

Inter (Part-I) 2015

Chemistry	Group-II	PAPER: I
Time: 20 Minutes	(OBJECTIVE TYPE)	Marks: 17

Note: Four possible answers, A, B, C and D to each question are given. The choice which you think is correct, fill that circle in front of that question with Marker or Pen ink in the answer-book. Cutting or filling two or more circles will result in zero mark in that question.

1-1- The wave number of the light emitted by a certain is $2 \times 10^6 \text{ m}^{-1}$. The wavelength of this light will be:

- (a) 500 nm ✓ (b) 500 m
(c) 200 nm (d) $5 \times 10^7 \text{ m}$

2- The enzyme used for hydrolysis of urea is:

- (a) Invertase (b) Urease ✓
(c) Lipase (d) Zymase

3- For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other:

- (a) $q_p = q_v$ (b) $q_p < q_v$
(c) $q_p > q_v$ ✓ (d) $q_p = \frac{q_v}{2}$

4- 2.7 g of Al will react completely with how much mass of O_2 to produce Al_2O_3 :

- (a) 0.8 g of oxygen (b) 1.6 g of oxygen
(c) 3.2 g of oxygen (d) 2.4 g of oxygen ✓

5- Which of the following is a pseudosolid:

- (a) NaBr (b) Glass ✓
(c) AgNO_3 (d) Naphthalein

6- Which of the hydrogen halides has the highest percentage of ionic character:

- (a) HF ✓ (b) HCl
(c) HBr (d) HI

7- The substance used for decolourization of undesirable colour in a crystalline substance is:

- (a) H_2SO_4 (b) Silica gel
(c) NaNO_3 (d) Animal charcoal ✓

- 8- The oxidation number of Cl in HClO_4 is:
(a) +2 (b) +3
(c) +5 (d) +7 ✓
- 9- Molarity of pure water is:
(a) 1 (b) 18
(c) 55.5 ✓ (d) 6
- 10- Pressure remaining constant, at which temperature the volume of a gas will become twice of what it is at 0°C :
(a) 546°C (b) 200°C
(c) 546 K ✓ (d) 283 K
- 11- When 50% reactants in a reversible reaction are converted into a product, the value of equilibrium constant K_c is:
(a) 2 (b) 1 ✓
(c) 3 (d) 4
- 12- Equal masses of methane and oxygen are mixed in an empty container at 25°C . The fraction of total pressure exerted by oxygen is:
(a) $\frac{1}{3}$ ✓ (b) $\frac{8}{9}$
(c) $\frac{1}{9}$ (d) $\frac{16}{17}$
- 13- The number of bonds in oxygen molecule is:
(a) One σ and one π ✓ (b) One σ and two π
(c) Three sigma only (d) Two sigma only
- 14- The mass of two moles of electrons is:
(a) 1.10 mg ✓ (b) 1.008 mg
(c) 0.184 mg (d) 1.673 mg
- 15- Bohr model of atom is contradicted by:
(a) Plank's quantum theory
(b) Dual nature of matter
(c) Heisenberg's uncertainty principle ✓
(d) All of these
- 16- The pH of $10^{-3}\text{ mol dm}^{-3}$ of an aqueous solution of H_2SO_4 is:
(a) 3.0 (b) 2.7 ✓
(c) 2.0 (d) 1.5
- 17- The boiling point of water at the top of Mount Everest is:
(a) 59°C (b) 69°C ✓
(c) 83°C (d) 75°C

Inter (Part-I) 2015

Chemistry	Group-II	PAPER: I
Time: 3.10 Hours	(SUBJECTIVE TYPE)	Marks: 83

SECTION-I

2. Write short answers to any EIGHT (8) questions: 16

- (i) What are isotopes? Why they have same chemical but different physical properties?

Ans Atoms of the same element can possess different masses but same atomic numbers. Such atoms of an element are called isotopes.

They have same chemical but different physical properties because isotopes are different kind of atoms of the same element having same atomic number, but different atomic masses.

- (ii) Write down stoichiometric assumptions.

Ans Following are the stoichiometric assumption:

- (1) All the reactants are completely converted into the products.

- (2) No side reaction occurs.

- (iii) Define molecular formula of a compound. How is it related with its empirical formula?

Ans Those compounds who have same empirical and molecular formulas, are numerous. For example, H_2O , CO_2 , NH_3 and $C_{12}H_{22}O_{11}$ have same empirical and molecular formulas. So, these compounds have:

Molecular formula = n (Empirical formula)

Their simple multiple 'n' is unity. Actually, the value of 'n' is the ratio of molecular mass and empirical formula mass of a substance.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

- (iv) Define sublimation and partition law.

Ans Sublimation:

Sublimation is a process in which a solid, when heated, vapourizes directly without passing through the liquid phase

and these vapours can be condensed to form the solid again. It is frequently used to purify a solid.

Partition law:

Partition law (Distribution law) states that a solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

(v) Differentiate between adsorption chromatography and partition chromatography.

Ans Chromatography in which the stationary phase is a solid, is classified as adsorption chromatography. While, chromatography in which the stationary phase is a liquid, is called as partition chromatography.

(vi) Write down the values of atmospheric pressure in four different units.

Ans The average pressure of atmosphere at sea level is 1 mm Hg = 1 torr. The S.I unit of pressure is expressed in Nm^{-2} . One atmospheric pressure, i.e., 760 torr is equal to 101325 Nm^{-2} .

1 Pascal = 1 Nm^{-2} . So, 760 torr = 101325

Pa = 101.325 kilopascals (kpa is another unit of pressure).

The unit pounds per square inch (psi) is used most commonly in engineering work, and $1 \text{ atm} = 760 \text{ torr} = 14.7 \text{ pounds inch}^{-2}$. The unit millibar is commonly used by meteorologists.

(vii) Write down any two applications of plasma.

Ans Following are two applications of plasma:

- (1) Plasma light up our offices and homes, make our computers and electronic equipment work.
- (2) They drive lasers and particle accelerators, help to clean up the environment, pasteurize foods and make tools corrosion-resistant.

(viii) Burning of candle is a spontaneous process. Justify it.

Ans Spontaneous process is defined as: "Once it is allowed to start, the process will proceed to the finish without any external intervention." You lit the candle, it was allowed to burn and it

would keep going without any help. Thus, candle burning is a spontaneous process.

(ix) **Differentiate between endothermic and exothermic reactions.**

Ans Those chemical reactions which release the heat are called exothermic reactions, while, those chemical reactions which absorb the heat are called endothermic reactions.

(x) **State the law of mass action.**

Ans Law of mass action states that, "The rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants."

(xi) **How the values of equilibrium constant help to predict the direction of a reversible reaction?**

Ans We know that, $K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$ for any reaction.

The value of ratio leads to one of the following three possibilities:

- (a) The ratio is less than K_c .
- (b) The ratio is greater than K_c .
- (c) The ratio is equal to K_c .

With the help of value of K_c , we can predict the direction of a reversible reaction.

(xii) **What are buffer solutions? How a basic buffer can be prepared?**

Ans **Buffer solution:**

"Those solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions."

Buffer solutions are mostly prepared by mixing two substances.

Basic buffer:

By mixing a weak base and a salt of it with a strong acid, solutions of basic buffer will be given with pH more than 7.

Mixture of NH_4OH and NH_4Cl is one of the best examples of such a basic buffer.

3. Write short answers to any EIGHT (8) questions: 16

(i) What is isomorphism? Give an example.

Ans Isomorphism is the phenomenon in which two different substances exist in the same crystalline form. For example, NaNO_3 , KNO_3 have 'rhombohedral' crystalline form, which means that structures of the negatively charged ions like NO_3^{-1} and CO_3^{-2} are the same. They have atomic ratio 1:1:3.

(ii) Transition temperature is the term used for elements as well as compounds. Explain.

Ans It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At this temperature, one crystalline form of a substance changes to another.

Transition temperature is same for elements as well as compounds but their forms can be changed from one to another.

(iii) The vapour pressure of diethyl ether is higher than that of water at same temperature. Give reason.

Ans The reason is that the difference in the strength of intermolecular forces in different liquids is directly related to their vapour pressures at a particular temperature.

(iv) What are dipole-dipole forces of attraction? Explain with an example.

Ans The positive end of one molecule attracts the negative end of the other molecule, these electrostatic forces of attraction are called dipole-dipole forces.

(v) State the Heisenberg's Uncertainty Principle and give its mathematical form.

Ans Certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

Suppose that Δx is the uncertainty in the measurement of the position and ΔP is the uncertainty in the measurement of momentum of an electron, then

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

This relationship is called uncertainty principle.

- (vi) Write down two defects of Rutherford's Atomic Model.

Ans Following are two of the defects of Rutherford's Atomic Model:

1. The outer electrons could not be stationary.
2. The behaviour of electrons remained unexplained in the atom.

- (vii) Give electronic distribution of $^{31}_{15}\text{P}$ and $^{66}_{29}\text{Cu}$.

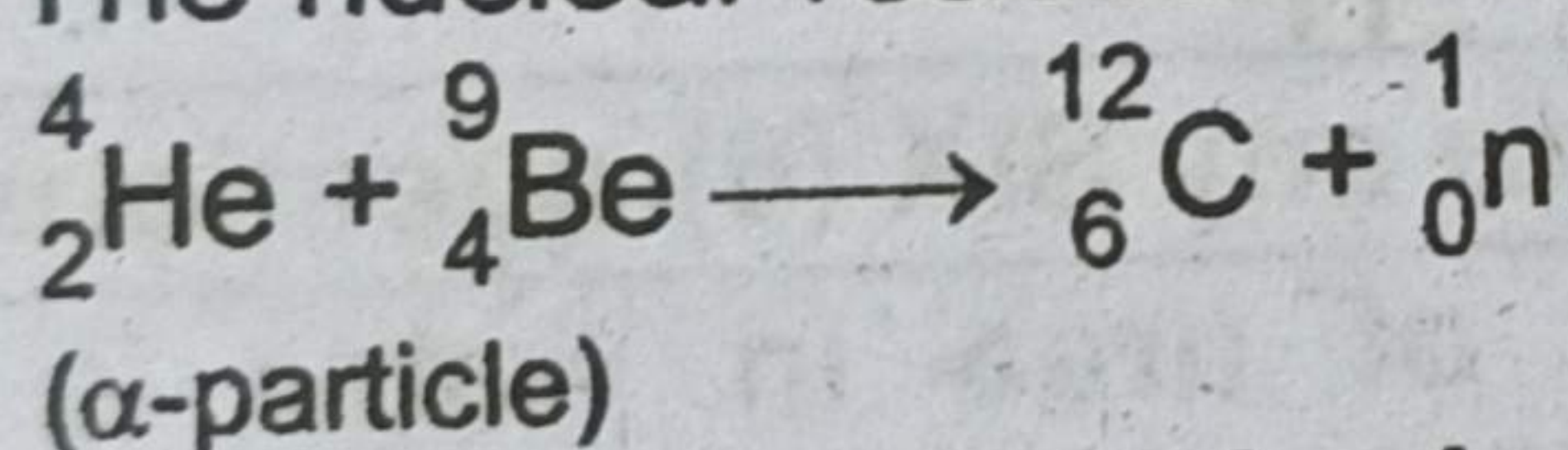
Ans

Element	Electronic Distribution
Phosphorous ($^{31}_{15}\text{P}$)	$[\text{Ne}]3s^2 3p_x^1 3p_y^1 3p_z^1$
Copper ($^{66}_{29}\text{Cu}$)	$[\text{Ar}] 4s^1 3d_{xy}^2 3d_{yz}^2 3d_{xz}^2 3d_{x^2-y^2}^2 3d_{y^2}^2$

- (viii) How neutrons were discovered by Chadwick? Give the equation of nuclear reaction involved.

Ans Chadwick discovered neutron in 1932 with an experiment:

A stream of α -particles produced from a polonium source was directed at beryllium (^9_4Be) target. It was noticed that some penetrating radiation were produced. These radiations were called neutrons because the charged detector showed them to be neutral. The nuclear reaction is as follows:



- (ix) How the percentage ionic character of a covalent bond is determined by dipole moment?

Ans For this purpose, we should know the actual dipole moment μ_{obs} of the molecule and actual bond length. The dipole moment of 100% ionic compound is represented as μ_{ionic} .

$$\% \text{ age of ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{ionic}}} \times 100$$

- (x) Differentiate between atomic orbital and molecular orbital.

Ans According to the idea of hybridization, atomic orbitals differing slightly in energy intermix to form new orbitals, which are called hybrid atomic orbitals. They differ from the parent atomic orbitals in shape and possess specific geometry.

While the molecular orbital approach considers the whole molecule as a single unit. It assumes that the atomic orbitals of the combining atoms overlap to form new orbitals called molecular orbitals which are characteristic of the whole molecule.

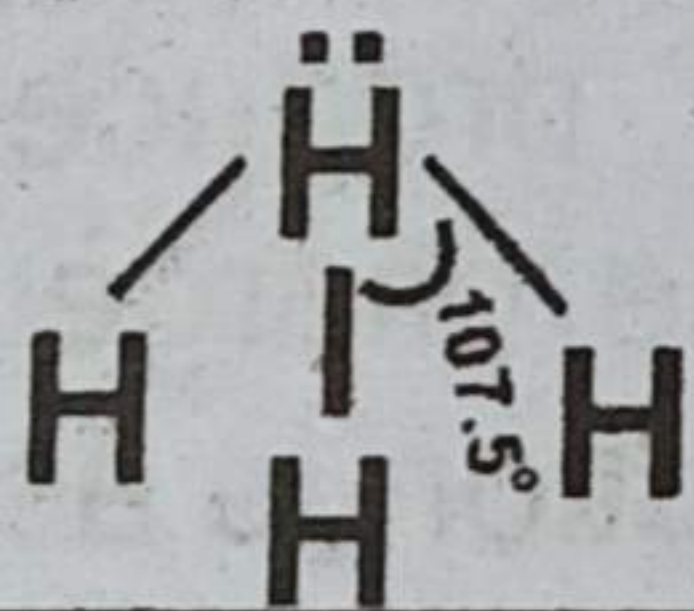
(xi) How the type of bonding affects solubility of compounds?

Ans It affects two types of solubility, i.e., solubility of ionic compounds and solubility of covalent compounds.

Mostly ionic compounds are soluble in water but insoluble in non-aqueous solvents. Similarly, in general, covalent compounds dissolve easily in non-polar organic solvent (benzene, ether, etc.).

(xii) State the geometry of NH_3 molecule on the basis of VSEPR theory.

Ans The geometry of NH_3 molecule on the basis of VSEPR theory is triangular pyramidal with bond angle of 107.5° .



4. Write short answers to any SIX (6) questions: 12

(i) One molal solution of urea in water is dilute as compared to one molar solution of urea but the number of particles of solute is same. Justify it.

Ans The molality of a solution is indirect expression of the ratio of the moles of the solute to the moles of the solvent. The molal aqueous solution of a solute, say glucose is dilute in comparison to its molar solution. The reason is that in molal solution, the quantity of the solvent is comparatively greater.

(ii) What is molarity? Calculate the molarity of a solution containing 9 grams of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in 250 cm^3 of solution.

Ans Molarity:

It is the number of moles of solute dissolved per dm^3 of the solution.

Mass of glucose dissolved (W_2) = 9 g

Volume of solution = 250 cm^3

= 0.25 dm^3

Molar mass of glucose = 180 g mol^{-1}

Molality of solution = ?

It is clear that one molar and one molal solutions urea contain equal number of molecules of solute because both contain one mole of urea.

$$\text{Molarity (M)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3}$$

Substituting the values

$$\text{Molarity (M)} = \frac{9 \text{ g}}{180 \text{ g mol}^{-1}} \times \frac{1}{0.25 \text{ dm}^3}$$

$$\text{Molarity (M)} = \frac{9}{180 \times 0.25} \text{ mole dm}^{-3}$$

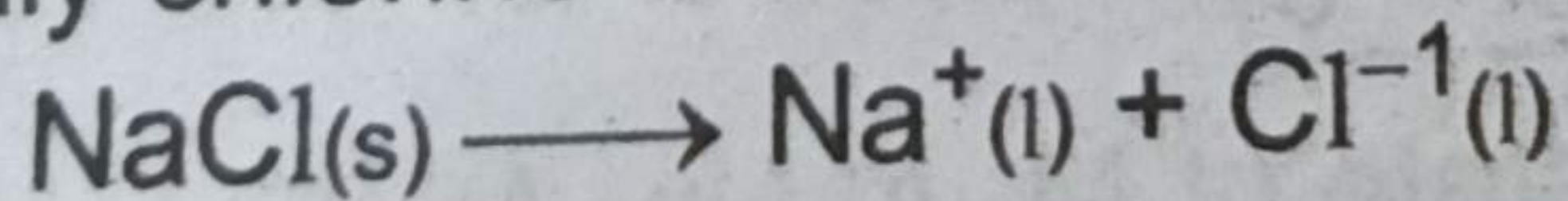
$$\boxed{\text{Molarity (M)} = 0.2 \text{ moles dm}^{-3}}$$

(iii) **Differentiate between hydration and hydrolysis.**

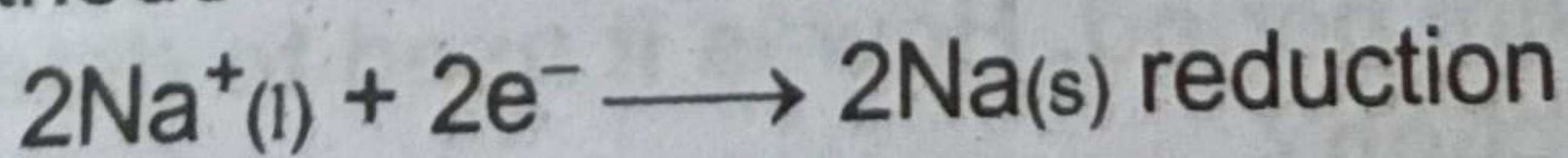
Ans The process in which water molecules surround and interact with solute ions or molecules is called hydration. While interactions between salts and water are called hydrolytic reactions and the phenomenon is known as hydrolysis.

(iv) **Give the chemistry of electrolysis of aqueous solution of sodium chloride.**

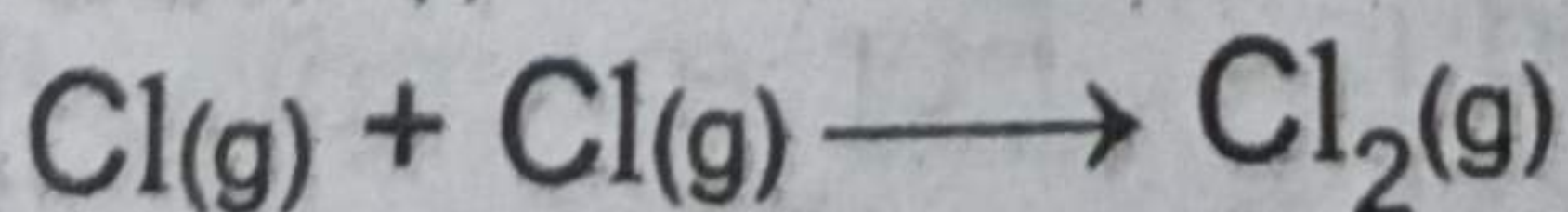
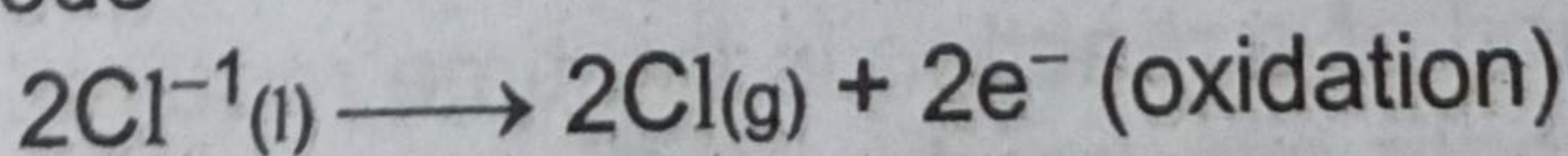
Ans Extraction of sodium by the electrolysis of fused sodium chloride is carried out in Down's cell. In this case, molten sodium chloride is electrolyzed between iron cathode and graphite anode. The cell is planted to get sodium metal and commercially chlorine is obtained as a by-product.



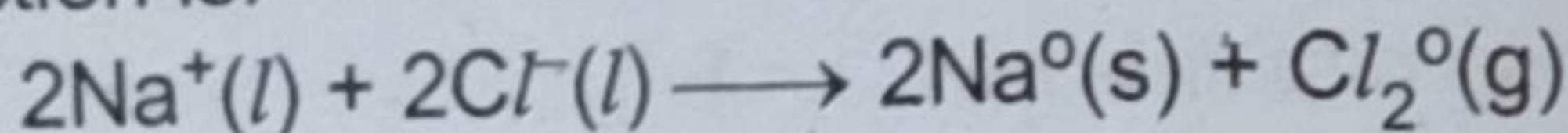
At cathode



At anode



By adding the two reactions at anode and cathode, the overall reaction is:



(v) **What is electrolysis? Give example.**

Ans In an electrolytic cell, a process called electrolysis takes place. In this process, electricity is passed through a solution or the fused state of electrolyte. The electricity provides sufficient energy to cause an otherwise non-spontaneous oxidation-reduction reaction to take place.

(vi) **Calculate oxidation number of Mn in KMnO_4 and Na_2MnO_4 .**

Ans

$$(\text{O.N of K} + \text{O.N of Mn}) + 4 (\text{O.N of O}) = 0$$

Where oxidation number of K = +1

Oxidation number of O = -2

Oxidation number of Mn = x

Let,

Putting these values in the above equation:

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

$$+1 + x - 8 = 0$$

$$x - 7 = 0$$

$$\boxed{x = 7}$$

Thus, the oxidation state of Mn in KMnO_4 is + 7.

Similarly, in Na_2MnO_4

$$2 (\text{O.N of Na}) + (\text{O.N of Mn}) + 4 (\text{O.N of O}) = 0$$

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

$$2 + x - 8 = 0$$

$$x - 6 = 0$$

$$\boxed{x = 6}$$

Thus, the oxidation state of Mn in Na_2MnO_4 is + 6.

(vii) **Define half-life period. How is it used to determine the order of reaction?**

Ans Half-life period of a reaction is the time required to convert 50% of the reactants into products. For example, the half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

If one knows the initial concentration and half-life period of a reaction, then order of that reaction can be determined.

(viii) **What is specific rate constant or velocity constant?**

Ans It states that the rate of reaction is proportional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction.

(ix) **Enzymes are specific in action. Justify.**

Ans Enzymes catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) **What is H-Bonding? Discuss H-Bonding in biological compounds. (4)**

Ans Hydrogen bonding is the electrostatic force of attraction between a highly electronegative atom and partial negatively charged hydrogen atom.

Hydrogen Bonding in Biological Compounds:

Hydrogen bonding exists in the molecules of living system. Proteins are the important part of living organisms. Fibres like those found in the hair, silk and muscles consist of long chains of amino acids. These long chains are coiled about one another into a spiral. This spiral is called a helix. Such a helix may either be right handed or left handed. In the case of right-handed helix, the groups like $>NH$ and $>C=O$ are vertically adjacent to one another and they are linked together by hydrogen bonds. These H-bonds link one spiral to the other. X-ray analysis has shown that on the average, there are 27 amino acid units for each turn of the helix, Fig. (a).

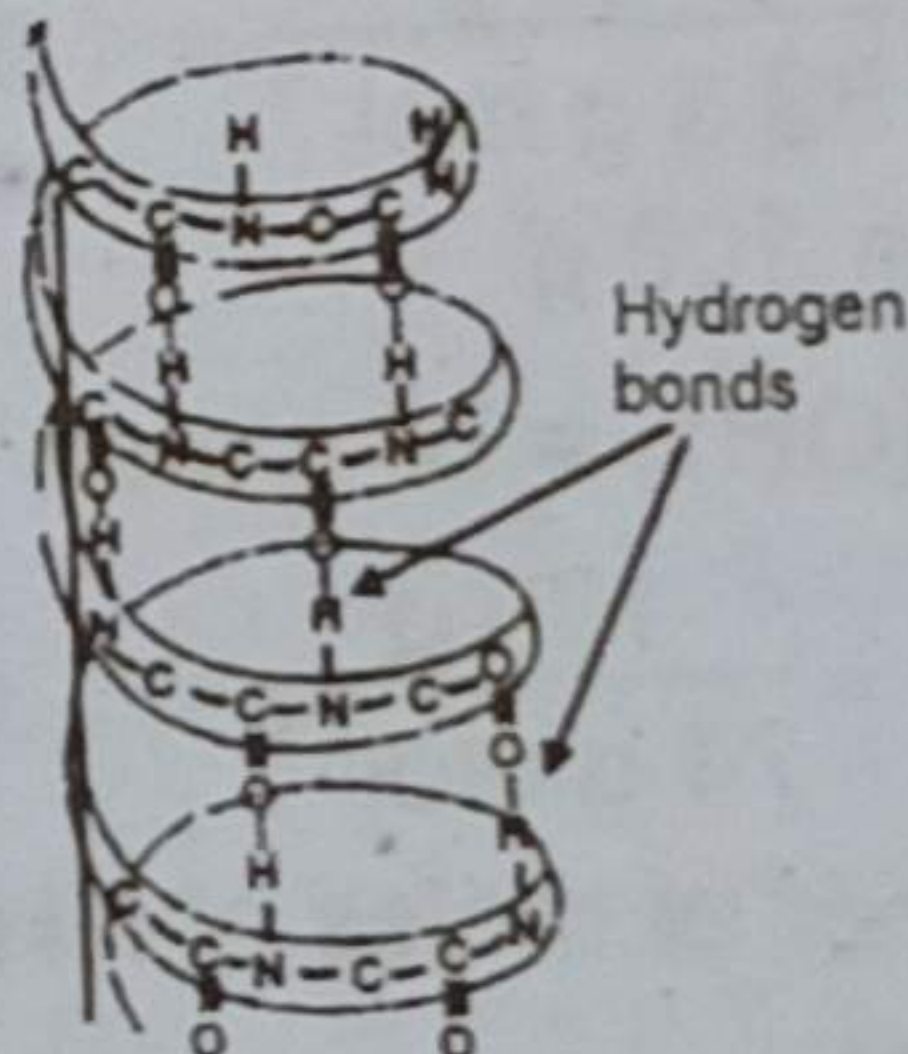


Fig. (a). Hydrogen bonding in proteins.

Deoxyribonucleic acid (DNA) has two spiral chains. These are coiled about each other on a common axis. In this way, they give a double helix. This is 18-20 Å in diameter. They are linked together by H-bonding between their sub-units, Fig. (b).

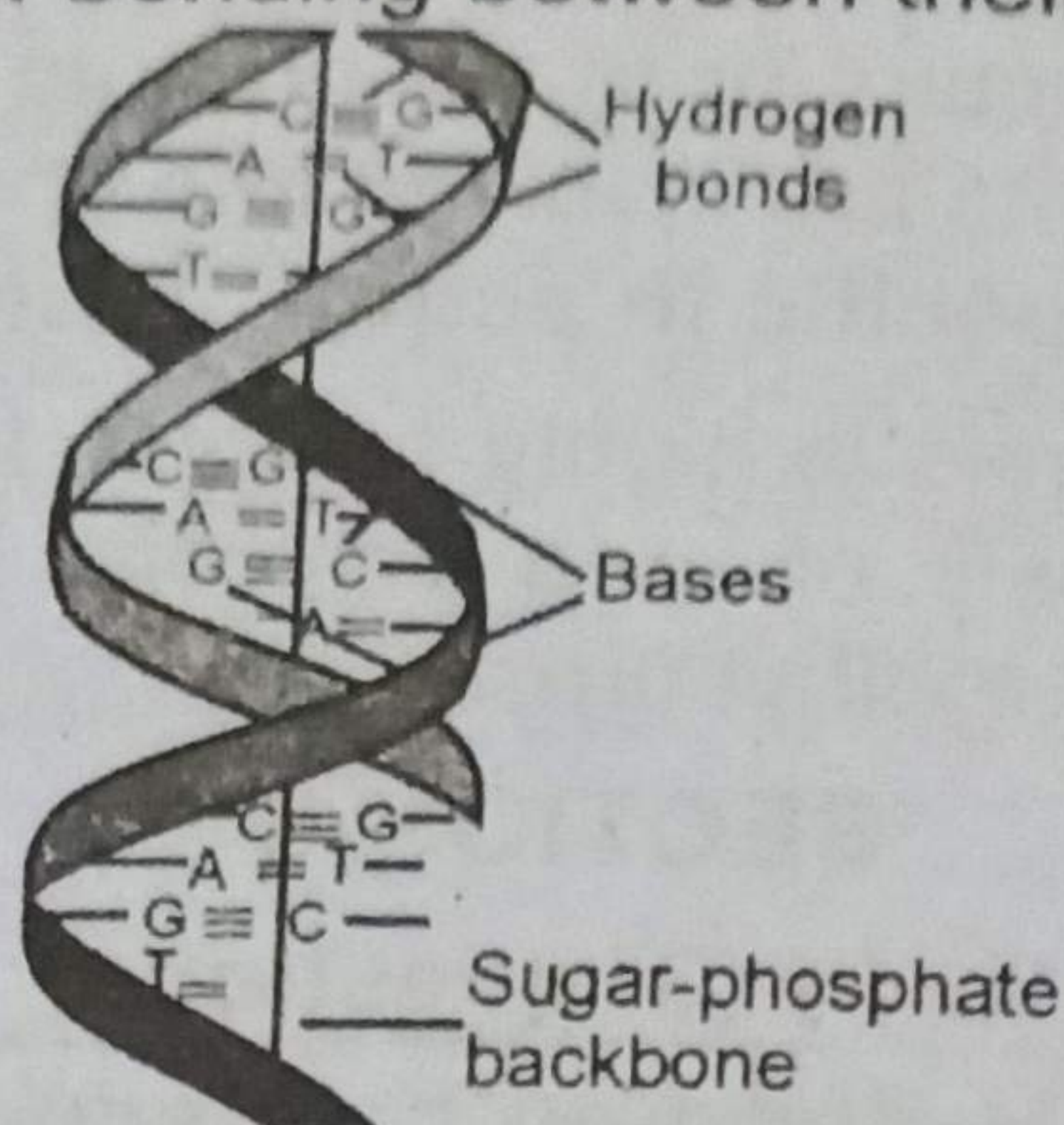


Fig. (b). Hydrogen bonding in DNA double helix.

The food materials like carbohydrates include glucose, fructose and sucrose. They all have -OH groups in them which are responsible for hydrogen bonding in them.

- (b) NH_3 gas can be prepared by heating together two solids NH_4Cl and Ca(OH)_2 . If a mixture containing 100 gm of each solid is heated then calculate the number of grams of NH_3 produced. (At mass of C = 12 g / mole, N = 14 gm / mole, H = 1 gm / mole, Ca = 40 gm / mole, Cl = 35.5 gm / mole, O = 16 gm / mole) (4)

Ans Convert the given amounts of both reactants into their number of moles.

$$\text{Mass of } \text{NH}_4\text{Cl} = 100 \text{ g}$$

$$\text{Molar mass of } \text{NH}_4\text{Cl} = 53.5 \text{ g mol}^{-1}$$

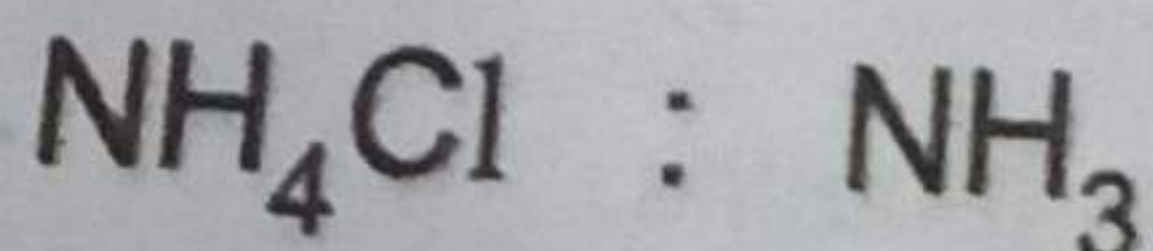
$$\text{Moles of } \text{NH}_4\text{Cl} = \frac{100 \text{ g}}{53.5 \text{ g mol}^{-1}} = 1.87$$

$$\text{Mass of } \text{Ca(OH)}_2 = 100 \text{ g}$$

$$\text{Molar mass of } \text{Ca(OH)}_2 = 74 \text{ g mol}^{-1}$$

$$\text{Moles of } \text{Ca(OH)}_2 = \frac{100 \text{ g}}{74 \text{ g mol}^{-1}} = 1.35$$

Compare the number of moles of NH_4Cl with those of NH_3



$$\begin{array}{rcl} 2 & : & 2 \\ 1 & : & 1 \\ 1.87 & : & 1.87 \end{array}$$

Similarly, compare the number of moles of Ca(OH)_2 with those of NH_3 .

$$\begin{array}{rcl} \text{Ca(OH)}_2 & : & \text{NH}_3 \\ 1 & : & 2 \\ 1.35 & : & 2.70 \end{array}$$

Since, the number of moles of NH_3 produced by 100 g or 1.87 moles of NH_4Cl are less, so NH_4Cl is the limiting reactant. The other reactant, Ca(OH)_2 is present in excess.

$$\begin{aligned} \text{Hence Mass of NH}_3 \text{ produced} &= 1.87 \text{ moles} \times 17 \text{ g mol}^{-1} \\ &= 31.79 \text{ g} \end{aligned}$$

Q.6.(a) Explain Dalton's law of partial pressure and give its applications in breathing process. (4)

Ans Dalton's Law of Partial Pressure:

John Dalton studied the mixture of gases and gave his law of partial pressure. According to this law, "the total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures."

Let the gases are designated as 1, 2, 3, and their partial pressures are p_1 , p_2 , p_3 . The total pressure (P) of the mixture of gases is given by:

$$P_t = p_1 + p_2 + p_3$$

The partial pressure of gas in a mixture of gases is the pressure that it would exert on the walls of container, if it were present all alone in that same volume under the same temperature.

Let us have four cylinders of the same volume i.e., 10 dm^3 each and three gases H_2 , CH_4 , and O_2 are separately enclosed in first three of them at the same temperature. Let their partial pressure be 400 torr, 500 torr and 100 torr, respectively. All three gases are transferred to a fourth cylinder of capacity 10 dm^3 at the same temperature. According to Dalton's law:

$$P_t = p_{\text{H}_2} + p_{\text{CH}_4} + p_{\text{O}_2} = (400 + 500 + 100) \text{ torr}$$

$$P_t = 1000 \text{ torr}$$

Molecules of each gas move independently, so the general gas equation ($PV = nRT$) can be applied to the individual gases in the gaseous mixture.

$$P_{H_2} V = n_{H_2} RT \quad P_{H_2} = n_{H_2} RT / V$$

$$P_{CH_4} V = n_{CH_4} RT \quad P_{CH_4} = n_{CH_4} RT / V$$

$$P_{O_2} V = n_{O_2} RT \quad P_{O_2} = n_{O_2} RT / V$$

$$P_{H_2} \propto n_{H_2}$$

$$P_{CH_4} \propto n_{CH_4}$$

$$P_{O_2} \propto n_{O_2}$$

RT / V is a constant factor for each gas. All these gases have their own partial pressures. Since, volumes and temperatures are the same, so their number of moles will be different and will be directly proportional to their partial pressures.

Adding these three equations:

$$P_t = P_{H_2} + P_{CH_4} + P_{O_2}$$

$$P_t = (n_{H_2} + n_{CH_4} + n_{O_2}) \frac{RT}{V}$$

$$P_t = n_t \frac{RT}{V} \quad \text{where } n_t = n_{H_2} + n_{CH_4} + n_{O_2}$$

$$P_t V = n_t RT$$

So, the total pressure of mixture of gases depends upon the total number of moles of the gases.

Applications:

Following are the three important applications:

1. Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and become moist. The pressure exerted by this moist gas is, therefore, the sum of the partial pressures of the dry gas and that of water vapours. The partial pressure exerted by water vapours is called aqueous tension.

$$P_{\text{moist}} = p_{\text{dry}} + p_{\text{w.vap}}$$

$$P_{\text{moist}} = p_{\text{dry}} + \text{aqueous tension}$$

$$P_{\text{dry}} = P_{\text{moist}} - \text{aqueous tension}$$

2. Dalton's law finds its application during the process of respiration. The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into lungs as the partial pressure of the oxygen in air is 159 torr, while the partial pressure of oxygen in lungs is 116 torr. CO_2 produced during respiration moves out in the opposite direction, as its partial pressure is more in the lungs than that in air.
3. At higher altitudes, the pilot feels uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

(b) Write down the properties of cathode rays. (4)

Ans Following are the properties of cathode rays:

- (1) Cathode rays are negatively charged.
- (2) They produce a greenish fluorescence on striking the walls of the glass tube.
- (3) Cathode rays cast a shadow when an opaque object is placed in their path.
- (4) These rays can drive a small paddle wheel placed in their path.
- (5) Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass.
- (6) Cathode rays can produce heat when they fall on matter.
- (7) Cathode rays can ionize gases.
- (8) They can cause a chemical change, because they have a reducing effect.
- (9) Cathode rays can pass through a thin metal foil like aluminium or gold foil.
- (10) The e/m value of cathode rays shows that they are simply electrons.

Q.7.(a) Explain paramagnetic behaviour of O_2 on the basis of MOT and prove MOT is superior to other theories.

(4)

Ans Oxygen O_2 :

The formation of molecular orbitals in oxygen molecule is shown in Fig.

The electronic configuration O_2 is

$$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x) < \pi(2p_y)^2 = \pi(2p_z)^2 < \pi^*(2p_y)^1 = \pi^*(2p_z)^1 < \sigma^*2p_x$$

The bond order in O_2 is $\frac{6-2}{2} = 2$, which corresponds to a double bond.

This is consistent with the large bond energy of 496 kJ mol^{-1} of oxygen molecule.

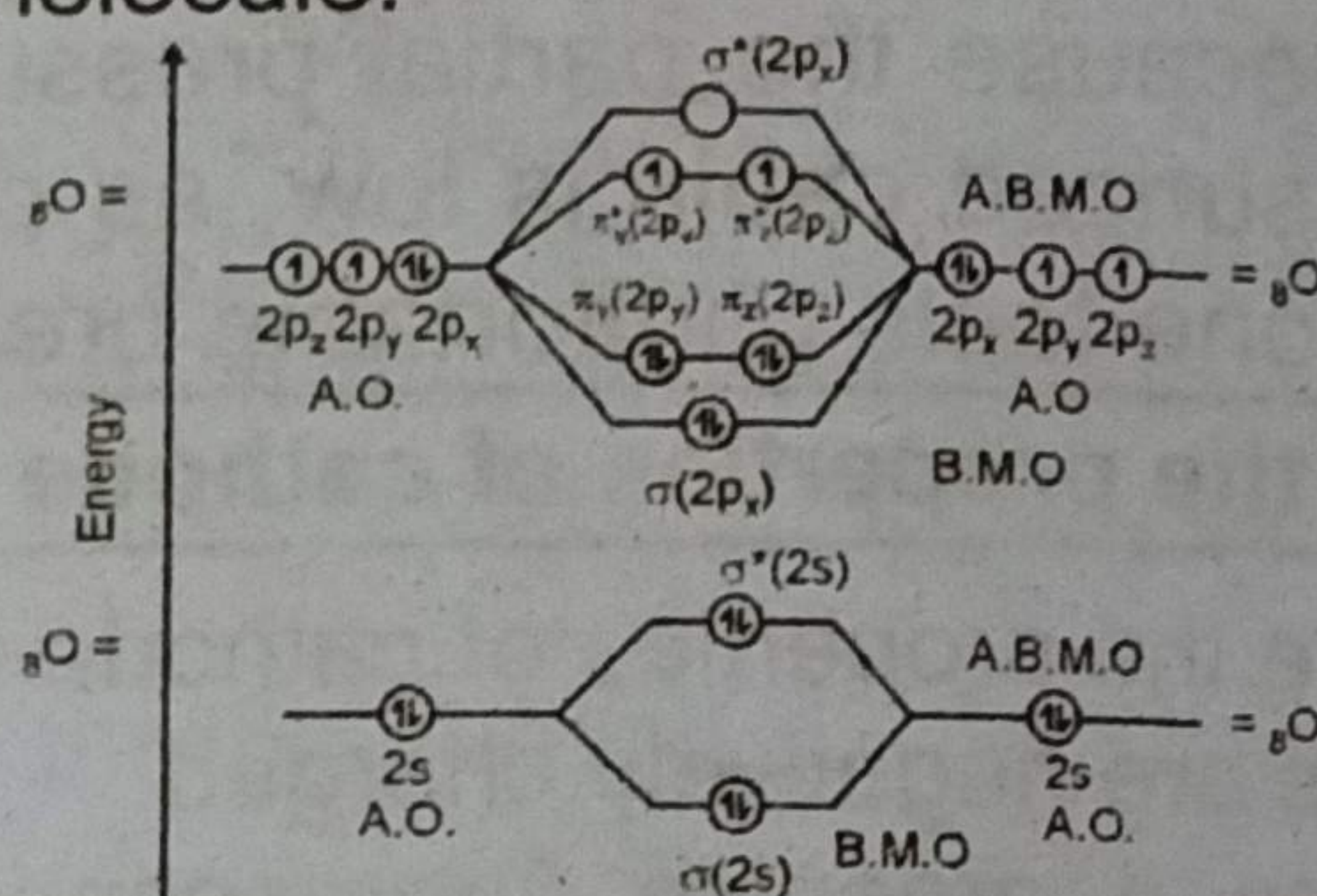


Fig. Molecular orbitals in O_2 molecule.

Fig. shows that the filling of molecular orbitals leaves two unpaired electrons in each of the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ orbitals. Thus, the electronic configuration of the molecular orbitals accounts admirably for the paramagnetic properties of oxygen. This is one of the greatest successes of the molecular orbital theory. Liquid O_2 is attracted towards the magnet.

Anyhow, when two more electrons are given to O_2 , it becomes O_2^{2-} . The paramagnetism vanishes. Similarly, in O_2^{2+} , the unpaired electrons are removed and paramagnetic property is no more there. Bond order of O_2^{2-} and are also different from O_2 and are one and three, respectively.

Similarly, M.O.T justifies that F_2 has bond order of one and Ne does not make a bond with Ne.

(b) What is molar heat of combustion? How it is measured by bomb calorimeter? (4)

Ans Molar heat of combustion:

It is the amount of heat evolved when one mole of a substance is completely burnt in excess of oxygen under standard conditions.

Bomb Calorimeter:

A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds. It consists of a strong cylindrical steel vessel usually lined with enamel to prevent corrosion. A known mass (about one gram) of the test substance is placed in a platinum crucible inside the bomb. The lid is screwed on tightly and oxygen is provided in through a valve until the pressure inside is about 20 atm. After closing the screw valve, the bomb calorimeter is then immersed in a known mass of water in a well-insulated calorimeter. Then, it is allowed to attain a steady temperature. The initial temperature is measured, by using the thermometer present in the calorimeter. The test substance is then, ignited, electrically by passing the current through the ignition coil. The temperature of water, which is stirred continuously, is recorded at 30 sec intervals.

From the increase of temperature ΔT , heat capacity (c) in kJ K^{-1} of bomb calorimeter including bomb, water, etc., we can calculate the enthalpy of combustion.

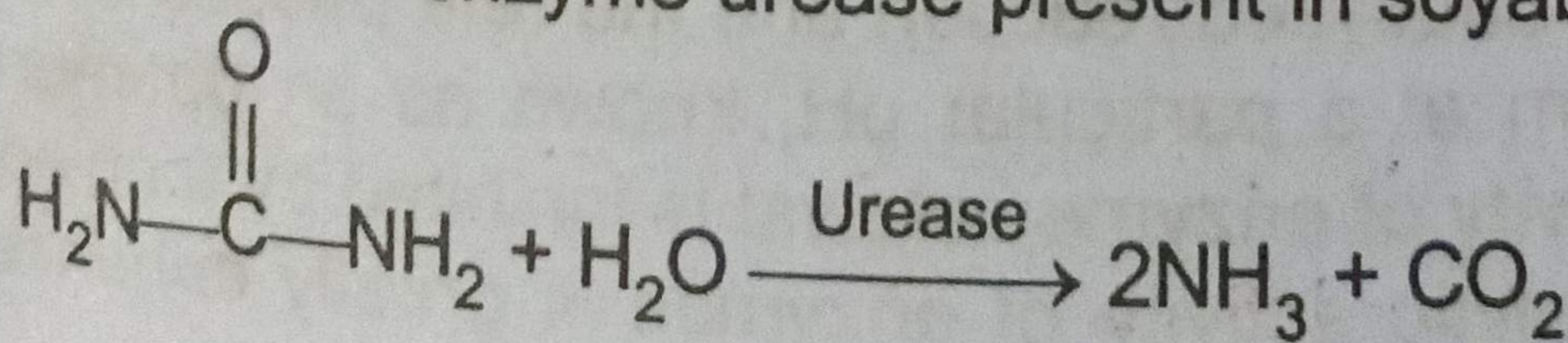
The heat capacity ' c ' of a body or a system is defined as the quantity of heat required to change its temperature by 1 kelvin.

$$q = c \times \Delta T$$

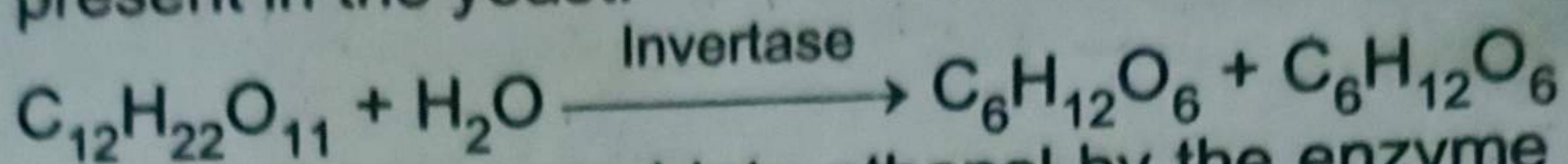
Q.8.(a) What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzymes. (4)

Ans Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells. Many enzymes have been identified and obtained in the pure crystalline state. However, the first enzyme was prepared in the laboratory in 1969. For example:

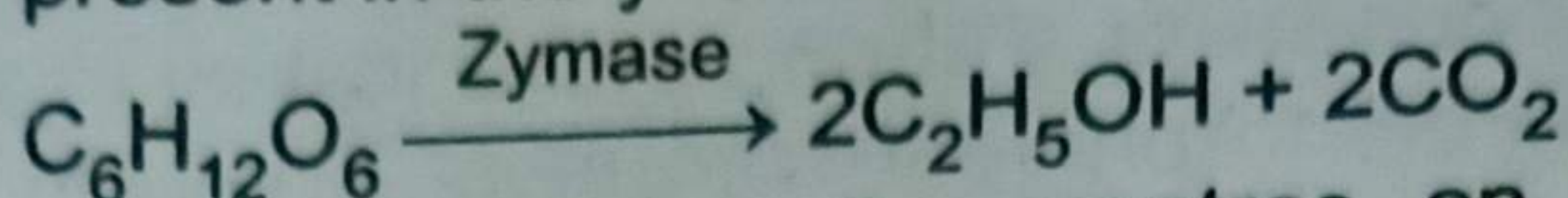
(i) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.



- (ii) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called invertase, present in the yeast.



- (iii) Glucose is converted into ethanol by the enzyme zymase present in the yeast.



Enzymes have active centres on their surfaces. The molecules of a substrate fit into their cavities just as a key fits into a lock, as in Fig. The substrate molecules enter the cavities, form the complex, reactants and the products get out of the cavity immediately.

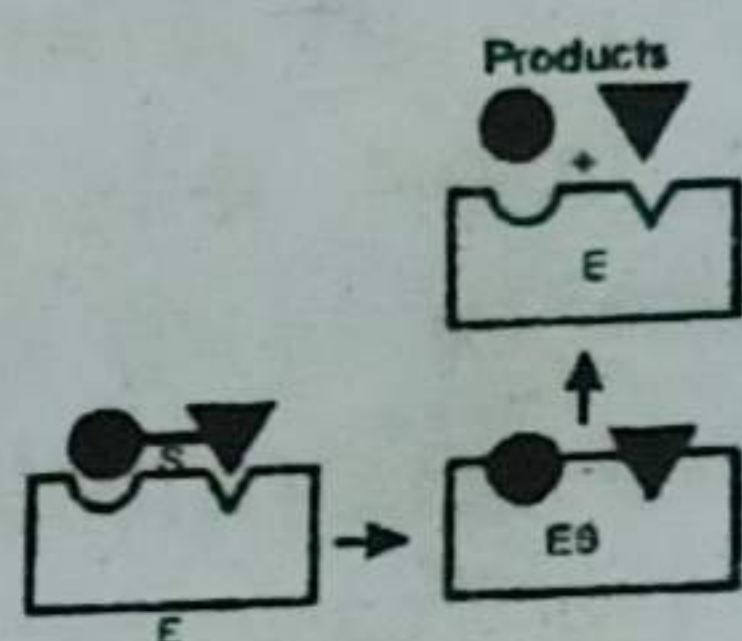
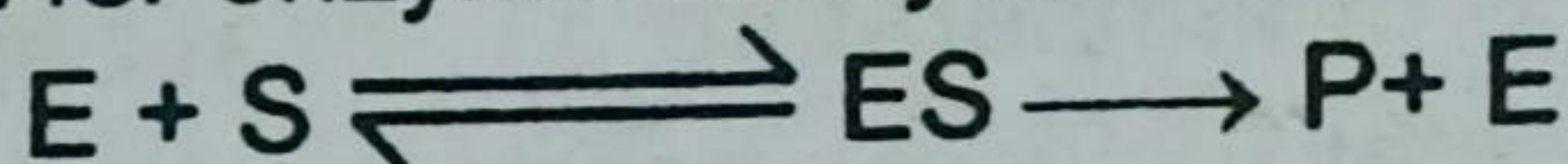


Fig. Lock and Key model of enzyme catalysis.

Michaulis and Menter (1913) proposed the following mechanism for enzyme catalysis



Where E = enzyme, S = substrate (reactant)

ES = activated complex, P = product

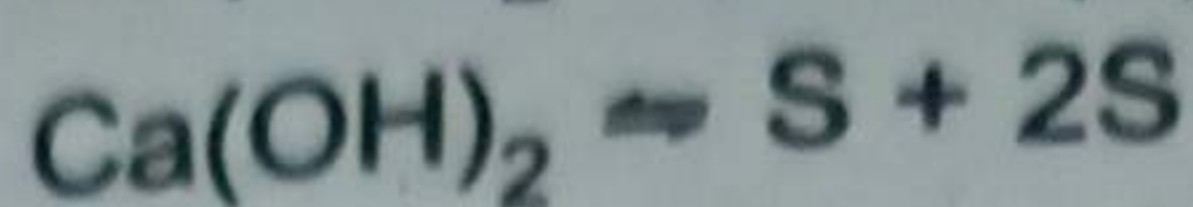
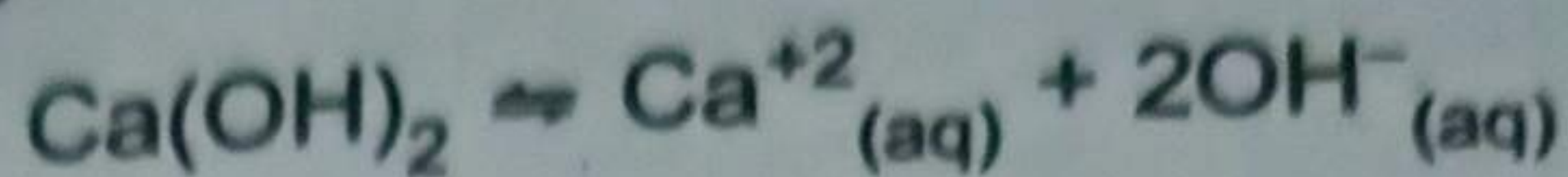
Characteristics of Enzyme Catalysis:

The role of enzyme as catalysts is like inorganic heterogeneous catalysts. They are unique in their efficiency and have a high degree of specificity. For example:

- (i) Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.
- (ii) Enzymes catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.
- (iii) Enzyme catalytic reactions have the maximum rates at an optimum temperature.
- (iv) The pH of the system also controls the rates of the enzyme catalysed reaction and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.
- (v) The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.

- (b) Ca(OH)_2 is a sparingly soluble compound. Its solubility product is 6.5×10^{-6} . Calculate the solubility of Ca(OH)_2 . (Atomic mass : $\text{Ca} = 40$) (4)

Ans



$$K_{\text{sp}} = [\text{Ca}^{+2}][\text{OH}^{-}]^2 = \text{S} \times (2\text{S})^2$$

$$4\text{S}^3 = 6.5 \times 10^{-6}$$

$$\text{S} = \frac{6.5 \times 10^{-6}}{4} = (1.625 \times 10^{-6})^{1/3}$$

$$\text{S} = 1.17 \times 10^{-2} \text{ mol / dm}^3$$

Q.9.(a) Give graphical explanation for elevation of boiling point of a solution. (4)

Ans Elevation of boiling point:

When the solute is added in the solvent and vapour pressures are plotted vs temperatures, then a curve CD is obtained. This curve is lower than the curve AB because vapour pressures of solution are less than those of pure solvent. Solution will boil at higher temperature T_2 to equalize its pressure to p^0 . The difference of two boiling points gives the elevation of the boiling point ΔT_b .

The higher of the concentration of solute, the greater will be the lowering in vapour pressure of solution and hence, higher will be its boiling point. So, elevation of boiling point ΔT_b is directly proportional to the molality of solution.

$$\Delta T_b = K_b m \quad (1)$$

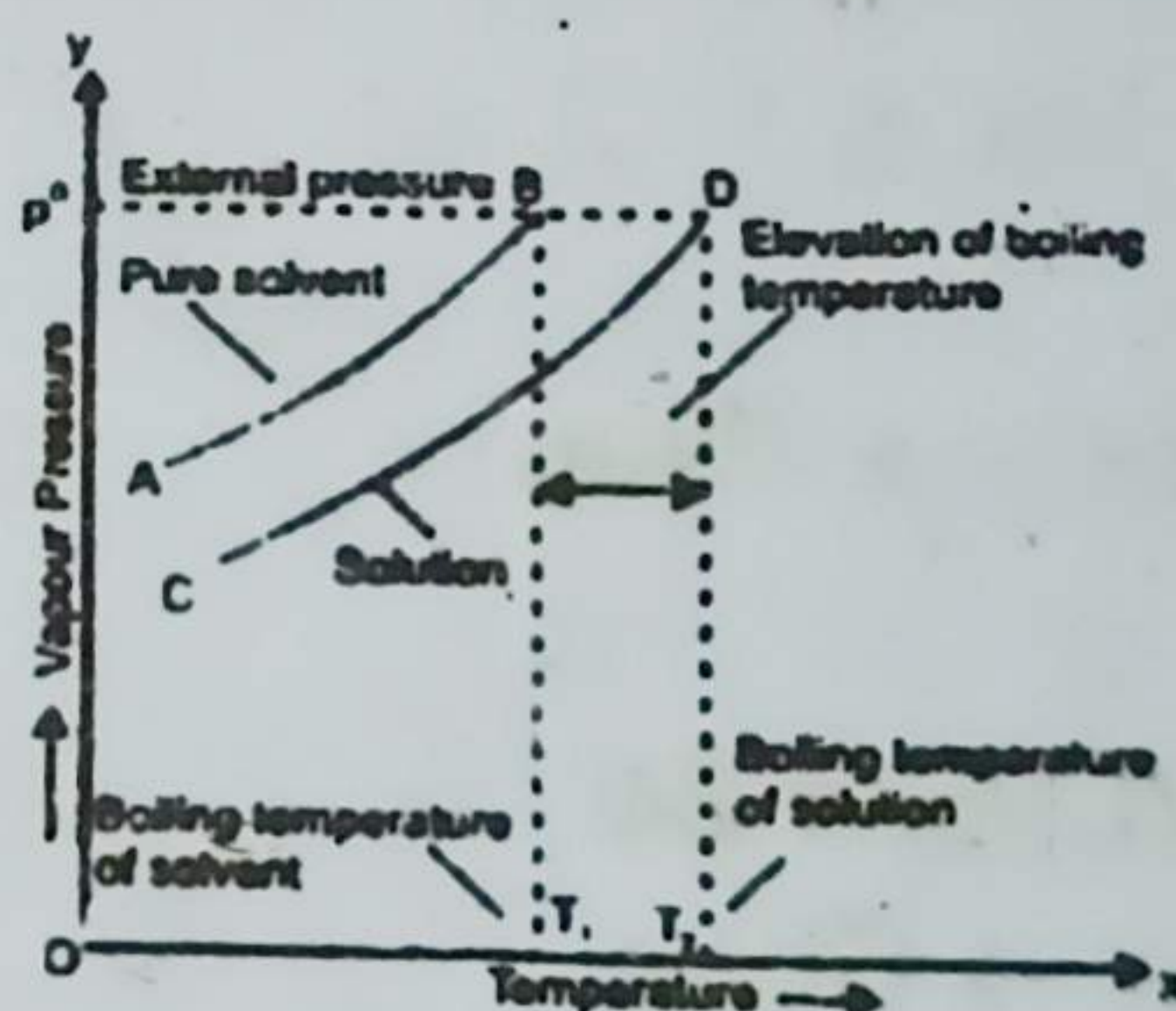


Fig. Elevation of boiling temperature curve.

According to equation (1), molality of any solute determines the elevation of boiling point of a solvent. You may dissolve 6 g of urea in 500 g of H_2O or 18 g of glucose in 500 g of H_2O both give 0.2 molal solution and both have same elevation of boiling points i.e., $0.1^\circ C$, which is $1/5^{th}$ of $0.52^\circ C$. We say that ΔT_b (not T) is a colligative property.

We know that

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

$$\text{or } m = \frac{W_2}{M_2} \frac{1}{W_1 / 1000} = \frac{1000 W_2}{M_2 W_1} \quad (2)$$

Putting the value of m from equation (2) into equation (1),

$$\Delta T_b = K_b \frac{1000 W_2}{M_2 W_1} \quad (3)$$

Rearranging equation (3),

$$\text{Molecular mass (M}_2\text{)} = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000 \quad (4)$$

Equation (4) can be used to determine the molar mass of a non-volatile and non-electrolyte solute in a volatile solvent.

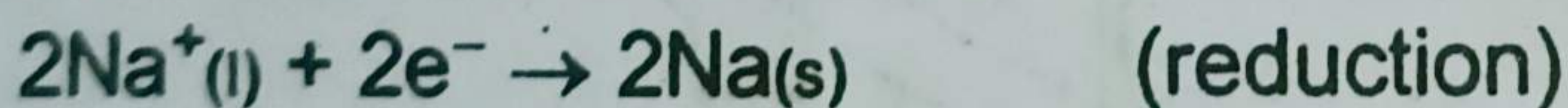
(b) Describe the electrolysis of molten NaCl and aqueous solution of NaCl. (4)

Ans **Electrolysis of molten NaCl:**

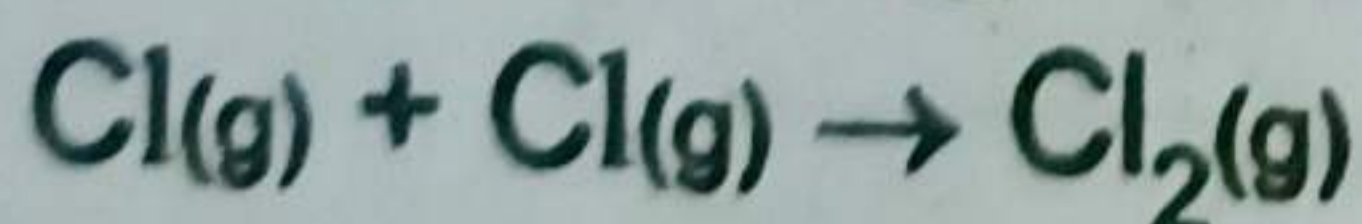
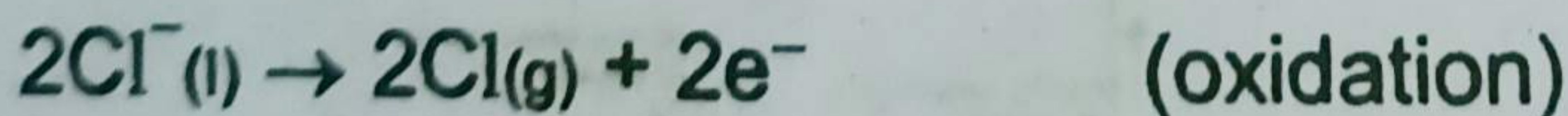
Extraction of sodium by the electrolysis of fused sodium chloride is carried out in Down's cell. In this case, molten sodium chloride is electrolyzed between iron cathode and graphite anode. The cell is planted to get sodium metal commercially. Chlorine is obtained as a by-product.



At cathode



At anode

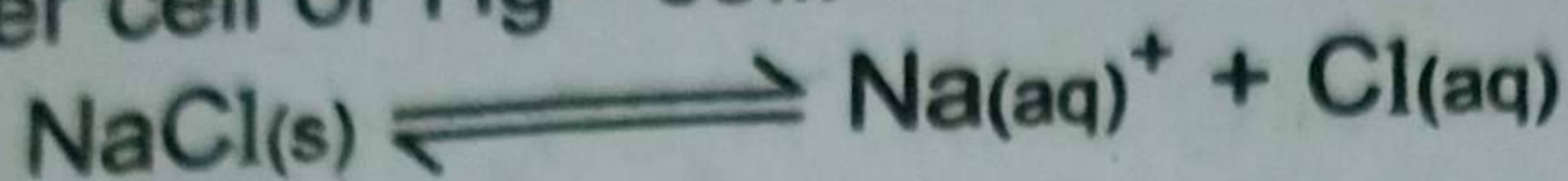


By adding the two reactions at anode and cathode, the overall reaction is:

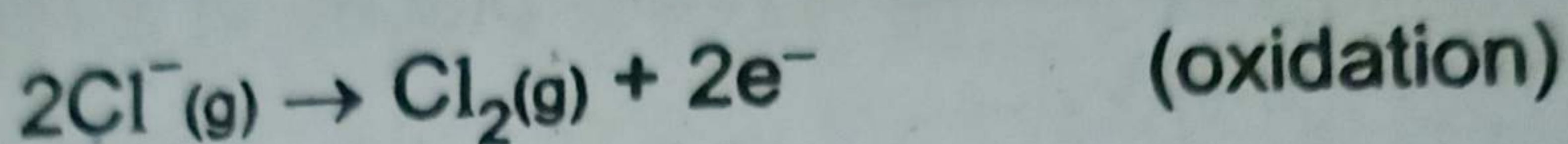


Aqueous solution of NaCl:

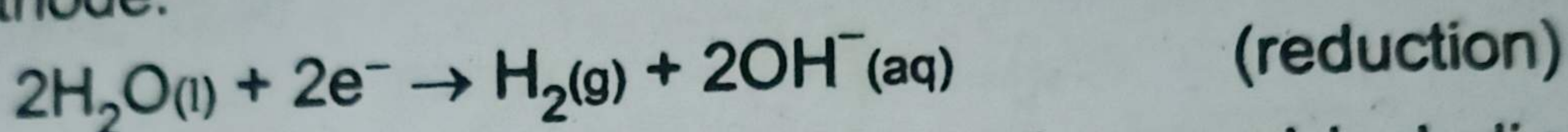
Caustic soda is obtained on industrial scale by the electrolysis of concentrated aqueous solution of sodium chloride using titanium anode and mercury or steel cathode. This electrolysis is carried out in Nelson cell and Castner-Kellner cell or Hg-cell.



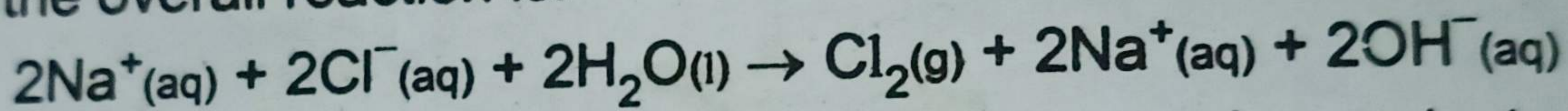
At anode:



At cathode:



By combining, the electrode reactions and including Na^+ ions, the overall reaction is:



Here, chlorine and hydrogen are obtained as by products, and Na^+ is not discharged at cathode.

SECTION-III

(Practical Part)

NOTE: (i) Attempt any THREE (3) questions.

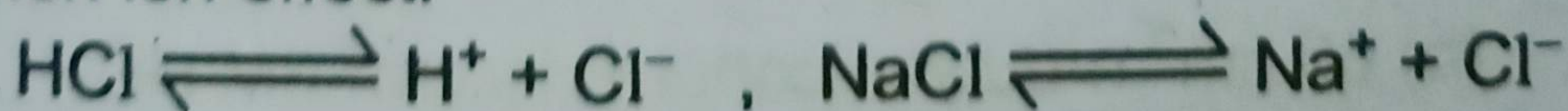
(ii) Write down standard solution, chemical equation with mole ratio, indicator with end point, procedure and supposed readings with calculations for Part C, D, and E. (1,1,1,1,1)

(iii) Write down material required, diagram and procedure for Part A and B. (1,1,3)

(A) Prepare pure sample of NaCl by common ion effect. (5)

Ans Theory of Common Ion Effect:

On passing HCl gas into saturated solution of NaCl, the stronger electrolyte HCl ionizes to give Cl^- ions and H^+ . Ionization of weak electrolyte NaCl is suppressed due to common ion effect.



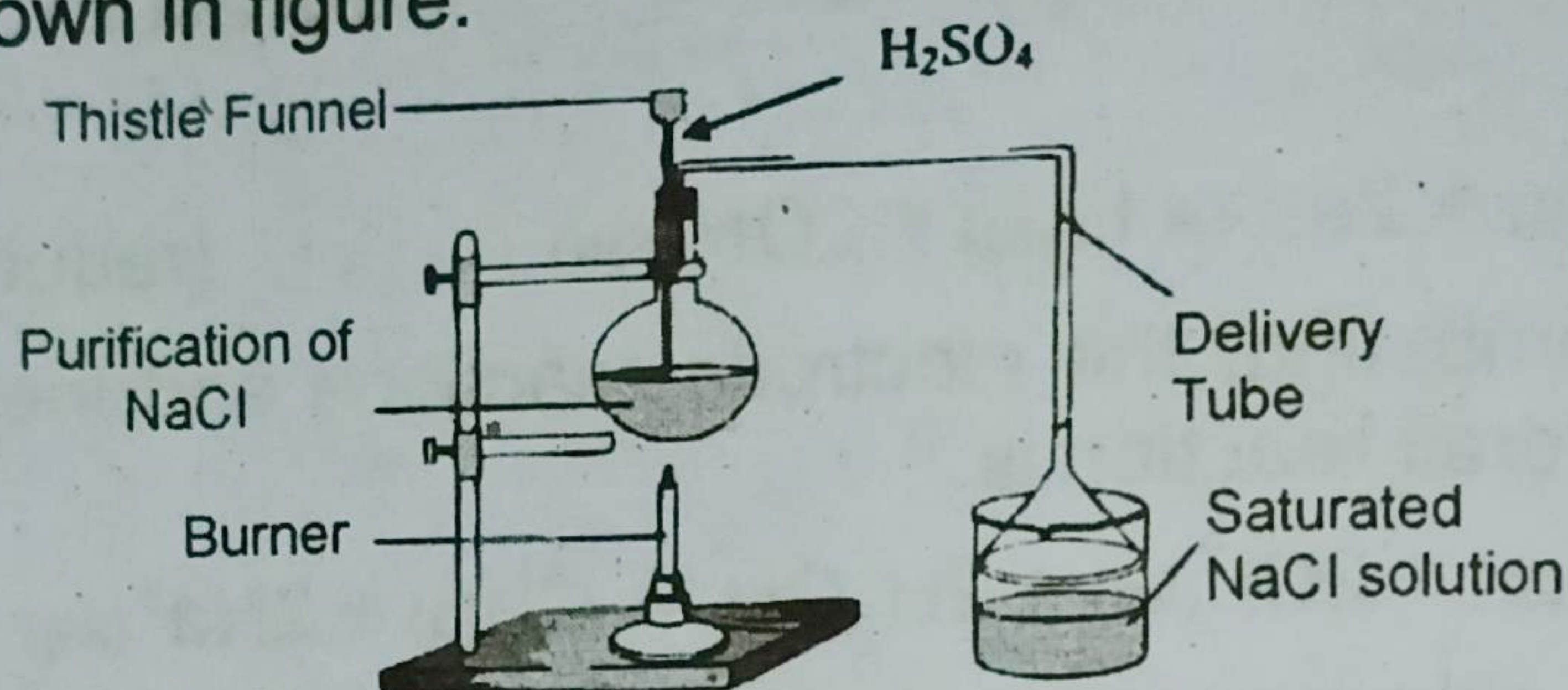
Apparatus:

Beakers, Funnel, Burner, Round bottom flask, Thistle funnel, Wire gauze, Delivery glass tube, etc.

Procedure:

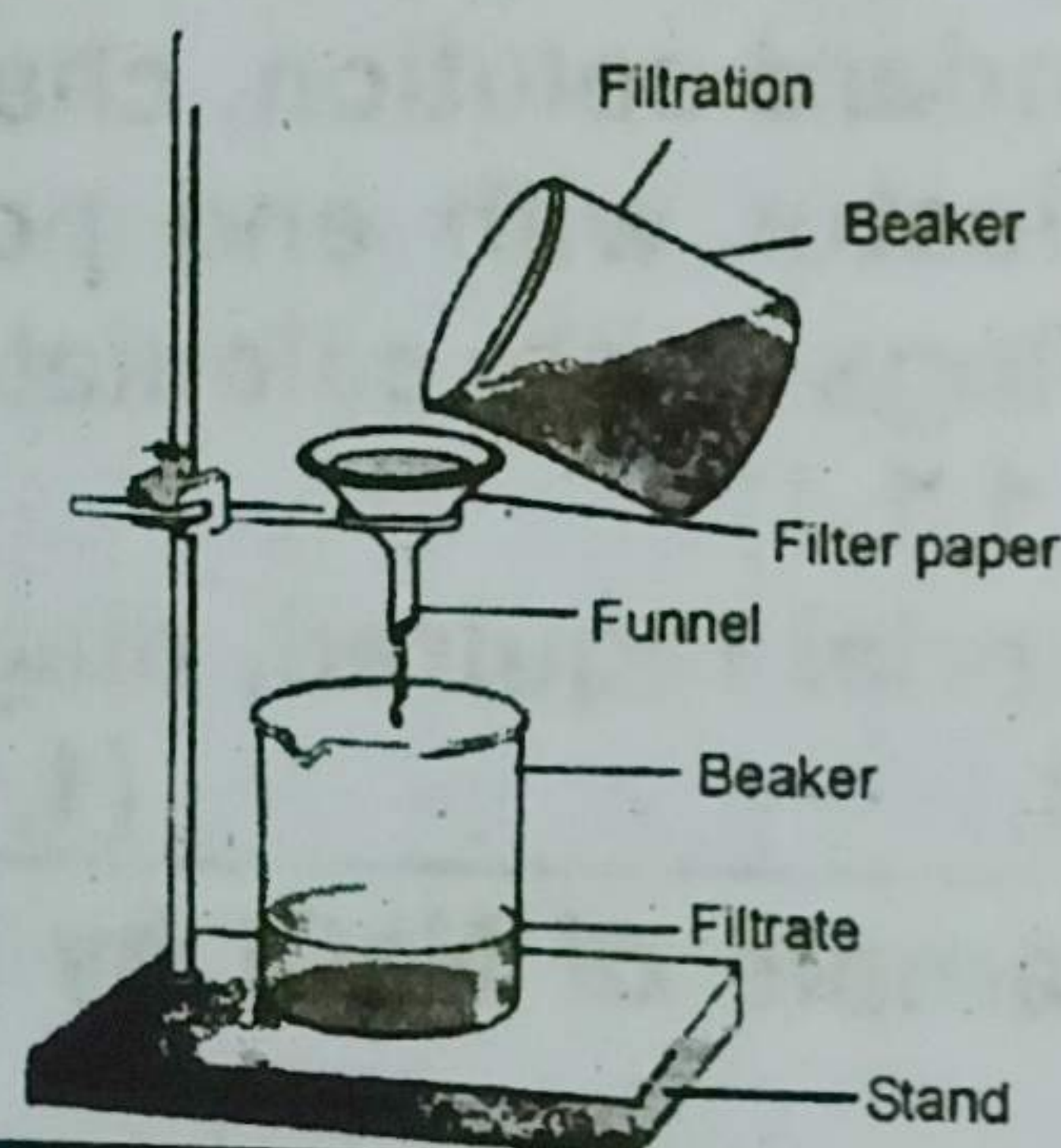
Dissolve the impure sample of NaCl in about 100 cm³ of distilled water in beaker with constant stirring till some of it remains undissolved. Filter this saturated solution in another beaker.

Prepare HCl gas by adding conc. H₂SO₄ through thistle funnel to the sodium chloride crystals placed in a round bottom flask as shown in figure.



Purification Apparatus for NaCl

Pass the HCl gas into the saturated solution of impure sodium chloride through inverted funnel, where pure crystals of NaCl precipitate out by common ion effect. Filter this precipitate. Dry the pure NaCl crystals in between the folds of filter paper.



(B) Separate the mixture of Pb²⁺ and Cd²⁺ ions by chromatography.

(5)

Ans Material Required:

(i) Solvent: (a) 88 cm³ ethyl alcohol + 12 cm³ 5M HCl

OR

(b) 85 cm³ n-butyl alcohol + 15 cm³ 3M HCl

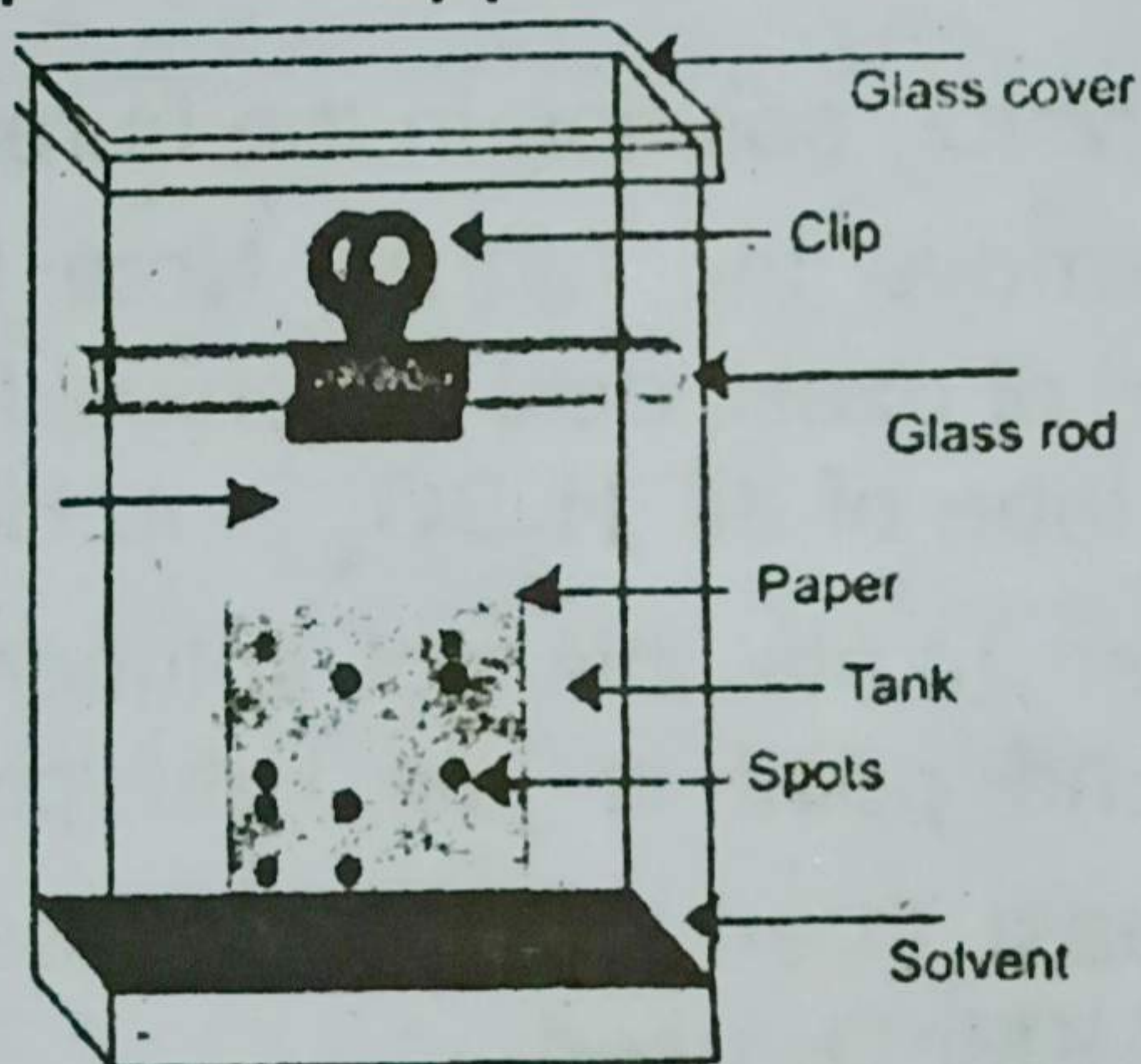
(ii) Spraying agent (Locating Agent): H₂S gas or H₂S + water.

Procedure:

Take about 25 cm^3 of solvent (eluent) in a cylinder or jar, cover it with watch glass and allow it to stand for 5 minutes to saturate the inner atmosphere of the jar with the solvent vapours. Take about 6 or 8 inches long and 1 to 1.5 inch wide strip of Whatman's filter paper and draw lines with lead pencil 1 inch from one end.

Prepare the mixture solution of the sample by mixing 1 cm^3 of each of Pb^{+2} and Cd^{+2} salts solutions and put one small drop of this mixture solution with the help of capillary tube on the one inch line and dry it in open air.

Suspend this paper strip in the cylinder in such a way that the impregnated end (marked end) just touches the solvent and the spot remains above the solvent. The cylinder must be covered fully. The ions (Pb^{+2} or Cd^{+2} ions) diffuse at different relative rates and the process is stopped when the solvent front has risen to about $\frac{3}{4}$ th of the length of paper. Care should be taken that the paper strip does not touch the sides of the cylinder. Remove the paper strip, mark the solvent front. Then spray H_2S water with the help of sprayer on the filter paper. Black and yellow spots will appear on the filter paper.



Paper chromatography

Dry the paper and determine the R_f values of these spots according to the formula:

$$R_1 = \frac{\text{Distance travelled by the ion from line}}{\text{Distance travelled by the solvent from line}}$$

Black spot shows Pb^{+2} ion and yellow exhibits the Cd^{+2} ion. Lower spot is black showing Pb^{++} ion.

- (C) 6.3 g of sample of $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \cdot x\text{H}_2\text{O}$ is dissolved per dm^3 of solution. Determine the value of "X" (number of water molecules) volumetrically. (5)

Ans Principle:

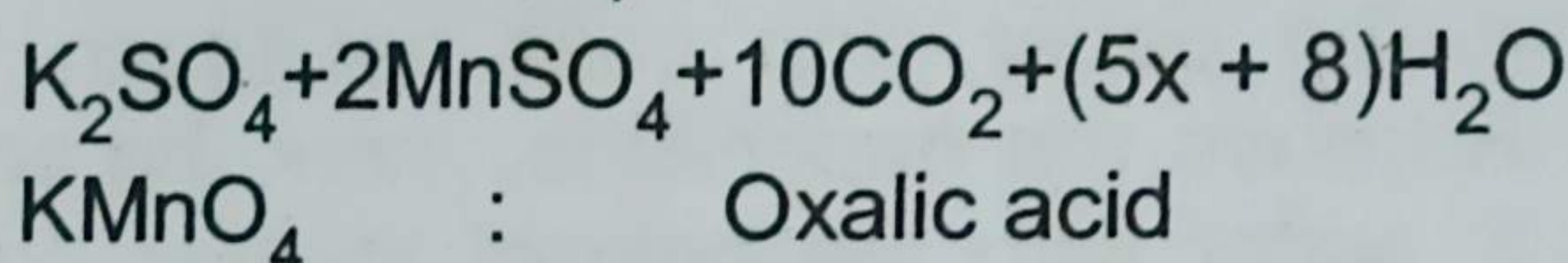
It is a redox titration. Oxalic acid is a reducing agent and can be oxidized to CO_2 by an oxidizing agent such as KMnO_4 in the presence of dil. H_2SO_4 at $60-70^\circ\text{C}$.

Standard Solution: 0.02 M KMnO_4

Indicator: KMnO_4 (itself)

End Point: Just light pink

Equation: $2\text{KMnO}_4 + 5 \begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \cdot x\text{H}_2\text{O} + 3\text{H}_2\text{SO}_4$



Mole Ratio: 2 : 5

Procedure:

Take given KMnO_4 solution in the burette with the help of funnel and then remove the funnel. Note the initial reading. Pipette out 10.0 cm^3 of oxalic acid in conical flask.

Add half test tube of dil. H_2SO_4 in it. Heat the solution up to $60-70^\circ\text{C}$ and then titrate this hot solution against standard KMnO_4 solution. End point is just light pink. Note the final reading. Take at least three concordant readings to calculate the exact volume of KMnO_4 used.

Observations and Calculations:

- (i) Vol. of oxalic acid taken for each titration = 10.0 cm^3
 (ii) Vol. of KMnO_4 used for each titration.

No. of Obs.	Initial Reading	Final Reading	Vol. of KMnO_4 used
1.	0.0	10.0	10.0 cm^3
2.	10.0	20.0	10.0 cm^3
3.	20.0	30.0	10.0 cm^3

Concordant Reading = 10.0 cm^3

Oxalic acid

 KMnO_4

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_1 = \frac{M_2 V_2}{n_2} \times \frac{n_1}{V_1}$$

$$M_1 = \frac{0.02 \times 10 \times 5}{2 \times 10} = 0.05 \text{M}$$

Amount of oxalic acid per dm^3 = Molar mass \times Molarity

$$6.3 = 0.05 \times (90 + 18x)$$

$$\frac{6.3}{0.05} = 90 + 18x$$

$$126 = 90 + 18x$$

$$126 - 90 = 18x$$

$$36 = 18x$$

$$x = \frac{36}{18} = 2$$

Result:

Water of crystallization of oxalic acid = 2.

(D) The given solution contains 30 g of partially oxidized $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved per dm^3 . Find out the percentage purity of the sample. (5)

Ans Principle:

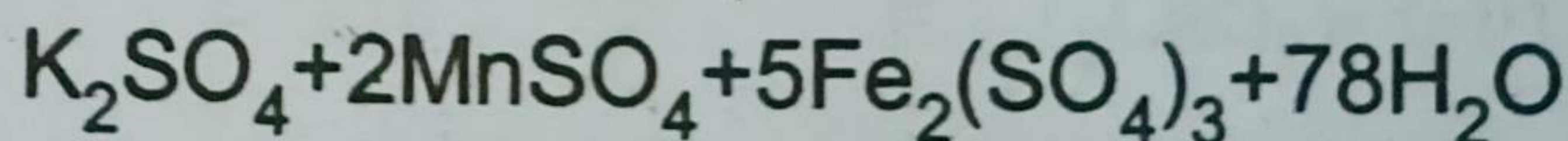
It is redox titration. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is a reducing agent and can be titrated against KMnO_4 in the presence of dil. H_2SO_4 .

Standard Solution : 0.02 M KMnO_4 Indicator : KMnO_4 (itself)

End Point : Just light pink

Equation : $2\text{KMnO}_4 + 10\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 8\text{H}_2\text{SO}_4$

↓



Mole Ratio: : KMnO_4 : $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

2

:

10

Procedure:

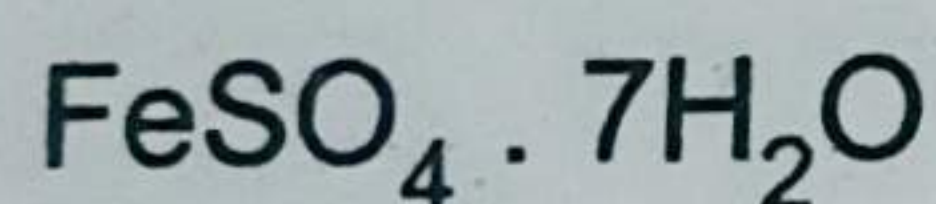
Take the given KMnO_4 in the burette and note the initial reading. Pipette out 10.0 cm^3 of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution in the conical flask. Then add half test tube of dil. H_2SO_4 in the flask. Titrate this solution against KMnO_4 in the burette. The end point is just light pink. Note the final reading. Take at least three concordant readings to calculate the exact volume of KMnO_4 used.

Observations and Calculations:

- (i) Vol. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution taken = 10.0 cm^3
 (ii) Vol. of KMnO_4 used for each titration.

No. of Obs.	Initial Reading	Final Reading	Vol. of KMnO_4 used
1.	0.0	10.0	10.0 cm^3
2.	10.0	20.0	10.0 cm^3
3.	20.0	30.0	10.0 cm^3

Concordant Reading = 10.0 cm^3



$$\frac{M_1 V_1}{n_1}$$

=

$$\frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 10.0}{10}$$

=

$$\frac{0.02 \times 10.0}{2}$$

$$M_1$$

=

$$\frac{0.02 \times 10.0}{2} \times \frac{10}{10.0}$$

$$M_1$$

=

$$0.1 \text{ M FeSO}_4 \cdot 7\text{H}_2\text{O}$$

Amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in g/dm^3 = Molarity \times Molar mass

$$= 0.1 \times 278$$

$$= 27.8 \text{ g/dm}^3$$

Amount of oxidized $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ = $30 - 27.8 = 2.2 \text{ g}$

$$\% \text{age of } [\text{Fe}_2(\text{SO}_4)_3] = \frac{2.2}{30} \times 100 = 7.33\%$$

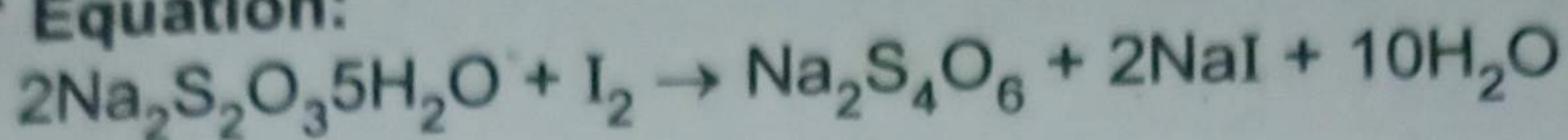
$$\% \text{ age of oxidation} = 7.33\%$$

Result:

The given solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ contains 7.33% of the sample.

- (E) The given solution contains 30.0 grams a mixture of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_4\text{O}_6$ dissolved per dm^3 . Find out the percentage of each component volumetrically.

Ans Equation:



Molar ratio:

2

Principle:

It is an iodimetric titration.

Standard soln:

0.05 iodine.

Indicator:

Freshly prepared starch solution.

End point:

Blue colour changes to colourless solution.

Procedure:

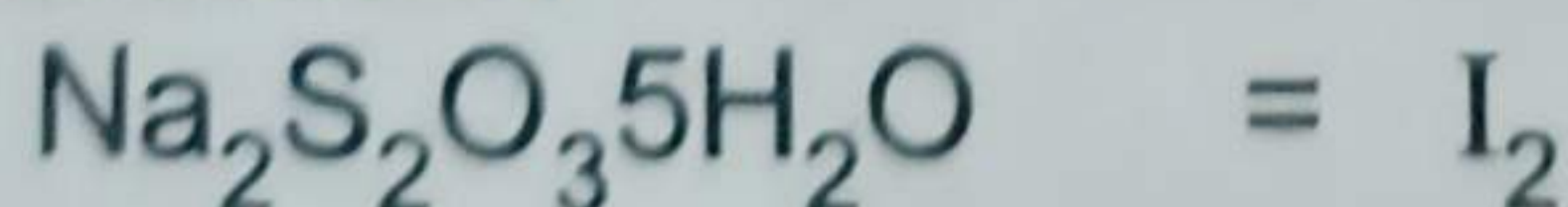
Take the given solution of hypo ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and $\text{Na}_2\text{S}_4\text{O}_6$ in the burette. Pipette out 10 ml of the standard solution of iodine into the iodine titration flask and add a test tube of water into it to dilute the iodine solution. Run down the hypo solution from the burette into the iodine titration flask gradually and shake till the colour of iodine in the flask changes to a pale yellow colour. Add 2 ml of freshly prepared starch solution into it. The solution is coloured blue. Continue the addition of hypo solution from the burette into the titration flask drop by drop and shake till the end point is reached. The blue colour is discharged to a colourless solution at the end point. Note the final reading of the burette. Repeat the titration to get three concordant readings.

Observations:

Sr. No.	Initial Reading	Final Reading	Volume of hypo used
1.	0	10	10 ml
2.	10	20	10 ml
3.	20	30	10 ml

Mean volume of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ used = 10 ml

Calculations:



$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 10}{2} = \frac{0.05 \times 10}{1}$$

$$M_1 \times 10 \times 1 = 0.05 \times 10 \times 2$$

$$M_1 = \frac{0.05 \times 10 \times 2}{10 \times 1}$$

$$M_1 = 0.1 \text{ M}$$

Molarity of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 0.1 \text{ M}$.

$$\begin{aligned} \text{Strength of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} &= \text{Molarity} \times \text{Mol.mass} \\ &= 0.1 \times 248 \\ &= 24.8 \text{ g/dm}^3 \end{aligned}$$

1000 cm^3 of mixture contain $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 30 \text{ g}$

30 g of solution contain $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 24.8 \text{ g}$

$$\begin{aligned} 100 \text{ g of solution} // // // &= \frac{24.8}{30} \times 100 \\ &= 82.67\% \end{aligned}$$

$$\% \text{ age of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 82.67\%$$

$$\% \text{ age of } \text{Na}_2\text{S}_4\text{O}_6 = 100 - 82.67$$

$$= 17.33\%$$