

Inter (Part-I) 2016

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- Which of the following species has unpaired electrons in antibonding molecular orbitals:
- (a) O_2^{2+} (b) N_2^{2-} ✓
 (c) B_2 (d) F_2
- 2- Which statement about the following equilibrium is correct:
- $$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -188.3 \text{ kJ mol}^{-1}$$
- (a) The value of K_p falls with a rise in temperature. ✓
 (b) The value of K_p falls with increasing pressure.
 (c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide.
 (d) The value of K_p is equal to K_c .
- 3- Pressure remaining constant at which temperature the volume of gas will become twice of what it is at 0°C :
- (a) 546°C (b) 200°C
 (c) 546 K ✓ (d) 273 K
- 4- A solution of glucose is 10% w/v. The volume in which one gram mole of it dissolved will be:
- (a) 1 dm^3 (b) 1.8 dm^3 ✓
 (c) 200 cm^3 (d) 900 cm^3
- 5- Quantum number value for 2p orbitals are:
- (a) $n = 2, l = 1$ ✓ (b) $n = 1, l = 2$
 (c) $n = 1, l = 0$ (d) $n = 2, l = 0$
- 6- If the salt bridge is not used between two half-cells then the voltage:
- (a) Decreases rapidly (b) Decreases slowly
 (c) Does not change (d) Drops to zero ✓

- 7- In order to mention the boiling point of water at 110°C , the external pressure should be:
(a) 765 torr (b) Between 200 torr and 760 torr
(c) Between 760 torr and 1200 torr ✓
(d) Any value of pressure
- 8- The volume occupied by 1.4 g of N_2 at STP is:
(a) 2.24 dm^3 (b) 22.4 dm^3
(c) 1.12 dm^3 ✓ (d) 112 cm^3
- 9- The change in heat energy of a chemical reaction at constant temperature and pressure is called:
(a) Enthalpy change ✓ (b) Bond energy
(c) Heat of sublimation (d) Internal energy
- 10- 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
- 11- Splitting of spectral lines of the hydrogen atom under the influence of magnetic field is called:
(a) Stark effect (b) Zeeman effect ✓
(c) Compton effect (d) Photoelectric effect
- 12- Solvent extraction method is particularly useful technique for separation, when the product to be separated is:
(a) Non-volatile or thermally unstable.
(b) Volatile or thermally stable.
(c) Non-volatile or thermally stable.
(d) Volatile or thermally unstable. ✓
- 13- Which of the following is a pseudo solid:
(a) CaF_2 (b) Glass ✓
(c) NaCl (d) All of these
- 14- Which of the following will have the same number of molecules at STP:
(a) 280 cm^3 of CO_2 and 280 cm^3 of N_2O ✓
(b) 11.2 dm^3 of O_2 and 32 g of O_2
(c) 44 g of CO_2 and 11.2 dm^3 of CO
(d) 28 g of N_2 and 5.6 dm^3 of oxygen

- 15- The number of bonds in nitrogen molecule is:
- (a) One σ and one π (b) Two σ and one π
(c) Three σ only (d) One σ and two π ✓
- 16- In zero order reaction, the rate is independent of:
- (a) Temperature of reaction
(b) Concentration of reactants ✓
(c) Concentration of products
(d) Pressure of reaction
- 17- One mole of SO_2 contains:
- (a) 6.02×10^{23} atoms of oxygen
(b) 6.02×10^{23} atoms of sulphur ✓
(c) 18.1×10^{23} molecules of SO_2
(d) 4 g atoms of SO_2

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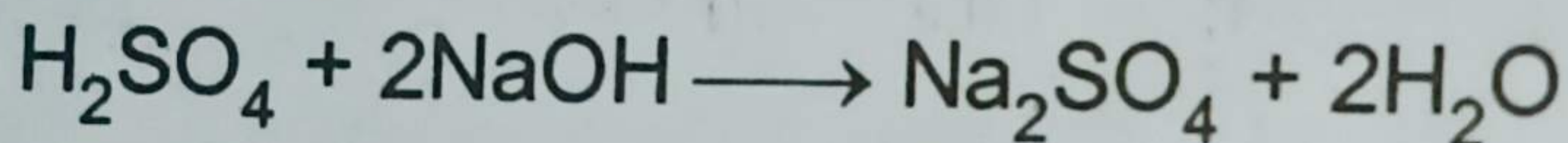
Chemistry	Group-II	PAPER: I
Time: 2.40 Hours	(SUBJECTIVE TYPE)	Marks: 68

SECTION-I

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

(i) One mole of H_2SO_4 should completely react with two moles of NaOH . How does Avogadro's number help to explain it?

Ans The balanced chemical equation between H_2SO_4 and NaOH is as follows:



One mole of H_2SO_4 releases two moles of H^+ in the solution. It needs two moles of OH^- ions for complete neutralization.

(ii) Describe that one mole of H_2O has two moles of bonds, three moles of atoms, ten moles of electrons and twenty eight moles of the total fundamental particles present in it.

Ans The molecule of $\text{H} - \text{O} - \text{H}$ has two bonds in it. Therefore, one mole of H_2O contains two moles of bonds and three moles of atoms. Similarly, there are eight electrons in oxygen and one electron in each of the two H atoms. One molecule of H_2O has 10 electrons. So, one mole of water contains 10 moles of electrons. There are 28 moles of all fundamental particles in one mole of water, 10 moles of electrons, 10 moles of protons, 8 moles of neutrons.

(iii) How N_2 and CO have same number of electrons, protons and neutrons?

Ans No. of electrons in $\text{N}_2 = 7 + 7 = 14$, number of protons in $\text{N}_2 = 7 + 7 = 14$ and number of neutrons $(14 - 7) = 7 + 7 = 14$.

In CO , number of electrons in $\text{C} = 6$, number of electrons in $\text{O} = 8$, total number of electrons $= 6 + 8 = 14$.

Number of protons in C = 6, number of protons in O = 8,
total number of protons = $6 + 8 = 14$.

Number of neutrons in C = 6, number of neutrons in O = 8,
total number of neutrons = $6 + 8 = 14$.

(iv) Why concentrated HCl and KMnO_4 solutions cannot be filtered by Gooch's crucible?

Ans Quick filtration can be done by placing the Gooch crucible in a suction filtering apparatus. It is useful for the filtration of precipitates, which need to be ignited at high temperature. If its perforations are covered with asbestos mat then it may be used to filter solutions that react with paper e.g., concentrated HCl and KMnO_4 solutions.

(v) Write names of major steps involved in crystallization.

Ans The process of crystallization has the following steps:

- (i) Choice of solvent
- (ii) Preparation of saturated solution
- (iii) Filtration
- (iv) Cooling
- (v) Collecting and washing of crystals
- (vi) Drying the crystalline substance
- (vii) Decolourization of undesirable colours

(vi) What do you mean by critical temperature of gases?

Ans Critical Temperature:

The temperature of a gas in its critical state, above which it cannot be liquefied by pressure alone.

(vii) What do you mean by absolute zero temperature of gases?

Ans Absolute zero is lowest possible temperature, at which point atoms of a substance transmit no thermal energy. They are completely at rest.

(viii) Why lighter gases diffuse more rapidly than heavier gases?

Ans The rate of diffusion of gases depends on greater molecular velocity. The lighter gases because of greater their molecular velocity diffuse faster than the heavier one.

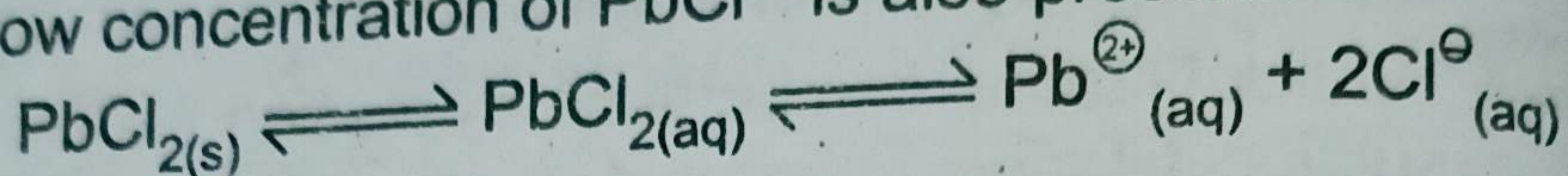
(ix) What is solubility product? What is solubility product expression for PbCl_2 ?

Ans Solubility Product:

"The product of molar solubilities of the ions of a weak electrolyte at equilibrium stage is called solubility product."

It is denoted by K_{sp} . The K_{sp} of the salts are very small quantities and they are temperature dependent.

When $PbCl_2$ is dissolved in water, it contains Pb^{2+} , Cl^- and sufficient amount of $PbCl_2$ which is undissociated. Extremely low concentration of $PbCl^+$ is also present.



(x) Why change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant?

Ans Those gaseous phase reversible reactions, which happen with changing number of moles, are affected by the change of volume at equilibrium stage. Their equilibrium position is disturbed, but equilibrium constant is not changed.

(xi) How the molality is independent of temperature but molarity depends upon temperature?

Ans In molal solutions, the mass of the solvent and that of the solute are also fixed. The masses of the substances are not temperature dependent.

In molar solutions, we have the volumes of solutions. Volume of a liquid is a temperature dependent. So, the molality is not influenced by temperature but molarity does change.

(xii) One molal solution of urea in water is dilute as compared to one molar solution of urea in water but the number of particles of solute in both solutions are same.

Ans In one molal solution of urea, 60 g of urea is dissolved in 1000 g of water, which is approximately 1000 cm³ of water. In one molar solution of urea, 60 g of urea is added in water to make total volume of solution as 1000 cm³. So, the volume of water in molar solution is less than 1000 cm³. Hence, molar solution is concentrated and molal solution is dilute.

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

(i) Describe that heat of sublimation is greater than heat of vaporization.

Ans In sublimation, a solid substance is to be directly converted into vapours without melting so, high amount of energy is needed to overcome inter-molecular forces. On the other hand, heat of

vaporization is comparatively low because a liquid substance is to be converted into vapour form. That's why.

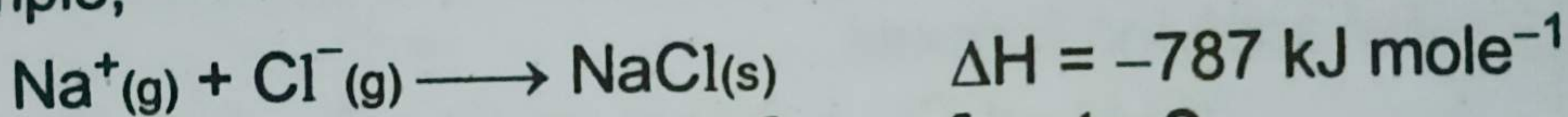
(ii) **Evaporation is a cooling process. Explain.**

Ans Evaporation causes cooling because when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of liquid falls and heat moves from surrounding to liquid and then temperature of surrounding also falls.

(iii) **Define lattice energy with an example.**

Ans The lattice energy is the energy released when one mole of the ionic crystal is formed from the gaseous ions. It is expressed in kJ mole^{-1} .

For example,



(iv) **Why ice floats over the surface of water?**

Ans It is because the chemical bonds between H_2O molecules are forced into being longer, expanding the water and forming a crystal. When something at constant mass increases in volume, its density decreases. Thus, ice is less dense than water causing it to float.

(v) **Write two defects of Rutherford's atomic model.**

Ans Following are the two defects of Rutherford's atomic model:

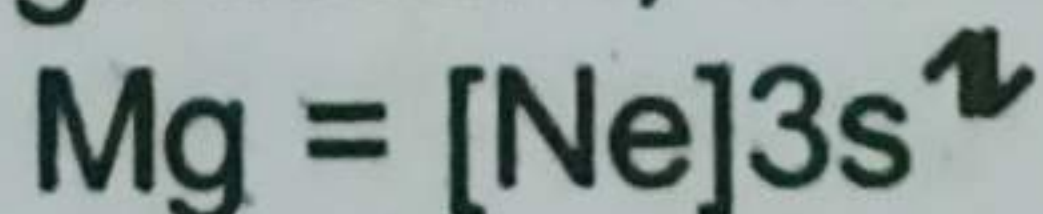
- (1) It is based on the laws of the motion and the gravitation. These laws are not for the charged bodies like electrons.
- (2) The atoms should give continuous spectra, but they give the line spectra.

(vi) **State Pauli's Exclusion Principle.**

Ans "It is impossible for two electrons residing in same orbital of a poly electron atom to have same values of four quantum numbers."

Example:

In Magnesium, the electrons have opposite spins.



(vii) **Give the electronic configuration of ${}_{24}\text{Cr}$.**

Ans $\text{Cr}_{24} : [\text{Ar}] 4s^1 3d_{xy}^1 3d_{yz}^1 3d_{xz}^1 3d_{x^2-y^2}^1 3d_z^2$

(viii) **Write two properties of neutron.**

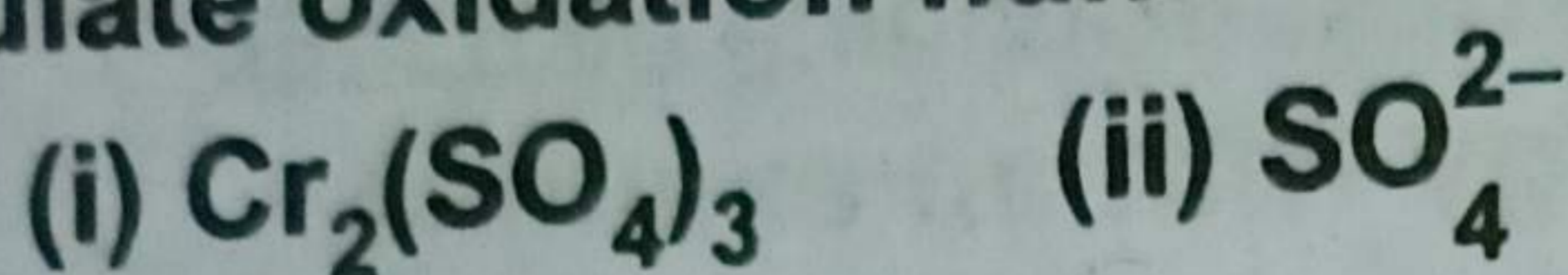
Ans Following are the two properties of neutron:

1. Neutrons cannot ionize gases.
2. Neutrons are highly penetrating particles.

- (ix) Describe that boiling point of solvent increase due to the presence of solute.

Ans The surface of the solution has molecules of solute as well. They do not allow the solvent to leave the surface as rapidly as in pure solvent. To boil the solutions, we have to increase the temperature of solutions in comparison to pure solvents.

- (x) Calculate oxidation number of 'S' in :



Ans (i) $\text{Cr}_2(\text{SO}_4)_3$:

Let the oxidation number of S = x

Oxidation number of Cr = +3

Oxidation number of O = -2

By applying formula,

$$2(\text{O.N. of Cr}) + 3(\text{O.N. of S}) + 3 \times 4 (\text{O.N. of O}) = 0$$

$$2(+3) + 3(x) + 12(-2) = 0$$

$$6 + 3x - 24 = 0$$

$$\boxed{x = 6}$$

(ii) SO_4^{2-} :

$$[\text{oxidation number of S}] + 4[\text{oxidation number of O}] = -2$$

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

$$x = +6$$

Thus, the oxidation number of sulphur in SO_4^{2-} is +6.

- (xi) Write recharging of lead accumulator battery.

Ans It is commonly used as a car battery. It is secondary or a storage cell. Passing a direct current through it must charge it. The charged cell can then produce electric current when required. The cathode of a fully charged lead accumulator is lead oxide, PbO_2 and its anode is metallic lead. The electrolyte is 30% sulphuric acid solution (density 1.25 g cm^{-3}). When the two electrodes are connected through an external circuit, it produces electricity by discharge. A single cell provides around 2 volts. For 12 volts, 6 cells are connected in series.

- (xii) Define electrochemistry.

Ans Electrochemistry is concerned with the conversion of electrical energy into chemical energy in electrolytic cells as well as the conversion of chemical energy into electrical energy in galvanic or voltaic cells.

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

(i) Why an ionic radius is greater than atomic radius?

Ans This creates a larger positive charge in nucleus than negative charge in electron cloud, causing the electron cloud to be drawn a little closer to nucleus as a ion. Non-metal -- the atomic radius of a non-metal -- is generally smaller than ionic radius of same element.

(ii) State electronegativity and electron affinity.

Ans The tendency of an atom to attract a shared electron pair towards itself is called its electronegativity.

The electron affinity of an atom is the energy released when an electron adds to an empty or partially filled orbital of an isolated gaseous atom in its valence energy level to form an anion having a unit negative charge.

(iii) Write two points of valence bond theory.

Ans Following are the two points of valence bond theory:

1. A covalent bond is formed due to the overlap of the partially filled atomic orbitals.
2. In overlapping orbitals, electrons become paired with opposite spin to stabilize them.

(iv) Ionization energy decreases down the group, although nuclear charge increases. Explain.

Ans In groups, the ionization energy 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. As the force of attraction between the nucleus and the outer electron decreases with the increase in distance, the electron can be removed more easily or with less energy.

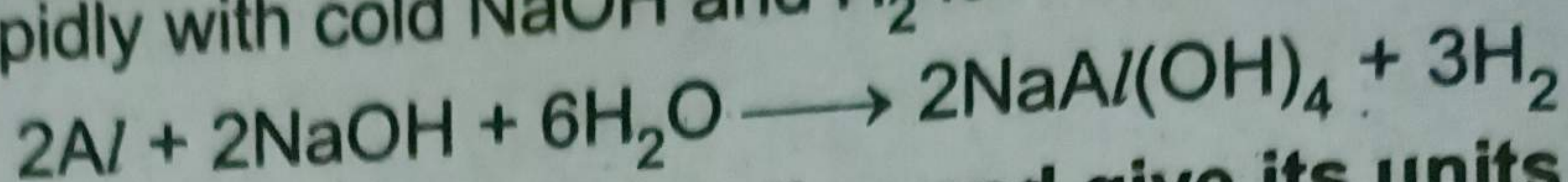
(v) What is internal energy of a system?

Ans The energy stored in a substance in terms of its kinetic and potential energies by virtue of its constituent particles is called its internal energy.

(vi) How surface area affects the rate of reaction? Give one example.

Ans The increased surface area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, Al

foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.



(vii) State rate of chemical reaction and give its units.

Ans Whenever we want to measure the rate of a chemical reaction, we need to measure the concentration of reactants or products at regular time intervals. With the passage of time, the concentration of reactants decrease while those of the products increase.

$$\begin{aligned} \text{Rate of reaction} &= \frac{\Delta c}{\Delta t} = \frac{\text{moles dm}^{-3}}{\text{s}} \\ &= \text{moles dm}^{-3} \text{ s}^{-1} \end{aligned}$$

The rate of a reaction is measured in $\text{moles dm}^{-3} \text{ s}^{-1}$.

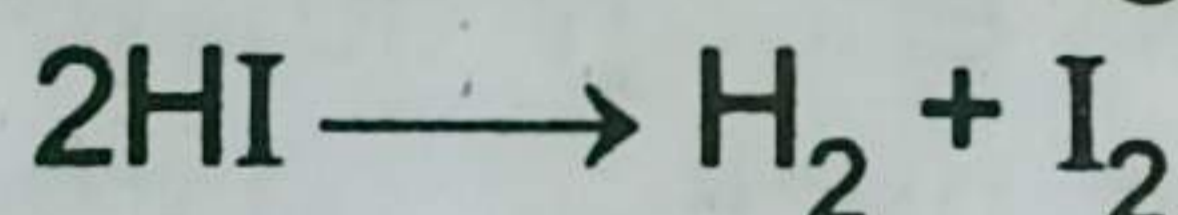
(viii) Define with example 2nd-order reaction.

Ans Order of Reaction:

The order of reaction is given by "the sum of all the exponents to which the concentrations in the rate equation are raised." The order of reaction may also be defined as "the number of reacting molecules, whose concentrations alter as a result of the chemical change."

Following are the example 2nd-order reaction:

1. Decomposition of HI in the gas phase



$$\text{Rate of reaction} = k [HI]^2$$

2. Decomposition of ozone.



$$\text{Rate of reaction} = k [O_3]^2$$

3. Decomposition of CH_3CHO



$$\text{Rate of reaction} = k [CH_3CHO]^2$$

4. Oxidation of NO with ozone



$$\text{Rate of reaction} = k [NO][O_3]$$

(ix) The radioactive decay is always a first order reaction. Explain.

Ans Radioactive substances have a single species at a moment, whose nucleus is being broken up without the help of any external agency. So, only one reactant is present and it follows the first order mechanism.

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) The combustion analysis of an organic compound shows it to contain 65.44% carbon, 5.50% hydrogen and 29.06% oxygen. What is the empirical formula of the compound? If the molecular mass of this compound is $110.15 \text{ gm mole}^{-1}$, calculate the molecular formula of the compound? (4)

Ans First of all, divide the percentage of each element by its atomic mass to get the number of gram atoms or moles.

$$\begin{aligned} \text{No. of gram atoms of C} &= \frac{65.44 \text{ g of C}}{12 \text{ g/mol}} \\ &= 5.45 \text{ gram atoms of C} \end{aligned}$$

$$\begin{aligned} \text{No. of gram atoms of hydrogen} &= \frac{5.50 \text{ g of H}}{1.008 \text{ g/mol}} \\ &= 5.45 \text{ gram atoms of H} \end{aligned}$$

$$\begin{aligned} \text{No. of gram atoms of oxygen} &= \frac{29.06 \text{ g of O}}{16.00 \text{ g/mol}} \\ &= 1.82 \text{ gram atoms of O} \end{aligned}$$

Molar ratio:

$$\begin{array}{ccc} \text{C} & : & \text{H} & : & \text{O} \\ 5.45 & : & 4.45 & : & 1.82 \end{array}$$

Divide the number of gram atoms by the smallest number
i.e., 1.82

$$\begin{array}{ccc} \text{C} & : & \text{H} & : & \text{O} \\ \frac{5.45}{1.82} & : & \frac{5.45}{1.82} & : & \frac{1.82}{1.82} \\ 3 & : & 3 & : & 1 \end{array}$$

Carbon, hydrogen and oxygen are present in the given organic compound in the ratio of 3:3:1. So the empirical formula is $\text{C}_3\text{H}_3\text{O}$.

In order to determine the molecular formula, first calculate the empirical formula mass.

$$\begin{aligned} \text{Empirical formula mass} &= 12 \times 3 = 1.008 \times 3 + 16 \times 1 \\ &= 55.05 \text{ g/mol} \end{aligned}$$

$$\text{Molar mass of the compound} = 110.15 \text{ g mol}^{-1}$$

$$\begin{aligned} n &= \frac{\text{Molar mass of the compound}}{\text{Empirical formula mass}} \\ &= \frac{110.15}{55.05} = 2 \end{aligned}$$

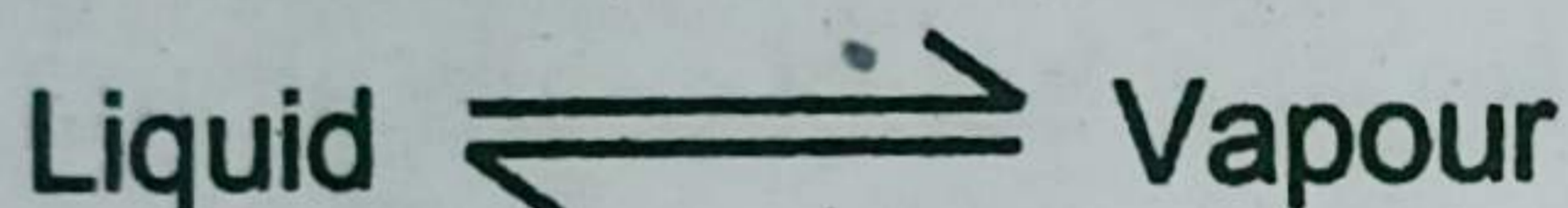
$$\text{Molecular formula} = n(\text{empirical formula})$$

$$= 2(\text{C}_3\text{H}_3\text{O}) = \boxed{\text{C}_6\text{H}_6\text{O}_2}$$

(b) What is vapour pressure of liquid? Also discuss its measurement by manometric method. (4)

Ans Definition:

The vapour pressure of a liquid is a pressure exerted by the vapours of the liquid in equilibrium with a liquid at a given temperature.



Manometric method:

Manometric method is comparatively an accurate method. The liquid whose vapour pressure is to be determined is taken in a flask placed in a thermostat, as shown in the Fig. One end of the tube from the flask is connected to a manometer and the other end is connected to a vacuum pump. The liquid is frozen with the help of a freezing mixture and the space above the liquid is evacuated. In this way, the air is removed from the surface of the liquid along with the vapours of that liquid. The frozen liquid is then melted to release any entrapped air. Liquid is again frozen and released air is evacuated. This process is repeated many times till almost all the air is removed.

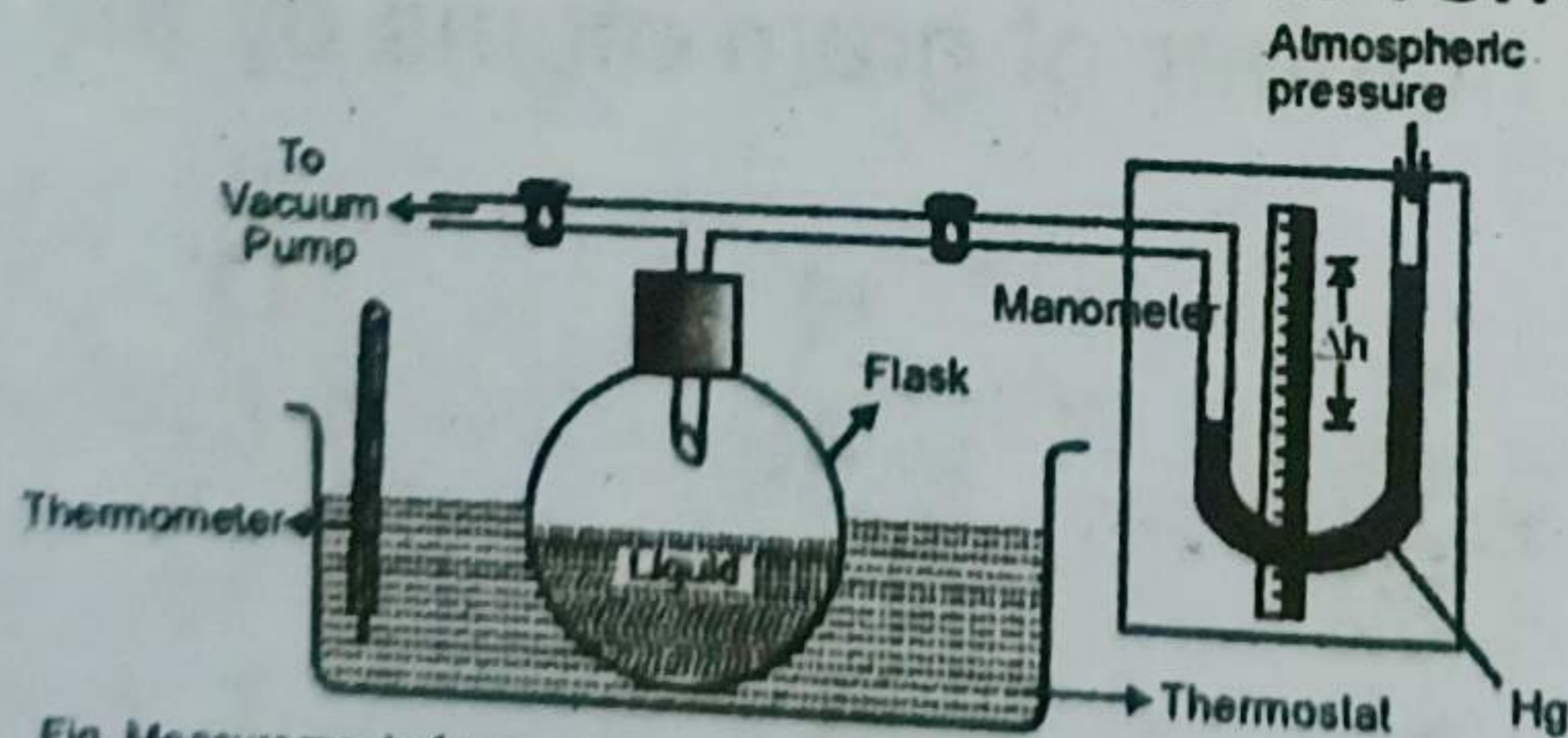


Fig. Measurement of vapour pressure of a liquid by manometric method.

Now, the liquid is warmed in the thermostat to that temperature at which the vapour pressure of the liquid in the flask is to be determined. Difference in the heights of the

columns of Hg in the two limbs of the manometer determines the vapour pressure of the liquid.

The column of mercury in the manometer facing the vapours of the liquid is depressed. The other column, which faces the atmospheric pressure, rises. Actually, the pressure on the surface of the liquid in the flask is equal to the sum of the atmospheric pressure and the vapour pressure of liquid. For this reason, the column of manometer facing the liquid is more depressed than facing the atmosphere, and it is given by the following equation

$$P = P_a + \Delta h$$

Where P = Vapour pressure of the liquid at one atm pressure.

P_a = Atmospheric pressure.

Δh = Difference in the heights of the mercury levels in the two limbs of the manometer, giving us the vapour pressure of liquid.

Q.6.(a) Give eight postulates of the KMT (Kinetic Molecular Theory). (4)

Ans Following are the fundamental postulates of this kinetic theory of gases:

1. Every gas consists of a large number of very small particles called molecules. Gases like He, Ne, Ar have monoatomic molecules.
2. The molecules of a gas move haphazardly, colliding among themselves and with the walls of the container and change their directions.
3. The pressure exerted by a gas is due to the collisions of its molecules with the walls of a container. The collisions among the molecules are perfectly elastic.
4. The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.
5. The molecules of a gas have no forces of attraction for each other.
6. The actual volume of molecules of a gas is negligible as compared to the volume of the gas.
7. The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them.

8. The average kinetic energy of the gas molecules varies directly as absolute temperature of the gas.

(b) Define quantum numbers. Discuss briefly Azimuthal quantum number. (4)

Ans Quantum Numbers:

Quantum numbers are the sets of numerical values which give the acceptable solutions to Schrodinger wave equation for hydrogen atom.

Azimuthal Quantum Number (l):

It has already been mentioned in the defects of Bohr's model that a spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very fine lines. This thing can be explained by saying that each shell is divided into subshells. So, only principal quantum number (n) is not sufficient to explain the line spectrum. There is another subsidiary quantum number called azimuthal quantum number and is used to represent the subshells. The values of azimuthal quantum number (l) are

$$l = 0, 1, 2, 3, \dots, (n - 1)$$

Its value depends upon n. These values represent different subshells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, diffused and fundamental, respectively. These are the spectral terms used to describe the series of lines observed in the atomic spectrum. The values of azimuthal quantum number always start from zero.

A subshell may have different shapes depending upon the value of 'l'. It may be spherical dumb-bell, or some other complicated shapes. The value of 'l' is related to the shape of the subshell as follows:

$l = 0$	s-subshell	spherical
$l = 1$	p-subshell	dumb-bell
$l = 2$	d-subshell	(complicated shape)

The relationship between principal and azimuthal quantum numbers is as follows.

$n = 1$	K-shell	{ $l = 0$	{ s-subshell	should be called as	1s
$n = 2$	L-shell	{ $l = 0$ $l = 1$	{ s-subshell p-subshell		2s
$n = 3$	M-shell	{ $l = 0$ $l = 1$ $l = 2$	{ s-subshell p-subshell d-subshell		2p 3s 3p 3d

n = 4	N-shell	$l = 0$	s-subshell	4s
		$l = 1$	p-subshell	4p
		$l = 2$	d-subshell	4d
		$l = 3$	f-subshell	4f

In 1s, 2s,, etc., the digit represents the value of principal quantum number. 'l' values also enable us to calculate the total number of electrons in a given subshell. The formula for calculating electrons is $2(2l + 1)$.

When $l = 0$	s-subshell	total electrons = 2
$l = 1$	p-subshell	total electrons = 6
$l = 2$	d-subshell	total electrons = 10
$l = 3$	f-subshell	total electrons = 14

Q.7.(a) Write the main points of valence shell electron pair repulsion theory and explain the structure of ammonia on the basis of this theory. (4)

Ans Valence Shell Electron Pair Repulsion Theory:

Sidgwick and Powell (1940) pointed out that the shapes of molecules could be interpreted in terms of electron pairs in the outer orbit of the central atom. Recently, Nyholm and Gillespie developed VSEPR theory, which explains the shapes of molecules for non-transition elements.

Basis Assumption:

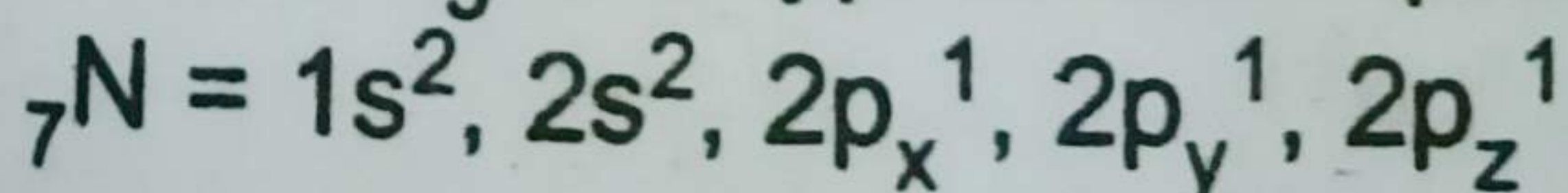
The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsions at a minimum.

Postulates of VSEPR Theory:

- Both the lone pairs as well as the bond pairs participate in determining the geometry of the molecules.
- The electron pairs are arranged around the central polyvalent atom, so as to remain at a maximum distance apart to avoid repulsions.
- The electron pairs of lone pairs occupy more space than the bond pairs.

In such cases, the charge cloud of lone pair electrons (non-bonding electrons) spreads out more than that of bonding electrons. As a result, somewhat large lone pair charge cloud tend to compress the bond angles in rest of the molecules.

Ammonia, $\overset{\cdot\cdot}{\text{N}}\text{H}_3$ is a typical example.



The non-bonding electron in 2s orbital takes up more space and exerts a strong repulsive force on the bonding electron pairs. Consequently, to avoid a larger repulsion, the bonding electron pairs move closer that reduces the ideal bond angle from 109.5° to 107.5° . This effect compels ammonia to assume a triangular pyramidal geometry instead of tetrahedral, as in methane.

(b) State and explain Hess's law of constant heat summation with an example. (4)

Ans Hess's law of constant heat summation:

This law states that:

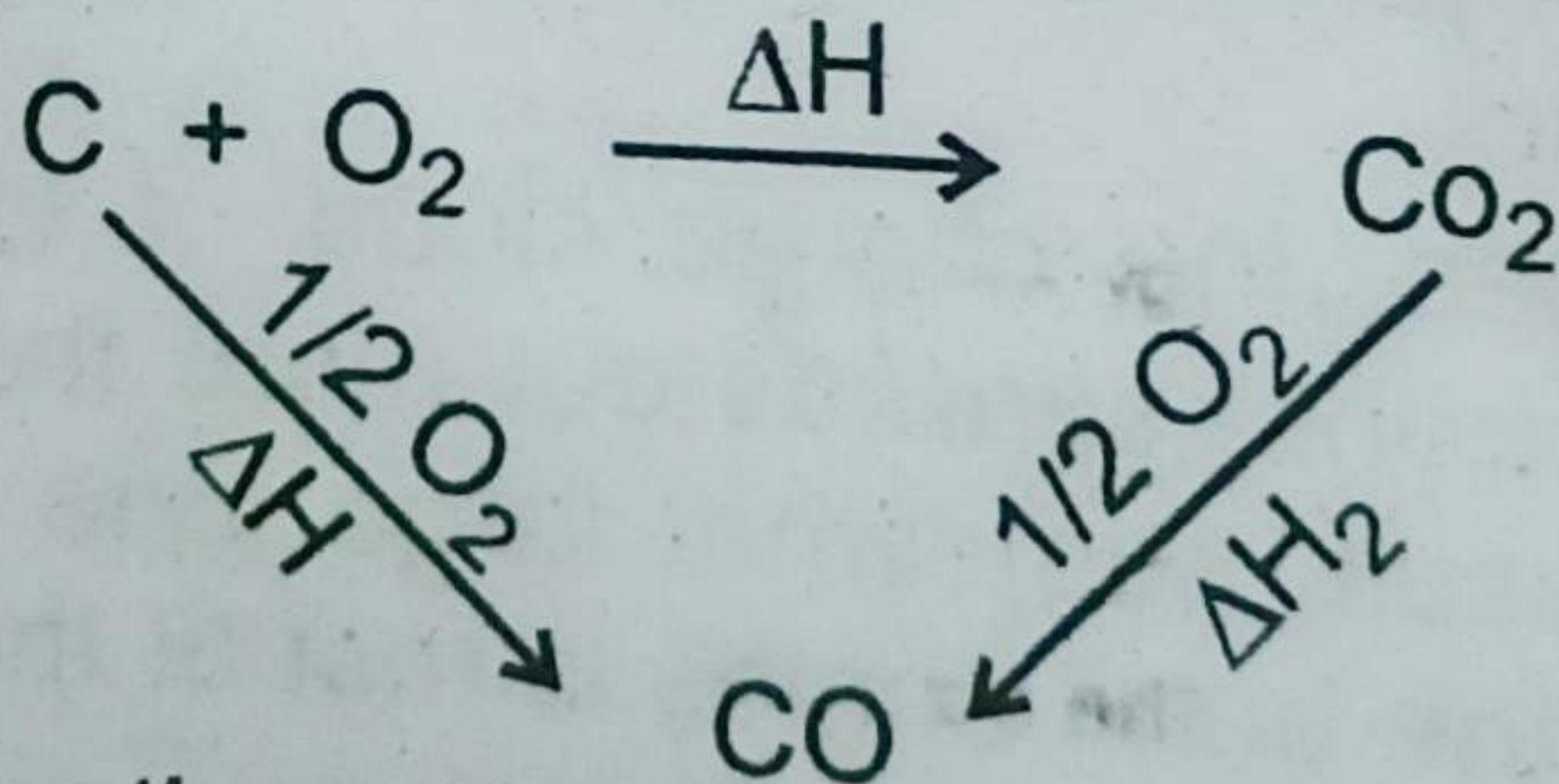
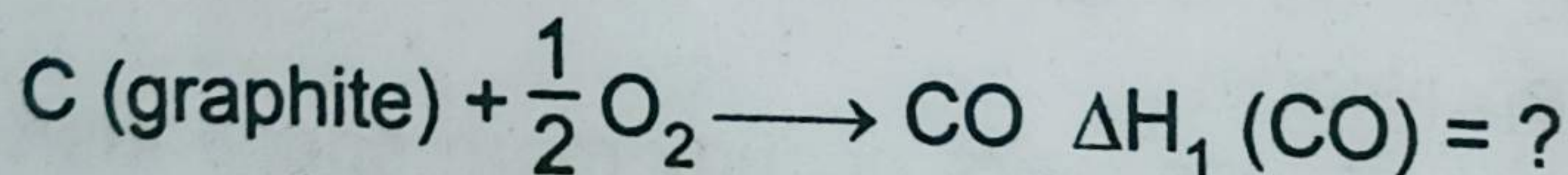
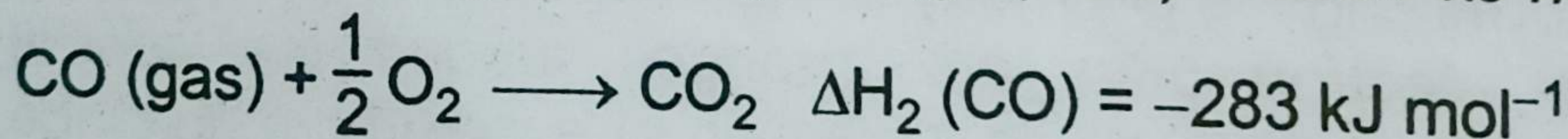
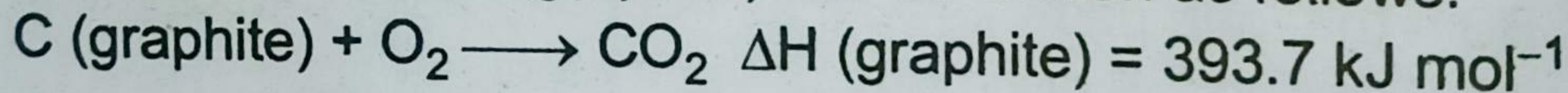
"If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same."

Let A can be converted to D directly in a single step and heat evolved is ΔH . If the reaction can have a route from $A \rightarrow B \rightarrow C$ as shown below:

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Mathematically, $\Sigma \Delta H$ (cycle) = 0

Example: If the enthalpy of combustion for graphite to form CO_2 and the enthalpy of combustion of CO to form CO_2 are known, we can determine the enthalpy of formation for CO. The oxidation of carbon (graphite) can be written as follows:



Applying equation of heat summation:

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta H - \Delta H_2$$

$$= -393 - (-283)$$

$$= -110 \text{ kJ mol}^{-1}$$

Q.8.(a) Ca(OH)_2 is a sparingly soluble compound. Its solubility product (K_{sp}) is 6.5×10^{-6} . Calculate the solubility of Ca(OH)_2 . (4)

Ans For Answer see Paper 2015, (Group-II), Q.8.(b).

(b) Explain effect of temperature on rate of reaction. (4)

Ans Effect of Temperature on Rate of Reaction:

The collision theory of reaction rates convinces us that the rate of a reaction is proportional to the number of collisions among the reactant molecules. Anything, that can increase the frequency of collisions should increase the rate. We also know, that every collision does not lead to a reaction. For a collision, to be effective the molecules must possess the activation energy and they must also be properly oriented. For nearly all chemical reactions, the activation energy is quite large; and at ordinary temperature, very few molecules are moving fast enough to have this minimum energy.

All the molecules of a reactant do not possess the same energy at a particular temperature. Most of the molecules will possess average energy. A fraction of total molecules will have energy more than the average energy. This fraction of molecules indicated as shaded area in Figure.

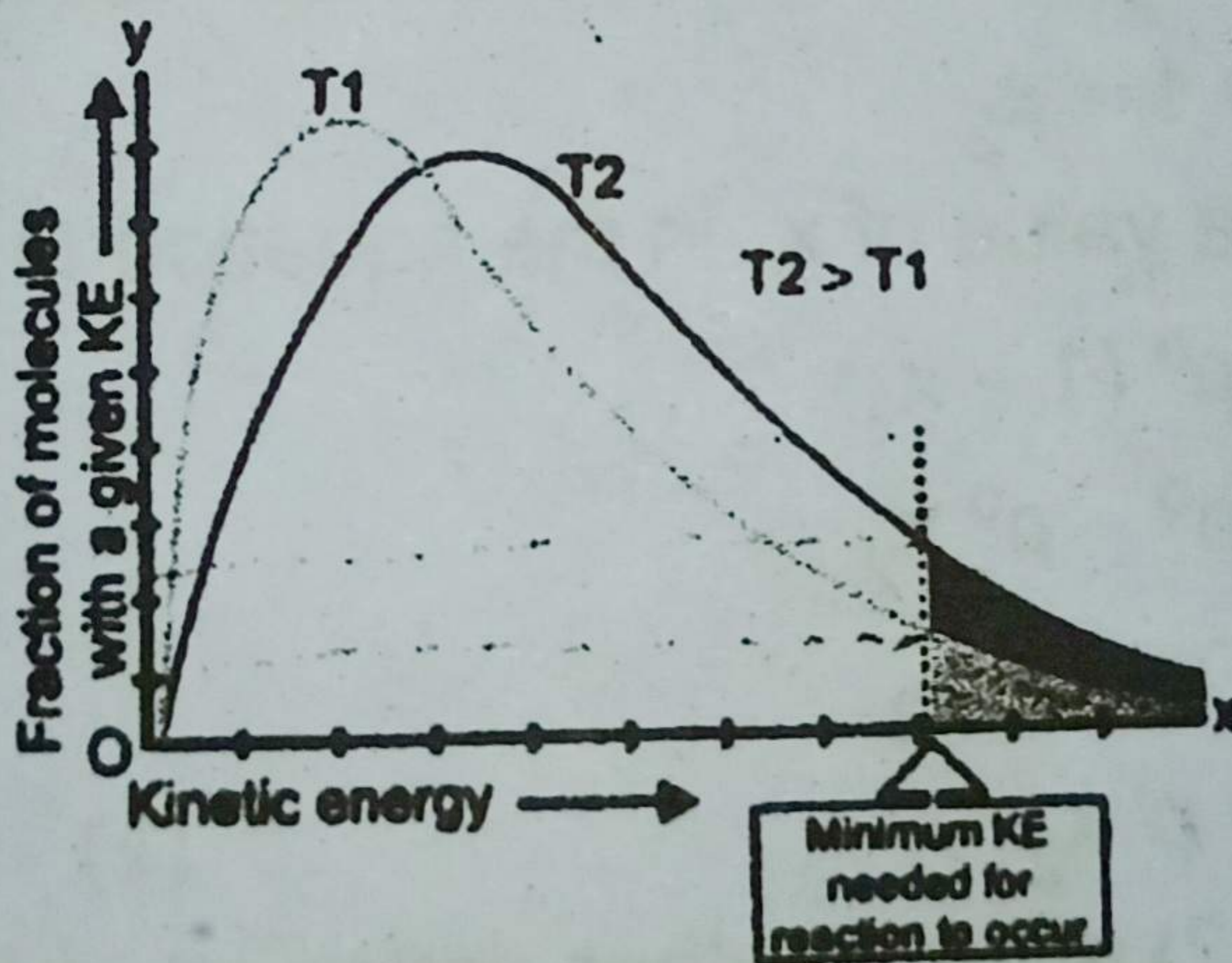


Fig. Kinetic energy distributions for a reaction mixture at two different temperatures. The size of the shaded areas under the curves are proportional to the total fraction of the molecules that possess the minimum activation energy.

As the temperature increases, the number of molecules in this fraction also increases. There happens a wider distribution

of velocities. The curve at higher temperature T_2 has flattened. It shows that molecules having higher energies have increased and those with less energies have decreased. So, the number of effective collisions increases and hence, the rate increases. When the temperature of the reacting gases is raised by 10 K, the fraction of molecule with energy more than E_a roughly doubles and so the reaction rate also doubles. Arrhenius has studied the quantitative relationship between temperature, energy of activation and rate constant of a reaction.

Q.9.(a) State different form of Raoult's law. How this law can help us to understand the ideality of a solution? (4)

Ans Raoult's Law:

This law can be defined in three ways.

First way:

The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of the solvent in a solution.

Mathematically, it can be written as follows:

$$p = p^{\circ} x_1 \quad (1)$$

where p is the vapour pressure of the solvent, m° the solution, p° is the vapour pressure of pure solvent and x_1 is the mole fraction of the solvent.

We also know that:

$$x_1 + x_2 = 1 \quad (x_2 \text{ is the mole fraction of solute})$$

$$\text{or } x_1 = 1 - x_2$$

Putting the value of x_1 in the equation (1),

$$p = p^{\circ} (1 - x_2)$$

$$p = p^{\circ} - p^{\circ} x_2$$

$$\text{or } p^{\circ} - p = p^{\circ} x_2$$

$$\text{or } \Delta p = p^{\circ} x_2 \quad (2)$$

Equation (2) gives another definition of Raoult's law.

Second way:

The lowering of vapour pressure is directly proportional to the mole fraction of solute.

Now rearrange equation (2) to get equation (3)

$$\frac{\Delta p}{p^{\circ}} = x_2 \quad (3)$$

$\frac{\Delta p}{p^{\circ}}$ is called relative lowering of vapour pressure and it is more important than actual lowering of vapour pressure (Δp). The equation (3) gives us another definition of Raoult's law.

Third way:

The relative lowering of vapour pressure is equal to the mole fraction of solute.

The relative lowering of vapour pressure:

- (i) is independent of the temperature.
- (ii) depends upon the concentration of solute.
- (iii) is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

Raoult's law can be applied to understand the relationship between mole fractions of two volatile components and their vapour pressures before making the solution and after making the solution. Consider two liquids 'A' and 'B' with vapour pressure p°_A and p°_B in the pure state at a given temperature. After making the solution, the vapour pressures of both liquids are changed. Let the vapour pressures of these liquids in solution state p_A and p_B with their mole fractions x_A and x_B , respectively.

Applying Raoult's law to both components.

$$p_A = p^{\circ}_A x_A$$

$$p_B = p^{\circ}_B x_B$$

$$P_t = p_A + p_B = p^{\circ}_A x_A + p^{\circ}_B x_B$$

(where p_t is total pressure)

$$\text{Since } x_A + x_B = 1$$

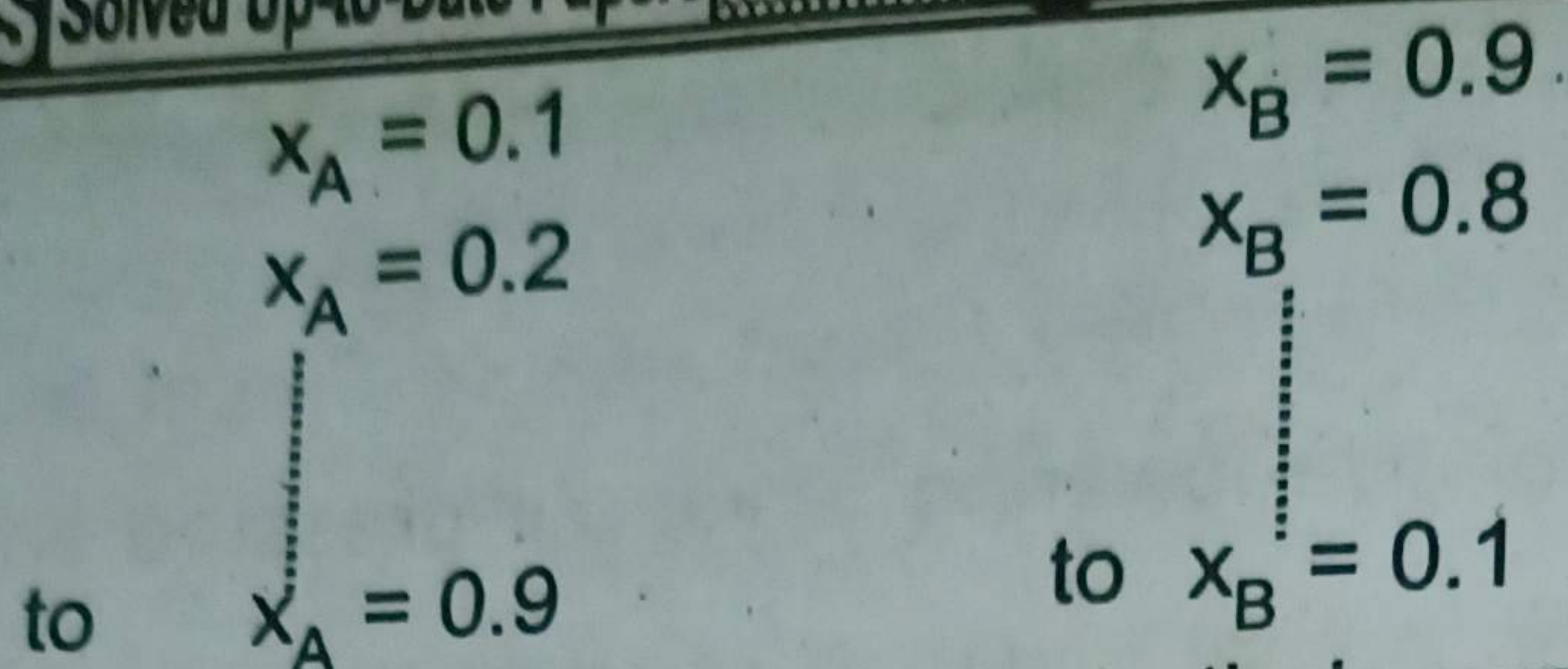
$$x_B = 1 - x_A$$

$$P_t = p^{\circ}_A x_A + p^{\circ}_B (1 - x_A)$$

$$P_t = p^{\circ}_A x_A + p^{\circ}_B - p^{\circ}_B x_A$$

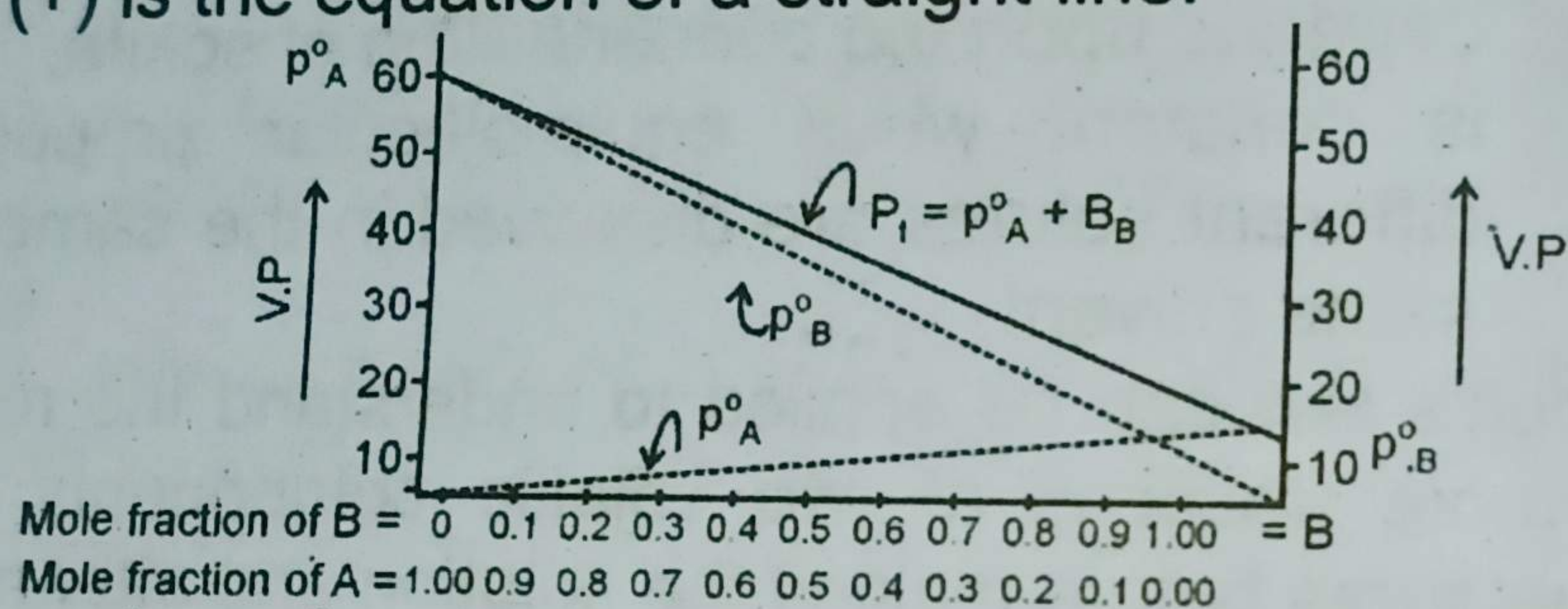
$$P_t = (p^{\circ}_A - p^{\circ}_B) x_A + p^{\circ}_B \quad (4)$$

In order to give the graphical shape to equation (4), let us prepare nine different solutions with the following compositions.



All these nine solutions have their own vapour pressures. These values of vapour pressures are the sum of vapour pressures of components in solution state.

Let us plot a graph between mole fraction of A and B on x-axis and vapour pressures of solutions on y-axis. When all the solutions behave ideally, then a straight line is obtained. Actually (+) is the equation of a straight line.



The value of mole fraction of A decreases from left to right. The values of mole fractions of component B, increase from left to right. p_B^0 is the vapour pressure of the pure component B. A is a low boiling liquid. p_A^0 is the vapour pressure of the pure component A. B is a high boiling liquid. That is why, its vapour pressure is less.

The values of the vapour pressure of all the nine solutions are on the straight line joining the two pure components. So, all such solutions are ideal solutions according to Raoult's law.

(b) What is electrochemical series? Explain any three applications of electrochemical series. (4)

Ans Electrochemical Series:

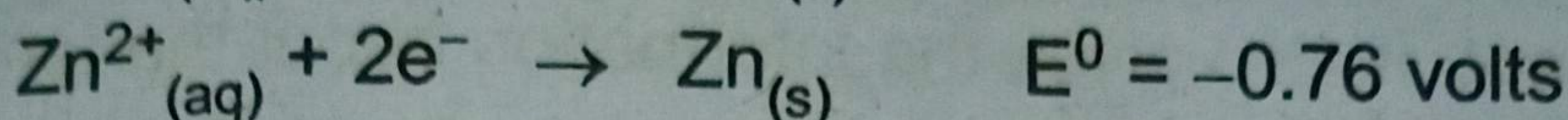
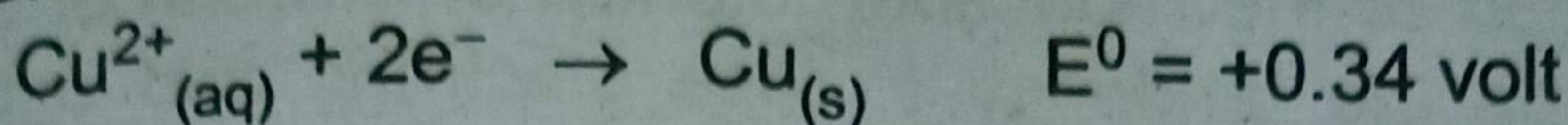
"When elements are arranged in order of their standard, electrode potentials on hydrogen scale, the resulting list is known as electrochemical series."

Applications of Electrochemical Series

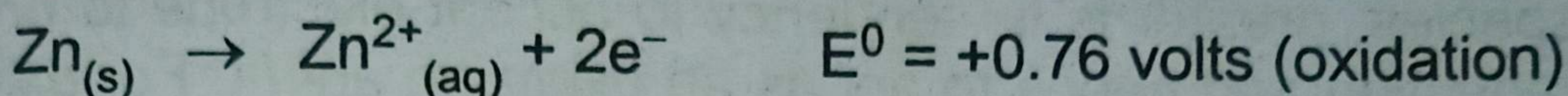
(i) Prediction of the Feasibility of a Chemical Reaction:

When we look at the electrochemical series, it is easy to predict whether a particular reaction will take place or not. For

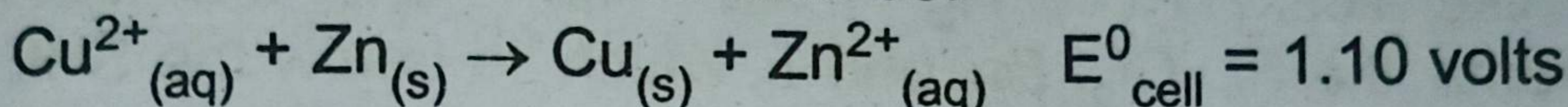
example, $\text{Cu}^{2+}_{(\text{aq})}$ can oxidize solid zinc but $\text{Zn}^{2+}_{(\text{aq})}$ cannot oxidize solid copper. Standard reduction potential values of copper and zinc can explain this.



Since, zinc is being oxidized so the reverse reaction will be considered.



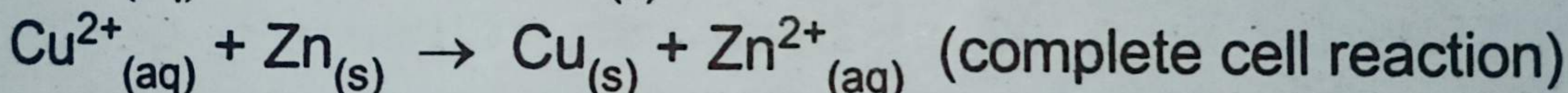
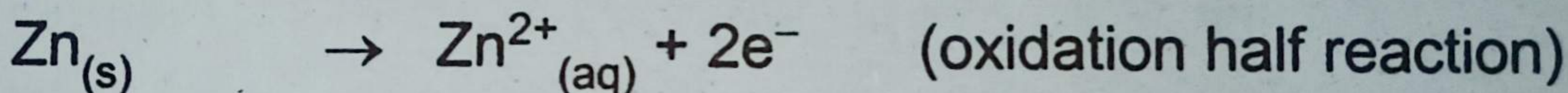
The overall reaction will thus be:



The overall positive value for the reaction potential suggests that the process is energetically feasible. If the sum of E° values of the two half-cell reactions is negative, then the reaction will not be feasible.

(ii) Calculation of the Voltage or Electromotive (emf) of Cells:

In a galvanic cell, the electrode occupying a higher position in the electrochemical series, will act as anode and oxidation takes place on it. Similarly, the electrode occupying the lower position in the series will act as a cathode and reduction will take place on it. Let us find out a cell potential or the emf of the cell already discussed as above. The half-cell reactions are:



The oxidation potential of Zn is positive. The reduction potential of Cu^{2+} is also positive.

The cell voltage or emf of the cell is given by:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxi}} + E^{\circ}_{\text{red}}$$

$$E^{\circ}_{\text{cell}} = 0.76 + 0.34 = 1.10 \text{ volts}$$

The cell voltage or emf measures the force with which electrons move in the external circuit and therefore measures the tendency of the cell reaction to take place. Galvanic cells, thus, give quantitative measure of the relative tendency of the various reactions to occur.

(iii) Comparison of Relative Tendency of Metals and Non-metals to Get Oxidized or Reduced:

The value of the reduction potential of a metal or a non-metals tells us the tendency to lose electrons and act as a reducing agent. It also gives the information about the tendency of a species to gain electrons and act as an oxidizing agent. Greater the value of standard reduction potential of a given species, greater is its tendency to accept electrons to undergo reduction and hence to act as an oxidizing agent. For example, ions like Au^{3+} , Pt^{2+} , Hg^{2+} , Ag^+ , Cu^{2+} and the non-metals elements like F_2 , Cl_2 , Br_2 and I_2 which lie below the SHE, have a strong tendency to gain electrons and undergo reduction.

The series tell us that strong oxidizing agents like F_2 , Cl_2 , Br_2 , etc. have a large positive value of standard reduction potentials, while strong reducing agents have large negative values like Li, K, Ca, Na, etc. which lie above SHE.