**EUCHARISTIC HEART OF ESUS MODEL COLLEGE, ILORIN.**

**SS II CHEMISTRY NOTE FOR SECOND TERM 2024/2025 ACADEMIC SESSION**

**Scheme of work**

**Lesson I - Energy and chemical reactions**

**Lesson II - Chemical thermodynamics**

**Lesson III - Chemical equilibrium**

**Lesson IV - Halogens**

**Lesson V - Nitrogen and its compounds**

**Lesson VI - Shapes of molecules**

**Lesson VII - Silicon and its compounds**

**ENERGY & CHEMICAL REACTION [Thermochemistry]**

Energy is defined as the ability to do work. It exists in different forms such as **potential** energy (stored energy), **kinetic** (energy of motion) energy, **heat** or **thermal** energy, **light** energy, **electrical** energy, **sound** energy, **chemical** energy and **nuclear** energy. The various forms of energy are interconvertible. For example, the food we eat contains chemical energy which is converted to heat energy (to keep us warm) and kinetic energy (to enable us do work). An electric bulb converts chemical energy to heat and light energy. When energy is converted from one form to another, the total amount of energy before and after conversion remains the same that is the Law of conservation of energy.

Energy changes occur in chemical reactions as reactants change to products because each of them possess different amount of chemical energy. These energy changes can be observed in the form of:

1. Heat e.g when a strong acid is mixed with a strong base
2. Sound and heat e.g when a mixture of hydrogen and oxygen is ignited
3. Light and heat e.g when Magnesium is burnt in air.

**UNIT OF ENERGY**

It is not possible to measure the absolute heat of any substance but we can measure the heat change during inter conversion. The unit of energy is the JOULE (J). 1000J = 1kJ

1 calorie = 4.18 joules = 4.2 joules

One joule is the energy required to raise the temperature of 1g of water by 0.239K.

**TERMINOLOGIES**

1. **Thermochemistry or energetics** is the study of heat changes which accompany physical and chemical changes e.g chemical reactions, formation of solutions or change of state.
2. **Thermodynamics**: This is the flow of heat energy in a chemical system
3. **System**: A material under study. A substance or mixture of substances in which a change occurs.
4. **Surrounding**: This is the portion of matter which is not under study but can exchange materials with the system. It is everything in the vicinity of the thermodynamic system.
5. **Isolated** **system** does not exchange heat energy or matter with its surrounding e.g a vacuum flask or a lagged container
6. **Open** **system** exchanges both heat energy or matter with its surrounding e.g a reaction in an open test tube or beaker
7. **Closed** **system** exchanges only heat energy with its surrounding e.g collection of a gas over water

**HEAT CONTENT AND HEAT OF REACTION**

**Heat** **content** or **enthalpy** is the characteristic internal energy possess b substance a due to its structure and physical state. In any reaction, since the heat contents of reactants are different, energy is either absorbed or evolved.

The heat (or energy) content of a substance is represented by the letter ‘**H**’ while the change in heat content during a reaction is represented as **∆H (delta H)** and is known as **enthalpy change**. (∆is a Greek letter meaning “change in”)

*Mathematically*,

**∆H =** [Heat content of product - Heat content of reactant ]

i.e ∆H = Hp - Hr

The heat change, **∆H** is written alongside the chemical equation for a given chemical change.

e.g 2H2(g) + O2(g) 2H2O(l) **∆H =** -571.16kJmol-1

For one mole, H2(g) + ½O2(g) H2O(l) **∆H =** -285.58kJmol-1

The same amount of energy must be supplied during electrolysis of water to split it into its molecules.

For one mole, H2O(l) → H2(g) + ½O2(g) **∆H** = + 285.58kJmol-1

**Activated** **complex** is the intermediate complex/ transition state that reactants must attain in order to form a product.

Two types of reaction can occur in a thermodynamic system (thermochemical reaction). They are:

1. Exothermic reaction
2. Endothermic reaction

**EXOTHERMIC REACTION**

This is a reaction in which heat energy is given out to the surrounding from the reacting system. This arises because the heat content of the product is less than that of the reactant i.e Hproduct  < Hreactant , therefore **∆H** will be negative. The excess energy is given off as heat. Since there is a rise in temperature, the reaction vessel feels warm to touch

Some examples of exothermic reactions are:

1. Reaction between an acid and a base

HCl(aq) + NaOH(aq) NaCl(s) + H2O(l) **∆H= -ve**

1. Reaction between calcium oxide and water

CaO(s) + H2O(l)  Ca(OH)2(s)

1. Combustion reactions
2. Dissolution of NaOH, KOH and SO3 in water
3. Addition of water to concentrated acid

Fig: Energy Profile Diagram for an Exothermic Reaction

**ENDOTHERMIC REACTION**

This is a reaction in which heat energy is absorbed from the surrounding into reacting system. This is because the heat content of the product is greater than that of the reactant particles i.e Hproduct > Hreactant, therefore **∆H** will be positive. Heat energy is absorbed from the surrounding for the reaction to proceed. Since there is a drop in temperature, the reaction vessel feels cold to touch.

Some examples of endothermic reactions are:

1. Dissolving potassium trioxonitrate (V), ammonium trioxonitrate and sodium ethanoate in water

KNO3(s) + H2O(l) KNO3(aq) **∆H= +ve**

1. Thermal decomposition of ammonium chloride

NH4Cl(s) NH3(g) + HCl(g) **∆H= +ve**

Fig: Energy Profile Diagram for an Endothermic Reaction

**Students’ Exercise:**

1. The formation of water gas is represented by the equation below:

C(s) + H2O(g) CO(g) + H2(g) **∆H = +**131 kJmol-1

Draw an energy profile diagram for the reaction showing the

1. activated complex
2. enthalpy of reactants

**HEAT OF REACTION AND CHEMICAL BONDS**

In any chemical reaction, the atoms or ions in the reactant molecule regroup themselves to form particles of the product. The bonds in the reactants are broken to form new bonds in the product. For bond breaking and bond formation to occur, there must be collision of the reactant particles. Chemical energy is the energy change which occur as a result of breaking or formation of bonds. Energy is absorbed when bonds are broken so it is an endothermic process. Energy is evolved when bonds are formed, so it is an exothermic process.

**HEATS OF CHEMICAL REACTION**

**Heat** **of** **reaction** is the energy changes that accompany a chemical reaction. The standard heat of reaction is the amount of heat evolved or absorbed when a chemical reaction occurs between molar quantities of the substances represented in the equation of reaction under standard conditions. The value of heat change, ∆H of chemical reaction is not fixed. It is dependent on the conditions under which the measurement is made. It is therefore necessary to state under what conditions the measurement of heat change is made. For accurate comparison of changes of different reactions, measurements are made under the **standard** conditions. The conditions are as follow:

1. Standard temperature = 298K or 250C
2. Standard pressure = 1 atm
3. Solution must have concentration of 1moldm-3
4. Substances involved must be in their normal physical states at standard temperature & pressure.

Standard heat change is denoted as ∆Hθ

The physical state of the reactants in a chemical reactants in a chemical reaction must be indicated as solids (s), liquid (l) and gas (g). The heat evolved when a given amount of sodium hydroxide is neutralized by hydrochloric acid is greater when hydrochloric acid gas than when hydrochloric acid is used for the reaction. This is because the HCl gas first dissolves in water with the evolution of heat (heat of solution)

**Measurement of Heat Change**

**Heat of Reaction:** is the enthalpy change when the numbers of moles of reactants as indicated in the balanced equation reacts together under standard conditions of temp (298K) and pressure (1 atm) e.g. N2(g) + 3H2(g) → 2NH3(g) ; ∆Hθ = - 92kJmol-1

The instrument used for measuring heat change **(∆H)** for a chemical reaction is the ***calorimeter***. A simple calorimeter consists of a smaller beaker placed inside a bigger beaker. The smaller beaker is lagged from the bigger one using cotton wool to minimise heat loss. Inside the smaller beaker is placed a stirrer and a thermometer. The diagram is as shown below:

There are two types of calorimeter:

1. Bomb calorimeter: used in nutrition studies and very sensitive
2. Glass calorimeter: used in chemical reactions.

The heat energy evolved or absorbed is known by recording the temperatures of the system before and after the reaction.

To calculate the **∆H** for a particular reaction mixture, we must know the

1. Temperature change
2. Mass of reactants
3. Specific heat capacity of the reaction mixture

**Types of Heat Change in chemical reactions**

It is possible to identify heat change in chemical reactions, depending on the type of reaction in which it occurs. These heat changes are

1. Heat of formation, ∆HӨf
2. Heat of combustion, ∆HӨc
3. Heat of neutralization, ∆HӨn
4. Heat of solution ∆HӨs
5. Heat of vaporization ∆HӨvap
6. Heat of fusion ∆HӨfus
7. Heat of hydrogenation ∆HӨh
8. Heat of atomization of a compound ∆HӨato
9. Heat of atomization of an element ∆HӨato

**Enthalpy of formation:** This is the amount of heat evolved or absorbed (enthalpy change) when a substance is formed from its constituent elements.

**Standard Heat of Formation:** Standard heat of formation (∆Hf Ө) is the enthalpy change when one mole of a substance is formed from its constituent elements under standard conditions e.g.

C(s) + H2(g)  CH4(g) ;∆Hf Ө = -749KJmol-1

H2(g) + ½ O2(g) H2O(g) ; ∆Hf Ө = -285. 58 KJmol-1

C(s) + 2S(s)  CS2(s) ; ∆Hf Ө = +90 KJmol-1

An element in its standard state (most stable state) has zero standard heat of formation

**Enthalpy of combustion/Standard Heat of Combustion (**∆HcӨ)**:** This is the amount of heat evolved (enthalpy change) when a mole of substance is completely burned in oxygen under standard conditions. Combustion is the rapid reaction of a substance with oxygen being accompanied by heat and light. It is an exothermic process. e.g.

C2H6(g) + ½ O2(g) 2CO2(g) + 3H2O(g) ; ∆HcӨ = -1559.5 KJmol-1

Heat of combustion is very important as many industrial and domestic processes require burning of fuel as source of energy. Internal biological combustion of food provides energy for use by the living body.

The heat of combustion is determined accurately with the aid of **bomb calorimeter.** It consists of a cylindrical vessel lined with enamel to prevent corrosion. A known mass (e.g 1g) of the test substance is placed in a platinum crucible and placed inside the bomb. The lid is screwed and Oxygen is pumped inside the bomb through a valve until the pressure is 20 atm. The valve is closed. The bomb is immersed in a known mass of water in a well lagged calorimeter and left to attain a steady temperature. The temperature is recorded. The test substance is ignited electrically by passing a current through the ignition coil. The temperature of the water which is stirred continuously is recorded at a 30-second interval until a maximum constant temperature is attained. The heat of combustion can be calculated knowing

1. Heat capacity of the whole system ( bomb calorimeter, water, thermometer, calorimeter and stirrer)
2. The temperature rise
3. Heat generated by the heating coil

**Estimation of Heat of Combustion of Ethanol**

***Aim:*** To determine the heat of combustion of ethanol

***Apparatus:*** Thermometer, retort stand with clamp, thin walled tin can, plastic cup, thick measuring cylinder and balance.

***Method:*** Take the thin walled can, weigh it and then re-weigh with about 100g of H2O. Find the exact mass of H2O used. Fill the spirit lamp half full of ethanol & assemble the lid and wick. The wick should be inside the ethanol. Weigh the lamp with ethanol before the experiment. Clamp the tin can above the specimen bottle, insert the thermometer and record the initial temp of the H2O. Light the spirit lamp at the bottom of the can and heat the water in it. Ensure the flame remains steady, stir the water frequently with a thermometer until the temp increases by approximately 250C. Record it, put out the flame and reweigh the lamp with ethanol.

***Specimen Result:***

Initial temp of H2O = 24.60C

Final temp of H2  = 49.40C

Mass of H2O in tin can = 100g

Mass of lamp + ethanol before burning = 32.05g

Mass of lamp + ethanol after burning = 31.65g

Mass of ethanol used = 0.40g

Heat Capacity of H2O = 4.2JK-1g-1

**Solution**

RMM of ethanol C2H50H = (12 x 2) + (1 x 5) + (16 x 1) + (1 x 1) = 46g/mol

No of mole of ethanol burned = Mass of ethanol = 0.40 = 0.0087mol

RMM of ethanol 46

Heat evolved = mcΔӨ → 100 x 4.2 x (49.4 – 24.6)

= 10416J

If 0.0087 moles of ethanol produce 10416J of heat

1 mole will produce = 10416 x 1

0.0087

= 1197000J

= -1197kJmol-1

**Note**: The standard heat of formation of CO2 is the same as the standard heat of combustion of carbon

**Enthalpy of Neutralization/Standard Heat of Neutralization (**∆HnӨ): is the amount of heat evolved (enthalpy change) 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 conditions e.g

HCl(aq) + NaOH(aq) NaCl + H2O(l) ;∆H= -57.3kJmol-1

H+ (aq) + OH- (aq) H2O ; ∆H= -57.3kJmol-1

The dilute solutions of HCl and NaOH are completely ionized. The only change that actually occurs is the formation of water molecules, H2O. Therefore the heat of neutralization is merely the heat of formation of one mole of water from its ionic components and that is about -57.4kJmol-1.

Thus the heat of neutralization of any strong acid and a strong base is approximately the same e.g

KOH(aq) + HNO3(aq) KNO3(aq) + H2O(l) ; ∆H= -57.3kJmol-1

2NaOH(aq) + H2SO4(aq) Na2SO4 + 2H2O(l) ; ∆H= (-57.3 X 2) kJmol-1

When weak acids or bases are involved, the heat of neutralization is less because the reactants are only partially or incompletely ionized in solutions. Energy is used up in drawing apart the undissociated ions before they can react. The heat of neutralization is only the net heat change and is less than 57.4kJmol**-**1 by the amount of energy needed to bring about the dissociation of the weak acids or base e.g

NH3.H2O**(aq)** + HCl **(aq)** NH4Cl **(aq)** + H2O**(l)** ;∆H= -51.5kJmol-1

NH3.H2O**(aq)** + HCN **(aq)** NH4CN **(aq)** + H2O**(l)** ;∆H= -41.4kJmol-1

NH3.H2O**(aq)** + CH3COOH**(aq)** CH3COONH4**(aq)** + H2O**(l)** ;∆H= -55.2kJmol-1

NH3.H2O**(aq)** + NaOH**(aq)** NaNH4**(aq)** + H2O**(l)** ;∆H= -51.5kJmol-1

**DETERMINATION OF HEAT OF NEUTRALIZATION**

**Aim:** To determine the heat of neutralization when HCl**(aq)** reacts with NaOH**(aq)**

**Apparatus:** 250cm3 beakers, thermometer, stirrer and cotton wool

**Reagents:** HCl(aq) and NaOH(aq)

**Method:** Pipette 100cm3 of 0.5M HCl into the beaker, record the temperature of the solution. Pipette 100cm3 of 0.5M NaOH into another beaker and record the temperature. Find the mean value of the two temperature readings. As rapidly as possible, add the NaOH solution to the acid in the beaker. Stir well with thermometer and record the highest temperature attained.

**Specimen results:**

Volume of 0.5M HCl solution = 100cm3

Volume of 0.5M NaOH solution = 100cm3

Initial temp of HCl = 26.0°C

Initial temp of NaOH = 27.0°C

Final temp of reaction mixture = 29.9°C = 302.9k

**Calculation**

Total mass of reaction mixture =100g

Total volume of reaction mixture = 200cm3 (100 + 100) and it has an approximate of 200g

Initial temp of reaction mixture = Average temperature of the two reactant solutions

= 26.0 + 27.0 = 26.5°C

2

Convert to Kelvin = 26.5 + 273

= 299.5K

Temp rise for the reaction mixture = final temp – initial temp = ( 302.9 - 299.5)K

= 3.4K

Taking the heat capacity of water = 4.2JK-1g-1

Total heat evolved = mass x specific heat capacity x temp rise = 200 x 4.2 x 3.4 = 2856J

Equation of the reaction

NaOH**(aq)** + HCl**(aq)** NaCl**(aq)** + H2O**(l)**

Since the molarity of HCl = 0.5M

Recall: molarity = Mol x 1000

Vol

Mole = molarity x vol OR n = CV = 0.5x 100 = 0.050mol of HCl

1000 1000

And molarity NaOH = 0.05M

Mole = Molarity x vol = 0.05 x 100 = 0.05mol of NaOH

1000cm3 1000

0.05 mole of HCl reacts with 0.05 mole of NaOH to produce 0.05mole of H2O

If 0.05mole of water evolves 2856J,

1 mole of water will evolve 1 x 2856

0.05 = 57120 J = 57.1kJ

**Conclusion:** The standard heat of neutralization of NaOH by HCl is –57.1KJmol-1

**Student’s exercise:** Describe an experiment to determine the heat of neutralization between equimolar concentrations of trioxonitrate (V) acid and potassium hydroxide

**Heat of Solution:** - Is the amount of heat evolved or absorbed (heat change) when one mole of a substance is dissolved in such an amount of water that further dilution results in no detectable heat change. The change may be exothermic or endothermic. Generally, the dissolution process of solute substances in water involves two steps: They are:

1. Water molecules splits up ions in the crystal into free ions. This process needs energy called **lattice** energy(endothermic process)
2. The free ions are then hydrated by water molecules due to attraction between the ions and dipolar water molecules. This process evolves energy known as **hydration** energy. (exothermic process)

If lattice energy < hydration energy, then dissolution is exothermic.

It is endothermic if lattice energy > hydration energy.

**Example**

If the heat of solution of potassium chloride is +24kJmol-1 and its lattice energy is -710kJmol-1, calculate its hydration energy.

Dissolution rate is affected by the relative amounts of solute and solvent. If a concentrated solution is diluted, there is a further heat change known as heat of dilution. Heat of dilution decreases with increase in the quantity of the diluents.

|  |  |  |
| --- | --- | --- |
| **Solute** | **Heat change** | **∆HsӨ** |
| NH4Cl | Endothermic | +15.1 |
| NaCl | Endothermic | +38 |
| NH4NO3 | Endothermic | +26.3 |
| NaOH | Exothermic | -43.0 |
| KOH | Exothermic | -54.9 |
| Na2CO3 | Exothermic | -25.0 |

Solids with negative value are more soluble than that with positive values. Solubility varies with change in temperature, a solute which dissolves exothermically would be more soluble at a lower temperature and a solute which dissolves endothermically would be more soluble at a higher temperature.

**Experimental data**

When 5.6g of potassium hydroxide is dissolved in 100cm3 of water, the following results were obtained:

Mass of water = 31.65g

Initial temperature of water = 25

Final temperature of water = 38

Temperature change = 38 – 25 = 13

Heat Capacity of H2O = 4.25JK-1g-1

**Solution**

**Molar Heat of vaporization** ∆HӨvap**:** Is the amount of heat absorbed (heat change) when one mole of a liquid is vaporized at its boiling point. It is always positive.

H2O(l) → H2O(g)  ; ∆HӨvap = + 41.4kJmol-1

**Molar Heat of fusion** ∆HӨfus**:** - Is the amount of heat evolved or absorbed (heat change) when one mole of a solid is melted.

S(s) → S(l)  ; ∆HӨvap = + 2.0kJmol-1

**Heat of sublimation** ∆HӨSub**:** Is the amount of heat evolved or absorbed (heat change) when one mole of a solid is converted to a gas under standard conditions.

C(s) → C(g)  ; ∆HӨSub = +718.0kJmol-1

**Molar Heat of hydrogenation** ∆HӨh**:** - Is the amount of heat evolved or absorbed (heat change) when one mole of an unsaturated organic compound is converted corresponding saturated organic compound by reacting with hydrogen under standard conditions.

C2H4(g) + H2(g) → C2H6(g) ; ∆HӨ = - 126 kJmol-1

**Heat of Atomization of an Element:**  is the enthalpy change when one mole of gaseous atom is formed from its element in its physical state under standard conditions of temperature (298K) and pressure (1 atm) e.g.

½ H2(g) → 2H(g)  ; ∆Hat (½H2) = + 218kJmol-1

**Heat of Atomization of a Compound:** is the enthalpy change when one mole of the compound is converted into gaseous atom under standard conditions of temp (298K) and pressure (1 atm) e.g

CH4(g)  C(g ) + 4H(g)  ; ∆Hat (CH4)g = +1622kJmol-1

**Heat of Transformation:** Is the amount of heat evolved or absorbed (heat change) when one mole of an allotropic form changes to another.

C(graphite) → C(diamond)  ; ∆HӨvap = + 2.0kJmol-1

**Calculations involving heat energy change**

**Example 1**

4.5g of liquid water was formed by burning hydrogen in oxygen. -72kJ mol-1 of energy was given off. Calculate the heat of formation of water.

**Solution**

**Example 2**

-57.4kJ mol-1 of heat was evolved when one mole of hydrogen ions H+ from a strong acid neutralized one mole of a hydroxyl ion OH-. Calculate the heat evolved when

a. 2 moles of H+

b. 0.5 moles of H+ is used

c. calculate the number of moles of H+ that would be produced by the liberation of -5.74kJ mol-1 of heat?

**Solution**

**Example 3**

When 100cm3 of 0.1M NaOH at 21°C was added to 100cm3 of 0.1M HCl at 20°C, the temperature of the mixture rose to 26.8°C. Calculate the heat of neutralization given that the specific heat capacity is 4.2JK-1g-1.

**Solution**

**Example 4**

When 4.60g of ethane was burnt in oxygen, the heat liberated raises the temperature of 100g of water from 30°C to 45.5°C. What is the heat of combustion of ethane given that the specific heat capacity of water is 4.2JK-1g-1

**Solution**

**Example 5**

The heat of solution of Ammonium trioxonitrate(V) solution is +26kJ mol-1. Calculate the quantity of heat absorbed when

1. 2 mole of NH4NO3 was dissolved
2. 5g of NH4NO3 was dissolved in a large volume of water.

**Solution**

**Example 6**

The amount energy required to change 20g of water to steam is +20kJ. Calculate the standard heat of vaporization.

**Solution**

**Example 7**

The heat of fusion of sulphur is +45.5kJ mol-1. Calculate the quantity of heat required to fuse

1. 3 moles of sulphur
2. 4g of sulphur
3. Determine the mass of sulphur that would require of heat for fusion

**Example 8**

The heat of combustion of carbon is -393kJmol-1. Calculate the heat change when 60g of carbon undergoes complete combustion

**Born Haber cycle and Hess law**

Enthalpy of reaction can be determined experimentally and theoretically. Heat of reaction can theoretically be determined using **Hess’ law of constant heat summation**. This law states that “**the total enthalpy change of a chemical reaction is constant regardless of the route by which the chemical change occurs provided that the conditions at the start of a reaction are the same as the final conditions”.**

A + B C + D

E + F

Hess’s law is another form of conservation of energy which can be represented in the form of Born-Haber cycle (a combination of energy cycle and energy level diagrams)

**Example**

Calculate the heat of formation of butane directly using the born-Haber cycle and Hess’s law if the heats of combustion of carbon, hydrogen and butane are as follows:

H2(g) + ½ O2(g) H2O(g) ; ∆Hc Ө = -285.58 KJmol-1

C(s) + O2(g)  CO2(g) ; ∆Hc Ө = -393 KJmol-1

C4H10(g) + 6½O2(g)  4CO2(g) +5H2O(g) ; ∆Hc Ө = -2887 KJmol-1

**Solution**

**BOND ENERGY/ DISSOCIATION ENERGY OF A COVALENT BOND**

Dissociation energy of a covalent bond is the enthalpy change that accompanies the breaking of a particular covalent bond when the reactants and products are in gaseous state.

Bond energy is the average amount of energy associated with making or breaking one mole of a particular bond in its gaseous state. Bond energy is same for homonuclear molecules (e.g H-H) but differ for heteronuclear molecules (e.g H-Cl). Bond energies indicate the strength of bonds. The higher the value of bond energy, the stronger the bond. Stable compounds have high bond energies while reactive compounds have low bond energies. This explains why the heats of combustion of alkanes increase with increase in number of carbon atoms. Bond energy is energy absorbed when a covalent bond is broken (endothermic) and energy evolved when a covalent bond is formed (exothermic).

ΔH(reaction) = E(bond broken) – E(bond formed)

**Example**

1. Calculate the enthalpy change for the reaction

H2(g) + Cl2(g) → 2HCl(g)

[Given EH-H = 437kJmol-1; ECl-Cl = 242kJmol-1; EH-Cl =433kJmol-1]

1. Calculate the bond energy for the hydrogenation of a molecule of ethyne [ECΞC=811, Ec=c =610, EC-H = 413, EH-H = 437]
2. Calculate the bond energy for the reaction: H2 + ½O2 → H2O Eo=o =498, Eo=H = 464]

**LATTICE ENERGY OF AN IONIC CRYSTAL**

It is the heat of formation of one mole of ionic compound from its gaseous free ions under standard conditions. Lattice energy helps to understand the stability of ionic crystals.

**CHEMICAL THERMODYNAMICS**

This is the study of the relationships between heat and other forms of energy

**FIRST LAW OF THERMODYNAMICS** states that “energy cannot be created nor destroyed but can be changed from one form to another”.

∆U = q + w *∆U= change in internal energy,*

*q = heat of the system, w = work done by the system*

For a gaseous system,

∆U = ∆H + P∆V

**SECOND LAW OF THERMODYNAMICS** states that “a spontaneous process occurs only if there is an increase in the entropy of a system and its sorroundings”

**SPONTANEOUS REACTION**

A spontaneous reaction is that which has the potential to occur on its own without the assistance of any external agent. The factors which determine whether a reaction occurs spontaneously are:

1. the entropy
2. the free energy
3. enthalpy

**Entropy(S)**: is a measure of the degree of disorderliness or randomness of a system. A change in entropy is represented as ΔS.

ΔS0 = Sθproduct – Sθreactant

The S.I unit of entropy is JK-1mol-1

A perfectly ordered system at 0K has an entropy value of zero. Entropy increases from the solid to liquid and to gaseous state. A **crystalline solid** with a perfectly ordered structure has low entropy because the molecules are fixed in a static position. **Liquids** have higher entropy value due to less ordered arrangement of molecules. **Gases** have the highest value due to great disorderliness of the molecules. Generally, for a given substance, as temperature increases entropy increases.

Examples of systems with positive entropy include

1. melting of a solid
2. evaporation or boiling of a liquid
3. expansion of a gas with increasing temperature of decreasing pressure
4. reactions involving gaseous products
5. decomposition reactions
6. dissolution of solid and liquids in water

For a reversible process at constant temperature and pressure, the change in entropy (ΔS) is equal to the enthalpy change of the reaction (ΔH) divided by the absolute temp T at which the process occurs

ΔS = ∆H

T

**Note**: Nature prefers conditions of low enthalpy and high entropy

**Example1**:

Calculate the entropy change for the reaction

H2(g) + Cl2(g) → 2HCl(g)

Given that: Sθ H2 = 131JK-1mol-1; SθCl2=223JK-1mol-1; SθHCl= 187 JK-1mol-1

**Solution**

ΔS = Sθproduct – Sθreactant

Since ΔSθ is positive, it means there is an increase in disorderliness/randomness of the system.

**Example 2**

Calculate the standard entropy change for the conversion of one mole of liquid water to vapour at 100°C given that the heat of vapourization of water is 2261Jg-1

**Solution**

**Example 3**

Nitrogen gas reacts with hydrogen gas to form ammonia gas. Given that the standard entropies of Nitrogen, hydrogen and ammonia gases are 192, 131, and 193 JK-1mol-1 respectively. Calculate the standard entropy change for the reaction.

**Solution**

**Gibb’s Free energy(G):** of a chemical system is the energy which is available for doing work. It is the driving force that brings about a chemical change.

ΔGθ = G θ product – G θreactant

**Example**

Calculate the standard free energy change for the reaction involving the decomposition of hydrogen peroxide to water at 25°C, given that the standard free energies of H2O2, H2O, and O2 are -120.4, -228.6 and 0.0

**Solution**

**SPONTANEITY OF REACTION**

ΔG = ΔH - TΔS

ΔG helps to predict if a chemical reaction will occur or not provided that enthalpy and entropy of the reaction are known. (Feasibility of reactions)

For a chemical change to occur **spontaneously**, ΔS must be **positive** and ΔG must be **negative**.

For a **non**-**spontaneous** chemical change to occur, ΔS must be **negative** ΔG must be **positive**.

For a chemical system is in a state of **equilibrium**. ΔG = 0

**Example 1**

Consider the reaction: C(s) + O2(g) CO2(g) carried out at a temperature of 57°C. If the enthalpy and entropy changes are -5000J and +15J respectively, calculate the free energy change.

State whether the reaction is spontaneous or not. Give reason(s) for your answer.

**Solution**

**Example 2**

Calculate the standard enthalpy change ∆HӨ, standard entropy change ∆SӨ and the standard free energy ∆GӨ at (a). 30°C (b). 500°C

Given that the standard entropies for Fe2O3, H2, Fe and H2O are 90, 131, 27 and 189 respectively and the standard enthalpies are -822, 0, 0 and -242

**Solution**

**Students exercise**

1. State three parameters that determine the spontaneity of a chemical reaction
2. Write an expression to show the relationship between the parameters
3. Explain why enthalpy data alone cannot be used to predict whether a reaction will occur spontaneously or not

**ENERGY EFFECTS & CHEMICAL EQUILIBRIUM**

Chemical equilibrium is the state of a system where there is no observable change in the properties of the system with respect to time. An example of a system in equilibrium is a saturated solution in which we have dissolution and precipitation taking place.

NaCl(s) NaCl(aq)

Liquid vapour

**Types of equilibrium systems**

1. **Static** equilibrium: the equilibrium system is at rest e.g a balanced see-saw
2. **Dynamic** equilibrium: The equilibrium system is at constant motion; rate of formation equals rate of decomposition e.g a saturated solution or a volatile liquid in a closed air tight container.

**Types of dynamic equilibrium**

1. **Physical**: This involves a physical change i.e no change in the composition of the substances involved
2. **Chemical**: This involves a chemical change i.e reactant undergo a change to form products while the product are reconverted to form the reactants at the same rate.

**Properties of a system in dynamic equilibrium**

1. It can only be achieved in a closed system. None of the reactants or products can leave the system.
2. A closed system is a reaction system whereby all the chemical species (reactants and products) are present and it takes place in a closed vessel
3. An open system is a reaction system whereby one or more of the chemical species (reactants and products) are being removed and it takes place in an open vessel. This reaction cannot attain equilibrium.

**Compare decomposition of calcium trioxocarbonate (IV) in an open and closed system**

1. It can be approached from the forward or backward reaction.
2. It is dynamic in nature i.e rate of forward and backward reaction is constant.
3. The concentration of all the chemical species remain constant as long as the conditions are not changed
4. A catalyst can alter the time required to attain equilibrium but does not affect the yield of the reaction
5. The free energy of an equilibrium reaction is zero
6. A system in equilibrium will resist a change

**EQUILIBRUM IN REVERSIBLE SYSTEMS**

A reversible reaction is one that proceeds in both directions (forward and backward) under suitable conditions. E.g. sometimes forward and backward reactions occur under the same the condition but at other times, they occur under different conditions.

Forward

A + B C + D

Backward

When A and B are mixed together in a closed container, the product C & D will be formed by the forward reaction at a fast rate but gradually slows down. However, C & D will begin to react to form A and B in the backward reaction. After a while, the forward & backward reactions will go on at the same rate. The concentrations of A, B, C and D remains constant (there is no observable change in the properties of the system with respect to time. Here, the system is said to be in dynamic equilibrium.

**Dynamic Equilibrium in reversible reaction:** A reversible reaction is in dynamic equilibrium when both the forward and backward reactions are occurring at the same rate thereby producing no net change in the concentration of the reactants or products.

**Information obtained from an equilibrium equation**

1. The two opposing reactions are occurring at the same time
2. The two opposing reactions are at equilibrium
3. The amounts (in moles) of reactants and products are equal to the stoichiometry of the reaction(balanced equation)
4. The forward reaction is exothermic, hence the backward reaction will be endothermic

**Limitations of an equilibrium equation**

Information that cannot be obtained from the equilibrium equation include

1. Time taken for equilibrium to be achieved
2. Concentrations of reactants and products at equilibrium
3. The mechanism of the reaction

**LE CHATELIER’S PRINCIPLE**

Le Chatelier’s Principle states that if a chemical system is in equilibrium and one of the factors such as temperature, pressure or concentration involved in the equilibrium is altered, the equilibrium will shift so as to annul or neutralize the effect of the change.

Every reversible reaction reaches its own equilibrium under a given set of conditions. Equilibrium is dependent on

1. Temperature of the reacting system
2. Pressure of the reacting system (gases)
3. Concentration of the reacting system

**Importance of Le Chatelier’s principle**

1. It defines the optimum conditions for chemical processes employed in industries
2. It reduces undesirable reversibility
3. It predicts the effect of an altered factor on the equilibrium position

**Effect of Change in Temperature on an equilibrium mixture**

Consider the following reactions:

A + B C ∆H = +ve (endothermic)

X + Y Z ∆H = –ve (exothermic)

According to Le Chatelier’s principle, a forward reaction which is an exothermic process is favoured by lowering the temperature while the forward reaction for an endothermic process is favoured by raising the temperature. e.g

N2(g) + O2(g) 2NO ;∆H = +90.4kJmol-1

Since the forward reaction is endothermic, increasing the temperature will shift the equilibrium to the **right** favouring the forward reaction i.e. more of NO is formed. The value of K will increase

When the temp is lowered, the equilibrium will be shifted to the **left** favouring backward reaction and more of 02 and N2 will be produced. The value of K will decrease

In the reaction below, the forward is exothermic.

N2(g) + 3H2(g) 2NH3 ∆H = – 46.1 kJmol-1

Since the forward reaction is exothermic, Increasing the temperature will shift the equilibrium to the **left** favouring the backward reaction i.e more of N2and H2 are formed and The value of K will decrease. Decreasing it will shift the equilibrium to the right leading to the production of more ammonia. The value of K will increase

We can illustrate the effect of temperature on an equilibrium system using dinitrogen(IV)oxide and nitrogen(IV) oxide system.

N2O4 2NO2

**Effect of Change in Pressure**

For a change in pressure to affect the position of equilibrium in a chemical system, the following conditions must be satisfied:

1. One of the reactants or products must be gaseous
2. The total number of moles of gaseous molecules on one side of the equation must be different from the total number on the other side of the equation.

Consider the following equation:

2SO2(g) + O2(g) 2SO3(g)

3moles/vol 2moles/vol

According to Le Chatelier’s principle, if the pressure is increased in an equilibrium position, the reaction which involves a reduction in volume will be favoured. i.e. the equilibrium position will shift to the side of lower volume ( i.e to the right, formation of SO3).

Similarly, a decrease in pressure will shift the equilibrium to the side of higher volume i.e. to the left. Formation of SO2 and O2

**In general, an increase in pressure pushes the equilibrium in favour of smaller volumes.**

**NB:** In reversible reactions involving the same number of gaseous molecules on both sides of the equation e.g.

Red heat

3Fe(s) + 4H2O(g) Fe3O4(s) + 4H2(g)

**Note**: A change in pressure has no effect on the equilibrium position.

**Effect of Change in Concentration**

If the concentration of one of the reactants present in an equilibrium system is increased without change in any of the other conditions then according to Le Chatelier’s principle, the position of the equilibrium will move to decrease the concentration (use up) of the added substance (i.e. to the right, favouring the forward reaction). This results in a proportional increase in the concentration of the products.

Another way of increasing the amount of product formed is by continually removing the products from the system. This also will shift the equilibrium to the right favouring the forward reaction.

Consider the equation: N2(g) + O2(g) 2NO(g)

If extra N2 or O2 is pumped into the system, the position of the equilibrium shifts to the right i.e there will more of NO in the system. Similarly, if N2 or O2 is removed from the system, the equilibrium will shift to produce more of the removed substance (i.e. equilibrium shift to the left).

Also, continuous removal of the product will shift the equilibrium to the right to produce more of NO.

However, addition of product or removal of reactant will favour the backward reaction

1. **Effect of Catalyst:** A catalyst has no effect on the equilibrium position of a reversible reaction. It only affects the time taken for a reaction to attain equilibrium by lowering the activation energy.

**EQUILIBRIUM CONSTANT [K]**

The effect of concentration on rate of equilibrium is known as the **law of mass action**. This law states that “**at constant temperature, the rate of reaction is proportional to the active masses of each of the reactants. This is known as the rate law**

Consider the reaction below:

nA + mB pC + qD

This means that ‘n’ molecules of A and ‘m’ molecules of B react to form ‘p’ molecules of C and ‘q’ molecules of D.

Equilibrium constant is a measure of the ratio of the concentration of the products of a reaction to the equilibrium concentration of the reactants.

For the above reaction, the equilibrium constant K = [C]p[D]q

[A]n[B]m

In which each concentration is raised to a power equal to its coefficient in the overall balanced equation for the reaction and [ ] stands for equilibrium concentration/ pressure for gaseous species

**Note:** A positive K (K˃1) value indicates that products (forward reaction) are favoured at equilibrium while

A negative K (K˂1) value indicates that reactants are favoured (backward reaction)

A neutral value of K shows that the concentration of reactants and products are constant.

The product of the equilibrium constants for the forward reaction and that of the backward reaction is unity i.e = 1

**Example 1**

Consider the following reaction : H2(g) + I2(g) 2Hl(g) .Calculate

(a) the equilibrium constant Kf for the reaction at 45°C

(b) the equilibrium constant Kb for the backward reaction

Given that the partial pressures of the following substances at 45°C are

[H2] = 0.068 atm, [ I2] = 0.43atm, [HI] = 0.214 atm

The above example is for homogenous equilibria. For heterogeneous equilbiria which involves two or more phases, pure solids and pure liquids are constants and so are omitted from the equilibrium law expression. For example

C(s) + O2(g) ⇋ CO2(g)

Kp = [CO2]

[O2]

**Example**:

Consider the equilibrium reaction:

PCl5(l) ⇋ PCl3(l) + Cl2(g) H = +xkJmol-1

1. Write an expression for the equilibrium constant Keq
2. What would happen to the equilibrium position if

I . pressure of the system is increased

II. temperature of the system is increased

III. concentration of the reactant is increased

IV. concentration of the product is increased

1. Calculate the volume of chlorine produced from 3.8g of phosphorus (V) chloride

**Equilibrium Constant, Free Energy and Electrode Potentials**

Reactions with ∆G<O would occur spontaneously while those with ∆G>O would not occur. The relationship between the free energy ∆G and the equilibrium constant K is given by

**∆G0 = - RTlnk**

but: ln K = -2.303log K therefore, ∆G = -2.303RTlogK

Where: *K = equilibrium constant*

*∆G0 = standard free energy change*

*R= Molar gas constant*

*T = Temp of the system in Kelvin*

In an electrochemical cell, oxidation occurs in one electrode and reduction at the other. If such a reaction is in equilibrium,e.g.

Zn(s) + Pb2+(aq) Zn2+(aq) + Pb(s)

Then, the relationship between standard electrode potential E0 and equilibrium constant is given by: **E0 = RTlnk**

**nF**

*Where, n = no of moles of electrons,*

*E0 = standard electrode potential*

*F = Faraday’s constant*

The relationship between electrode potential and free energy change of an electrochemical cell is expressed as: **∆G = –nFE**

**Example:**

1. Calculate the standard free energy change and the equilibrium constant for the reaction at 250C:

PCl5(l) PCl3(l) + Cl2(g)

given that the free energy values of formation of PCl5, PCl3 and Cl2 at 25°C are –305, –268 and 0.00KJ mol-1 respectively [molar gas constant = 8.314 JK-1mol-1]

**Solution**

1. ΔG° = G°product – G°reactant

**Example 2:** The equilibrium constant at 25°C for the reaction:

H2(g) + S(g) H2S(g)  is 6.0 x 105.Calculate the

1. Standard enthalpy change, ΔH°
2. Standard free energy change, ΔG°
3. Standard entropy change ΔS°

Given that the enthalpy values for H2(g), S(s) and H2S(g) are 0.0, 0.0 and -21KJmol-1 respectively {R=8.314 Jk-1mol-1}

**Solution**

1. Calculate the standard electrode potential, E° for Cu/Cu2+//Zn2+/Zn system at 25C, Keq= 1.8x10-2 [temp= 298K]
2. 2SO2 + O2 → 2SO3 given that ΔG = +3.9kmol-1, temp= 25°C]. Calculate the equilibrium constant for the reaction and state which gas exists at equilibrium

**EQUILIBRUM IN PRACTICE**

1. **Haber Process**

N2(g) + 3H2(g) 2NH3 ∆H = – 46.1 kJmol-1

The forward reaction will be favored by

1. Decrease in temperature
2. Increase in pressure
3. Nitrogen and hydrogen are continuously added while ammonia is removed by liquefaction
4. Addition of catalyst is shortens production time
5. Recycling of unreacted gases

Industrial Conditions for optimum yield are temperature of 450°C, pressure of 200 atm, finely divided iron (catalyst) = 15% yield

1. **Contact** **Process**

2SO2(g) + O2(g) 2SO3(g) –395.7 kJmol-1

The forward reaction will be favored by

1. Decrease in temperature
2. Increase in pressure
3. An excess of air is used while SO3 is removed by dissolving it in conc. H2SO4 to form oleum
4. Addition of catalyst is shortens production time
5. Recycling of unreacted gases

Industrial Conditions for optimum yield are temperature of 450 - 500°C, pressure of 1atm, finely divided Vanadium(V) oxide (catalyst) = 98% yield

**ACID-BASE EQUILIBRUM**

Equilibrium exists between an acid and its associated base

According to **Arrhenius**, an acid dissociates in water to yield hydroxonium ions while a base dissociates in water to yield hydroxide ions.

HCl + H2O → H3O+ + Cl-

NaOH → Na+ + OH-

When an acid is dissolved in water, an equilibrium is established

HA + H2O ⇋ A- + H3O+

Ka = [H3O+][A-]

[HA] Ka is called the equilibrium constant or acidity/ionization constant

Bronsted-Lowry on the other hand described an acid as a substance which donates a proton while a base is a substance that accepts a proton

CH3COOH + H+ ⇋ CH3COO- + H+

acid base base acid

HCl + H2O ⇋ Cl- + H3O+

acid base base acid

The equations represented are **conjugate acid-base pair** because in the forward reaction, the acid donates proton while the base accept a proton but in the reverse reaction, the acid radical acts as a base.

**WATER, SOLUTION AND SOLUBILITY**

**WATER**

Water is one of the most abundant substances on earth. It is present in plants and animal tissues. Princely (1781) was the first to observe that the explosion of a hydrogen gas and oxygen gas mixture yields water vapour. Later, Cavendish established their ratio by volume.

**Water as an oxide of hydrogen:** when dry hydrogen gas is ignited in air, it burns with a faint blue flame to give steam which will condenses when in contact on any cold surface to form water

2H2(g) + O2(g) 2H2O(g)

Hydrogen Oxide (water)

Oxygen

Hydrogen

**Water as a Universal Solvent**

The most common solvent in nature is water. It is referred to as the universal solvent because it can dissolve most substances. Water molecules have a structure which is polar in nature. i.e one side of the molecule is positively charged and the other side is negatively charged. As a result of this polar structure, water is an excellent solvent (for electrovalent solutes) such as mineral acids and bases. These are mainly organic compounds. All covalent compounds which contain the hydrogen group will also dissolve equally in water. e.g organic solids like sugar and organic liquids like alcohol.

**Physical properties of water**

1. Pure water is colourless, odourless and tasteless
2. It has a boiling point of 100oC and melting point of 0oC
3. Maximum density of 1gcm-3 at 4oC
4. Water is neutral to litmus.

**Chemical properties of water**

1. Water reacts with metals in a number of ways with the degree of reactivity depending on the position of the metal in the electrochemical series. Thus,
2. Na, K and Ca react with cold water to form alkalis and liberate hydrogen gas

2K(s) + H2O(l) K2O(aq) + H2(g)

2Na(s) + H2O(l) Na2O(aq) + H2(g)

Ca(s) + H2O(l) CaO(aq) + H2(g)

1. Mg and Zn react only with steam (hot water) to liberate hydrogen form oxide

Mg(s) + H2O(g) MgO(aq)  + H2(g)

Zn(s) + H2O(g) ZnO(aq)  + H2(g)

1. Fe reacts only with excess steam at red heat

3Fe(s) + 4H2O(g) Fe3O4(aq)  + H2(g)

1. Cu, Au, Ag and Hg do not react with water in any form
2. Water reacts with organic and inorganic compounds. Such reaction are generally described as ***hydrolysis*** e.g.

Na2 SO3 (s)  + 6H2O(l) 2Al(OH) 3(aq)  + H2S(g)

CH3COOC2H5(g)  + H2O(l) ⇋C2H5OH(aq)  + CH3COOH(aq)

**Unique properties of water**

1. High boiling point and melting point due to hydrogen bonds.
2. Water has high surface tension which makes it behave like a skin
3. Water is less dense when it solidifies as opposed to most solids which become denser. Ice molecules form an open lattice structure which is not crowded together as in liquid water. This is the reason why ponds and lakes in polar regions do not freeze completely preventing aquatic life from being killed.
4. Water expands when it freezes. This is responsible for weathering

**Confirmatory Test for Water**

The reagents used to test water in the laboratory are:

1. White anhydrous copper (II) tetraoxosulphate (VI): it turns blue

CuSO4 (s) + 5H2O CuSO4 **.**5H2O

White Anhydrous

Blue Hydrate

2. Blue cobalt (II) chloride: it turns pink

CoCl2 + 6H2O CoCl2**.**6H2O

Pink Hydrate

Blue

Anhydrous

**Uses of water**

1. Water is the foundation of every living thing
2. It is used in homes for laundry, cooking, bathing, cleaning and drinking
3. Plants absorbs nutrients dissolved in water in order to sustain growth and in photosynthesis
4. Water is used in most industrial processes as solvent and in cooling processes
5. Distilled water is used in pharmaceutical industry to make drugs and intravenous fluid

**[**

**Types of Water**

1. ***Natural water:*** e.g. rain water, spring water, and well water. Rain water is the purest form of natural water because it is formed as a result of condensation of water vapour in the atmosphere. Spring water contains a considerable amount of mineral salt but very little suspended impurities such as dust and bacteria, so it is a good source of drinking water. Well water contains a lot of clay and other mineral salts.
2. ***Treated Water***: is usually prepared for a special purpose e.g. distilled water(chemically pure) for use in laboratories and pharmaceutical plants, pipe borne water for township and chlorinated water for the use in swimming pools.

**Water Treatment for township water supply (municipal)**

Pipe borne water is prepared in a water-heated plant. This water is usually dust-free but it contains mineral salts like NaCl. Water from rainfall, rivers, lake is stored in reservoirs. This water is purified by various methods which include

1. Aeration
2. Screening
3. Coagulation
4. Sedimentation
5. Filtration
6. Disinfection
7. Testing and distribution

**Aeration** is a process in water treatment where air and water are brought into close contact to remove dissolved gases present in the water. **Screening** removes objects such as rags, paper, plastics and metals to prevent damage and clogging of the equipments. The untreated water is passed through large settings tanks where chemicals like potash alum, KAl(SO4)2 or sodium aluminate(III), NaAlO2 are added to cause **coagulation** or flocculation. The impurities clump together to form big particles of dirt or flocs which settle down rapidly.

Next, the water is passed through a filter bed to remove the remaining fine particles of dirt (**filtration** ). Then the water is treated with chemicals like chlorine, iodine and fluorine in the correct amount as disinfectant, food supplement to prevent goiter and tooth decay respectively. Finally, the water which is now clean and free from germs is stored in reservoir, the pH and some other tests are carried out. The treated water is distributed to the town after the results of the tests have complied with standard specifications.

Fig: Chart showing steps involved in water treatment

**HARDNESS OF WATER**

This is the ease with which soap lathers with water. Based on this, there are two types of water: **hard** water and **soft** water.Hard water will not form lather easily with soap due to the presence of dissolved calcium tetraoxosulphate (VI), CaSO4; Magnesium tetraoxosulphate (VI), MgSO4; calcium hydrogen trioxocarbonate (IV), Ca(HCO3)2 and magnesium hydrogen trioxocarbonate (IV), Mg(HCO3)2. The most ions present in hard water are Mg2+ and Ca2+.

**Origin of hardWater**: Water acquires hardness when it dissolves gypsum [CaSO4.2H2O] or limestone, CaCO3 from the soil over which it flows.

**Types of Hard Water**

1. Temporary hardness of water
2. Permanent hardness of water

Temporary hardness of water is caused by dissolved calcium hydrogen trioxocarbonate (IV). It can easily be removed by:

1. **Boiling**: Ca(HCO3)2(aq) 2CaCO3(s)  + H2O(l)

Soluble

Insoluble

1. **Addition of slaked lime Ca(OH)2**

Ca(HCO3)2(aq) + Ca(OH)2(s) 2CaCO3 (s) + H2O (l)

Soluble

Insoluble

Slightly

Soluble

The soluble Ca(HCO3)2 is precipitated as the insoluble CaCO3, thus removing the calcium ions(Ca2+) in which are responsible for hardness

**Effects of Temporary Hardness**

1. **Furring of kettles & boilers**: when a kettle or boiler is used to boil temporary hard water for some time, the inner surface becomes coated with a white fur- like layer. This layer is due to the gradual deposition of calcium trioxocarbonate (IV),CaCO3 from the decomposition of Ca(HCO3)2
2. **Stalagmites & stalactites:** These are pillars of limestone found in hot caves. When hard water temporarily flows on top of a cave, drops of water tend to drip from the roof through cracks. The CaCO3 in the water becomes decomposed by the heat in the cave, leaving deposits CaCO3 of on the roof and on the floor. A CaCO3 structure growing downward from the roof is called **stalactite** while the one growing from the floor is called **stalagmite**.

**Permanent Hardness:** This form of hardness can only be removed by using chemicals. It is caused by the presence of calcium and magnesium ions in the form of soluble tetraoxosulphate (VI) and its chlorides.

**Removal of Permanent Hardness**

1. **Addition of washing soda (Na2CO3)**: removes the Ca2+ & Mg2+ ions as the insoluble calcium and magnesium trioxocarbonates (IV) respectively.

Na2CO3(aq) + CaSO4(aq) Na2SO4(aq) + CaCO3(s)

Soluble

Insoluble

2. **Addition of Caustic Soda ( NaOH):** removes calcium and magnesium ions from water as insoluble calcium and magnesium hydroxides respectively.

2NaOH(aq) + CaSO4(aq) Ca(OH)2(s)  + Na2SO4(aq)

Soluble

Insoluble

3. **Ion-exchange resin (permutit or zeolite)**: is used industrially and in the homes for softening water. It is naturally occurring sodium aluminum trioxosilicate (IV) commonly known as zeolite. When the hard water is passed through the resin, the anions will go into solution while the unwanted Ca and Mg ions take their place in the complex salt e.g

Na+Y+ CaSO4 Ca2+Y + Na2SO4

Soluble Insoluble

When the permutit is used up, it can be regenerated by pouring a strong solution of common salt through the resin

NaCl + CaY NaY + CaCl2

Distillation can also be used to remove both types of hardness because as the water evaporates, the ions are left behind though it is not economical

**Advantages of Hard water**

1. Hard water tastes better than soft water because of the dissolved minerals
2. Calcium present in hard water is used in the building of strong bones and teeth
3. Hard water helps animals like snails and crabs to make their shells. These shells are made mainly of CaCO3.
4. Hard water can be supplied in pipe made of lead, as this type of water does not dissolve lead. Soft water dissolves lead if supplied in lead pipes, it will cause poisoning.

**Disadvantages of Hard Water**

1. It wastes lots of soap because it does not lather easily with soap
2. Hard water causes furring of kettles & boilers while soft water dose not
3. It cannot be used in dyeing and tanning as the salts in it interfere with the mode of action of these processes.

**Students** **exercise**: Write 2 advantages and disadvantages of soft water

**WATER POLLUTION**

This is the indiscriminate dumping of solid and liquid waste into water bodies such that the water becomes unfit for intended use. It threatens aquatic life and makes water bodies unsightly and foul- smelling. Common pollutants include:

1. **Refuse and sewage**: These are organic matter discharged into water bodies. The micro-organisms in the water decompose the organic matter into simple substances thereby using up the dissolved oxygen leading to a decrease in the BOD (Biochemical Oxygen Demand). BOD is the oxygen required by the micro-organisms to break down or oxidize a given amount of organic matter. If sewage in the water is too much, the oxygen is used up and the aquatic life begins to die and the river becomes clogged up and foul smelling. Disease-causing organisms are present in the water.
2. **Industrial and agricultural waste:** Most factories empty their chemical waste directly into rivers and seas without converting them into harmless substances. Fertilizers and insecticides are washed by rain into lakes, ponds and rivers. The pollutants are acids, alkalis, mercury compounds, organic solvents, detergents, fertilizers and insecticides. Some of these substances are non-biodegradable i.e they cannot be broken down into harmless substances by living organisms. They remain in water and tend to accumulate in the body of aquatic organisms like fish. Mercury is a good example. When we eat such fish, it accumulates in the body and eventually lead to mercury poisoning. Fertilizers which contain phosphates and nitrates encourage the growth of large amount of algae (algal bloom). Nitrates in larger concentrations are toxic to most higher organisms
3. **Crude oil spills**: Accidents and carelessness in oil rigs and tankers causes crude oil spills mainly in the coastal areas. The oil floats on water and kills most of the marine life in that water. The oil can be washed up the beach such that it cannot be used for recreation. Sometimes detergents can be used to clean up oil spills but they contain chemicals which are harmful and promotes the growth of algae and weeds.
4. **Thermal pollution**: Many industries like oil refineries, steel mills, breweries use water for cooling and discharge the water into nearby water bodies. Usually water from the river is pumped in and used for cooling and warm water is pumped out into the river. This raises the temperature of the water leading to decrease in the amount of dissolved oxygen in the water.

**CONTROL OF WATER POLLUTION**

1. Refuse should be buried or burnt in an incinerator with built-in devices to prevent air pollution.
2. Sewage should be processed, treated or converted to useful fertilizers in sewage plants.
3. Chemical waste should be converted to harmless biodegradable substances before being dumped into the sea.
4. Safety measures should be implemented to prevent crude oil spills.
5. Strict laws should be passed to control water pollution by individuals and companies
6. The public should be educated on the consequences of pollution precious water bodies.

**SOLUTION AND SOLUBILITY**

A solution can defined as a uniform homogeneous mixture of two or more substances where the particles are so small to be seen with the naked eye.

Solute + solvent = solution

CuSO4 + 5H2O CuSO4.5H2O

A solute is a dissolved substance which may be solid, liquid, gas.

A solvent is a substance (usually a liquid, although it may solid, liquid, or gas) which dissolves a solute (the dissolving medium). Water is referred to as the universal solvent because it can dissolve most substances. It is polar in nature i.e with positive and negative charges so electrovalent solids or covalent compounds which have the OH group can dissolve in it. **In general, polar substances dissolve polar substances while non- polar substances dissolves non-polar substances**

**Examples of solution.**

**Solution Solute (State) Solvent (State)**

Brine sodium chloride(s) water(s)

Anti freeze alkanol(l) water(l)

Soda water carbon (IV) oxide(g) water (l)

Brass zinc (s) copper(s)

Air mainly oxygen nitrogen(g)

**Solute Suitable Solvent**

Sodium chloride Water

Copper (II) tetraoxosulphate(VI) Water

Sugar Water

Iodine Ethanol

Naphthalene Ethanol

Grease Petrol

Sulphur Carbon (IV) Sulphide

Rubber Benzene

Paint Turpentine

Quicklime None

Solutions can be classified into two:

1. **Aqueous solution:** is a solution with water as a solvent.
2. **Chemical solution:** is when the apparent solution of a solute in a solvent is accompanied by a chemical reaction e.g when Mg appears to dissolve in dilute HCl, what actually happen is that the Mg attacks the acid to form MgCl2 which dissolves in water present

**Uses of solution**

1. Petrol, kerosene and ammonia solution are used in laundry to remove fat, oil or grease stain. Turpentine is used to remove paint stain, borax solution is used to remove tea or coffee stains
2. Petrol is used in general cleaning of homes and offices to remove stains of wax, grease, fat or oil
3. Ethanol is used in the manufacture of aromatics and perfumes to dissolve essential oils(esters)
4. Ethanol is used to extract chlorophyll from plants
5. Vulcanizer’s solution (for mending punctures in tubes) is made by dissolving phosphorus, rubber and sulphur in benzene
6. Iodine solution for dressing wounds is made by dissolving solid iodine in ethanol
7. Turpentine is used to mix water-proof paint for painting walls

**COLLOIDS; True Solutions & False/Colloidal Solution**

**True solutions**: When solute particles dissolve such that they are able to get in between the solvent particles, the resultant homogeneous mixture is called a **true solution** e.g aqueous solution of NaCl, CuSO4. The solute particles which are simple molecules or ions are too small to be seen by the naked eyes and are called **crystalloids**.

**A colloidal solution or** **false solution** is a homogeneous mixture of substances in which one substance is dispersed in another one. In colloidal solutions, the individual solute particles are larger than the particle of the true solution but not large enough to be seen by the naked eye e.g starch, jelly, glue, albumen, milk, fog, smoke, insecticide e.t.c.

**Types of colloids.**

1. Sols and gels: Sols are solid-liquid colloidal systems which solidify to form gels e.g starch, agar, gelatin, jelly and clay.
2. Emulsions: These are liquid-liquid colloidal system e.g milk, hair cream, cod liver oil, butter
3. Aerosols: These are liquid-gas or solid-gas colloidal systems e.g fog, smoke, sprays of insecticides and perfumes from aerosol cans, foam or lather

**Differences between true and false solutions**

|  |  |
| --- | --- |
| **True solution** | **False solution** |
| Solution can be dialysed i.e the solutes can pass through a semi-permeable membrane | Solution cannot be dialysed |
| The solution do not scatter light rays | The solution scatters light raysi.e they exhibit tyndall effect(scattering of light rays) |

**SUSPENSIONS:** are heterogeneous mixtures of undissolved particles in a given medium where the particles are usually large enough to be seen without the aid of an instrument and they eventually settle down if left standing e.g the harmattan wind.

**Students** **exercise**: Write 2 characteristics of true solution, false solution and suspension in a tabular form

**SOLUBILITY**

The solubility of a solute at a particular temperature is defined as the maximum amount of the solute in moles or grams that will dissolve in 1dm3 of the solvent at that temperature. It compares the extent to which different solutes can dissolve in a solvent at a particular temperature

Solubility = mole x 1000cm3 OR Solubility=mass x 1000cm3

Volume Volume

The S.I unit is moldm-3 S.I Unit is moldm-3

**Saturated, Unsaturated and Super saturated Solution**

A **saturated** solution at a particular temperature is one which contains as much solute as it can dissolve at that temperature in the presence of undissolved solute particles. The composition of a saturated solution is not affected by the presence of excess solute particles. The concentration of a saturated solution varies with temperature, solute and solvent. **The dissolved solute and the undissolved solutes are in a state of equilibrium at that particular temperature.** Increase in temperature results in increase in solubility while a decrease in temperature results in precipitation of the excess solute

**Unsaturated** solution is one which contains less amount of a solute that it can normally dissolve at a particular temperature, it can dissolve more solutes, if added until the solution becomes saturated. It contains lower concentration of solutes.

**Supersaturated Solution:** is one which contains much more of the solute than it can normally hold at a particular temperature. It is unstable and the excess solute will separate out if the solution is slightly disturbed by scratching, shaking or if any tiny crystal of one solute or even a dust particle is dropped into it.

**Determination of solubility**

It involves two stages:

1. Preparing a saturated solution of a given solute at a particular temperature
2. Taking a known mass of the saturated solution and heating it to dryness so that the exact mass of the solute can be calculated

**Experiment** to determine the solubility of potassium trioxonitrate (V) in water at room temperature

**Apparatus**: Beaker, stirrer, KNO3 salt, distilled water, filtration apparatus

**Procedure**: Place 50cm3 of distilled water in a beaker, add KNO3 salt (a little at a time) while stirring continuously until no more salt can dissolve. Filter the solution. The filtrate is a saturated solution of KNO3 at the prevailing room temperature. Then weigh a clean, dry evaporating dish. Put some of the saturated solution into the dish and weigh again to determine the mass of the solution. Heat the solution to dryness on a water-bath. Place the dish in a desiccator to dry. Weigh the crucible again to find the mass of the solute that was present in the solvent. Express the concentration in moles per dm3.

**NOTE**: Use dry apparatus to avoid diluting the saturated solution

**Specimen result:**

Mass of saturated solution = 55.27g

Mass of solvent evaporated = 43.40g

Mass of dry residue = 11.87g

Molar mass of KNO3  = 101g/mol

**Solubility**

**Calculations on Solubility**

**Example** **1**

If 12.2g of Pb(NO3)2 were dissolved in 21g of distilled H2O at 20°C. Calculate the solubility of the solute in (a) moldm-3 (b) gdm-3

**Solution**

Density of water = 1gcm-3

**Example 2**

25.0g of potassium chloride were dissolved in 80g of distilled water at 30oC. Calculate the solubility of the solute in mol/dm3

**Solution**

**Example 3**

500cm3 of a saturated solution of Aluminium chloride contains 26.7g dissolved in it at 45°C. What is the solubility in mole per dm3 at this temperature?

**Solution**

**Example 4**

Water as added to 50g of sodium chloride to produce 100cm3 of a saturated solution at 20°C if the solubility of the salt at this temperature is 7 moles per dm3. Calculate the number of moles of undissolved salt.

**Solution**

**Example 5**

The solubility of KNO3is exactly 1800g per 1000g water at 830C and 700g per 1000 water at 40oC. Calculate the mass of KNO3 that will crystallize out of solution if 155g of the saturated solution at 83oC is cooled to 40oC

**Solution**

Solvent + solute = solution

**Solubility Product**

Solubility is the equilibrium concentration of a substance in water. Sparingly soluble salts do not ionize completely in water. Solubility product constant, Ksp, is used to describe the equilibrium constant of sparingly soluble ionic salts. The solid does not appear in the equilibrium constant equation since it is not in the same phase as the ions e.g silver chloride, calcium phosphate, Lead (II) chloride e.t c

Examples

1. A saturated solution of AgCl was found to have a concentration of 1.3x10-5mol/dm3. Calculate the solubility product of the salt.
2. Calculate the concentration of barium fluoride in water at 25°C if the Ksp is 1.9x10-6.

**Factors that affect solubility of a solid in a liquid**

1. Nature of the solute and solvent: Polar solutes are soluble in polar solvents while non-polar solvents are soluble in non-polar solvents. **Like dissolves like**.
2. Temperature: solubility increases when the solution is heated.
3. Common ion effect: The solubility of sodium chloride in water is higher than its solubility in HCl because of the common ion in the solute and solvent

**Factors that increase solubility of a solid in a liquid**

1. Stirring the mixture
2. Heating the mixture
3. Grinding the solid to powder

**Solubility Graph/Curve**

If the solubilities of a solute in a given solvent are plotted against their respective temperatures, a solubility graph or curve showing the effect of temperature on the solubility of the substance will be obtained.

Fig: Solubility Graph for Some Salts

**Deductions from the Solubility Curves**

From the graph above, we can deduce the following from the temperature range of O0C to 1000C

1. Solubilities of KClO3 and KNO3 increase very rapidly with increase in temperature
2. Solubilities of NaCl and Ca(OH)2 are independent of temperature.
3. Na2SO4 shows a solubility curve with a sharp break at 360C. This is because the salt exist in solution as sodium tetraoxosulphate ( VI) decahydrate, Na2SO4 .10H2O at temperatures below 36°C to give up its water of crystallization to become anhydrous at temperatures above 36°C. Thus, 36°C is referred to as the **transition** point. If cooled, a saturated solution of Na2SO4 will be deposited.
4. At all temperatures between O°C and 100°C, Ca(OH)2 has the lowest solubility which decreases at temperatures over 70°C.
5. Solubility of KCl increases at a constant rate with the rise in temperature.

**Applications of Solubility Curves**

1. Solubility curves enables pharmacists to determine the amount of solid drugs that must be dissolved in a given quantity of solvent to give a prescribed drug mixture.
2. It also enables chemists and research workers to determine the most suitable solvent to be used at various temperatures for the extraction of chemicals from various natural resources.
3. With the help of solubility curves, a given mixture of solutes can be separated or purified by fractional crystallization.

**Solubility of gases**

The solubility of most gases decreases with increase in temperature with the exception of HCl gas

The solubility of a gas in a liquid is affected by pressure, temperature and chemical reaction of the gas.

**Students exercise**: Write three differences between solubility of solids in liquids and gases in liquids

**HALOGENS AND THEIR COMPOUNDS**

Halogens are the group seven (7) elements on the periodic table. They are following: Chlorine, Bromine, Iodine and Astatine They are all very reactive non-metals. They do not occur free in nature but in the combined state. They react with most metals to form electrovalent salt–like compound. Halogen means salt producers. Fluorine is the most reactive and most electronegative element.

**Electronic configuration**

This describes how electrons of atoms are arranged in the sub-shells, shells and orbitals. In filling the available orbital, electrons will enter the orbital with lowest total energy content ‘f’ electronic have more quanta (energy) than ‘d’ , d has more energy than ‘p’ and p more than ‘s’ electrons for the same value of n’ the electronic configuration of some elements are given below.

**Electronic Configuration of some Halogens**

9F : 2, 7 or 1s22s22p5.

17Cl : 2, 8, 7 or 1s22s22p63s23p5.

35Br : 2, 8,18,7 or 1s22s22p63s23p64s23d104p5.

53I : 2,8,18,18,7 or 1s22s22p63s23p64s23d104p64d105s25p5

Each halogen member has 7 electrons in it outer most shell and so needs only one electron to complete its octet. This account for their electronegativity values of the halogens and their great reactivity.

**GENERAL PROPERTIES OF THE HALOGENS**

1. They are all composed of covalent molecules containing two atoms (diatomic molecules) where x is a halogen. This accounts for their low melting and boiling points and their solubility in covalent non- polar liquids
2. At room temperature, fluorine and chlorine are gases. Bromine is liquid and iodine solid. The boiling point increases with increases in atomic mass.(group trend)
3. Halogens are colored with typical penetration odors’. The colours deepen down the group: fluorine is pale yellow, chlorine is greenish yellow, bromine is red and iodine is violet. (group trend)
4. Halogens are very reactive element. The reactivity decreases down the group.
5. All halogens are strong oxidizing agents. Fluorine oxidizes water to peroxide, chlorine reacts slowly with water to give Oxochlorate (I) acid (HClO). Oxidizing power decreases down the group.
6. They combine with metals to form ionic compounds and with non-metals to form covalent compounds.
7. They combine with hydrogen to form gaseous covalent **halides**
8. The halogens disproportionate in water

Disproportionation is a redox reaction in which a substance acts as the oxidizing agent as well as the reducing agent in the same reaction.

H2O(g) + Cl2(g)  2HCl(g) + HOCl(aq)

0 0 -1 +1

1. They form complexes with silver(except fluorine) which can be used as test for halides

Volatility, reactivity, Oxidising ability, electronegativity and solubility decreases down the group due to increasing atomic number of the halogens.

**CHEMISTRY OF IODINE, FLUORINE AND BROMINE**

**Fluorine**

Fluorine is the first and the most reactive element among the halogen it does not occur free in nature due to its high reactivity, it is too reactive to be safely prepared in the laboratory. Fluorine is found mainly in minerals like cryolite [NaF.AlF3] and fluorspar [CaF2].

**Preparation of fluorine**

It is prepared by the electrolysis of potassium fluoride in anhydrous hydrogen fluoride using carbon as anode and a steel vessel as cathode

**Physical properties of Fluorine**

1. It is a poisonous yellow gas with an irritating smell.
2. It has a boiling point of -1880C.
3. It is the most reactive element found on earth.
4. It is the most electronegative element as a result of its small size and electronic structure.

**Chemical Properties**

1. Fluorine combines directly with other non-metals except Nitrogen, Helium, Neon, Oxygen and rare gases to form fluorides like PF5 and SF6.

P2(S) + 5F2 (g) → 2PF5

S2(S) + 6F2 (g)  → 2SF6

Xe(g) + 2F2 (g) → XeF4

1. It has a great affinity for hydrogen. It reacts explosively with hydrogen or hydrogen containing compound to form hydrogen fluoride

H2(g) + F2(g)  → 2HF(l)

2NH3(g) + 3F2(g) → 6HF(l) + N2(g)

CH4(g) +4F2(g)  → 4HF(g) + CF4(l)

1. Fluorine is a powerful oxidizing agent. it vigorously oxidizes water in a complex reaction which gives mainly hydrogen fluoride and oxygen together with traces of hydrogen peroxide and oxygen diflouride, F2O

2F2(g) + 2H2O(l) 4HF(l) + O2(g)

4.It can displace all other halogens from aqueous solution of their compounds

2NaCl(aq) + F2(g) 2 NaF(aq) +Cl2(g)

5.It can also react with the most reducing agents and the noble gases like krypton and xenon Xe(g)+ 2F2(g)  + Xe XeF4(s)

**USES OF FLOURINE**

* 1. Fluorine compounds are used as refrigerants, anaesthetic, in atomic research and as aerosol propellant.
  2. Tin (IV) fluoride is used in much toothpaste to prevent tooth decay. Sodium fluoride is used in minute quantities for the fluoridation of drinking water.
  3. Hydrofluoric acid is used in etching glass and in cleaning steel.
  4. Fluorine and hydrogen fluoride are used to make uranium hexafluoride which is used in separating the isotopes of uranium.
  5. Fused cryolite is used as solvent for bauxite

**CHLORINE**

Chlorine is the most important element of all the halogens. It was first isolated by Scheele in 1794 when he heated some conc. HCl(aq) with manganese(IV)oxide. The gas was named “chlorine” in 1810 by Davy from the Greek word “chloros” meaning greenish yellow.

Chlorine does not occur free in nature because it is very reactive but in combined state as chlorides.

**Laboratory preparation of chlorine**

Chlorine is generally prepared by the oxidation of conc. hydrochloric acid [HCl] with a strong oxidizing agent such as manganese (IV) oxide [MnO2] or potassium tetraoxomanganate (VII) KMnO4.

1. Using **Manganese (IV) oxide:** Add mixture of manganese (VI) oxide and conc. Hydrochloric acid. The acid is oxidized to liberate chlorine which is then passed through a wash bottle containing water to dissolve any hydrogen chloride that might be present. The gas is dried using conc. H2SO4 and it collected by upward displacement of air or downward delivery.

MnO2(s) + 4HCl(ag) heat MnCl2(aq) + 2H2O(l) + Cl2(g)

Alternatively, chlorine can be prepared by heating a mixture of NaCl, MnO2 and conc. H2SO4.

2NaCl(s) + MnO2(s) + 2H2SO4(aq) Na2SO4(aq) + MnSO4(aq) + 2H2O(l)

1. Using **potassium tetraoxomanganate (VII) KMnO4.** Conc. Hydrochloric acid is oxidized to liberate chlorine gas

2KMnO4(aq) + 16HCl(aq) 2KCl(aq) + 2MnCl2(aq) +8H2O(l) + 5Cl2(g)

The water removes impurities like hydrogen chloride gas while conc. H2SO4 dries the gas. The gas is collected by downward delivery because it is denser than air

**INDUSTRIAL PREPARATION OF CHLORINE**

Chlorine is manufactured industrially by the electrolysis of:

1. Brine
2. The chloride of molten Na, Mg or Ca.

The chlorine is then liquefied and stored under pressure in steel cylinders.

**PHYSICAL PROPERTIES OF CHLORINE**

1. Chlorine is a greenish yellow gas with a choking, irritating and unpleasant smell.
2. It is about 2.5 times denser than air
3. It is slightly soluble in water (about 2.3cm3 will dissolve in 1 cm3 of water)
4. Chlorine is easily liquefies under a pressure of about 6 atm and stored in iron cylinder
5. Chlorine is a very poisonous gas. (about 20ppm will damage the mucous ling of the lungs)

**CHEMICAL PROPERTIES**

The Chemical reactivity of Chlorine is great due to its strong electronegative character.

1. Direct combination with other elements: Chlorine combines directly with most other element to form chlorides.
2. With **metals**: metals react readily with chlorine especially when heated to form the corresponding chloride

2Na(s) + Cl2(g) 2NaCl(s)

Mg(s) + Cl2(g) MgCl2(s)

**NB:** If the Metal forms more than one type of chloride, the higher one is formed e.g. in the case of iron, FeCl3 is formed and not FeCl2. This is due to the oxidizing nature of chlorine.

1. With **non**-**metal**: with the exception of noble gas, oxygen, nitrogen and carbon, all other non metals burn in chlorides

2P + 5Cl2 2PCl5

Hydrogen and chloride combine explosively in bright sunlight, although the reaction is slower in diffused light.

1. **Displacement of other halogen**: With the exception of fluorine, chlorine can displace any of the other halogens from solution of their respective acids and salts.

2NaBr(aq) + Cl2(g) 2NaCl(aq) + Br(l)

2HI(aq) + Cl2(g) 2HCl(aq) + I2(S)

1. **As an oxidizing agent**: Chlorine is a powerful oxidizing agent because of its ability to remove hydrogen and its readiness to accept electrons from reducing agent to form chloride.

Chlorine readily removes hydrogen from its compound to form hydrogen chloride.

1. 2NH3(g) + 3Cl2(g) N2(g) + 6HCl(g)

The hydrogen chloride formed reacts with excess ammonia to form ammonium chloride.

HCl(g) + NH3(g) NH4Cl(s)

1. **With hydrocarbons:** a piece of filter paper saturated with warm turpentine [C10H10] will rapidly catch fire in a jar of chorine forming a black soot and misty fumes of hydrogen chloride C10H10 + 8Cl2(g) 10C(g) + 16HCl(g)

Under sunlight chlorine reacts with a saturated hydrocarbon e.g. methane [CH4] to produce chlorine. This is known as substitution reaction.

CH4(g) + Cl2(g) CH3Cl(g) + HCl(g)

1. **With hydrogen sulphide:** when chlorine and hydrogen sulphide are mixed together a yellow deposit of sulphur is formed as a result of the oxidation of the sulphide by chlorine.

H2S(g) + Cl2(g)  2HCl(g) + S(s) yellow deposit.

1. **With water:** chlorine reacts with water to form to form oxochlorate(I) acid whch decomposes to for hydrogen chloride and oxygen. Chlorine water(chlorine bubbled through water) decomposes when exposed to sunlight

H2O(g) + Cl2(g)  2HCl(g) + HOCl(aq)

HOCl(aq)  2HCl(g) + O2(g)

1. **With iron (II) chloride solution**: Chlorine oxidizes a solution of green iron (II) chloride to brown iron (III) chloride.

2FeCl2(aq) + Cl2(g) 2FeCl3(aq)

Fe2+  Fe3+ + e-

1. **With trioxosulphate (IV) in (SO32-):** when chlorine gas is bubbled through a freshly prepared solution of trioxosulphate (IV) acid, it oxidizes the SO32- to tetraoxosulphate (VI) acid.

H2SO3(aq) + H2O(l) + Cl2(s) H2SO4(aq) + 2HCl(aq)

1. **Reaction with alkalis**:
2. With **dilute** **alkali** solution: chlorine form a pale yellow of sodium oxochlorate (I) when bubbled through a cold dilute solution of NaOH.

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

Bleaching powder is produced by bubbling chlorine through a freshly prepared solution of slaked lime.

Ca(OH)2(ag) + Cl2(g) CaOCl2.H2O(s)

Slaked lime bleaching powder

1. With **concentrated** **alkali** solution: when Chlorine is bubbled through a hot conc. Solution of NaOH, a mixture of the trioxochlorate (V) and chloride of the metal is formed.

3Cl2(g) + 6NaOH(aq) NaClO3(aq) + 5NaCl(aq) + 3H2O

Sodium trioxochlorate(V)

**Uses of chlorine**

1. Chlorine is used as a bleaching agent in the laundry and dyeing industry for cloths, cottons, and paper.
2. It is used as a powerful germicide (b/c of its oxidizing nature) in the sterilization of water and in sewage treatment.
3. It is used in aerosol propellants.
4. Chlorine is used in the manufacture of
5. Hydrochloric acid
6. Important organic solvent such as trichloromethane,(CHCl3) tetrachloromethane, (CCl4), trichloroethanal (chloral for making insecticides, etc.
7. Plastic as polyvinyl chloride [PVC] and synthetic rubber.

**Test for chlorine**

The presence of Cl2 can be confirmed by its action on damp litmus paper and starch iodide paper.

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

Chlorine turns starch iodide paper blue because it displaces iodine from the iodide. The liberated iodide then turns the starch blue

2KI(aq) + Cl2(g) → 2KCl(aq) + I2(s)

**HYDROGEN CHLORIDE**

Hydrogen chloride exists as a gas at s.t.p and when it dissolves in water, it forms hydrochloric acid. It can be found in the atmosphere as an industrial by-product. In the atmosphere, it is considered as an air pollutant but can readily be washed down by rain because of its solubility in water.

**Laboratory preparation:**

HCl is prepared by the action of hot conc. H2SO4 on NaCl

**Method**: Put some NaCl in a round bottom flask. Add conc. H2SO4 acid through the thistle funnel and water on. The gas formed is passed though a wash bottle containing conc. H2SO4 drying and is then collected in a gas jar by down and delivery denser than air

NaCl(aq) + H2SO4(aq) NaHSO4(ag) + HCl(g).

**Industrial preparation**

HCl is prepared in large amount by the direct combination of hydrogen and chlorine gases obtained from the electrolysis of brine. The HCl obtained is very pure and it dissolved in water to form hydrochloric acid.

H2(g) +Cl2(g) 2HCl(g)

**Physical Properties of Hydrogen chloride**

1. HCl gas is a colorless gas with a choking irritating smell.
2. It is very soluble in water, forming an aqueous solution of hydrochloric acid.
3. It does not burn nor support combustion, hence it extinguished a glowing splinter .
4. It turns damp blue litmus paper red, showing that it is acidic in aqueous solution.
5. It is dense than air (about 1.25 times).
6. Dry HCl gas readily dissolved in non-solvent like chloroform and toluene.

**Chemical properties**

1. **Reaction with metal:** Hydrogen chloride reacts with many metals (especially when heated to form the respective chloride and hydrogen.

Zn(s) + 2HCl(g) ZnCl2(s). + H2(g)

If the metal can form two chlorides, the lower chloride is usually formed

Fe(s) + 2HCl(g) FeCl2(s) + H2(g)

1. **Direct combination with ammonia:** HCl react with NH3 to formed dense white fumes of ammonium chloride

HCl(g) + NH3(g) NH4Cl(g)

**Fountain experiment:**

**Aim**: To show that hydrogen chloride is extremely soluble in water.

**Method**: Fit a dry round button flask with a rubber bung carrying two delivery tubes A and B. Fill the flask completely with hydrogen chloride through tube A. at the same time, open the clip on tube B to allow the air inside the flask to displaced. When the flask is full gas, add a few drop of water through tube B and immediately close the clip at A and B. allow the water run down the flask into a through of water containing a few dry of blue litmus.

Open the clip at B. the water dissolves some of hydrogen chloride and partial vacuum is created in the flask. This causes more water to be sucked into the top flask and a foundation is seen. The litmus turns red (showing that the gas is acidic in aqueous solution).

The hydrochloric acid formed the fountain continues until all the hydrogen chloride has dissolved

**HYDROCHLORIC ACID**

**Properties**

**1. As an acid:** hydrogen chloride gas dissolves in water to form hydrochloric acid which exhibits all the usual properties of acid

**With** **metals**: metals which are more than hydrogen in the series liberate hydrogen gas form hydrochloric acid e.g Zinc

2HCl(aq) + Zn(s) → ZnCl2(aq) +H2(g)

**With** **Bases** : it neutralists bases or alkali to form salt and water only

NaOH(aq)+ HCl(aq) →NaCl(aq) +H2O

ZnO(l) +2HCl(aq) →ZnCl2(aq)

It liberates carbon(IV)oxide from trioxocarbonates (IV) and hydrogen trioxocarbonate(IV)

2HCl(aq) + Na2CO3(s) → 2NaCl(aq) +H2O(l) + CO2(g)

HCl(aq) + NaHCO3(s) → 2NaCl(aq) +H2O(l) + CO2(g)

2 **As a precipitating agent**: when hydrochloric acid is added to AgNO3 or Pb(NO3)2 solution, a white precipitate of Ag or Lead(II)chloride is formed

3. **Reaction with oxidizing agents**: Conc. hydrochloric acid is easily oxidized by strong oxidizing agents such as KMnO4 or MnO2 to liberate chlorine

Note: This is why hydrochloric acid is never used for acididfying solution of oxidizing agents instead; tetraoxosulphate (VI) acid is used.

**Test for Hydrogen chloride**

If the unknown gas is colorless with an irritating smell, fumes in moist air and turns blue litmus paper red, then it is probably hydrogen chloride

**With ammonia**: Place a glass rod dipped in ammonia solution at the mouth of a gas jar containing the unknown gas the formation of dense white fumes of ammonium chloride confirms the gas as hydrogen chloride

**With silver trioxonitrate (V):**  Add a few drops of AgNO3 solution to a gas jar containing the unknown gas and shake. The formation of a white ppt. of AgCl which is not soluble in water confirms the gas at hydrogen chloride.

AgNO3(aq) + HCl(laq) → AgCl(s)

**Uses of hydrogen chloride**

1 Hydrogen chloride gas is used in the manufacture of chloroethene.

2 It is used to remove oxides from metal before electroplating.

3 It is used in the preparation of drugs and dyes

4 It is also used in the manufacture of gelatin and glue (from the tendons of animals, also in the production of glucose from starch.

**[**

**NITROGEN & ITS COMPOUNDS**

Nitrogen occurs as a free element in the air, constituting 78% of the earth’s atmosphere. It acts as a diluent in air to slow down oxidation of metals and combustion it exists in the combined from as trioxonitrates(V) of Na and ammonium salts. It can also be found in organism matter such as proteins, urea and vitamin B compounds. It was discovered by David Rutherford in 1772

**Laboratory preparation of Nitrogen**

1. **From the atmosphere:** Since Nitrogen makes up a large percentage of air, it can be obtained by removing the other constituents of air.

CO2 and O2 can be removed by passing air through caustic soda and copper turning respectively Nitrogen obtained through this method contains 17% by volume of gases as impurities and is denser than pure nitrogen

1. **By decomposition of ammonium dioxonitrate(III).** NH4NO2 is unstable and decomposes exothermically. It is generated by the reaction of sodium dioxonitrate(III) and ammonium chloride in ratio 5:7.

NaNO2(aq) + NH4Cl(s) → NaCl(s) + NH4NO2

The ammonium dioxonitrate (III) formed is decomposed to produce nitrogen and steam

NH4NO2(aq) → N2(g) + 2H2O(g)

If the ammonium dioxonitrate (III) is heated directly, it may get out of control and cause an explosion.

3. **From Ammonia:** passing NH3 over red hot copper(II) oxide oxidizes the ammonia to Nitrogen and the CuO is reduced to Cu

2NH3(g) + 3CuO(s) + 3H2O(l) +N2(g)

4. **From dinitrogen (I) oxide**: When dinitrogen (I) oxide is passed over red hot copper, the gas is reduced to nitrogen

N2O(g) +Cu(s) → CuO + N2(g)

5. **From ammonium heptaoxodichromate(VI)** When The heptaoxodichromate heated, it decomposes to yield nitrogen.

(NH4)2Cr2O7(s) → N2(g) + Cr2O3(s) + 4H2O(g)

**Industrial preparation**

Nitrogen is prepared industrially by the fractional distillation of liquid air from which dust, water vapour and CO2 has been removed. The air is then subjected to successive compression and cooling processes at 200atm and -200°C. Upon distillation, nitrogen gas is first evolved at -196°C and is separated from oxygen. The nitrogen is then stored in steel cylinders or sold as compressed gas.

**Physical properties**

* 1. Nitrogen is a colourless, odourless and tasteless gas
  2. Pure nitrogen is slightly lighter than air
  3. It is only slightly soluble in water. 2 vols will dissolve in 100 vols of water
  4. The melting point of nitrogen is -210°C while the boiling point is -196°C

**Chemical properties**

Nitrogen belongs to group V of the periodic table and have valence electrons. However, However, it achieves stable octet structure by forming covalent bonds in its compounds. It also forms the nitride ion N3- in combinations with group 1 and 2 metals. Nitrogen shows oxidation states varying from -3 to +5 in its various compounds. Nitrogen exists in air as a diatomic molecule with triple covalent bond between its atoms (N≡N).The high bond energy (946KJmol-1) makes the bond very stable and accounts for the unreactive nature of nitrogen under ordinary conditions. However at high temperatures, nitrogen combines directly with hydrogen, oxygen and certain metals.

1. **With Metals**

Nitrogen combines directly with very electropositive metals e.g Magnesium, calcium, aluminium and iron to form nitride is hydrolyzed to give ammonia gas .

1. **With Non-Metals**

Nitrogen combines reversibly with hydrogen to produce ammonia. It combines directly with oxygen at very high temperature (abt 2000oC) or in the presence of a high voltage electric spark to form small amounts of nitrogen (II) oxide. In nature, this reaction occurs in the atmosphere when lightning flashes.

**NAME OF COMPOUND FORMULA OXIDATION STATE**

Ammonia NH3 -3

Hydrazine N3H4 -2

Hydroxylamine NH2OH -1

Nitrogen N2 0

Dinitrogen (I) oxide N20 +1

Nitrogen(II) oxide NO +2

Dinitrogen (III) oxide N2O3 +2

Dioxonitrate (III) NO2- +3

Nitrogen (IV) oxide NO2 +4

Dinitrogen (V) oxide N2O5 +5

Trioxonitrate (V) NO3- +5

**Uses of Nitrogen**

1. Nitrogen is used in the manufacture of ammonia, cyanide, trioxonitrates (V) and fertilizers
2. Liquid nitrogen is used as a refrigerant (cooling agent)
3. Due to its inert nature, nitrogen is used

As a preservative to prevent rancidity in packaged foods

As a carrier gas in gas chromatography

In providing an inert atmosphere for certain industrial processes

**COMPOUNDS OF NITROGEN**

These include: ammonia, oxides of nitrogen, trioxonitrate (V) acid, trioxonitrate (V) salts.

**AMMONIA**

Ammonia is a hydride of nitrogen, formed when an ammonia salt is heated with a non-volatile base. In nature, ammonia is produced when nitrogen matter decays in the absence of air by the action of heat or putrefying bacteria. Ammonia is present in trace amount air but it is very soluble in water and as a result dissolves in rainwater and finds its way into the soil where it may be converted into other compound

**Laboratory Preparation of Ammonia**

Ammonia is prepared by heating any ammonia salt with a non-volatile base e.g. ammonia chloride or calcium hydroxide (slaked lime) Ca(OH)2 is prepared because it is cheap and not deliquescent like caustic soda since both reactants are solids, they are grounded to increase the surface area.

Ca(OH)2 + 2NH4Cl(s) CaCl2 (s) + 2H2O(i) + 2NH3(g)

Drying agent for ammonia is Calcium oxide since conc. H2SO4 and fused calcium chloride

2NH3(g) + H2SO4  (NH4)2SO4 (g)

4NH3(g) + CaCl2(g) CaCl2.4NH3(g)

**Industrial Preparation of Ammonia**

It is manufactured industrially by the Haber process. The combination of nitrogen with hydrogen is a reversible reaction. The conditions for optimum yield are.

1. Finely divided iron (catalyst)
2. Temperature of 450°C
3. Pressure of 200 atm

Yield of ammonia is 15%. It is liquefied and stored

**Structure of the Ammonia Molecule**

Ammonia molecule has 3 single covalent bonds between nitrogen and hydrogen and a pairs of lone electrons. The shape is that of a trigonal pyramidal. Ammonia molecule is polar due to the lone pair of electrons and the electronegativities of nitrogen and hydrogen. As a result, hydrogen bonds forms easily between ammonia and water molecule.

**Physical Properties of Ammonia**

1. It is a colorless gas with a characteristic pungent choking smell
2. It is less dense than air about 1.7 times
3. It is an alkaline gas, turning moist red litmus paper blue
4. It is very soluble in water to gives aqueous ammonia which ionizes slightly to produce hydroxide ion and ammonia in ion

NH 3(g) + H2O(i) NH3H2O(i)

NH3.H2O(g)  ⇋ NH4+ + OH-(aq)

On warming, aqueous ammonia liberates ammonia gas

1. Ammonia liquefies at -34.4°C into a colorless liquid
2. It has a boiling point of -77.7°C and a melting point of -34.4°C
3. Concentrated solution of ammonia (880 ammonia) has a density of 0.880gcm-3 which contains 35% by mass of the gas.

**Chemical properties of ammonia**

1. Ammonia does not burn in air but burns in oxygen with a greenish- yellow flame to form water vapor and nitrogen

4NH3(g) + 3O2(g) → 6H2O(g) + 2N2(g)

In the presence of a catalyst (heated platinum) ammonia reacts with excess air to produce nitrogen (ll) oxide (NO) and water

4NH3(g) + 5O2(g) → 4NO(g) + 6H2O(l)

1. It reduces heated copper(ll) oxide to copper while it is itself oxidized to water and nitrogen

3CuO(s) + 2NH3(g) 3Cu(s) + 3H2O(l) + N2(g)

Ammonia obtained from heating ammonia chloride and slaked lime is dried and passed over copper (ll) oxide the anhydrous copper (ll) tetraoxosulphate(VI) in the second u-tube turns blue showing that water is one of the combustion tube. Reduction of copper (ll) oxide (CuO) by ammonia

1. It reduces chlorine to Hydrogen chloride and Nitrogen. The hydrogen chloride reacts with excess ammonia to produce dense white form of ammonia chloride.

2NH3(g) + 3Cl2(g) 6HCl(g) + N2(g)

6NH3(g) + 6HCl(g) 6NH4Cl (s)

Cl2(g) + 8NH3(g) 6NH4Cl (s)

4. Chlorine is in excess, Nitrogen(lll) chloride NCl3 an explosive and oily liquid is formed

NH3(g) + 3Cl(g) NCl3(l) + 3HCl(g)

5. It reacts with carbon(IV) oxide at 150°C and 150atm to produce u**rea** an important organic compound

2NH3(g) + CO2(g) (NH2)2CO(s) + H2O(l)

6. It reacts as a base (a weak base). It reacts with acids to form ammonia salt

2NH3(g) + H2SO4(aq) (NH4)2SO4(s)

NH3(g) + HCl(aq) NH4Cl(s)

7. It acts as a precipitating agent. It precipitates the insoluble hydroxides of metal form solution of their salts. It is useful in precipitating amphoteric hydroxides which dissolve in excess of strong alkali

Pb(NO3)2(aq) + 2NH3(aq) Pb(OH)2(s) + 2NH4NO3(aq)alkali

Pb2+ + 2OH- Pb(OH)2(s) *white gelatinous ppt*

Zn2+ + 2OH- Zn(OH)2(s) white gelatinous ppt

Fe3+ + 3OH- Fe(OH)3(s) reddish brown gelatinous ppt

Cu2+ + 2OH- Cu(OH)2(s) blue gelatinous ppt

However some metal hydroxides like Cu2+ and Zn2+ will dissolve in excess ammonia solution to form complex ions. The lone pair of electron in the ammonia molecule allows it form complex ions

Cu(OH)2(s) + 4NH3(aq) Cu(NH3)4(aq) + 2OH-(aq)

Zn(OH)2(s) + 4NH3(aq) Zn(NH3)4(aq) + 2OH-(aq)

The complex ion formation is used as a confirmatory test for copper and zinc because other metallic hydroxides do not dissolve in excess ammonia

9. Ammonia is decomposed at temperatures above 500c or by prolonged to yield nitrogen and hydrogen 2NH3(g)  → N2(g) + 3H2(g)

**Test For Ammonia**

Ammonia has a characteristic choking smell which is easily recognizable. It can be confirmed by

1. **Action on litmus paper:** Hold a damp red litmus paper into the jar containing the unknown gas, if the litmus paper turn red, ammonia is confirmed.
2. **Action with dilute hydrogen acids**: Dip a glass rod in concentrated hydrochloric acid and insert into a test tube containing the unknown gas, dense white fumes are formed if its ammonia.

**USES OF AMMONIA**

1. It is used to manufacture trioxonitrate(V) acid and sodium trioxocarbonate (IV)
2. It is used to manufacture nitrogenous fertilizer like ammonia tetraoxosulphate (VI) and ammonium tetraoxophosphate (V)
3. Aqueous ammonia is used in laundry as a solvent for removing stains and grease
4. It is used in softening temporary hard water
5. It is used as a cooling agent in refrigerator although it is replaced by less reactive fluorocarbons.

**Ammonium Salts**

Ammonia salts are electrovalent compound which contains the ammonium ions NH4+ as the cation. They resemble the corresponding alkali metal salt in solubility and structure.

Ammonia salts are prepared by dissolving ammonia in appropriate acid or neutralizing aqueous ammonia with an appropriate acid. The ammonia salts are separated out of solution by crystallization and not by evaporation because they are decomposed by heat.

NH3(aq) + HCl(aq) NH4Cl(s) + H2O(l)

NH3(aq) + HNO3(aq) NH4NO3(aq) + H2O(l)

NH3(aq) + H2SO4(aq) (NH4)2SO4(aq) + H2O(l)

Ammonia trioxocarbonate (IV) (NH4)2CO3 is prepared by heating a mixture of ammonium tetraoxosulphate (IV) with calcium trioxocarbonate (IV) which sublimes as a white solid in the cooler parts of the beaker

(NH4)2SO4(aq) + CaCO3(s) (NH4)2CO3(s) + CaSO4(s)

**Properties of Ammonia Salts**

1. **Solubility**: All ammonia salts are white crystalline solid which dissolve readily in water. They are completely ionized in solution and are strong electrolytes.
2. **Action of heat**: All ammonia salts decompose on heating some however sublime.

NH4Cl ⇋ NH3(g) + HCl(g)

(NH4)2SO4 ⇋ 2NH3(g) + H2SO4(aq)

NH4NO2 ⇋ N2(g) + 2H2O(g)

**Ammonium dioxonitrate (III)**

NH4NO3(s) N2O(g) + 2H2O(g)

**Ammonia trioxonitrate (V)**

(NH4)2CO3(s) 2NH3(g) + CO2 (g) + H2O(l )

1. **Reaction with bases:** All ammonia salts liberate ammonia gas when heated with bases. This reaction helps to distinguish ammonia salts from normal metal salts.

NH4+(s) + OH-(aq) NH3(g) + H2O(l)

**TEST FOR AMMONIUM SALTS**

Heat the unknown substance with sodium hydroxide solution. (ammonia gas) a gas with choking smell which form red litmus paper to blue is given off

NH4+(s) + NaOH(aq) Na+ + NH3(g) + H2O(l)

**AMMONIUM CHLORIDE (NH4Cl)**

This is a white crystalline salt that does not contain water of crystallization and sublimes on heating if heating is continued, it dissociates into ammonia and hydrogen chloride gases but when cooled recombines to form solid ammonia chloride

Ammonia chloride is used in Leclanche and dry cells. It is also used as a flux to increase fusibility of solders and as an analytical reagent in the laboratory.

**Ammonia tetraoxosulphate(VI)(NH4)2SO4**

It is prepared by neutralization of H2SO4 with aqueous ammonia in the laboratory. In the industry, it is manufactured by passing ammonia and carbon(IV) oxide into a fine suspension of calcium tetraoxosulphate(VI) or gypsum in water. CaCO3 is precipitated and filtered off leaving the soluble (NH4)2SO4 which is recovered by crystallization

CaSO4(aq) + CO2(g)+H2O(l) (NH4)2SO4(aq) + CaCO3(s)

It is used as a fertilizer and as a weed killer when it is concentrated

**AMMONIA TRIOXONITRATE(V) NH4NO3**

It is prepared in the laboratory by neutralization of aqueous ammonia with trioxonitrate (V) acid which on crystallization, yield colorless crystals

NH4+(aq)+ OH-(aq)+HNO3(aq) NH4NO3(aq) +H2O(l)

It dissolves readily in water. It is used as a freezing mixture, as fertilizer (nitrochalk) and in making explosives eg amatol or ammonal.

**Ammonia Trioxocarbonate(IV) (NH4)2CO3**

It is prepared by heating a mixture of ammonia tetraoxosulphate(VI) and calcium trioxocarbonate(IV) which is collected as a sublimate. The sublimate contains NH4HCO3 and (NH4)2CO3. when ammonia is added to the sublimate, pure (NH4)2CO3 is obtained.

(NH4)2SO4(s) +CaCO3(s) (NH4)2CO3(s) + CaSO4(s)

It is used as an analytical regent in the laboratory and in smelling salt to present dizziness and and fainting.

**OXIDE OF NITROGEN**

Nitrogen forms different oxides by direct combination of nitrogen and oxygen

**NITROGEN (I) OXIDE N2O (LAUGHING GAS)**

**LABORATORY PREPARATION**

N2O is liberated by thermal decomposition of ammonia trioxonitrate(V). Direct heating of NH4NO3 is uncontrollable and exothermic. It is prepared by gently heating a mixture (finely ground) of potassium trioxonitrate(V) and ammonia chloride . The gas is collected over warm water as the gas is fairly soluble in cold water.

KNO3(s) + NH4Cl(s)KCl(s) + NH4NO3(s)

NH4NO3(s) 2H2O(l) + N2O(g)

Laboratory preparation of dinitrogen (I) oxide

**Physical properties**

1. Nitrogen (i) oxide is a colourless gas with a faint, pleasant but sickly smell and sweetish taste.
2. It is fairly soluble in cold water
3. It is 1.5 times denser than air.
4. It is neutral to moist litmus paper.

**Chemical properties**

1. N2O does not burn in air
2. It decomposed rapidly at red heat (600°C)into N2and O2

2N2O(g) → 2N2(g) +O2(g)

1. It rekindles a brightly glowing splinter but extinguish a feeble glowing one (not hot enough to decompose the gas )
2. It support the combustion of any burning substance which is hot enough to decompose it to yield nitrogen

S(s) +2N2O(g) → SO2(g) + 2N2(g)

Mg(s) + N2O(g) → MgO + N2(g)

1. it is reduced to nitrogen when it passes over copper or iron

Cu(s) + N2O(g) N2(g) + CuO(s)

**TEST FOR NITROGEN(I) OXIDE**

Insert a brightly glowing splinter into a test tube containing the unknown gas. If the gas is rekindled, it is either oxygen or nitrogen (I) oxide N2O has a pleasant smell but oxygen is odourless.

**USES**

1. It is used as a mild anesthetic for minor surgical operation e.g dental surgery with about 20% oxygen (keep patient alive) and trace of carbon(IV) oxide ( maintain breathing) .

Nitrogen (II) oxide NO

Discovered by Cavendish in 1770 as one of the products obtained by passing electric spark through air. It is difficult to obtain in the pure state because of its great affinity for oxygen.

**Laboratory preparation**

NO is prepared by the action of dilute trioxonitrate (V) acid on most metals. Usually a 50% acid solution and copper turnings are used.

3Cu(s) + 8HNO3(aq) → 3Cu(NO3)2(aq) + 4H20(l) +2N0(g)

Preparation of nitrogen (II) oxide brown forms of nitrogen (iv) oxide are always produced in the flask when some of the nitrogen (II) oxide formed reacts with oxygen in the flask but NO2 is very soluble in water and is removed when the gases are bubbled through water

2NO(g) +02(g) →2NO2(g)

**Physical properties**

1. NO is a colorless, poisonous gas. Its smell is unknown because it changes to NO2 on exposure to air
2. It is almost insoluble in water
3. It is slightly denser than air it is neutral to litmus.

**Chemical** **properties**

1. It combined with air to from nitrogen (IV) oxide

2NO(g) + 02(g) ) →2NO2(g)

1. It decomposes into equal volumes of nitrogen and oxygen at high temperature of 10000C. It will only support the combustion of strongly burning substances to from nitrogen and their oxides

2Mg(s) + 2NO(g) → 2MgO(s) + N2(g)

P4(g) +10NO(g) → P4O10(s) + 5N2(g)

It extinguishes a burning splinter or burning sulphur

1. It is reduced to nitrogen by heated metals
2. 2Mg(s) + 2NO(g) → 2MgO(s) + N2(g)
3. It is a weak reducing agent, it decolorized acidified potassium tetraoxomanganate(VII) very slowly.

3Mn04-(aq) + 4H+(aq) + 5N0(g) → 3Mn2+(aq) + 5NO3(aq) + 2H2O(l)

1. It reacts with cold iron (II) tetraoxosulphate (VI) solution to from dark brown solution of an addition compound which decomposes when heated. this is the basis of the brown ring test

FeS04(aq) +NO(g) ⇋ FeS04.NO(aq)

This reaction is used to detect the presence of NO and for purifying or removing it from a mixture of gases.

**TEST FOR NITROGEN (II) OXIDE**

1. When a test tube containing the gas is exposed to air, if the gas is turns reddish brown it is nitrogen (II) oxide
2. When a solution of iron (II) tetraoxosulphate (VI) which has been acidified by a little dilute tetraoxosulphate (VI) acid is formed in to a texture containing the gas, if the solution turns dark brown, the gas is nitrogen (II) oxide

**NITROGEN (IV) OXIDE NO2**

This is the reddish brown gas given off when trioxonitrates (V) of heavy metals are heated. The yellowish colour of bench HNO3 acid is due to the production of NO2 and its subsequent dissolution in the acid. It has an oxidation number is +4

**Laboratory preparation of Nitrogen (IV) oxide**

NO2 is prepared in the laboratory by thermal decomposition of lead (II) trioxonitrate(V) Pb(NO3)2 crystals do not contain any water of crystallization which might interfere with the reaction.

On strong heating, Pb(NO3)2 crackle (cracking sound), melt and decompose to yield lead (II) oxide, oxygen and Nitrogen (IV) oxide. These gases are passed through a U- tube immersed in a freezing mixture. The NO2 formed is liquefied as a green liquid (yellow if pure) while the oxygen escapes. The residue, lead (II) oxide is left in the boiling tube. It is reddish brown when hot but yellow on cooling.

Fig: Laboratory Preparation of Nitrogen (IV) oxide

2 Pb(NO3)2(s) → 2Pb0(s) +4NO2 + 02

**Physical Properties**

1. It is a reddish-brown gas
2. It is poisonous with an irritating pungent smell
3. It is readily soluble in water to form an acidic solution
4. It turns red litmus paper blue
5. It condenses (liquefies) at 220C into a yellow liquid
6. It is denser than air and can be poured downwards.

**Chemical properties**

1. **Action of heat**: At low temperatures Nitrogen (IV) oxide NO2 exists as nitrogen (IV) oxide N2O4. On warming this molecule dissociates into two molecules of NO2 at about 140°C. Above 140°C NO2 dissociate into nitrogen (II) oxide, NO, and oxygen which is complete at 620°C. The reverse changes takes place on cooling
2. **Combustion**: NO2 will not support combustion but will support and burning substance which is not enough to decompose it into oxygen and nitrogen

2N02(g) )→ N2(g) + 202(g)

As a supporter of combustion, it is intermediate between NO2 and NO. It does not rekindle splinter but will allow a rigorously burning splinter/sulphur/carbon/phosphorus/magnesium to continue burning

2C(s) + 2NO2 (g) → 2CO(g) + N2(g)

4Mg(s) + 2NO2 → 4Mg0 + N2(g)

1. **Reducing Agents:** NO2 is reduced to nitrogen by heated copper or iron

4Cu(s) + 2NO2 (g) → 4Cu0(g) + N2(g)

It is also reduced to nitrogen (I) oxide by hydrogen sulphide and carbon (II) oxide

H2S (g) + NO2 (g) →H2O(l) + NO (g) + S(s)

CO (g) + NO2 (g) → CO2 (g)+NO(g)

1. **Water**: It dissolves in water to give an acidic mixture of dioxonitrate (III) acid and trioxonitrate(V) acid. The gas is a mixed anhydride Dioxonitrate (III) acid decomposes at room temperature to form nitrogen (II) oxide and trioxonitrate (V) acid

2N02(g) + H2O(l) → NO2(g)+ HNO2(g) + HNO3(aq)

3 HNO2 (aq) → HNO3(aq) + 2NO2(g)+ H2O(l)

In excess oxygen only trioxonitrate (V) acid is obtained as the dioxonitrate (III) is oxidized to trioxonitrate (V) acid.

1. **Alkalis**: it reacts with alkalis to yield a mixture of dioxonitrate (III) and trioxonitrates (V) salts

2KOH(aq)+2NO2(g) →NaNO3 (aq) + H2O(l)

2NaOH(aq)+2NO2(g) →NaNO3(aq)+NaNO2(aq) + H2O(l)

**Trioxonitrate (V) acid HNO3**

This was first prepared by Glauber in 1658. The early alchemists used the acid to separate gold from silver. It is formerly known as aqua fortis (strong water) because of its corrosive nature on metals

**Laboratory preparation of HNO3**

It is prepared by displacing it from trioxonitrate (V) by concentrated H2SO4 because HNO3 is a less volatile acid. All glass apparatus are used because HNO3 vapor attacks rubber or cork

KNO3(s) + H2O → KHSO4(aq) + HNO3(aq)

NaNO3(s) + H2SO4(aq) → NaHSO4(g) + HNO3(aq)

Trioxonitrate (V) of K and Na are used because they are cheap

HNO3 obtained is yellow due to the dissolution of brown forms of NO2 in the acid which is an impurity. Pure colourless HNO3 can be obtained by bubbling air through the acid to remove Nitrogen (IV) oxide impurity

**Industrial preparation (Ostwald process)**

Industrially HNO3 is obtained by the Catalytic oxidation of a ammonia. the ammonia reacts with excess air in the presence of platinum—Rhodium catalyst at 700°C to produce Nitrogen (II) oxide is cooled and mixed with air to produce nitrogen (IV)oxide. In the presence of more air, the nitrogen (IV) oxide is dissolved in a spray of hot water to yield trioxonitrate(V) acid with a concentration of about 50%. In more modern plants Nitrogen (IV) oxide is absorbed under pressure to obtain more concentrated solution of the acid

2NO(g) + O2(g) →2NO2(g).

4NO2(g)+2H2O(l)+ O2(g) → 4HNO3(aq)

**Physical properties**

1. HNO3 is a forming liquid with a sharp choking smell it is colourless when pure but yellow when contaminated with nitrogen (IV) oxide
2. Pure HNO3­ boils at 860°C and melts at 47°C. The pure acid is very corrosive and readily destroys organic matter such as skin, rubber, cork, clothing
3. Trioxonitrate (V) acid is miscible with water in all proportions and forms a constant boiling mixture at 121°C

**Chemical properties**

This depends on its concentration since it is a strong oxidising agent and a strong acid

1. **As an acid**

**with bases**: it neutralises bases and alkalis to form metallic trioxonitrates (V) and water only NaOH(aq)+ HNO3(aq) → NaNO3(aq) + H20(g)

CaO (aq)+HNO3(aq) → Ca(NO3)2(g )+ H20(i)

**With trioxocarbonate:** it reacts with trioxocarbonate to liberate carbon (IV) oxide

CaCO3(g) + HNO3(aq) → Ca(NO3)2(aq) + CO2(g)

**With metals**: They rarely react with metals to produce hydrogen gas because the hydrogen produced is oxidized to form water but they can liberate hydrogen gas with calcium, magnesium or manganese

C (g) +HNO3(g) → Ca(NO3)2(aq) + H2(g)

Mg(s) + HNO3 (aq) → Mg(NO3)2(aq) + H2(g)

1. **As an oxidizing agent**: It readily accepts electrons and is a strong oxidizing agent. It can undergoes reduction many ways these include NO2, HNO2,NO,NO2, N2H4 and NH4 depending on the acid concentration, strength of the reducing agent and the Temperature

**With metals.**

Pure trioxonitrate (V) acid oxidizes copper to copper (II) trioxonitrate(IV) while it is reduced to nitrogen (IV) oxide

Cu(s) + HNO3(aq) → Cu2+2NO3- + 2H20(l) + 2N02(g)

Concentrated trioxonitrate(V) acid oxidized copper to copper (II) trioxonitrate (V) but it is reduced to nitrogen (II) oxide

3Cu(s) + 8H+NO3-(aq) →3Cu2+2NO3-(aq) + 4H2O(l) + 2NO(g)

Other metals which will behave like copper include lead, mercury and silver. Aluminium and iron do not react with the concentrated acid due to the formation of a surface coating of the oxide which is passive and stops any further reaction by the acid.

**Note: That is why HNO3 is transported in containers lined with aluminium of iron. Magnesium, Zinc and Iron reacts with dilute HNO3 to form their respective trioxonitrates (V) and ammonium trioxonitrate (V) or nitrogen (IV) oxide.**

4Zn(s) + 10HN03(aq) → 4Zn(NO3)2 + 3H2O(l) + NH4NO3(aq

Tin reacts with the concentrated acid to form hydrated oxide instead of a trioxonitrate (V)

Sn(s)+4HNO3(aq) → Sn02.H20(s) + H2O(l) + 4N02(g)

Gold and platinum are not attacked by trioxonitrate(V) acid at all.

**With non-metals**

Hot concentrated trioxonitrate(V) acid oxidizes non-metals to form the corresponding acid while it is reduced to nitrogen (IV) oxide

C(s) + 4HNO3(aq) → C02(g)+2H20(l)+N2O(g)

S(s) + 6HNO3(aq) → H2SO4(aq)  + 2H20(l)+6N02(g)

P(s) + 5HNO3(aq) → H3PO4(aq)+H20(l) +5NO2(g)

I(s) +10HNO3 (aq) →2HIO3 (aq) 4H20(l) +10N02(g)

**With reducing Agents**

Trioxonitrate(V) acid also undergoes redox reaction with common reducing agents.

A. It oxidizes hydrogen sulphide to sulphur and it is reduced to nitrogen (IV) oxide

H2S (g) +2HNO3 (g) → S(s) + 2H20(l) + 2NO2(g)

B. It oxidises iron (II) salts to iron (III) salts

6Fe2+(aq) + 8H+(aq) +2NO3(aq) → 6Fe3+(aq)+ 4HO2(l)+2N02(g)

1. **Decomposition:**

Trioxonitrate(V) acid decomposes slowly at room temperature when heated

4HN03(aq) →2H20(l) + 4N02 (g) + 02(g)

1. **Nitration**

In the presence of conc. H2SO4, HN03 dissociates to form the nitryl cation (nitronium ion) N02+ which can replace hydrogen ions from many inorganic compounds like benzene, methylbenzene and phenol. This process is called Nitration

C6H6 (I) +HN03(aq) → C6H5NO2(l) + H20(l)

Nitrobenzene

**USES OF HNO3**

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

**TRIOXONITRATES (V)**

These are normal salts formed from Trioxonitrate (V) acid.

**Preparation**

They can be prepared by

1. Neutralization of trioxonitrate(V) acid with an appropriate alkali
2. Action of trioxonitrate(V) acid on a metal, a metallic oxide or a trioxocarbonates (IV) since all trioxonitrates (V) are soluble, they are recovered from their solution by dry heating

**PROPERTIES**

1. **Action to heat**

All trioxonitrates(V) are decomposed by heat. The products of decomposition of a metallic trioxonitrate(V) depends on the position of the metal in the electrochemical series. All trioxonitrates (V) salts except that of sodium, lead (II) and potassium contain water of crystallization on heating; these salts crackle and dissolve in their own water of crystallization. The salt will decompose after all the water of crystallization has been driven off and therefore must be heated carefully

K they decompose to give the dioxonitrates (III) and oxygen

Na 2NaNO3(g) → 2NaNO2(g) + O2(g)

Ca decompose to give the corresponding oxides of the metals, oxygen and brown fumes of N02

Mg

Zn 2Zn(NO3)2(g)  → 2ZnO(g) + O2(g) + 4NO2(g)

Pb

H

Cu

Hg decompose to give the corresponding metals oxygen and brown fumes of nitrogen (IV) oxide

Ag 2AgNO3(g) →2Ag(s) + NO2(g) + 2NO2 (g)

Au

**Examples are**

2NaNO3(g) → 2NaNO3(g)+ O2(g)

*White pale yellow*

2Zn(NO3)2(g) → 2ZnO(g) + O2(g) + 4NO2(g)

*Colourless yellow (hot) brown*

*White (cold)*

2Pb(NO3)2(g) → 2PbO(s) + O2(g) + 4NO2(g)

*White reddishbrown(hot)*

*Yellow (cold)*

2Cu(NO3)2(g) → 2CuO(s) + O2(g) + 4NO2(g)

*Black brown*

2AgNO3(g) → 2Ag(s) + O2(g) + 2NO2(g)

*Colourless lustrous White brown*

Ammonium trioxonitrates(V) decompose to give nitrogen (I) oxide and water

NH4NO3(s)  → N2O(g) +2H2O(l)

**Action of tetraoxosulphate (VI) acid**

All trioxonitrate(V) liberate trioxonitrate(V) acid when it reacts with tetraoxosulphate (VI) acid

N03-+ H2SO4(aq) →HSO4-(aq)+ HNO3(g)

**Brown ring formation**

When concentrated tetraoxosulphate (VI) acid is added slowly down the side of test-tube containing an aqueous solution of a trioxonitrate(V) and iron (II) tetraoxosulphate (VI), the acid sinks to be bottom and two layers are formed. At the junction of the two layers, the trioxonitrate(V) concentrated acid and the iron (II) tetraoxosulphate (VI) react to form a brown compound.

NO3 reacts with conc. H2SO4 to yield HNO3

Some of the HNO3 is reduced to Nitrogen(II) oxide by iron(II) tetraoxosulphate(VI)

2HNO3(aq) 3H2SO4(aq)+ 6FeSO4(aq) → 3Fe2(SO4)3(aq) + 4H2O(l) + 2NO(g)

The NO combines with more iron (II) tetraoxosulphate (VI) to form a brown addition compound FeS04.NO which appears at the junction of the two liquid layer as a **brown** **ring**

FeSO4(aq) + NO(aq) →FeSO4.NO(aq)

The brown ring disappears if the solution is shaken because the addition compound is decomposed by heat produced when water mixes with the concentrated tetraoxosulphate (VI) acid.

**TEST FOR TRIOXONITRATES(V)**

1. **Brown ring test**

Fill a test-tube with a solution of the unknown compound to a depth of 2cm. Acidify the solution with a little dilute tetraoxosulphate (VI). Add some freshly prepared iron (II) tetraoxosulphate (VI) solution and shake well to mix hold the test-tube in a slanting position and carefully pour a stream of concentrated tetraoxosulphate (VI) acid down the side of the tube. If the unknown compound is a trioxonitrate (V), a brown ring appears at the junction of the acid and aqueous layers

The brown ring test is unreliable in the presence of oxides and bromides since they give coloured rings. Dioxonitrate(III) form a brown solution before the addition of conc. H2SO4 and so must be removed before the test is carried out. Metallic radicals may also interfere with the test since it forms insoluble tetraoxosulphate (VI)

1. **With Tetraoxosulphate (VI) acid.**

Warm the unknown solid with a little conc. H2SO4 acid in a test tube. If a trioxonitrate (V) is present, some trioxonitrate rate (v) acid will be condensed as only drop on the upper part of the tube. On further heating the acid will decomposed to yield brown fumes of nitrogen (IV) oxide

H2SO4(aq) →NO3- (aq) → HNO3(aq)+HSO4-(aq)

4HNO3 → 4NO2(aq) + O2(g) + 2H2O(l)

1. **Copper turnings**

Warm a mixture of the unknown solid and copper turnings conc. H2S04 acid. If a trioxonitrate(V) acid is present, reddish-brown fumes of nitrogen (IV) oxide will be formed

H2S04(aq) + NO3(aq) → HNO3(aq)+ H2SO4(aq)

Cu(s) +4HNO3(aq) →HNO3(aq) +2N02(g)+2H2O(l)

**NITROGEN CYCLE**

This is the continuous circulation of nitrogen between free gaseous nitrogen in the atmosphere and the combined nitrogen in the proteins of living tissues

**Process using soil Trioxonitrate (V)**

All living cells contain protoplasm which consist mainly of proteins. Nitrogen is an essential component of protein. Animal consume protein directly by eating plants or animals since they cannot synthesize protein plants can synthesize their own protein from ammonium or trioxonitrate(V) salts present in the salt. Denitrifying bacteria convert trioxonitrate(V) in the soil to gaseous nitrogen. The process is called **Denitrification**.

**Processes that replenish soil trioxonitrates (V)**

a. **Oxidation of atmospheric nitrogen** by electrical discharge in the lightning. Oxides of nitrogen are dissolved in water as dioxonitrate (III) and trioxonitrate(V) acids which are absorbed by the plants

b. **Action of nitrogen fixing bacteria** such as Rhizobium(symbiotic) and Nostoc, Clostridium and Azotobacter (free Living) which live in the root nodules of plants are able to fix nitrogen directly into the soil. The process is called **nitrogen fixation.**

**c. Decay of organic matter:** nitrogenous matter in dead organisms and excretory are converted into ammonia by putrefying bacteria. Nitrifying bacteria eg Nitrosomonas and nitrobacter convert the ammonia to trioxotrate (V). This process is known as **nitrification**.

**Maintenance of soil Nitrogen**

Under natural conditions, the process which use the soil nitrogen are in equilibrum.

However some activities upset this balance

1. Soil erosion: soil is washed into the sea
2. Discharge of human waste into the sea
3. Production of fertilizer from Haber process

**Method of replacing soil nitrogen include**

1. Application of fertilizer
2. Application of compost/ manure
3. Crop rotation using leguminous plants

Nitrogen cycle

**SHAPES OF MOLECULES AND SOLIDS**

**POLAR AND POLAR MOLECULES**

Substances that are deflected by a non-uniform electrostatic field are said to be polar eg water, trichloromethane, ethanol while substances which are not deflected by a non uniform electrostatic field are said to be non-polar eg Toluene, benzene and tetrachloromethane.

Polar substances consist of polar molecule (they have positive and negative poles). They have a partial positive charge and partial negative charge. In hydrogen chloride, chlorine is more electronegative than hydrogen. The centre of the negative charge in HCl is closer to the chlorine atom than to the hydrogen atom. This results in distortion of the changes in the molecule.

**Polarization**: This is the overall distortion of charge in a molecule due to unequal distribution or sharing of electron. This results in an electron cloud. Such molecules are said to be DIPOLAR and the separation of charges in the molecules is called a DIPOLE. As the centre of positive charge and that of negative charge do not coincide, a permanent dipole results.

When polar liquids flow past a positively charged rod, the negative ends are attracted towards it and with a negatively charged rod, the positive ends are attracted. In non polar liquids, they usually have a symmetrical distribution of similar atoms. In tetrachloromethane, each of the four bonds is a dipole C + Cl which cancel each other because the dipoles are equal making the compound non-polar but in trichloromethane, the structure is assymetrical and the dipoles do not cancel each other. Thus the compound is polar.

**FACTORS AFFECTING POLARITY OF MOLECULES**

1. The polarity of the covalent bond
2. The number and position of lone pairs
3. The shape of the molecule

**ELECTRONEGATIVITY**

Linus Pauling defined electronegativity of an atom as the power of that atom in a molecule to attract shared pair of electrons to itself. Electronegativity increases across the periodic table and decreases down the group. The most electronegative element is Fluorine while the least electronegative is Caesium

Electronegativity values can be used to estimate the polarity of different bonds.

1. Bonds between elements of widely different electronegativities are polar i.e ionic (metal and non metal) bonds between elements of similar electronegativities are non-polar i.e covalent (oxygen and sulphur)

The existence of a dipole makes a covalent molecule partially ionic.

Polarity increases with increase in ionic character.

**Differences between a sigma bond and a pi bond**

|  |  |
| --- | --- |
| **Sigma bond** | **Pi bond** |
| Head on (end to end) overlap of atomic orbitals | side to side overlap of atomic orbitals |
| Determines the shape of the molecule | Does not determine the shape of the molecule |
| Very reactive covalent bond | Less reactive covalent bond |
| It allows rotation of the orbitals | It restricts the rotation of the orbitals |
| It involves hybridized and unhybridized orbitals | It involves unhybridized orbitals only |

**SHAPES OF MOLECULES**

In covalent molecules, bond is formed by overlap of two atomic orbitals, each occupied by a single electron. The bond will be orientated in the direction of the orbitals which provide the electrons, so it is said to be directional and influence the shape and structure of the molecule.

Electron pair repulsion theory states that the shape adopted is the one that keeps repulsive forces to a minimum. It is used to predict the shapes of simple molecules by considering the repulsions between pairs of electrons (lone pairs and bond pairs) within the molecule.

Lone pairs - lone pairs > lone pairs and bond pairs > bond pairs and bond pairs

**Methane CH4 (PO43-, SO42-, ClO4-)**

Carbon has the following electronic configuration

It has only two unpaired electrons available for bond formation in its valence shell. In methane, carbon shows a valency of four, one of the 2s electrons is promoted to occupy the empty 2pz orbital creating four unpaired electrons (One s and three p) in its valence shell

Carbon in methane has four unpaired electron, which form a bond with a hydrogen atom to form four pairs of electrons in its valence shell (stable octet electronic configuration is achieved). The C-H bond are identical and consist of one S and three P orbitals. The 2s and three 2p orbitals merge or hybridize to form four new orbitals that are identical to each other. This new set of four hybrid orbitals are called sp3. The electron clouds of the four bond pairs of electrons are all equally negatively charged so they repel one another to an equal extent to minimize the repulsion, the four electrons pairs become widely spread so that the four electron pairs are directed toward the corners of a regular **tetrahedron**. Carbon lies in the centre with the four hydrogen atom situated at the apices of the tetrahedron. The bond angle between any two covalent bonds is approximately 109°

**AMMONIA**

Nitrogen has the following configuration

It has three unpaired electrons in the 2p orbital and one lone pair in the 2s orbital of its valence shell. Each of the three unpaired electron forms a covalent bond with an electron of a hydrogen atom. The nitrogen atom in ammonia has three bond pairs of electrons and one lone pair in its valence shell.

The electron clouds of the four pairs of electrons are spaced out into **trigonal** **pyramidal** shape. Ammonia contains one lone pair of electron but methane has none. Lone pairs have a greater repelling effect than bond pairs.

Due to the large repulsive force exerted by lone pairs, the three hydrogen atoms occupy the corners of the triangular base with the lone pair occupying a large space at the top bond angle between two N-H bond is approximately 1070

**Water**

Water has the following configuration

Its valence shell has two lone pairs (2s22p2). Each of the unpaired electron forms a covalent bond with an electron from a hydrogen atom. Water molecule has two lone pairs and two unpaired electrons. The two lone pairs squeeze the other two bond pairs of electrons closer together such that the structure is **V- shaped** or **angular**.

Bond angle between two O-H bond is 1050

**CARBON (IV) OXIDE (Cl2, O2, H2)**

Carbon (IV) oxide has double bonds. By forming two double bonds with neighboring oxygen atoms, the carbon atom achieves the covalent bonds are equal and so repel each other because of similar charge, and proximity. The bonds are distorted under strain and give the molecules a linear shape. Other molecules include oxygen O2, Hydrogen H2 and chlorine Cl2

**Summary of some molecules, their shapes and hybridisation**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| No. of electron region | No. of bonding regions | No. of non bonding regions | Molecular geometry | hybrid orbitals | Examples | Graph |
| 2 | 2 | 0 | Linear | sp | CO2, HCN, N2, Cl2 |  |
| 3 | 3  2 | 0  1 | Trigonal planar  Bent | sp2  sp2 | BF3, BCl3, SO3, CO32-  SO2, NO2 |  |
| 4 | 4  3  2 | 0  1  2 | Tetrahedral  Trigonal pyramidal  Bent | sp3  sp3  sp3 | CH4, SiCl4,  POCl3  NH3, PF3  H2O, H2S, BrO3- |  |
| 5 | 5  4  3  2 | 0  1  2  3 | Trigonal bipyramidal  Distorted tetrahedron (see-saw)  T- shape  Linear | dsp3  dsp3  dsp3  dsp3 | PH3, PCl5, SbF5, IO3F7  SF4, IF4+  ClF3, BrF3  XeF2, I3- |  |
| 6 | 6  5  4 | 0  1  2 | Octahedral  Square pyramidal  Square planar | d2sp3  d2sp3  d2sp3 | SF6, PF6-  IF3, XeOF4  XeF4, BrF4- |  |

**INTERMOLECULAR FORCES**

These are forces existing between molecules and they are

1. Dipole –dipole attraction
2. Van der waals forces
3. Hydrogen bonding

**Dipole – dipole attraction**: This is the non-symmetrical distribution of charges within a molecule such that the positive end of a polar molecule (positive dipole) attracts the negative end of another molecule (negative dipole). These are called dipole attractions which hold the polar molecules together in liquids. Therefore polar molecules are held together more strongly than non-polar molecules of the same mass eg water, trichloromethane, ethanol

Dipole-dipole attractions

**Van der waal forces**

In 1873, a Dutch physicist, Van der waal postulated the existence of weak, short range force of attraction between non-polar molecules. Electrons in a non-polar molecule such as hydrogen are close to one nucleus as the other and so the electron cloud may be concentrated at one end to cause a temporary dipole (a partial positive charge while the other one acquires a partial negative charge of equal magnitude). Electron movement in the molecules cause the concentration of the electron clouds to shift sides but the attractive force remains constant. This how Van der waal forces are set up. These forces exist between atoms and between molecules in the solid, liquid and gaseous states. As the size of the molecule increases, the number of constituent electron increases and the temporary dipole-dipole attractions become stronger.

This is illustrated by the increase in boiling point of the halogens and alkanes

The van der waal forces between layers in graphite is strong enough to hold the layer together but weak enough to allow them slide over each other. This is why graphite is used as a solid lubricant.

**HYDROGEN BONDS**

A hydrogen bond is a weak dipole-dipole attraction between:

1. Hydrogen atom attached to a strongly electronegative atom e.g. NH3, H2O, HF
2. Strong electronegative atom with a lone pair of electrons.

Lone pairs of electrons are present in Nitrogen, oxygen and fluorine atoms and thus hydrogen bonds form readily between the molecules of each hydride as such. Hydrogen bonds cause the molecules to aggregate and form chains. This is responsible for their high boiling point. Though hydrogen bonds are weak and break off easily when heated. The strongest hydrogen bonds are found in Fluorine (HF) since it is the most electronegative element. In ice crystals, water molecules are held together by hydrogen bonds.

**Structure of Solids**

Generally, solids are rigid with definite volumes and shapes. The particles are closely packed together in a fixed pattern. The can vibrate about a fixed position but cannot translate.

Solids with definite geometric shapes are said to be crystalline.

The shape of crystal depends on the spatial arrangement of the particles that make up the crystal.

The crystal lattice is the three dimensional arrangement of particles in a crystal.

The unit cells are the smallest portions of the crystal lattice which shows the complete pattern of the particles in their relative positions.

The shape of the unit cell depends on

1. Force of attraction between particles
2. Whether the particles are same or different and on their relative sizes if they are different.

**Kinds of Unit Cells**

1. Simple cubic structure: Particles are placed on at each corner of the cube.
2. Face-centered cubic structure: particles are placed on at each corner of the cube and one in the centre of each face of the cube.
3. Body-centered cubic structure: Particles are placed at one at each corner of a cube and one at the centre of the cube.

**Types of Crystalline Solid**

Crystals can be classified according to the chemical nature of their particles. They are:

**Covalent Solids**

These are made up to atoms joined by covalent bonds to form a grant lattice. They are quite hard, have low melting point and poor conductors of electricity.

Diamond is covalent solid which is octahedral is shape. The crystal lattice is build from a basic three dimensional tetrahedral unit cell. (A carbon atom is linked to four other carbon atoms by covalent bonds of equal lengths which are directed towards the apices of a regular tetrahedron). The basic unit cell is repeated indefinitely forming a giant three-dimensional molecule.

Due to the strength, uniformity and stability of the bonds, a rigid stable crystal lattice is formed.

Diamond is the hardest known substance, resistant to high temperatures and chemical attack. Diamond is compact crystal which has a density of 3.5gcm-3. It does not conduct electricity due to the fact that there are no free valence electrons in the crystal. All the four valence electrons has been used to form covalent bonds.

In graphite, each carbon atom is joined to three others by covalent bonds. The three covalent bonds lie in the same plane with an angle of 120°C between them. The carbon atoms arrange themselves at the corners of adjacent hexagons forming planes or layers. The layers are arranged parallel, one above the other in the crystal lattice. The atoms in a layer are held together by strong covalent bonds but the forces. That is why layers can slide over or past one another, making graphite a solid lubricant. It is soft, slippery and flakes easily.

Graphite has a more open structure, making it less dense and more prone to chemical attack than diamond (it can be oxidized to 6-carbon atom organic compounds under suitable conditions).

Graphite can conduct electricity because it has one free valence electron (mobile electron) since only three electrons are held in definite (covalent) bond.

**Ionic Solids**

In ionic solids, the positive and negative ions are arranged in a regular pattern to give a giant crystal lattice. The strong electrostatic attractions which occur between these opposite ions provide the binding force which holds the crystals together. The crystal lattice formed depends on:

1. the sizes of the ions;
2. their charges

When a crystal is formed, the ions rearrange themselves to maximize attractions and minimize repulsions. Ionic crystals are hard and have high melting points because the electrostatic forces holding the ions are strong. They are poor conductors in the solid state because the ions are held rigidly in place and cannot translate.

When melted or dissolved in water, the ions are free to move about and so they can conduct electricity. Ionic solids are brittle (they shelter when stuck) because as the planes of ions slip pass one another. They pass from state of mutual attraction to that of mutual repulsion.

**Molecular Solids**

Molecules are arranged in regular patterns to give crystal lattices. The molecules are held together by weak intermolecular forces such as Van der Waals forces, dipole-dipole attractions and hydrogen bonds.

1. Van der Waals forces e.g. Naphthalene, iodine, dry ice crystals
2. Dipole-dipole attractions (polar molecule) e.g. Sulphur (IV) oxide
3. Hydrogen bonding (solids) dry ice, water, ammonia, hydrogen fluoride.

Molecular solids have small lattice energies and are easily deformed. They have low melting points and are poor conductors of electricity because the electrons are bound to individual molecules and are not able to move freely through the solid.

**Metallic Solids**

Metal particles are held together in a lattice of closely packed spheres with a relatively few valence electrons. They are unable to form normal covalent bonds with the eight or twelve nearest neighbours in a solid metallic crystal. These valence electrons are very loosely held and they tend to separate from their particular nuclei and move at random through the crystal lattice forming a combined electron cloud. The resultant positively charged metallic ions tend to repel one another but are held together by the attractive force of this electron cloud. The strength of the bonds varies among the metals. It is stronger in iron than sodium or potassium.

When force is applied, layers of metallic ions can slide over one another without shattering the crystal lattice. This is because there are no rigid, directed bonds in a metallic crystal just the moving electron clouds which can adjust itself to a new arrangement. Sometimes, the sliding action can be hindered by the addition of another metal. Alloys, therefore, are less malleable but have greater mechanical strength than pure metals.

Metals are good conductors of electricity because when a metal wire is connecter to the terminals of a car battery (when a potential difference is applied to the two ends of the metal wire), the electrons in the electron cloud will loose their random movement and flow through the wire in a particular direction. Metals are good conductors of heat because the freely moving electrons can convey heat energy.

*How sliding can be prevented by alloy*

The structure of metals is dependent on the way in which the atoms are packed together.

Metallic structure includes face-centered cubic packing, hexagonal close packing and body-centered cubic packing. Some exist in more than one type of structure. Iron for example has a body-centered cubic lattice below 906°C and exists as a face-centered structure between 906 –1440°C

**SILICON AND ITS COMPOUND**

Silicon is a metalloid which belong to group IV of the periodic table. It does not occur free in nature but in combined form as silicon(IV) oxide and trioxosiliate(IV). Silica (Silicon(IV) oxide SiO2) is found in pure form as quartz and less pure forms opal, flint, jasper, and horn-stone.it is the major constituent of sand and keiselghur. Metallic trioxosilicates are formed in slate and igneous rocks like granite and basalt.

It is present in clay and kaolin as hydrated aluminium trioxosilicates(IV)

**PREPARATION**

It is prepared by heating pure dry sand and magnesium powder in a fire-clay crucible. Dilute HCl acid is added to dissolve any unreacted magnesium or its compounds. The residue contains mainly silicon.

Crystalline silicon is made by heating crushed coke (carbon) in an excess of sand in an electric furnace

Very pure silicon is made by heating silicon (IV) chloride SiCl4 with Zinc or by reducing trichlorosilane SiHCl3 with hydrogen at high temperature.

**Physical Properties**

1. It is a non-volatile solid with very high melting point
2. It is insoluble in most common solvents
3. It does not exhibit allotropy though it exists as brown amorphous powder or grey lustrous crystals. Both forms possess diamond-like structure
4. Amorphous silicon is more reactive than carbon(graphite) and crystalline silicon

**Chemical Properties**

1. **Heat**: It forms silicon(IV) oxide when heated strongly in air
2. **Steam**: It decomposes steam at red heat to liberate hydrogen gas
3. **Chlorine**: it combines with chlorine to form silicon tetrachloride. Graphite does not give the reaction
4. **Concentrated alkali**: It reacts with hot concentrated sodium hydroxide or KOH to form the corresponding trioxosilicates and evolution of hydrogen gas. Graphite does not give the reaction

**USES OF SILICON**

1. It is used in bronze and steel alloys to increase its tensile strength
2. Very pure silicon is used in making semi-conductors in computers and electronics
3. It is used to make silicone (water-like liquid/solid which are insoluble in water and chemically unreactive). Silicones are used as lubricant, water repellants and electric insulators and in paints, varnishes and polishes.

**SILICON (IV) OXIDE**

It occurs in three crystalline forms: quartz, tridymite and crystabalite. It is prepared by heating silicon in air or by warming sodium trioxosilicate(IV) with conc. HCl

**Properties**

1. It is a colourless crystalline solid when pure
2. It is a macromolecular solid. Si and O2 atoms are linked tetrahedral unit.
3. Silicon (IV) oxide is non-volatile and hard whereas its analogue CO2 is a gas at ordinary temperature
4. It melts at about 1500°C and cools to form a glass-like solid known as quartz glass or fused silica. It is heat resistant, acid resistant and has low expansivity.

**Chemical Properties**

1. It is insoluble in most common solvents except hydrogen fluoride.
2. It reacts with hot concentrated alkalis to form trioxosilicates(IV).It is an acidic oxide.
3. It displaces more volatile acidic oxides from their salts.
4. It combines with metallic oxides at high temperature to form trioxosilicates(IV).
5. It reacts with carbon at high temperature to form silicon carbide, silicon used to make abrasives due to its hardness.

**Uses of SiO2**

1. As sand, it is used in making mortar, cement , concrete, glass and refractory silica blocks
2. Fused silica is used to make optical lenses, prisms, heat-resistant articles and scientific apparatus.
3. Very fine thread of fused quartz are used to suspend component of electrical equipment.
4. Large quartz crystals are used for making optical lenses(since they are transparent to UV-light).They are also used for accurate control of radio transmitters.
5. Powdered quartzis used to make silicon carbide, silicon tetra fluoride, sodium trioxosilicate(IV) and silica bricks for lining furnaces.
6. keiselghur absorbs liquid readily and so it is used as an absorbent for nitroglycerine (explosive) in making dynamite.
7. Keiselghur is used in medicine for making dry antiseptic dressings.

**TRIOXOSILICATES(IV)**

These are salts of trioxosilicate(IV) acid H2SiO3.They occur in nature as trioxosilicates of Al, Fe and magnesium and as gem-stones e.g. emerald and jade. All trioxosilicates(IV) are insoluble in water except those of akail metals. All triosilicates(IV) are thermally stable.

**SODIUM TRIOXOSILICATE(IV) (Na2SiO3)**

It is prepared by heating 2 parts of Silicon(IV) oxide with one part of sodium trioxocarbonate until it melts. It is a colourless glass-like solid with a melting point of 1090°C

**WATER GLASS**

Sodium trioxosilicate(IV) dissolves in hot water under pressure to form a viscous liquid called water glass.

**USES**

1. For sizing paper

2. For fire proofing wood and textiles

3. For making glue

4. For preserving eggs. Eggs are immersed in a solution of water glass to form insoluble CaSiO3 which blocks the tiny pores in the eggshell and prevent entry of germs.

**SILICA GEL**

When water glass is acidified, it sets into a gel SiO2.xH2O. When the gel is heated and dehydrated, a hard porous material known as silica gel is obtained. It is a good absorbent. It is used to dry gases, recover valuable vapors from industrial effluents and refine petroleum.

**GLASS**

Glass is a mixture of metallic trioxosilicates(IV). It is prepared by heating a mixture of silicon(IV) oxide and appropriate metallic trioxocarbonate and oxides at 1300-1400oC . Sometimes powdered glass and coke are to improve quality.

**LIME-SODA GLASS (ORDINARY GLASS)**

It is made by heating Silicon (IV) oxide, washing soda and limestone.CO2 is given off and trioxosilicates (IV) of sodium and calcium are left behind.

Na2CO3(g)+SiO2(g) → Na2SiO3(s) + CO2(g) CaCO3(s)+SiO2(g) → CaSiO3(s) + CO2(g)

**PROPERTIES**

1. It is soft and easily scratched
2. It melts at low temperatures

It cracks by sudden changes in temperature. This is because glass is a poor conductor of heat, it does not contract or expand uniformly. This sets up a strain in the glass causing it to break easily. A better quality glass is obtained by using potassium trioxocarbonate (IV) instead of Na2CO3 or by increasing the proportion of SiO2.

**FLINT GLASS**

It contains trioxosilicate of lead. It is high refractive index and looks brilliant when cut. It is used in prisms and achromatic lenses

**HEAT RESISTANT GLASS (pyrex)**

It contains Silicon (IV) oxide, Boron (III) oxide, Aluminium and sodium oxides. It has lower coefficient for expansion. It is used to make heat resistant instruments like laboratory apparatus and cooking utensils

**COLOURED GLASS**

This is obtained by adding small pieces of metallic compounds to molten glass. Glass is known as supercooled liquid because its molecules are arranged randomly as in a liquid but not a definite crystal as in a solid.

**CLAY**

This is formed by weathering of certain silicate rocks to form hydrated aluminium trioxosilicate(IV) and silicon (IV) oxide. It is coloured by impurities usually iron (III) oxide. The purest form of clay is china clay or kaolin. It is soft, slippery and white. It is made up of layers loosely bounded to each other just like in graphite. It is used to make various types of pottery and ceramics, tiles, bricks and cement and it act as fillers for papers, rubber soap and paint

**ZEOLITES AND RESINS**

Aluminium trioxosilicates(IV) or zeolites are used as water softeners. Sodium aluminium trioxosilicates(IV) or resins are used in ion-exchange columns for removal of calcium ions