## Inter (Part-I) 2017

| 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-** Equal masses of methane and oxygen are mixed in 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) $\frac{16}{17}$

**2-** Sum of $pK_a$ and $pK_b$ is equal to:

(a) 7

(b) 9

(c) 11

(d) 14 ✓

**3-** In order to mention the boiling point of water at 110°C, the external pressure should be:

(a) Between 760 torr and 1200 torr ✓

(b) 765 torr

(c) Between 200 torr and 760 torr

(d) 100 torr

**4-** Which of the following has linear structure:

(a) $CO_2$ ✓

(b) $NH_3$

(c) $CH_4$

(d) $H_2O$

**5-** The largest number of molecules are present in:

(a) 3.6 g of $H_2O$ ✓

(b) 4.8 g of $C_2H_5OH$

(c) 2.8 g of CO

(d) 5.4 g of $N_2O_5$

**6-** Splitting of spectral lines when atoms are subjected to electric field, called:

(a) Zeeman effect

(b) Stark effect ✓

(c) Photoelectric effect

(d) Compton effect

7- If rate equation of reaction $2A + B \rightarrow$ product is, rate = $k[A]^2 [B]$, and A is present in large excess then order of reaction is:

(a) 1 ✓

(b) 2

(c) 3

(d) 4

8- The units of $K_c$ for reaction $N_2 + O_2 \rightleftharpoons 2NO$ will be:

(a) moles / $dm^3$

(b) $mole^{-1}$ / $dm^3$

(c) $mole^{-2} dm^{+6}$

(d) No unit ✓

9- The voltage of Nickel Cadmium Cell is:

(a) 1 V

(b) 1.2 V

(c) 1.4 V ✓

(d) 1.6 V

10- One mole of $SO_2$ contains:

(a) $6.02 \times 10^{23}$ atoms of oxygen.

(b) $18.1 \times 10^{23}$ molecules of $SO_2$.

(c) $6.02 \times 10^{23}$ atoms of sulphur. ✓

(d) $4.8 \times 10^{23}$ atoms of sulphur.

11- Bohr's model is contradicted by:

(a) Planck's theory

(b) Pauli's exclusion principle

(c) Heisenberg uncertainty principle ✓

(d) Hund's rule

12- Relative lowering of vapour pressure is equal to:

(a) Mole fraction of solute ✓

(b) Mole fraction of solvent

(c) Molarity

(d) Molality

13- Which of the following has bond angle of 120°:

(a) $BeCl_2$

(b) $BF_3$ ✓

(c) $CH_4$

(d) $NH_3$

14- For the reaction $NaOH + HCl \rightarrow NaCl + H_2O$, the change in enthalpy is called:

(a) Heat of reaction

(b) Heat of formation

(c) Heat of neutralization ✓

(d) Heat of combustion

15- The partial pressure of oxygen in lungs is:
   (a) 159 torr
   (b) 116 torr ✓
   (c) 100 torr
   (d) 90 torr

16- Which of the following is pseudo solid:
   (a) $CaF_2$
   (b) Glass ✓
   (c) $NaCl$
   (d) $KNO_3$

17- Solvent extraction is an equilibrium process and controlled by:
   (a) Law of mass action
   (b) Amount of solute used
   (c) Distribution law ✓
   (d) Hess's law

## Inter (Part-I) 2017

| Chemistry | Group-II | PAPER: I |
|---|---|---|
| Time: 2.40 Hours | (SUBJECTIVE TYPE) | Marks: 68 |

### SECTION-I

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

**(i) What is the function of electric field in mass spectrometer?**

**Ans** Mass spectrometer is the instrument employed to separate positively charged particles on the basis of their m/e values and get the record on the photographic plate or electrometer.

**(ii) With the help of two examples show that molecular formula is a multiple of empirical formula.**

**Ans** The empirical formulas of benzene and glucose are CH and $CH_2O$, respectively. So for these compounds the molecular formulas are the simple multiple of empirical formulas. Hence,

Molecular formula = n (Empirical formula)

**(iii) Define Avogadro's number and molar volume.**

**Ans** **Avogadro's number:**

It is the number of atoms, molecules or ions in one gram atom of an element, one gram mole of a compound or one gram ion of an ionic substance.

**Molar volume:**

The volume occupied by one mole of an ideal gas at standard temperature and pressure −22.414 $dm^3$ is called the molar volume.

**(iv) How crystals are dried in an oven?**

**Ans** Crystals are dried through drying agents which are used in an oven. Those agents are $CaCl_2$, silica gel or phosphorus pentaoxide.

**(v) State distribution law.**

**Ans** If a salute X distributes itself between two non-miscible solvents A and B at constant temperature and X is in the same molecular condition in both the solvents, then:

$$K_d = \frac{\text{Concentration of X in A}}{\text{Concentration of X in B}}$$

**(vi)** **What is partition chromatography?**

**Ans** The type in which separation involves distribution of components is called partition chromatography e.g., Paper chromatography.

**(vii)** **Define absolute zero. What is its value?**

**Ans** The temperature of $-273.16°C$ at which the volume of the gas theoretically becomes zero is called absolute zero. Its value is taken as zero on the Kelvin scale of temperature.

**(viii)** **Derive an expression to calculate density of a gas from ideal gas equation.**

**Ans** For calculating the density of an ideal gas, we substitute the value of number of moles (n) of the gas in terms of the mass (m), and the molar mass (M) of the gas.

$$n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT \tag{1}$$

Equation (1) is another form of general gas equation that may be employed to calculate the mass of a gas whose P, T, V and molar mass are known. Rearranging equation (1),

$$PM = \frac{m}{V} RT$$

$$PM = d\, RT \qquad\qquad (d = \frac{m}{V})$$

$$d = \frac{PM}{RT}$$

**(ix)** **Write down any two applications of plasma.**

**Ans** **Applications of Plasma:**

**(i)** Plasma light up our homes and offices, make our computers and electronic equipment work.

**(ii)** They drive lasers and particle accelerators, help to clean up environment, pasteurize foods and make tools corrosion-resistant.

**(x)** **State 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 we can check extent of reaction with the help of equilibrium constant?

**Ans** With the help of equilibrium constant, we can check extent of reaction as:

1. If the equilibrium constant is very large, this indicates that the reaction is almost complete.

2. If the value of $K_c$ is small, it reflects that the reaction does not proceed appreciably in the forward direction.

3. If the value of $K_c$ is very small, this shows a very little forward reaction.

**(xii)** What is meant by ionic product of water? Write down its value.

**Ans** Water is a very weak electrolyte and ionizes to a slight degree. The extent of this auto-ionization is expressed by ionic product of water called $K_w$, having a value $10^{-14}$ at $25^\circ C$.

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

**(i)** Water is liquid at room temperature while $H_2S$ is a gas, comment.

**Ans** When we consider the hydrides of group V-A, VI-A, then $NH_3$, $H_2O$ and HF show maximum boiling points in the respective series. The reason is, the enhanced electronegative character of N, O and F. That is why, water is liquid at room temperature, but $H_2S$ and $H_2Se$ are gases.

**(ii)** Why one feels sense of cooling under fan after bath?

**Ans** The water particles clinging to our skin and body evaporates very quickly with the help of the fan. When the water droplets evaporate, they take away the energy from our body heat. That's why, we feel the cooling effect.

**(iii)** What is cleavage and cleavage plane?

**Ans** Cleavage:

Cleavage is the tendency of crystalline materials to split along definite crystallographic structural planes.

Cleavage plane:

Whenever the crystalline solids are broken, they do so along definite planes. These planes are called cleavage planes.

**(iv) Define crystalline solid and crystallites.**

**Ans Crystalline solids:**

Those solids in which atoms, ions or molecules are arranged in a definite three-dimensional pattern are called crystalline solids.

**Crystallites:**

The crystalline parts of otherwise amorphous solids are known as crystallites.

**(v) State Moseley's law and give its mathematical form.**

**Ans** Moseley's law states that

"The frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it."

$$\sqrt{v} = a \, (Z - b)$$

Here 'a' and 'b' are the constant characteristics of the metal under consideration. This linear equation is known as Moseley's law.

**(vi) What is orbital? Draw the shape of p-orbitals.**

**Ans Orbital:**

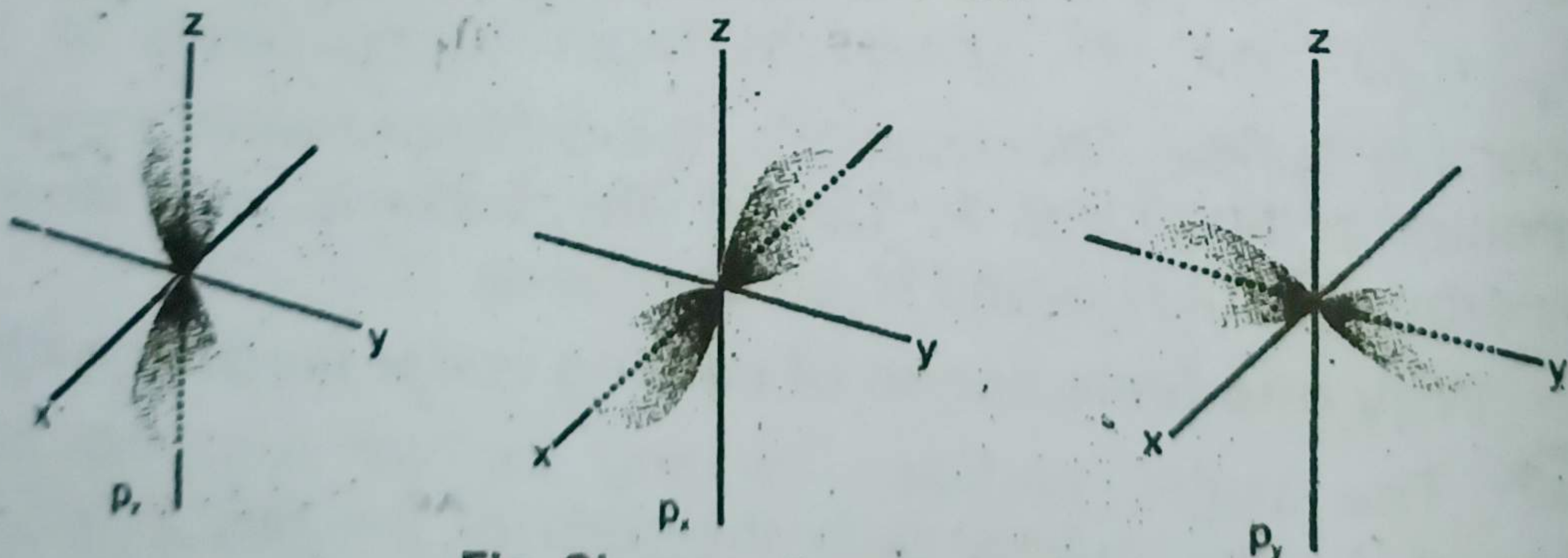The volume of space in which there is 95% chance of finding an electron is called atomic orbital.



Fig. Shapes of p-orbitals.

**(vii) Calculate the mass of electron when $\dfrac{e}{m} = 1.7588 \times 10^{11}$ C / kg.**

**Ans Mass of Electron:**

The value of charge on electron is $1.602 \times 10^{-19}$ coulombs, while e/m value of electron is $1.7588 \times 10^{11}$ coulombs kg$^{-1}$, so

$$\frac{e}{m} = \frac{1.6022 \times 10^{-19} \text{ coulombs}}{\text{Mass of electron}} = 1.7588 \times 10^{11} \text{ coulombs kg}^{-1}$$

$$\text{Mass of electron} = \frac{1.6022 \times 10^{-19} \text{ coulombs}}{1.7588 \times 10^{11} \text{ coulombs kg}^{-1}}$$

Mass of electron $= 9.1095 \times 10^{-31}$ kg

**(viii) What are the defects of Rutherford's Atomic Model.**

**Ans** The defects of Rutherford's Atomic Model are as following:

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

**(ix) Explain why $CuSO_4$ give acidic solution, when dissolved in water.**

**Ans** The reason is that $CuSO_4$ is soluble in water and exists as hydrated $Cu^{2+}$ ions and $SO_4^{2-}$ ions. The pH of a 0.2 M solution is 4.0. Copper (II) ion reacts with water to make the weak base $CuOH^-$ and leaves $H^+$ in solution.

**(x) The sum of mole fractions of all the components is always equal to unity for any solution. Justify.**

**Ans** As,

$$\text{Mole fraction} = \frac{\text{No. of moles of a solute}}{\text{Total no. of moles in solution}}$$

Suppose no. of moles of solute is $n_1$ that of solvent is $n_2$.

Then, corresponding mole fractions will be $\dfrac{n_1}{n_1 + n_2}$ and $\dfrac{n_2}{n_1 + n_2}$.

So, sum of mole fractions will be $\dfrac{n_1}{n_1 + n_2} + \dfrac{n_2}{n_1 + n_2} = 1$

**(xi) Define oxidation state with two examples.**

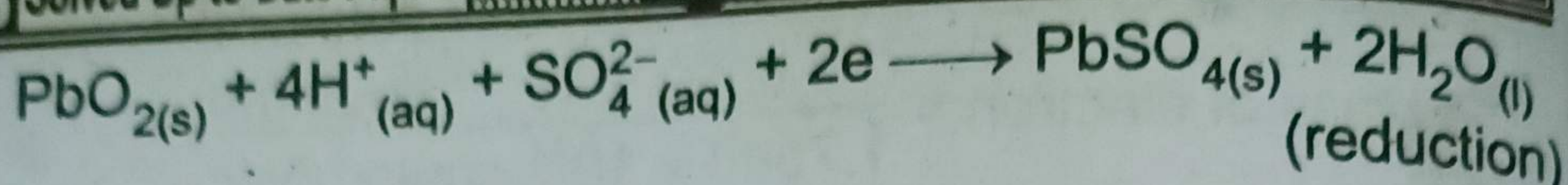**Ans** **Oxidation State:**

Oxidation state is the apparent charge on an atom of an element in a molecule or an ion. It may be positive or negative or zero.
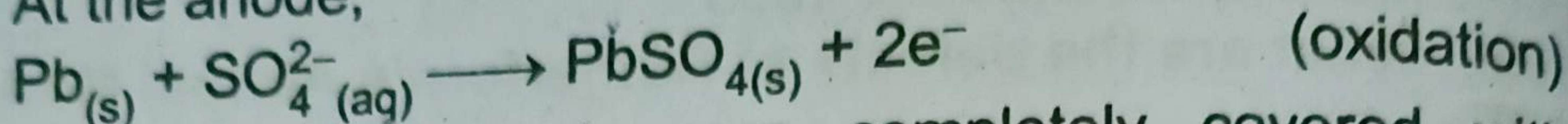
**Examples:**

1. The oxidation state of Mn in $KMnO_4$ is +7.
2. The oxidation state of sulphur in $SO_4^{2-}$ is +6.

**(xii) Write down electrode reactions during discharging in lead accumulator battery.**
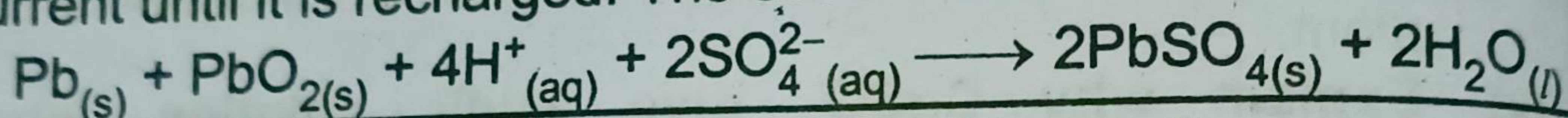
**Ans** At the cathode,

$$PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4\,(aq)} + 2e \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$
(reduction)

At the anode,
$$Pb_{(s)} + SO^{2-}_{4\,(aq)} \longrightarrow PbSO_{4(s)} + 2e^- \qquad \text{(oxidation)}$$

When both electrodes are completely covered with $PbSO_4$ deposits, the cell will cease to discharge any more current until it is recharged. The overall reaction is

$$Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO^{2-}_{4\,(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

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

**(i) Briefly explain the atomic and ionic radii with examples.**

**Ans Atomic Radius:**

The atomic radius means the average distance between the nucleus of the atom and its outermost electronic shell.

For example, the atomic radii can be determined by measuring the distances between the centres of adjacent atoms with the help of X-rays or by spectroscopic measurements.

**Ionic Radius:**

The ionic radius of an ion is the radius of the ion while considering it to be spherical in shape.

For example, the ionic radius for metals is for positive ions and for elements of group number VA to VIIA are for negative ions.

**(ii) Why π bonds are more diffused than σ bonds?**

**Ans** σ-bond is formed by head-to-head overlap of two half-filled orbitals. The electronic cloud density is symmetrically distributed along the bond axis.

π-bond is formed due to the side way or parallel overlap of two half-filled p-orbitals. The electronic cloud density is not symmetrical along the bond axis. It has two regions of electron density, above and below the bond axis. Therefore, the π-bonds are more diffused than σ-bonds.

**(iii) Why ionization energy (IE) values are decreased from top to bottom in a group?**

**Ans** The ionization energy (IE) decrease in spite of the increase in proton number or nuclear charge. This is due to successive addition of electronic shells as a result of which the

valence electrons are placed at a larger distance from the nucleus.

**(iv)** $NH_3$ **can form coordinate covalent bond with $H^+$ but $CH_4$ not. Justify.**

**Ans** In $CH_4$, there is no lone pair of electrons to donate $H^+$ for the formation of coordinate covalent bond. Therefore, $NH_3$ and $H_2O$ can form coordinate covalent bond with $H^+$ but $CH_4$ cannot do so.

**(v)** **Explain the term enthalpy.**

**Ans** **Enthalpy:**

"The total heat content of the system is termed as enthalpy of a system."

It is defined as the heat change when one mole of a substance is dissolved in a specified number of moles of solvent at a given temperature.

**(vi)** **Define system and surrounding.**

**Ans** **System:**

Any portion of the universe which is under study is called a system.

**Surrounding:**

The remaining portion other than system is known as its surrounding.

**(vii)** **A catalyst is specific in its action. Justify.**

**Ans** A catalyst is specific in its action. When a particular catalyst works for one reaction, it may not necessarily work for any other reaction. If different catalysts are used for the same reactant then the products may change. For example,

Formic acid is decomposed by $Al_2O_3$ to $H_2O$ and $CO$ while $Cu$ causes its decomposition to $H_2$ and $CO_2$.

$$HCOOH \xrightarrow{Al_2O_3} H_2O + CO$$

$$HCOOH \xrightarrow{Cu} H_2 + CO_2$$
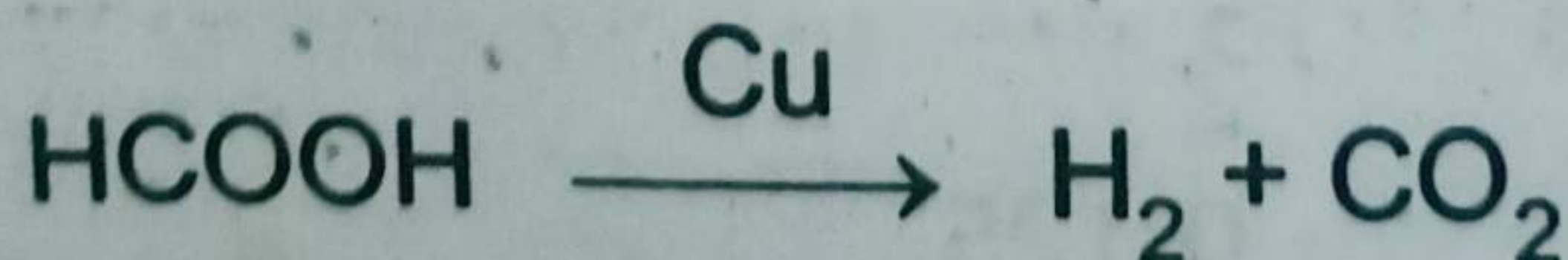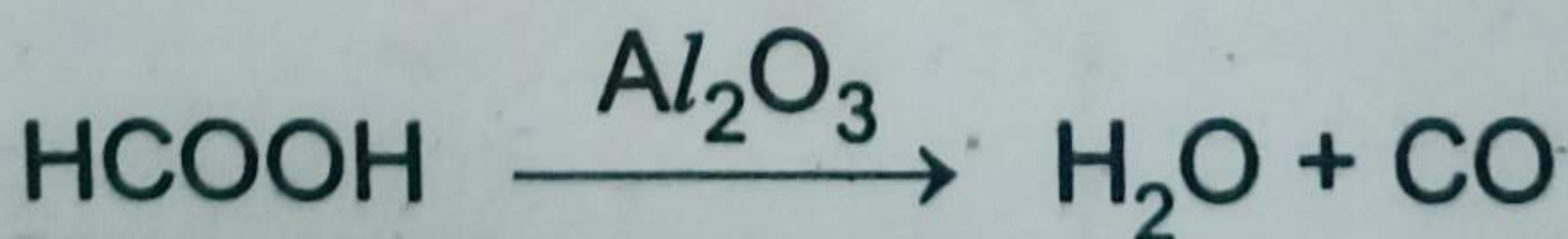
**(viii)** **What is meant by half-life period? Give one example.**

**Ans** Half-life period of a reaction is the time required to convert 50% of the reactants into products. For example, th

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.

**(ix) Define negative catalyst with an example.**

**Ans** When the rate of reaction is retarded by adding a substance, then it is said to be a negative catalyst or inhibitor. For example, tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition.

## SECTION-II

**NOTE: Attempt any Three (3) questions.**

**Q.5.(a)** Calculate the no. of grams of $K_2SO_4$ and water produced, when 14.0 g of KOH are reacted with excess of $H_2SO_4$. Also calculate the number of molecules of water produced. **(4)**
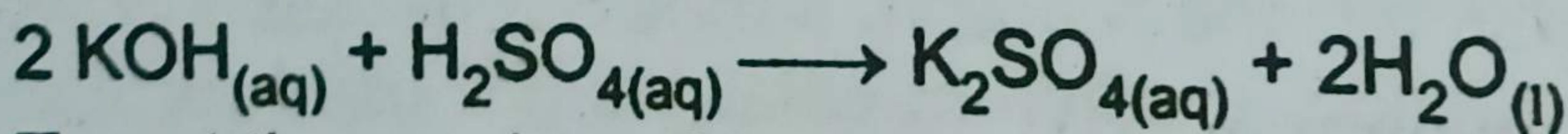
**Ans** Solution:

For doing such calculations, first of all convert the given mass of KOH into moles and then compare these moles with those of $K_2SO_4$ with the help of the balanced chemical equation.

$$\text{Mass of KOH} = 14.0 \text{ g}$$
$$\text{Molar mass of KOH} = 39 + 16 + 1 = 56 \text{ g/mol}$$
$$\text{No. of moles of KOH} = \frac{14.0 \text{ g}}{56 \text{ g mol}^{-1}} = 0.25$$

**Equation:**

$$2\,KOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} + 2H_2O_{(l)}$$

To get the number of moles of $K_2SO_4$, compare the moles of KOH with those of $K_2SO_4$.

| KOH | : | $K_2SO_4$ |
|---|---|---|
| 2 | : | 1 |
| 1 | : | $\frac{1}{2}$ |
| 0.25 | : | 0.125 |

So, 0.125 moles of $K_2SO_4$ is being produced from 0.25 moles of KOH.

$$\text{Molar mass of } K_2SO_4 = 2 \times 39 + 96$$
$$= 174 \text{ g/mol}$$

$$\text{Mass of } K_2SO_4 \text{ produced} = \text{No. of moles} \times \text{molar mass}$$
$$= 0.125 \text{ moles} \times 174 \text{ g mol}^{-1}$$
$$= 21.75 \text{ g}$$

To get the number of moles of $H_2O$, compare the moles of KOH with those of water.

| KOH | : | $H_2O$ |
|-----|---|--------|
| 2 | : | 2 |
| 1 | : | 1 |
| 0.25 | : | 0.25 |

So, the number of moles of water produced is 0.25 from 0.25 moles of KOH.

$$\text{Mass of water produced} = 0.25 \text{ moles} \times 18 \text{ g mol}^{-1}$$
$$= 4.50 \text{ g}$$

$$\text{Number of molecules of water} = \text{No. of moles} \times 6.02 \times 10^{23}$$
$$= 0.25 \text{ moles} \times 6.02 \times 10^{23}$$
$$\text{molecules per mole}$$
$$= \boxed{1.50 \times 10^{23} \text{ molecules}}$$

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**(b)** **What are covalent solids? Describe types of covalent solids and explain properties of covalent solids. (Only four properties)** **(4)**

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**Ans** **Covalent Solids:**

Covalent solids are also called atomic solids, because they are composed of neutral atoms of the same or of different elements. These atoms are held together by covalent bonds.

**Types of Covalent Solids:**

(i) When the covalent bonds join to form giant molecules like diamond, silicon carbide or aluminium nitride.

(ii) When atoms join to form the covalent bonds and separate layers are produced like that of graphite, cadmium iodide and boron nitride.

**Properties of Covalent Crystals:**

1. The bonding in covalent crystals extend in three dimensions. They contain a network of atoms. The valencies of atoms are directed in definite directions, so the packing of atoms in these crystals is looser than those

of ionic and metallic crystals. Thus, covalent crystals have open structure.

2. These crystals are very hard and considerable amount of energy is required to break them. They have high melting points and their volatility is very low.

3. Due to the absence of free electrons and ions, they are bad conductors of electricity. However, graphite has a layered structure and the electrons are available in between the layers. These electrons are delocalised and conductivity becomes possible. Graphite is not a conductor perpendicular to the layers.

4. Mostly covalent crystalline solids are insoluble in polar solvents like water but they are readily soluble in non-polar solvents like benzene and carbon tetrachloride.

**Q.6.(a) State and explain general gas equation. Calculate value of 'R' in SI-units.** (4)

**Ans** **General Gas Equation:**

While describing Boyle's and Charles' laws, some of the variables are held constant during the changes produced in the gases. According to Boyle's law,

$$V \propto \frac{1}{P}$$   (when 'n' and 'T' are held constant.)

According to Charles' law,

$$V \propto T$$   (when n and P are held constant.)

It is a well-known fact that volume of the given gas at constant temperature and pressure is directly proportional to the number of moles (Avogadro's law).

$$V \propto n$$   (when P and T are held constant)

If we think for a moment that none of the variables are to be kept constant then all the above three relationships can be joined together.

$$V \propto \frac{nT}{P}$$

$$V = \text{constant} \frac{nT}{P}$$

The constant suggested is R which is called general gas constant.

$$V = R \frac{nT}{P}$$

$$PV = n RT \qquad\qquad (1)$$

The equation (1) is called an ideal gas equation. It is also known as general gas equation. This equation shows that if we have any quantity of an ideal gas then the product of its pressure and volume is equal to the product of number of moles, general gas constant and absolute temperature. This equation is reduced to Boyle's law, Charles' law and Avogadro's law, when appropriate variables are held constant.

$PV = n RT$, when T and n are held constant,

$PV = k$ (Boyle's law)

$V = R\dfrac{nT}{P}$, when P and n are held constant,

$V = kT$ (Charles' law)

$V = R\dfrac{nT}{P}$, when P and T are held constant

$V = kn$ (Avogadro's law)

For one mole of a gas, the general gas equation is

$$PV = RT \qquad \text{or} \qquad \dfrac{PV}{T} = R$$

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**(b)　Explain Rutherford atomic model. Give its defects. (4)**

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**Ans　Rutherford's Model of Atom (Discovery of Nucleus):**

In 1911, Lord Rutherford performed a classic experiment. He studied the scattering of high speed $\alpha$-particles, which were emitted from a radioactive metal (radium or polonium),

A beam of $\alpha$-particles was directed onto a gold foil of 0.00004 cm thickness as target through a pin-hole in lead plate, Fig.
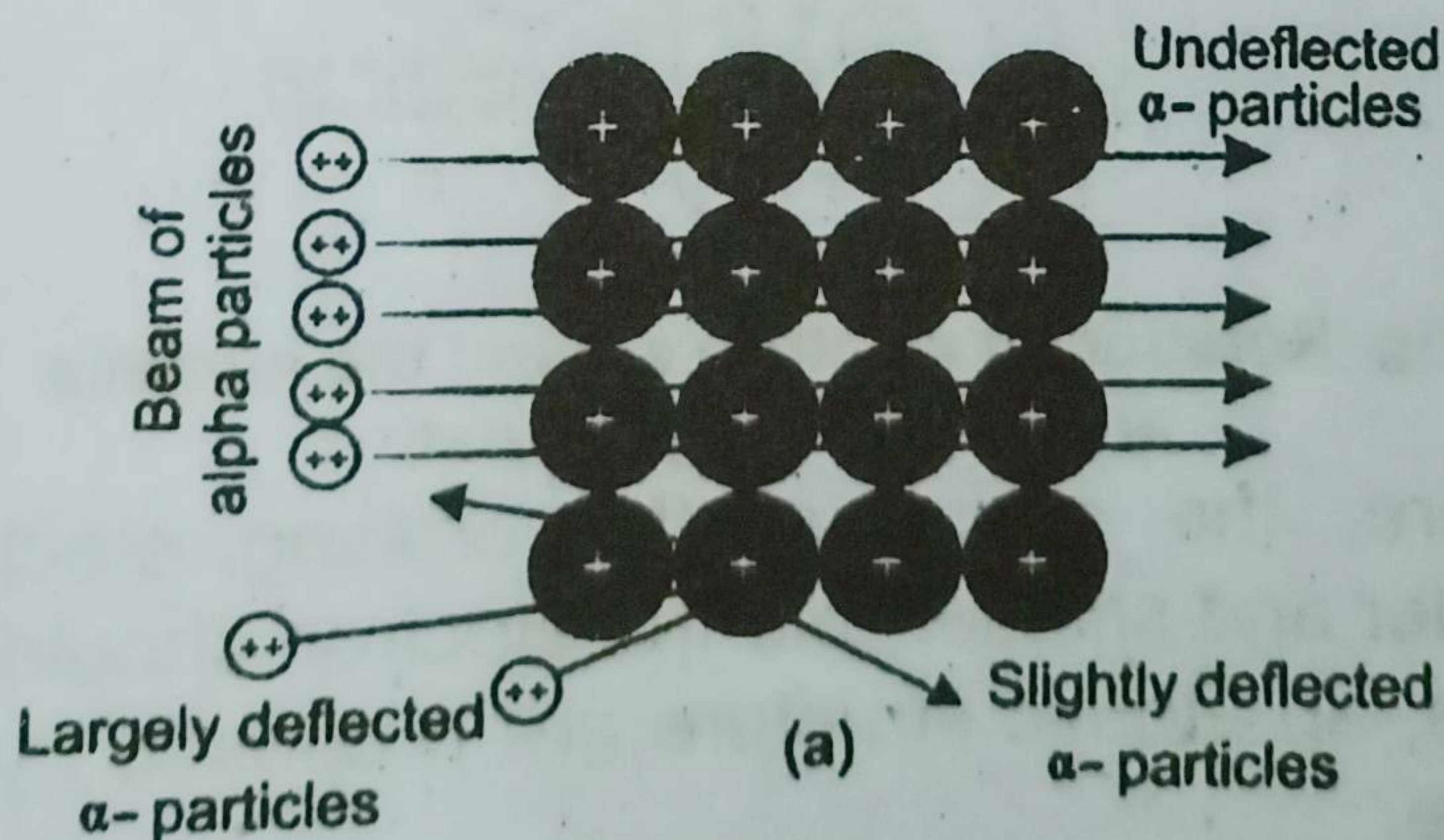


Fig. Rutherford's experiment for scattering of $\alpha$-particles.

A photographic plate or a screen coated with zinc sulphide was used as a detector. Whenever, an $\alpha$-particle

struck the screen, a flash of light was produced at that point. It was observed that most of the particles went through the foil undeflected. Some were deflected at fairly large angles and a few were deflected backward. Rutherford proposed that the rebounding particles must have collided with the central heavy portion of the atom which the called as nucleus.

**Conclusion:**

On the basis of these experimental observations, Rutherford proposed the planetary model (similar to the solar system) for an atom in which a tiny nucleus is surrounded by an appropriate number of electrons. Atom as a whole being neutral, therefore, the nucleus must be having the same number of protons as there are number of electrons surrounding it.

In Rutherford's model for the structure of an atom, the outer electrons could not be stationary. If they were, they would gradually be attracted by the nucleus till they ultimately fall into it. Therefore, to have a stable atomic structure, the electrons were supposed to be moving around the nucleus in closed orbits. The nuclear atom of Rutherford was a big step ahead towards understanding the atomic structure, but the behaviour of electrons remained unexplained in the atom.

**Defects of Rutherford's Model:**

Rutherford's planet-like picture was defective and unsatisfactory because the moving electron must be accelerated towards the nucleus. Fig.
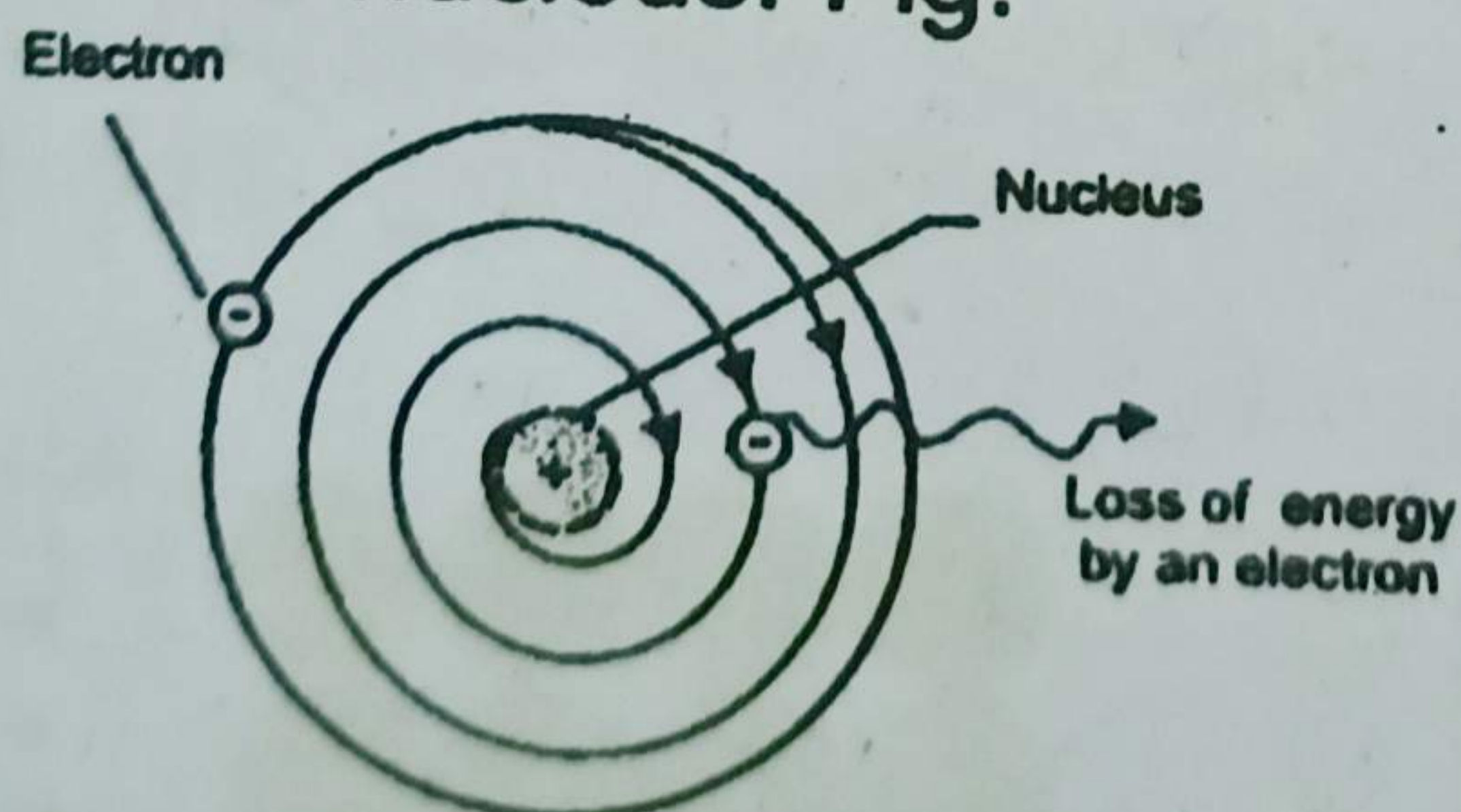


**Fig. Rotation of electron around the nucleus and expected spiral path.**

Therefore, the radius of the orbiting electron should become smaller and smaller and the electron should fall into the nucleus. Thus, an atomic structure are proposed by Rutherford would collapse.
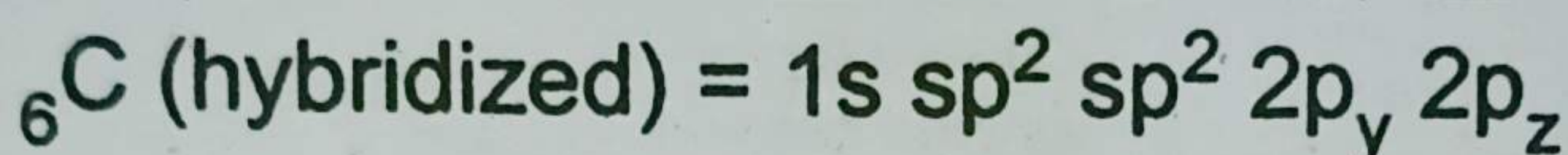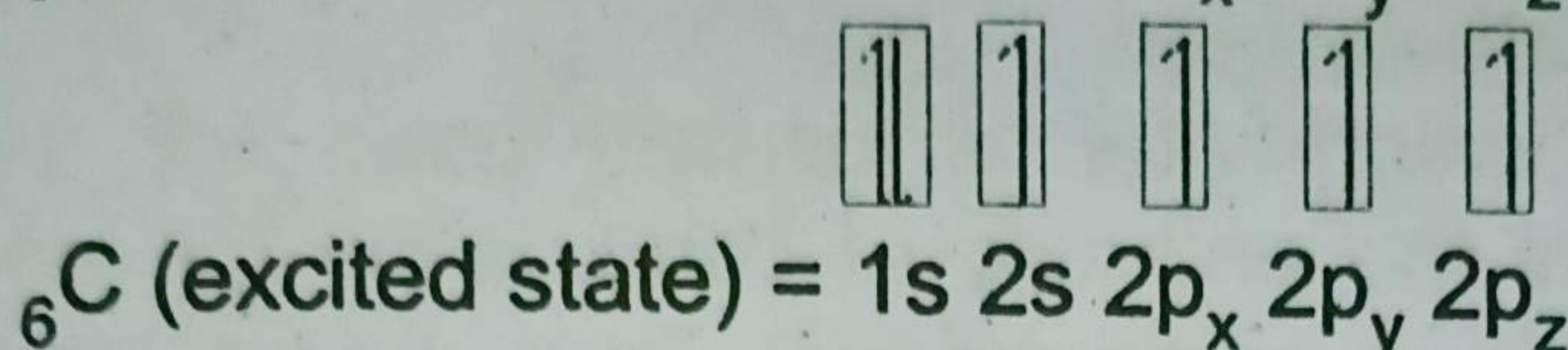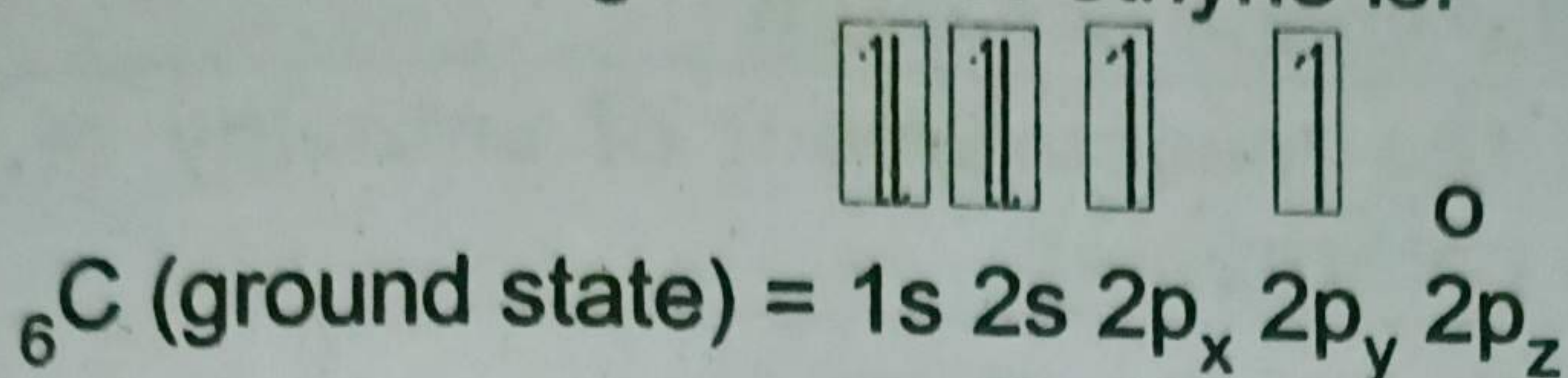
**Q.7.(a) Write a note on sp-hybridization and give example of ethyne.** (4)

**Ans** **sp-Hybridization:**

In sp hybridization, one 's' and one 'p' orbitals intermix to form two sp-hybrid orbital called sp hybrid orbitals.

**Ethyne (CH≡CH):**

The electronic configuration of ethyne is:

$$_6C \text{ (ground state)} = 1s\ 2s\ 2p_x\ 2p_y\ 2p_z$$

$$_6C \text{ (excited state)} = 1s\ 2s\ 2p_x\ 2p_y\ 2p_z$$

$$_6C \text{ (hybridized)} = 1s\ sp^2\ sp^2\ 2p_y\ 2p_z$$

Ethyne is formed as a result of sp hybridization of carbon atoms and subsequent formation of $\sigma$ and $\pi$ bonds. Each carbon atom undergoes sp-s overlap with one hydrogen atom and sp-sp overlap with other carbon atom. Each carbon atom is left with two unhybridized p orbitals perpendicular to the plane of sp hybrid orbitals. The two half-filled p orbitals (on separate carbon atoms) are parallel to each other in one plane while the other two p orbitals are parallel to each other in another plane. The sideways $\pi$ overlap between the p-orbitals in two planes results in the formation of two $\pi$ bonds as shown in Fig.



Overlap of hybrid orbitals gives a sigma bond

σ-bond

Overlap of p orbitals gives a pi bond
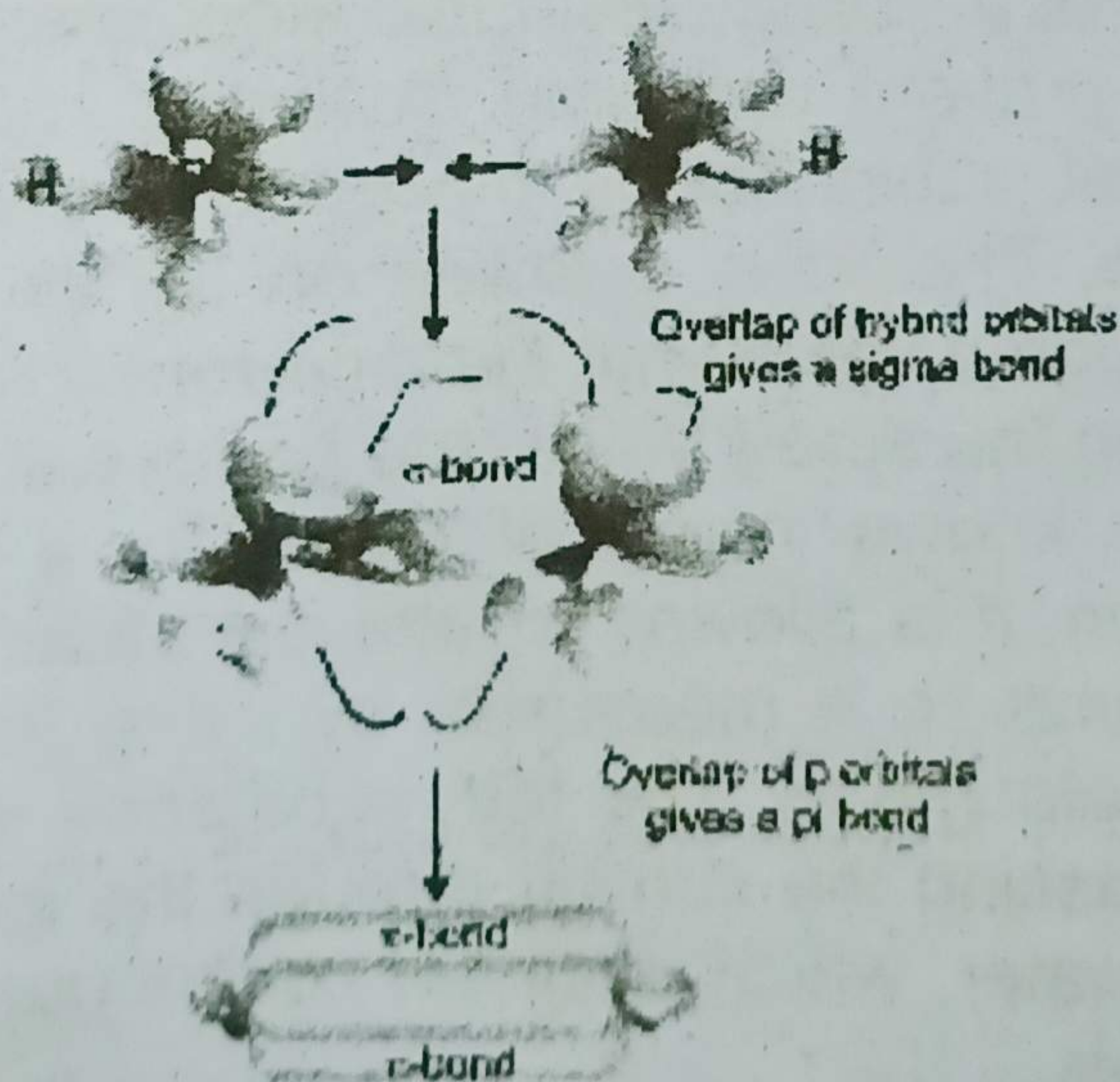
π-bond

σ-bond

**Fig. Formation of one sigma and two pi-bonds in $C_2H_2$ (ethyne).**

Ethyne molecule contains one σ and two π bonds between the two carbon atoms and each carbon atom is bonded with one H atom through a σ bond. Actually, four electronic clouds of two π-bonds intermix and they surround the sigma bond in the shape of a drum.

**(b)** **Describe the measurement of enthalpy of a reaction by bomb calorimeter.**

(4)

**Ans** **Bomb Calorimeter:**

A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds. A bomb calorimeter is shown in the following Fig.
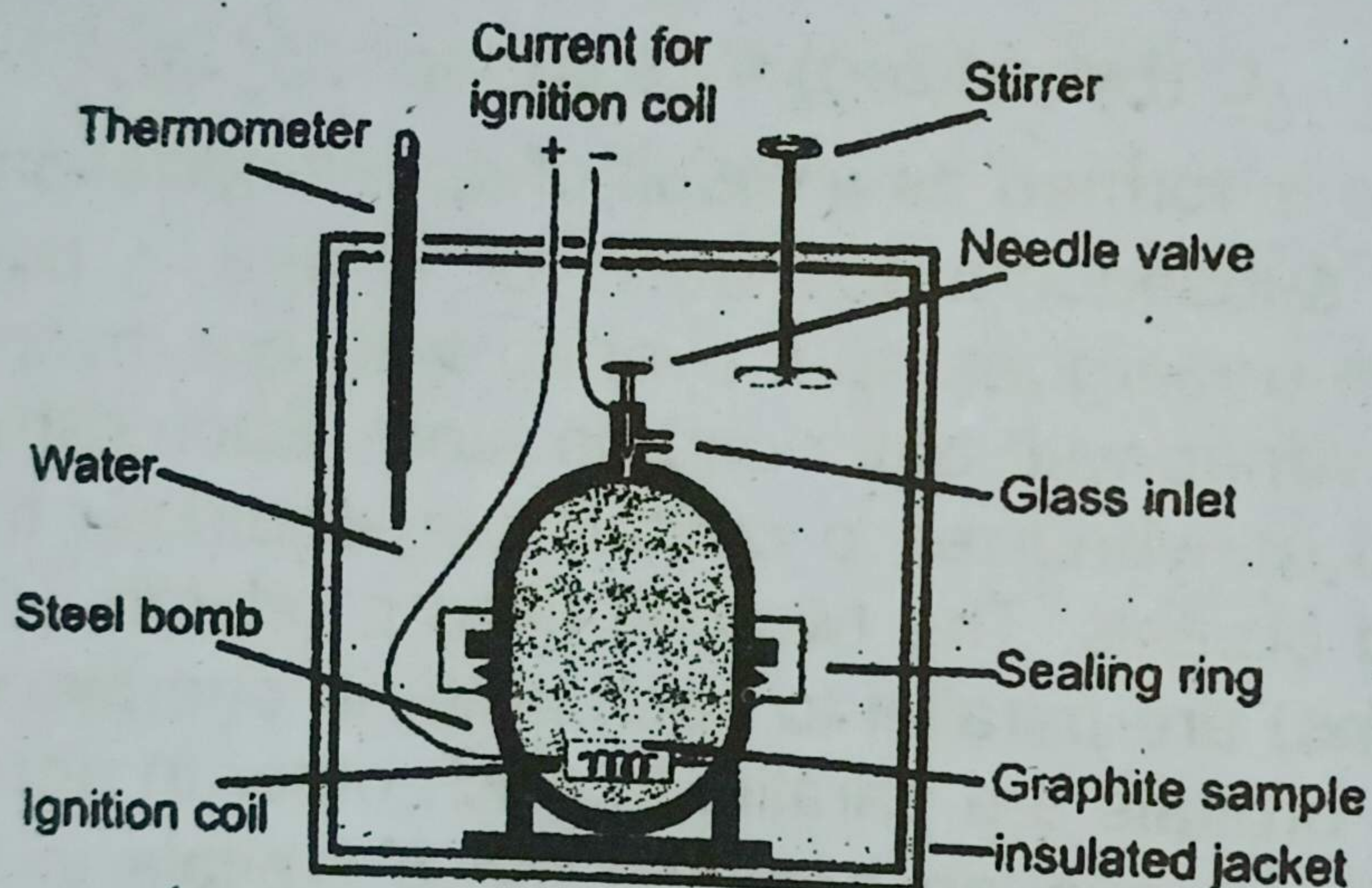


Fig. Bomb calorimeter.

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 $\Delta T$, heat capacity (c) in $kJK^{-1}$ 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)** The solubility of $CaF_2$ in water at 25°C is found to be $2.05 \times 10^{-4}$ mol $dm^{-3}$. What is the value of $K_{sp}$ at this temperature? (4)

**Ans** For Answer see Paper 2016 (Group-I), Q.8.(a).

**(b)** Describe fuel cells. Give their uses. (4)

**Ans** For Answer see Paper 2015 (Group-I), Q.9.(b).

**Q.9.(a)** What are non-ideal solutions? Briefly explain positive and negative deviation from Raoult's law. (4)

**Ans** Non-Ideal Solutions (azeotropic mixtures):

Non-ideal solutions are those solution which do not behave ideally. They show deviations from Raoult's Law due to differences in their molecular structures i.e., size, shape and intermolecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy. The vapour pressure deviations may be positive or negative in such solutions.

The deviations of solutions are of two types:
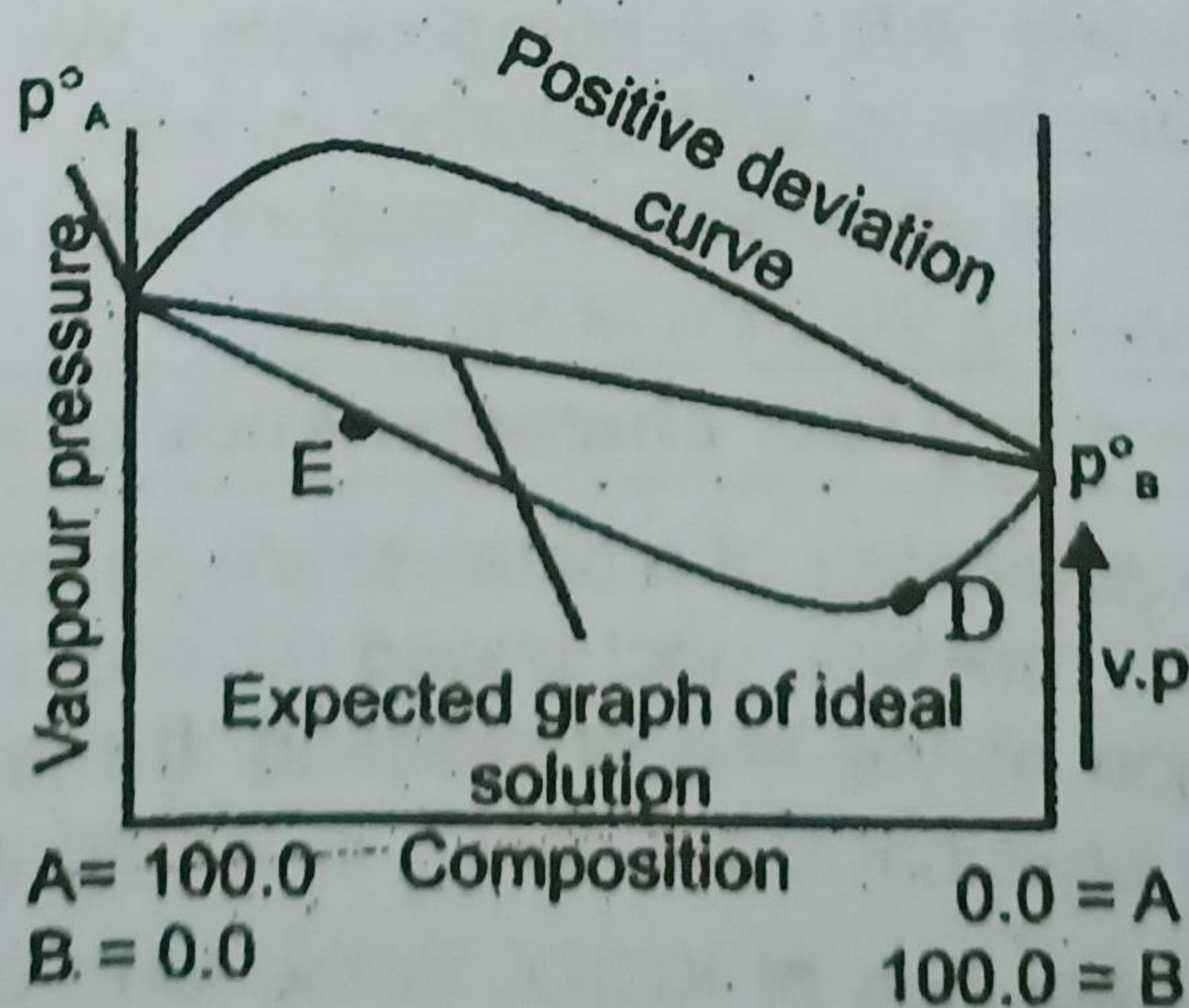
(a) Positive deviations          (b) Negative deviations



Fig. Non-ideal solutions and azeotropic mixtures for positive deviation.

## (a) Positive Deviations:

If a graph is plotted between composition and vapour pressure of a solution which shows positive deviation from Raoult's law, the total vapour pressure curve rises to a maximum. The vapour pressure of some of solutions are above the vapour pressure of either of the pure components.

Let us consider the mixture of A and B components at point C in the above Fig. At the point C, the mixture has the highest vapour pressure and, therefore, the lowest boiling point. On distilling this type of solution, the first fraction will be a constant boiling point mixture i.e., azeotropic mixture having a fixed composition corresponding to the maximum point. For this type of solution, it is not possible to bring about complete separation of components by fractional distillation. Ethanol-water mixture is an example of this type. It boils at 78.1°C with 4.5 % water and 95.5 % alcohol. 78.1°C is lower than the boiling point of ethanol (78.5°C) and water (100°C).

## Negative Deviations:

For this type of solution, the vapour pressure curve shows a minimum. Let us consider a point E in the above Fig. Here, the more volatile component A is in excess. On distilling this solution, the vapours will contain more of A and the remaining mixture becomes richer in less volatile component B'. Finally, we reach the point D where vapour pressure is minimum and the boiling point is maximum. At this point, the mixture will distill unchanged in composition.

Therefore, it is not possible to separate this type of solution completely into its components. We can give the example of hydrochloric acid solution in water for this type of solutions. HCl forms an azeotropic mixture with water, boiling at 110°C and containing 20.24% of the acid.

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**(b)** **Write down any four characteristics of a catalyst. (4)**

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**Ans** Four characteristics of a catalyst are as following:

1. A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state. $MnO_2$ is added as a catalyst for the decomposition of $KClO_3$ in the form of granules. It is converted to fine powder at the end of reaction. It has

been found in many cases that the shining surfaces of the solid catalyst become dull.

2.    Sometimes, we need a trace of a metal catalyst to affect very large amount of reactants. For example, 1 mg of fine platinum powder can convert 2.5 dm$^3$ of $H_2$ and 1.25 dm$^3$ of $O_2$ to water. Dry HCl and $NH_3$, don't combine, but in the presence of trace of moisture, they give dense white fumes of $NH_4Cl$. Thousands of dm$^3$ of $H_2O$, can be decomposed in the presence of 1 g of colloidal platinum.

3.    A catalyst is more affective, when it is present in a finely divided form. For example, a lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils, finely divided nickel is used.

4.    A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.