2.H_2O(s) + H_2O(l) + 4NO_3(g)$

(v) Gold and platinum are not attacked by HNO_3 at all.

With reducing agents

(i) HNO_3 oxidizes H_2S to sulphur, some of which may be further oxidized to H_2SO_4. The HNO_3 is itself reduced to NO_2.

$H_2S(g) + 2HNO_3(aq) \longrightarrow S(s) + 2H_2O(l) + 2NO_2(g)$

(ii) iron (II) salts are oxidized to iron (III) salts by HNO_3. The acid is then reduced to NO, which on exposure to air is converted to NO_2.

$6Fe^{2+}(aq) + 8H^+(aq) + 2NO_3^-(aq) \longrightarrow 6Fe^{3+}(aq) + 4H_2O(l) + 2NO(g)$

3. **Decomposition**

HNO_3 decomposes slowly at room temperature (especially in the presence of sunlight) and rapidly when heated to yield NO_2 and O_2.

4. **Nitration reactions**

HNO_3 dissociates in the presence of conc. H_2SO_4 to form the nitryl cation (nitronium ion), NO_2^+. The nitronium ion can replace the hydrogen ion from many compounds like benzene, methyl benzene and phenol. The process is called nitration and is very important in the industries.

$C_6H_6(l) + HNO_3(aq) \longrightarrow C_6H_5NO_2(l) + H_2O(l)$

Nitrobenzene

Uses of HNO_3.

- It is used as an acid, oxidizing agent and nitrating agent in the laboratory.
- It is used as a rocket fuel

- It is used as an oxidizing agent in the production of important polymers like nylon and terylene.
- A mixture of hydrochloric acid and HNO3 in ratio 3:1 (known as aqua regia) is used as a solvent for gold and platinum.
- It is used as an important starting material in the production of many trioxonitrates (V) and organic nitro-compounds which are used for the production of fertilizers, dyes, drugs and explosives e.g. methyl-2,4,6-trinitrobenzene – TNT)

TRIOXONITRATES (V)

Trioxonitrates (V) can be prepared by any of the general methods used for preparation of salts e.g.

- Neutralization of HNO_3 with appropriate alkali
- Action of HNO_3 on metals, a metal oxide or a trioxocarbonate (IV) Precipitation method cannot be used for the preparation of trioxonitrates(V) because they are all soluble. Crystallization is the only suitable method for recovering the trioxonitrate (V) salt from the aqueous solution because they decompose easily on heating.

Action of heat on trioxonitrates(V)

All trioxonitrate(V) salts decompose on heating but the product depend on the position of the metal in the electrochemical series. Below are the products of the decomposition of trioxonitrates(V).

Metal Decomposition of trioxonitrate (V)

K
Na
The Trioxonitrates (V) decompose to dioxonitrate (III) and oxygen
$2KNO_3(s)$ $2KNO_2(s) + O_2(g)$
Ca
Mg
Zn
Pb
H Cu
The trioxonitrates (V) decompose to give the metallic oxide, oxygen and brown fumes of nitrogen (IV) oxide e.g.
$2Zn(NO_3)_2(s) \longrightarrow 2ZnO(s) + O_2(g) + NO_2(g)$
Hg
Ag
Au
The trioxonitrate(V) decompose to give the metal, oxygen and brown fumes of nitrogen (IV) oxide e.g.
$2AgNO_3(s) \longrightarrow 2Ag(s) + O_2(g) + 2NO_2(g)$

Unlike the metallic trioxonitrate (V), ammonium trioxonitrate (V) decomposes on heating to produce nitrogen (I) oxide and water.

$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$

Action of H_2SO_4

All trioxonitrate (V) salts liberate HNO3 when heated with conc. H_2SO_4.

$NO_3^-(aq) + H_2SO_4(aq) \longrightarrow HSO_4^-(aq) + HNO_3(aq)$

Formation of brown ring

When conc. H_2SO_4 is added slowly down the side of a test tube containing an aqueous solution of a trioxonitrate(V) and $FeSO_4$, the acid sinks to the bottom and two layers are formed. A brown ring is formed at the junction of the two layers. This formation of brown ring can be used as a test for trioxonitrates (V) but it is unreliable because iodide and bromides too give coloured rings. Metallic radicals which form insoluble tetraoxosulphate (VI) also interfere with the test.

Test for trioxonitrate (V)

- With H_2SO_4: warm the unknown solid with a little conc. H_2SO_4 in a test tube. If trioxonitrate (V) is present, some HNO_3 will be condensed as oily drops on the upper part of the tube. On further heating, the acid decomposes to yield brown fumes of NO_2.

$H_2SO_4(aq) + NO_3^-(aq) \longrightarrow HNO_3(l) + HSO_4^-(aq)$
$4HNO_3(l) \longrightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$

- With copper turnings: warm the mixture of the unknown solid and copper turnings with some conc. H_2SO_4. If a trioxonitrate (V) is present, reddish brown fumes of NO_2 will be formed.

$H_2SO_4(aq) + NO_3^-(aq) \longrightarrow HNO_3(aq) + HSO_4^-(aq)$

$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

Tutorial questions

1. How do we test for trioxonitrates (V) in the laboratory?
2. With the aid of balanced chemical reactions show the thermal decomposition of;
(i) sodium trioxonitrate (V)
(ii) copper (II) trioxonitrate (V) and
(iii) Silver trioxonitrate (V)
3. State three uses of trioxonitrate (V) acid
4. Briefly describe the acidic properties of trioxonitrate (V) acid
5. How is HNO3 produced in the laboratory?

WEEK: 9

TOPIC: SULPHUR AND ITS COMOUNDS

Sulphur is a non-metal in the same family (Group VI) with oxygen in the Periodic Table. Sulphur is different from oxygen in that:

- it is a solid at room temperature
- it shows the valencies of -2, +4 and +6

The electronic configuration of sulphur is $1S^2,2S^2,2P^6, 3S^2,3P^4$ (2,8,6). It gains two electrons from a metallic element to form an ionic bond or shares two pairs of electrons with other non-metallic element to form covalent bond.

Allotropes of sulphur

Allotropy is a phenomenon whereby an element occurs in two or more free forms in the same physical state. The different forms are called isotopes. The main allotropes of sulphur are:

- Rhombic sulphur(α sulphur)
- Monoclinic or prismatic sulphur (β sulphur)
- Amorphous sulphur (δ sulphur) and
- Plastic sulphur

Rhombic sulphur

It is the only stable allotrope of sulphur at temperature below 960C. They are bright yellow and octahedral crystals. They are made up of S8 molecules. Each S8 molecule consists of a ring of 8 atoms. Rhombic sulphur is prepared by allowing a saturated solution of sulphur in carbon (IV) sulphide to evaporate slowly. The octahedral structure will gradually be deposited. The preparation is done in the fume cupboard because of the poisonous and highly inflammable nature of carbon (IV) sulphide.

Monoclinic sulphur

It is the only stable allotrope at temperature between 960C and 1190C. The crystals are long, thin and needle-shaped. They consist of S8 molecules. At room temperature, they slowly revert to rhombic sulphur crystals. The S8 molecules in monoclinic sulphur are more tightly packed; hence, monoclinic sulphur is less dense than rhombic sulphur.

To prepare monoclinic sulphur, some powdered sulphur is heated in a crucible till it melts. Add more; continue heating and stirring at the same time. Repeat the process until the crucible is almost filled with molten sulphur. Allow the molten sulphur to cool. After sometime, a hard crust will be formed at the top. Pierce two holes through the crust and pour off the remaining molten sulphur from inside before removing the crust. Needle-shaped crystals of monoclinic sulphur can be found as deposit on the sides of the crucible. The relationship between rhombic and monoclinic sulphur is shown below.

Between 960C and 1190C
Rhombic sulphur monoclinic sulphur
Below 960C

Comparison between the two allotropes

Property	Rhombic	Monoclinic
Colour	Bright yellow	Amber

Shape Octahedral Needle-shaped
Density (g/cm3) 2.08 1.98
Melting point (0C) 113 119
Stability Below 960C Between 960C and 1190C
Note: 960C is the transition temperature between the two allotropes.

Amorphous sulphur

It has no regular crystalline shape. It is pale yellow in colour and can be prepared in two ways;
- By bubbling hydrogen sulphide through water for a long time and the saturated solution exposed to the air; $2H_2S(g) + O_2(g) \rightarrow 2H_2O(l) + 3S(s)$
- By chemical reaction e.g action of dilute hydrochloric acid on a trioxothiosulphate (VI) solution;

$S2O_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(S)$

Plastic sulphur

It is generally not considered to be a true allotrope of sulphur because it is unstable and reverts to rhombic sulphur on standing. It is regarded as a super-cooled form of sulphur. It is prepared by heating yellow sulphur and pouring it in cold water. It rolls up into yellow ribbons which look like plastic material. It is soft and elastic and does not dissolve in carbon (IV) sulphide.

Physical properties of sulphur

1. It is a yellow solid which exists in two forms; amorphous and crystalline
2. It is insoluble in water but soluble in carbon (IV) sulphide and methyl benzene (toluene)
3. It is a bad conductor of heat and electricity
4. The density depends on the allotropic form
5. The melting point is 1190C and the boiling point is 4440C

Chemical properties of sulphur

Sulphur is a Group VI element. It gains two electrons from Group I or II elements to form sulphide ion; S^{2-}. It also shares electrons with other non-metals to obtain its octet structure. The oxidation state ranges from -2 to +6. The chemical properties include;

Direct combination with other elements.

- With metals: sulphur combines directly with many metals to form sulphides when heated in the absence of air. Reactive metals may not require heat if the metals and the sulphur are finely divided; $Fe(s) + S(s) \rightarrow FeS(s)$
- With oxygen: when heated in a plentiful supply of air, sulphur burns with a bright blue flame to form SO_2 and a small amount of SO_3; $O_2(g) + S(s) SO_2(g)$
- With carbon: sulphur combines with coke in an electric furnace to form a colourless liquid known as carbon (IV) sulphide (CS_2) which vaporizes to form poisonous and highly inflammable fumes;

$C(s) + 2S(s) \rightarrow CS_2(l)$

- With other non-metals: sulphur combines with other non-metals to form various sulphides e.g. disulphide dichloride; $S2Cl_2$, sulphur hexafluoride SF_6.

Reaction with oxidizing acids

When warmed with conc. H_2SO_4, sulphur is oxidized to form sulphur (IV) oxide; SO_2.

$2H_2SO_4(aq) + S(s) \rightarrow 2H_2O(l) + 3SO_2(g)$

With conc. HNO_3 when warmed and using bromine as catalyst, sulphur is oxidized to H_2SO_4.

$6HNO_3(aq) + S(s) \rightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$

Action of hot conc. Alkalis:

When sulphur is reacted with hot. Conc. Alkaline solutions, a mixture of sulphides and trioxosulphate (IV) are formed. In the presence of excess sulphur, a polysulphide and a trioxothiosulphate (VI) are formed respectively.

$3S(s) + 6OH^-(aq) \rightarrow 2S^{2-} + SO_3^{2-} + 3H_2O$
$S^{2-} + nS Sn+1$
2- (where n = 1 – 8)
$SO_3^{2-} + S S2O_3^{2-}$

Uses of sulphur

- It is used to produced SO_2 for the manufacturing of H_2SO_4

- It is used in the vulcanization of rubber
- Sulphur and some of its products are used as fungicides and insecticides for spraying crops.
- It is used to manufacture the bleaching agent used in the pulp and paper industry
- It is used for the production of CS_2, skin ointments, dyes and as sulphides in the manufacture of matches, fireworks and gunpowder.

HYDROGEN SULPHIDE

It occurs naturally in volcanic gases, sulphur springs, coal gas and gases formed during the decay of organic matter containing sulphur.

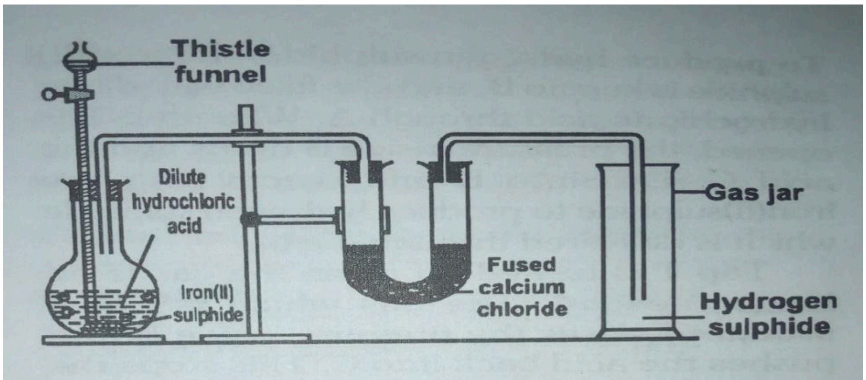
Preparation

Both in the laboratory and commercially, H2S is produced by the action of a dilute acid on a metallic sulphide e.g.

$2HCl(aq) + FeS(s) \longrightarrow FeCl_2(aq) + H_2S(g)$

Ionically; $2H^+(aq) + FeS(s) \longrightarrow Fe^{2+}(aq) + H_2S(g)$

The gas is easily liquefied and stored in steel cylinder for sale.



[redacted] Preparation of dry hydrogen sulphide

Physical properties of H_2S

- It is a colourless gas with a repulsive smell like that of a rotten egg.
- It is very poisonous
- It is about 1.18 times denser than air
- It is moderately soluble in water to form a very weak acidic solution
- It burns with a pale blue flame.

Chemical properties

As an acid:

When H_2S dissolves in water, it ionizes slightly to form a weak, dibasic acid;

$H_2S(g) + H_2O(l) \longrightarrow H_3O^+(aq) + HS^-(aq)$

$HS^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + S^{2-}(aq)$

It reacts with alkali to produce normal salt and water but when H2S is in excess, an acidic salt will be produced.

$2NaOH(aq) + H_2S(g) \longrightarrow Na_2S(aq) + 2H_2O(l)$

$NaOH(aq) + H_2S(g) \longrightarrow NaHS\ (aq) + H_2O(l)$

Excess acid salt

As a precipitating agent

When H_2S is bubbled through the solution of the salts of some metals, coloured sulphides are precipitated e.g.

$ZnSO_4(aq) + H_2S(g) \longrightarrow ZnS(s) + H_2SO_4(aq)$

White

$Pb(CH3COO)_2(aq) + H_2S(g) \longrightarrow PbS(s) + 2CH_3COOH(aq)$

Black

Reaction with oxygen

Although it doesn't support combustion, H_2S burns in a plentiful supply of air with a bright blue flame to produce SO_2. With limited supply of oxygen, a deposit of sulphur may be formed.

$2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(l) + 2SO_2(g)$

Excess supply

$2H_2S(g) + O_2(g) \longrightarrow 2H_2O(l) + 2S(s)$

Limited supply

As a reducing agent

H_2S releases 2 electrons to oxidizing agents in a redox reaction. The H_2S is itself oxidized to sulphur.

$H_2S \rightarrow 2H^+ + S^{2-}$

$S^{2-} \rightarrow S + 2e-$

- ***With acidified $KMnO_4$***

$2KMnO_4(aq) + 3H_2SO_4(aq) + 5H_2S(g) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l) + 5S(s)$

Ionically; $2MnO_4^-(aq) + 6H^+(aq) + 5H_2S(g) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5S(s)$

Purple pale pink

- ***With acidified $K_2Cr_2O_7$***

$K_2Cr_2O_7(aq) + 4H_2SO_4(aq) + 3H_2S(g) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3 (aq) + 7H_2O(l) + 3S(s)$

Ionically: $Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S(g) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3S(s)$

Orange green

- ***With halogens:***

In the presence of moisture, H_2S is oxidized by halogens to sulphur.

$Cl_2(g) + H_2S(g) \rightarrow 2HCl(g) + S(s)$

- ***With $FeCl_3$:***

$2FeCl_3(aq) + H_2S(g) \rightarrow 2FeCl_2(aq) + 2HCl(aq) + S(s)$

Brownish yellow green

- ***With SO_2;***

H_2S is a stronger reducing agent than SO_2. It reduces SO_2 to sulphur in the presence of moisture.

$SO_2(g) + 2H_2S(g) \qquad 2H_2O(l) + 3S(s)$

- ***With oxidizing agents***

Oxidizing acids convert hydrogen sulphide to sulphur. Meanwhile, conc. HNO_3 being a very strong oxidizing acid converts H_2S to H_2SO_4

$H_2SO_4(aq) + H_2S(g) \rightarrow 2H_2O(l) + SO_2(g) + S(s)$

$2HNO_3(aq) + H_2S(g) \rightarrow 2H_2O(l) + 2NO_2(g) + S(s)$

$8HNO_3(aq) + H_2S(g) \rightarrow 4H_2O(l) + 8NO_2(g) + H_2SO_4(aq)$

Test for H_2S

The gas can be suspected by its odour. It smells like rotten egg. To confirm the gas, moisten a piece of filter paper with $Pb(NO_3)_2$ solution and drop it in a gas jar containing the unknown gas. If the gas is H_2S, the paper will turn black due to the formation of PbS.

$Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq)$

Note: lead (II) ethanoate also gives the same reaction with H_2S.

Uses of H_2S

It is used in the analysis of ores and metals. The presence of certain metals is often indicated by its colour. Also the sulphides of metals have different solubility in acids and alkalis.

SULPHIDES

Almost all sulphides except Na, K and NH_4 – sulphides are insoluble in water. Some of the insoluble sulphides are however soluble in dilute HCl while others are not.

Preparation of sulphides

- Neutralization: the three soluble sulphides are prepared by bubbling H2S through the corresponding alkalis e.g. $2NaOH(aq) + H_2S(g) \rightarrow Na_2S(aq) + 2H_2O(l)$

- By direct combination: FeS and ZnS can be prepared by heating a mixture of the metal and sulphur e.g. $Fe(s) + S(s) \rightarrow FeS(s)$

- By precipitation: insoluble sulphides are prepared by bubbling H2S through a solution of the corresponding salts e.g. $SnCl_2(aq) + H_2S(g) \rightarrow SnS(s) + 2HCl(aq)$

Dark brown

Properties of sulphides

Reaction with oxygen

Except mercury (II) sulphide which yields the metallic mercury, most metallic sulphides when heated in air or oxygen produce the corresponding metallic oxides and sulphur (IV) oxide. This reaction is used for the extraction of metals from their naturally occurring sulphides.

$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$

$HgS(s) + O_2(g) \longrightarrow Hg(l) + SO_2(g)$

Reaction with dilute hydrochloric acid

When heated with HCl(aq), most sulphides yield H_2S. This reaction is used to test for sulphide. However, sulphides which are insoluble in dilute hydrochloric acid must first be fused with sodium trioxocarbonate (IV) before the test is carried out.

$PbS(S) + 2HCl(aq) \longrightarrow PbCl_2(s) + H_2S(g)$

Uses of sulphides

- FeS is reacted with dilute hydrochloric acid in the kipp's apparatus to obtain an immediate supply of H_2S in the lab.
- ZnS is used to coat the inside of television screen as it fluoresces when exposed to light
- Tin (IV) sulphide is used in paints

Tutorial questions

- What is allotropy? List four allotropes of sulphur
- State four physical properties of hydrogen sulphide
- With two balanced chemical equations, show the reducing action of hydrogen sulphide
- State five physical properties of sulphur
- Describe the laboratory test for S^{2-}.

WEEK: 10

TOPIC: SULPHUR AND ITS COMPOUNDS

TRIOXOSULPHATE (IV) ACID – H_2SO_3

It is an unstable acid formed when SO_2 dissolves in water. It is dibasic and decomposes readily to yield SO_2 and water.

$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$

Preparation of H_2SO_3

It is prepared by adding conc. HCl to Na_2SO_4 and heating the mixture gently. The SO_2 liberated is then dissolved in water to form H_2SO_3.

Physical properties

- It is a colourless and unstable acid
- It smells strongly of SO_2, which is a product of its decomposition.
- It turn blue litmus paper red.

Chemical properties

1. **Action on air:** when exposed to air for sometimes, H_2SO_3 becomes oxidized by the atmospheric oxygen to H_2SO_4:

$2H_2SO_3(aq) + O_2(g) \longrightarrow 2H_2SO_4(aq)$

2. **As a reducing agent and bleaching agent:** H2SO3 is responsible for all the bleaching and reducing action of SO_2.

3. **As an acid:** H_2SO_3 as a weak dibasic acid forms both acid and normal salts with alkalis.

$NaOH(aq) + H_2SO_3(aq) \longrightarrow NaHSO_3(aq) + H_2O(l)$

$2NaOH(aq) + H_2SO_3(aq) \longrightarrow Na_2SO_3(aq) + 2H_2O(l)$

Uses of H_2SO_3

- It is used for bleaching straw and other fabrics.
- It is used as a germicide

TRIOXOSULPHATES (IV)

These are normal salts formed when SO_2 or H_2SO_3 reacts with excess alkalis e.g.

$H_2SO_3(aq) + 2KOH(aq) \longrightarrow K_2SO_3(aq) + 2H_2O(l)$

$SO_2(g) + 2NaOH(aq) \longrightarrow Na_2SO_3(aq) + H_2O(l)$

Preparation of trioxosulphates (IV)

1. **By neutralization:** SO_2 dissolves in excess KOH and NaOH to produce K_2SO_3 and Na_2SO_3 respectively. H_2SO_3 also reacts with excess of these alkalis to produce the corresponding salt.

2. By precipitation: when SO_2 is bubbled through a solution of metallic salt, the corresponding insoluble trioxosulphate (IV) are precipitated out e.g.

$SO_2(g) + H_2O(l) + Zn(NO_3)_2(aq) \longrightarrow ZnSO_3(aq) + 2HNO_3(aq)$

Properties of trioxosulphates (IV)

1. **Solubility:** only the trioxosulphates (IV) of NH_4, K, Na and Ca are soluble in water. All other trioxosulphates (IV) are insoluble.
2. **Reaction with acids:** they liberate SO_2 when heated with conc. Or dilute acids e.g.
$CaSO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + SO_2(g)$
3. **Reaction with air:** when exposed to the air, trioxosulphates (IV) are slowly oxidized to tetraoxosulphates (VI). The reaction is more rapid when some other oxidizing agents are used.
4. **As a reducing agent:** they are good reducing agents when in dilute acidified solution.

Test for trioxosulphates(IV)

- Warm the unknown substance with a dilute acid. If it is trioxosulphate(IV), SO_2 will be evolved.

$2H^+(aq) + SO_3^{2-}(aq) \longrightarrow SO_2(g) + H_2O(l)$

- Add some $Ba(NO_3)_2$ to a solution of the unknown substance. A white precipitate of $BaSO_3$ will be formed. If the unknown solution is trioxosulphate (IV), the precipitate will dissolve in dilute HNO_3 with the evolution of SO_2.

$Ba^{2+}(aq) + SO_3^{2-} \longrightarrow BaSO_3(s)$

$BaSO_3(s) + 2HNO_3(aq) \longrightarrow SO_2(g) + Ba(NO_3)_2(aq)$

TETRAOXOSULPHATE (VI) ACID – H_2SO_4

It is a heavy chemical. Almost all manufacturing processes make use of it directly or indirectly.

Industrial preparation of H_2SO_4 (contact process)

The steps involved can be summarised as follows;

- SO_2 which is obtained by burning sulphur in dry air or by roasting sulphide ore is catalytically combined with oxygen to form SO_3.

$S(s) + O_2(g) \longrightarrow SO_2(g)$

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) + heat$

Note: SO_2 is usually mixed with excess air and passed through an electric chamber to remove the impurities and dusts that could kill the catalyst. The gaseous mixture is then passed through conc. H_2SO_4 to remove moisture before the gases are delivered into the reaction chamber or contact chamber. The SO_2 and O_2 combine in the contact chamber in the presence of vanadium (V) oxide catalyst at a temperature of $450^0C – 500^0C$ and atmospheric pressure to yield SO_3.

- The SO_3 is cooled and passed into an absorption chamber where it dissolves in conc. H_2SO_4 to produce a very thick liquid called oleum;

$SO_3(g) + H_2SO_4(aq) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7}$

- The oleum is diluted with calculated amount of water to produce the 98% H_2SO_4 used in the labs. Other desired concentration can also be obtained depending on the amount of water added.

Note: SO_3 is not dissolved directly in water because the process would evolve enough heat to cause the acid solution to boil, thereby producing a mist of acid droplets which would spread throughout the factory.

Contact process at a glance

O_2 conc. H_2SO_4 H_2O

$S + O_2 \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2S_2O_7 \longrightarrow H_2SO_4$

Physical properties of H_2SO_4

- Conc. H_2SO_4 (oil of vitriol) is a colourless, viscous liquid with a density of 1.84gcm-3
- It is very corrosive
- It turn blue litmus paper red
- Conc. H_2SO_4 has a great affinity for water. Hence, it dissolves readily in water.
- Conc. H_2SO_4 is hygroscopic

Chemical properties of H_2SO_4

1. As an acid: the acid properties of dilute H_2SO_4 is shown in its reaction with metals, bases and trioxocarbonates (IV) e.g.

$H_2SO_4(aq) + Zn(s) \longrightarrow ZnSO_4(aq) + H_2(g)$
$H_2SO_4(aq) + MgO(s) \longrightarrow MgSO_4(aq) + H_2O(l)$
$H_2SO_4(aq) + CuCO_3(aq) \longrightarrow MgSO_4(aq) + H_2O(l) + CO_2(g)$

Note: H_2SO_4 is a dibasic acid. It can form both acid and normal salts.

2. As an oxidizing agent: Hot conc. H2SO4 accept electrons from reducing agents. The oxidation number of sulphur hence changes from +6 to +4 e.g.

$Zn(s) + 2H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + 2H_2O(l) + SO_2(g)$
$C(s) + 2H_2SO_4(aq) \longrightarrow CO_2(g) + 2H_2O(l) + 2SO_2(g)$
$H_2S(s) + H_2SO_4(aq) \longrightarrow SO_2(g) + 2H_2O(l) + S(s)$

3. As a dehydrating agent: Conc. H_2SO_4 removes water molecules from compounds like sugar, ethanol, methanoic acid and ethanedioic acid. This removal of water from compounds is called dehydration reaction.

$C_{12}H_{22}O_{11}(s)$ - 11$H_2O(l)$ 12C
Sucrose conc. H2SO4 sugar charcoal
CH2OH-H2O(l) C2H2(g) CH2OH (l) conc. H_2SO_4

The dehydration reaction of H_2SO_4 accounts for:

- The corrosive action of the acid on cloth, paper, wood, skin etc
- Removal of water of crystallization from hydrated salts to produce anhydrous salts e.g.

$CuSO_4.5H_2O \longrightarrow 5H_2O(l) + CuSO_4$
Blue conc.H2SO4 white

4. Displacement of other acids from their salts: conc. H_2SO_4 displaces volatile acids from their salts e.g.

$KCl(s) + H_2SO_4(aq) \longrightarrow KHSO_4(aq) + HCl(g)$
$NaNO_3(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$

The reactions depend solely on the boiling point of the acids. HCl and HNO_3 distil over as gases.

Uses of H_2SO_4

1. Production of fertilizer; $Ca(HSO_4)_2$ and $(NH_4)_2SO_4$
2. Production of pigments e.g titanium (IV) oxide used in paint and dyes
3. For making cellulose film, natural and artificial fabrics and plastics.
4. Purification of crude oil and manufacturing of artificial silk
5. To clean or pickle metals before electroplating or enamelling
6. Used as drying agent for many gases except alkaline gas (NH_3) and reducing gases like H_2S
7. Used in the preparation of many important chemical compounds like HCl, HNO_3 etc

TETRAOXOSULPHATES (VI)

They are the normal salts formed when all the H+ in H2SO4 are replaced by metallic metallic or ammonium ion. Most of them are crystalline and soluble in water. The insoluble ones are $CaSO_4$, $PbSO_4$, $BaSO_4$ and Hg_2SO_4

Laboratory preparation

They are prepared in the laboratory by any of the standard methods used for the preparation of salts depending on the position of the metallic radical in the electrochemical series and the nature of the tetraoxosulphate (VI). The table below shows the methods:

Metal Method of preparation of SO4

K
Na

By the action of dil. H_2SO_4 on the oxides, hydroxides or the trioxocarbonates(IV) of the metal e.g.

$H_2SO_4(aq) + CaO(s) \longrightarrow CaSO_4(aq) + H_2O(l)$
Ca $H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

Mg
Al
Zn
Fe

By the action of dil. H_2SO_4 on the metals, their oxides or their trioxocarbonates (IV) aluminium requires the action of conc. H_2SO_4 e.g.

$H_2SO_4(aq) + Mg(s) \longrightarrow MgSO_4(aq) + H_2(g)$
$H_2SO_4(aq) + ZnO(s) \longrightarrow ZnSO_4(aq) + H_2O(l)$
$H_2SO_4(aq) + FeCO_3(s) \longrightarrow FeSO_4(aq) + CO_2(g) + H_2O(l)$
Pb. By double decomposition e.g.
$Pb(NO_3)_2(aq) + Na_2SO_4(aq) \longrightarrow PbSO_4(s) + 2NaNO_3(aq)$
Cu
Hg
Ag
By the action of hot. Conc. H_2SO_4 on the metals e.g.
$Hg(l) + 2H_2SO_4(aq) \longrightarrow HgSO_4(aq) + 2H_2O(l) + SO_2(g)$
$2Ag(s) + 2H_2SO_4(aq) \longrightarrow Ag_2SO_4(aq) + 2H_2O(l) + SO_2(g)$

Properties of tetraoxosulphates(VI)

- Most of them are colourless and crystalline
- The soluble ones form hydrated salts/crystals
- The tetraoxosulphates (VI) of Na, K and Ca are very stable to heat while those of metals lower in the electrochemical series tend to decompose on heating.
- When the hydrated tetraoxosulphate (VI) of Zn^{2+}, Cu^{2+} and Fe^{2+} are heated, they lose their water of crystallization in stages. Further heating of the anhydrous salts brings about their decomposition into metallic oxides, sulphur (IV) oxides and trioxosulphates (IV).

Uses of tetraoxosulphates (VI)

- Na_2SO_4 and $MgSO_4$ are used as laxatives
- $(NH_4)_2SO_4$ is used as fertilizer
- For the production of SO_2
- BaSO4 is used in the production of paints
- For the production of plaster of paris PoP

Test for tetraoxosulphate (VI)

Put some of the unknown solution in a test tube and acidify it with dilute HCl. Then add a few drops of $BaCl_2$ solution. A white precipitate of BaSO4 is formed if the unknown solution contains SO_4^{2-}
The precipitate remains insoluble in an excess of the dilute acid.
$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO4(s)$
Note: the acidification process is important to prevent the precipitation of other insoluble barium compounds like $BaSO_3$ or $BaCO_3$ which are soluble in the acidic solution.
Dilute HNO_3 and $BaNO_3$ can also be used instead of HCl and $BaCl_2$.
Assignment

Tutorial questions

- Briefly describe the contact process
- State three physical properties of H_2SO_4
- Describe any two chemical properties of H_2SO_4. Balance chemical equations important
- State three uses of H_2SO_4.
- State a laboratory test to distinguish between SO_3^{2-} and SO_4^{2-}.
- State the method of preparation of the tetraoxosulphates (VI) of (i) lead (ii) zinc