

DAV CENTENARY PUBLIC SCHOOL
PASCHIM ENCLAVE, NEW DELHI-87

100
PERCENT

**Exam
Ready**

CBSE 2021-22
TERM-II

CHEMISTRY

Based on Latest
**Competency Based
Education (CBE)**

STRICTLY BASED ON
LATEST TERM WISE
CBSE SYLLABUS

CHAPTERWISE

 **RECAP NOTES**

MCQs | Case Based | A&R Type Questions

Very Short | Short | Long Answer Type Questions

3 Practice Papers with Detailed Solutions

11

Two more chapters are added in TERM-2 examination (Redox Reactions and Basic principles and technique of organic chemistry)

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***As per the Circular Issued by CBSE on July 05, 2021, Special Scheme of Assessment for Board Examination for the Session 2021-22 is as follows :**

Term II Examination/Year-end Examination :

- At the end of the second term, the Board would organize Term II or Year-end Examination based on the rationalized syllabus of Term II only (i.e. approximately 50% of the entire syllabus).
- This examination would be held around March-April 2022 at the examination centres fixed by the Board.
- The paper will be of 2 hours duration and have questions of different formats (case-based/ situation based, open ended- short answer/ long answer type).
- In case the situation is not conducive for normal descriptive examination a 90 minute MCQ based exam will be conducted at the end of the Term II also.
- Marks of the Term II Examination would contribute to the final overall score.

To cope up with ongoing unpredictable pandemic situation, this book contains chapterwise objective as well as subjective questions.

In **Objective Section**, each question carry 1 mark and in **Subjective Section**, each **VSA** carry 1 mark, **SA I** carry 2 marks, **SA II** carry 3 marks and **LA** carry 5 marks.

States of Matter : Gases and Liquids

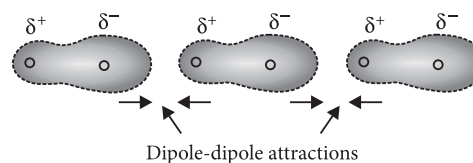


Recap Notes

- **Matter :** Matter exists in three states : solid, liquid and gas.
 - ▶ The main differences in the three states can be explained on the basis of their energy content and forces of attraction between molecules.
 - ▶ Energy of molecules is maximum in the gaseous state and forces of attraction between molecules are maximum in the solid state.
 - ▶ Gases are non-metallic elements, highly compressible, can diffuse easily and form homogeneous mixtures, whereas vapour is the gaseous state of any substance which is usually a liquid or solid at room temperature.
- **Intermolecular forces :** These are the forces of attraction and repulsion that exist between molecules of a compound. These cause the compound to exist in a certain state of matter – solid, liquid or gas and affect the melting and boiling points of compounds as well as the solubilities of one substance in another. Attractive intermolecular forces are also called *van der Waals' forces*. These are weak forces. Different types of intermolecular forces are :
 - ▶ **London or dispersion forces :** This is the weakest intermolecular force. It is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms to form temporary dipoles. This force is sometimes called an *dipole-induced dipole attraction*.
London or dispersion forces increase with
 - increase in number of electrons in molecules

- increase in molecular size
- increase in molecular weight.

- ▶ **Dipole-dipole forces :** This is the second strongest van der Waals' force. These forces exist between polar molecules where the positive end of one molecule attracts the negative end of another molecule.



Dipole-dipole forces are characteristically weaker than ion-dipole forces.

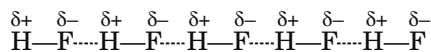
These forces increase with

- increase in molecular size of molecule
- increase in molecular weight of molecule
- increase in polarity of molecule.

- ▶ **Dipole-induced dipole forces :** These forces operate between the polar molecules having permanent dipole and the molecules having no permanent dipole.

- ▶ **Hydrogen bonding :** It is the electrostatic force of attraction between hydrogen atom and highly electronegative atom (N, O, and F atoms) of another molecule. It is represented by dotted line. It is of two types :

- **Intermolecular hydrogen bonding :** It is the force of attraction that exists between H-atom and highly electronegative atom between several molecules of the same substance. For example, hydrofluoric acid.

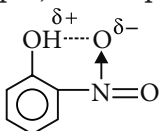


Intermolecular hydrogen bonding

– **Intramolecular hydrogen bonding :**

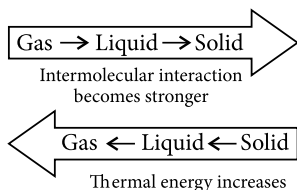
It is the force of attraction that exists between H-atom and highly electronegative atom within the same molecule.

For example, *o*-nitrophenol



Intramolecular H-bonding

- **Thermal energy :** The energy which arises by motions of atoms or molecules of a body is known as thermal energy. It is the measure of average kinetic energy of the particles of matter and it is directly proportional to the temperature of the substance.
- **Intermolecular forces vs thermal energy :**



- **Gaseous State :**

- ▶ There are few parameters which are important to understand the gaseous state *viz.* mass, volume, pressure and temperature.

- **Mass :** Mass of a gas is expressed in gram (g) or kilogram (kg).
- **Volume :** Volume of a gas is generally expressed in litre (L) or millilitre (mL). SI unit of volume is m^3 .
- **Pressure :** There are various units used to express pressure of a gas, like atmosphere, bar, N m^{-2} , Pascal, etc.
 $1 \text{ atm} = 76 \text{ cm Hg} = 760 \text{ mm Hg}$ or 760 torr
 $1 \text{ bar} = 0.987 \text{ atm} \approx 1 \text{ atm} = 10^5 \text{ Pa}$
- **Temperature :** There are three different scales to measure temperature *viz.* Centigrade or Celsius, Fahrenheit and Kelvin scale.

$$^{\circ}\text{C} = \frac{5}{9}(^{\circ}\text{F} - 32) \quad \text{or} \quad ^{\circ}\text{F} = \frac{9}{5}(^{\circ}\text{C}) + 32$$

$$\text{K} = ^{\circ}\text{C} + 273.15 \approx ^{\circ}\text{C} + 273 \quad \text{or} \quad ^{\circ}\text{C} = \text{K} - 273$$

SI unit of temperature is Kelvin (K).

- **Boyle's law :** This law states that, 'volume of a given mass of a gas is inversely proportional to its pressure, keeping the temperature constant', *i.e.*,

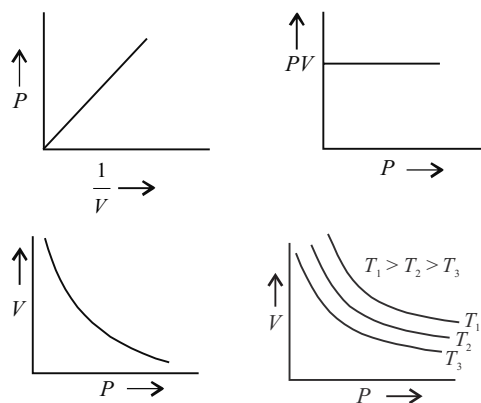
$$V \propto \frac{1}{P} \quad (\text{at constant temperature})$$

or $PV = \text{constant}$

$$P_1 V_1 = P_2 V_2 \quad (\text{mass and temperature constant})$$

(Initial state) (Final state)

- ▶ **Graphical representations of Boyle's law :**



- ▶ **Relationship between pressure and density :**

According to Boyle's law,

$$V \propto \frac{1}{P} \quad \text{but} \quad V \propto \frac{1}{d} \quad (\text{where, } d \text{ is density})$$

$$\text{and } d = \frac{m}{V}$$

$$\therefore \frac{1}{d} \propto \frac{1}{P} \quad \text{or} \quad d \propto P \quad \text{or} \quad \frac{d}{P} = \text{constant}$$

$$\text{Thus, } \frac{d_1}{P_1} = \frac{d_2}{P_2} \quad (\text{temperature and mass constant})$$

- ▶ **Significance of Boyle's law :** With the use of Boyle's law, it can be concluded that gases are compressible. Since the gas density is directly proportional to pressure, so more the gas is compressed, denser it becomes.
- **Charles' law :** This law states that, 'at constant pressure the volume of a given mass of a gas increases or decreases by $1/273$ of its volume at 0°C for every rise or fall of one degree in temperature'.

$$V_t = V_0 + \frac{V_0}{273} \times t \quad (\text{at constant pressure})$$

$$= V_0 \left[1 + \frac{t}{273} \right], \quad V_t = V_0 \left[\frac{273+t}{273} \right]$$

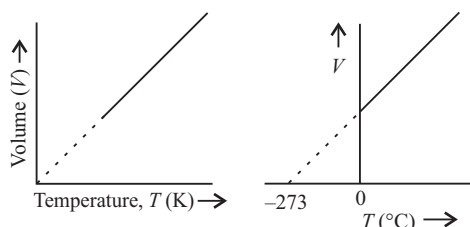
where, V_0 = volume at 0°C , V_t = volume at $t^\circ\text{C}$ and t = temperature.

From the above expression, it can be seen that at temperature -273°C , the volume of gas becomes zero. This temperature is known as *absolute zero*.

- ▶ **Absolute zero** : It is the theoretical or hypothetical temperature at which the gas is supposed to possess zero volume. At this temperature, the total kinetic energy of the molecules is zero and hence, molecular motion ceases.
- ▶ **Absolute scale of temperature** : This is also called *thermodynamic scale of temperature*.
- ▶ At constant pressure, if V_1 is the volume at T_1 and as temperature changes to T_2 , volume will change to V_2 , then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- ▶ **Graphical representations of Charles' law** : A plot of V vs T (temperature in Kelvin scale) for a given mass of a gas at constant pressure is a straight line passing through origin.



- ▶ **Significance of Charles' law** : Since density and temperature are inversely proportional to each other. Hence, hot air is lighter than atmospheric air. It means air expands on heating as its density decreases. This fact is applied in filling hot air balloons which ultimately rise up.

- **Gay Lussac's law (pressure-temperature relationship)** : This law states that 'at constant volume, the pressure of a given mass of a gas increases or decreases by $1/273$ of its pressure at 0°C for every rise or fall of 1°C in temperature'.

$$P_t = P_0 + \frac{P_0}{273} \times t = P_0 \left(1 + \frac{t}{273} \right)$$

$$= P_0 \left(\frac{273+t}{273} \right) = P_0 \frac{T}{273}$$

where, P_0 and P_t are the pressures at 0°C and $t^\circ\text{C}$ respectively, t and T are the temperature in $^\circ\text{C}$ and Kelvin respectively. Thus, $P_t \propto T$ (since P_0 and 273 both are constant) or simply $P \propto T$

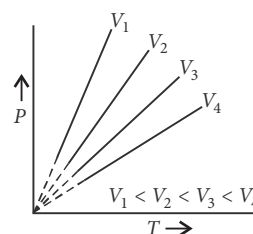
$$\text{i.e., } \frac{P}{T} = \text{constant} \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

(at constant volume)

This pressure-temperature relationship is also known as *Amonton's law*.

- ▶ **Graphical representation of Gay Lussac's law** : A plot of P vs T for a given mass of gas at constant volume is a straight line.

- P - T curves drawn at constant volume are known as *isochor*.



- **Avogadro's law** : This law states that equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules. One mole of a gas contains 6.023×10^{23} number of molecules (Avogadro's number). It means one mole of each gas has same volume under the given conditions of temperature and pressure. It means samples of different gases which contain the same number of molecules occupy same volume.

$$V \propto n \quad (T, P \text{ constant}) = \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

- **Ideal gas equation** :

- ▶ By combining Boyle's law and Charles' law, an equation can be derived that gives the simultaneous effect of the changes of pressure and temperature on the volume of the gas. This is known as *combined gas equation*.

$$V \propto 1/P \quad (\text{constant } T) \quad (\text{Boyle's law}) \quad \dots(\text{i})$$

$$V \propto T \quad (\text{constant } P) \quad (\text{Charles' law}) \quad \dots(\text{ii})$$

$$V \propto n \quad (\text{constant } P \text{ and } T) \quad (\text{Avogadro's law})$$

... (iii)

Combining eqns. (ii) and (iii),

$$V \propto \frac{nT}{P} \text{ or } V = R \frac{nT}{P}$$

$$\therefore \frac{PV}{T} = nR \text{ or } PV = nRT$$

For one mole ($n = 1$), $PV = RT$ (Ideal gas equation or equation of state for gases).

Units of pressure	Units of volume	Values of gas constant (R)	Units of gas constant (R)
atm	L	0.0821	L atm K ⁻¹ mol ⁻¹
atm	cm ³	82.1	atm cm ³ K ⁻¹ mol ⁻¹
dynes cm ⁻²	cm ³	8.314 × 10 ⁷	ergs K ⁻¹ mol ⁻¹
dynes cm ⁻²	cm ³	1.987	cal K ⁻¹ mol ⁻¹
Pa or N m ⁻²	m ³	8.314	J K ⁻¹ mol ⁻¹

$$\frac{P_1 V_1}{T_1} = nR ; \frac{P_2 V_2}{T_2} = nR$$

where 'R' is constant of proportionality and is called universal gas constant. Its value varies with the units in which pressure and volume are expressed.

Now, if V_1 is the volume of a gas at temperature T_1 and pressure P_1 , V_2 is the volume of same amount of gas at temperature

T_2 and pressure P_2 , then $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{constant}$

► **Relationship between molar mass and density :** Let m be the mass of gas in grams and M be the molar mass of gas.

$$\text{We know, } n = \frac{m}{M}$$

$$\text{Now, } PV = nRT = \frac{m}{M} RT$$

$$P = \frac{m}{V} \frac{RT}{M} = \frac{dRT}{M} \text{ or } M = \frac{dRT}{P}$$

$\frac{dT}{P} = \frac{M}{R}$, since M and R are constant for a gas.

$$\therefore \frac{dT}{P} = \text{constant}$$

$$\therefore \frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2}$$

► **Partial pressure:** In a mixture of different gases which do not react chemically, each gas behaves independently of the other gases and exerts its own pressure called its *partial pressure*.

► **Dalton's law of partial pressures :** The total pressure exerted by a mixture of gases is the sum of partial pressures of each component of the mixture.

$$P_{\text{Total}} = p_1 + p_2 + \dots + p_n \text{ (at constant } T, V) \quad \dots(i)$$

where P_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2, \dots, p_n are the partial pressures of n gases present in the mixture.

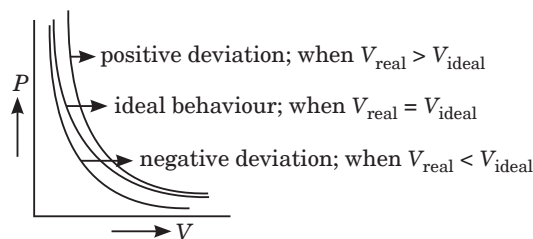
$$\therefore P_{\text{gas}} = P_{\text{Total}} \times x_{\text{gas}}$$

i.e., partial pressure = total pressure × mole fraction.

• **Behaviour of real gases (deviation from ideal gas behaviour) :**

► Real gases do not obey ideal gas equation under all conditions. They nearly obey ideal gas equation at higher temperatures and very low pressures. However, they show deviations from ideality at low temperatures and high pressures.

► The isotherms obtained by plotting pressure, P against volume, V for real gases do not coincide with that of ideal gas, as shown :



V_{real} = Volume of the real gas at given pressure.
 V_{ideal} = Volume of the gas calculated by ideal gas equation at given pressure.

► The deviation from ideal gas behaviour can also be expressed by compressibility factor, Z .

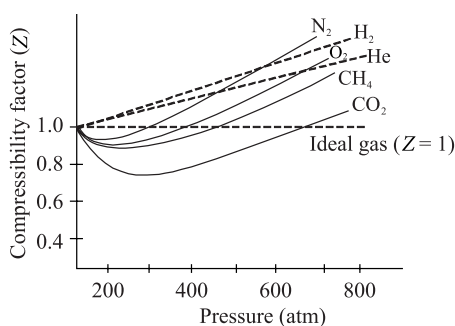
– **Compressibility factor (Z) :** The ratio of volume of real gas, V_{real} to the ideal volume of that gas, V_{ideal} calculated by ideal gas equation is known as *compressibility factor*.

$$Z = \frac{PV_{\text{real}}}{nRT} = \frac{V_{\text{real}}}{V_{\text{ideal}}} \left(\because V_{\text{ideal}} = \frac{nRT}{P} \right)$$

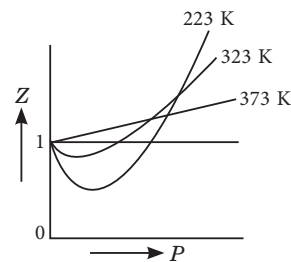
- For ideal perfect gases, the compressibility factor, $Z = 1$.
- But for real gases, $Z \neq 1$.

S.No.	If $Z > 1$	If $Z < 1$
1.	$V_{\text{real}} > V_{\text{ideal}}$	$V_{\text{real}} < V_{\text{ideal}}$
2.	Repulsive forces > attractive forces	Attractive forces > repulsive forces
3.	Gas cannot be compressed easily.	Gas can be compressed easily.
4.	For permanent gases like He, CH_4 , CO_2 , H_2 .	For gases like

- ▶ The isotherms for one mole of different gases, plotted against the Z value and pressure, P at 0°C are shown as :



- ▶ For gases like He, H_2 the Z value increases with increase in pressure (positive deviation). It is because, the repulsive forces become more significant and the attractive forces become less dominant. Hence, these gases are difficult to impress.
- ▶ For gases like CH_4 , CO_2 , NH_3 , etc., the Z value decreases initially (negative deviation) but increases at higher pressure. It is because at low pressures, the attractive forces are more dominant over the repulsive forces, whereas at higher pressures the repulsive forces become significant as the molecules approach closer to each other.
- ▶ But for all the gases, the Z value approaches one at very low pressures, indicating the ideal behaviour.
- ▶ Graph of Z vs P for N_2 gas at different temperatures is shown as :



In the given graph, the curves are approaching the horizontal line with increase in the temperature *i.e.*, the gases approach ideal behaviour at higher temperatures.

- **van der Waals' equation :** The deviations from ideal gas behaviour can be ascertained to the following faulty assumptions by kinetic theory of gases :

- ▶ The real volume of the gas molecules is negligible when compared to the volume of the gas.
- ▶ There are no forces of attraction or repulsion between the gas molecules. Hence, van der Waals suggested the following corrections :

- Volume correction, $V_{\text{ideal}} = V - nb$
- Pressure correction :

$$P_{\text{ideal}} = P_{\text{real}} + a \left(\frac{n^2}{V^2} \right)$$

- ▶ Now, the ideal gas equation can be modified by introducing this volume and pressure correction as : $\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$

- ▶ (van der Waals equation of state)

$$\text{For 1 mole of gas, } \left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

- where, V_m = molar volume of a real gas,
 a = van der Waals constant of attraction.
 $a \propto$ attraction between gas molecules
 \propto compressibility \propto ease of liquefaction.
 b = excluded volume of the gas
- ▶ Units of 'a' and 'b' :
Unit of a = $\text{atm L}^2 \text{mol}^{-2}$, Unit of b = L mol^{-1}



OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

- Which one of the following statements is wrong for gases?
 - Gases do not have a definite shape and volume.
 - Volume of the gas is equal to volume of container confining the gas.
 - Confined gas exerts uniform pressure on the walls of its container in all directions.
 - Gases are not compressible.
- Which of the following is true about gaseous state?
 - Thermal energy = molecular attraction
 - Thermal energy \gg molecular attraction
 - Thermal energy \ll molecular attraction
 - Molecular forces \gg those in liquids
- Intermolecular forces in solid hydrogen are
 - covalent forces
 - van der Waals forces or London dispersion forces
 - hydrogen bonds
 - all of these.
- For the type of interactions; (I) covalent bond, (II) van der Waals forces, (III) hydrogen bonding, (IV) dipole-dipole interaction, which represents the correct order of increasing stability?
 - (I) < (III) < (II) < (IV)
 - (II) < (III) < (IV) < (I)
 - (II) < (IV) < (III) < (I)
 - (IV) < (II) < (III) < (I)
- The types of attractive forces between a polar molecule and a non-polar molecule are
 - dipole-dipole forces
 - hydrogen bonds
 - dipole-induced dipole forces
 - dispersion forces.
- Dipole-induced dipole interactions are present in which of the following pairs?
 - HCl and He atoms
 - SiF_4 and He atoms
 - H_2O and alcohol
 - Cl_2 and CCl_4
- If P , V and T represent pressure, volume and temperature of the gas, the correct representation of Boyle's law is
 - $V \propto 1/P$ (P is constant)
 - $PV = RT$
 - $V \propto 1/P$ (at constant T)
 - $PV = nRT$
- At 25°C and 380 mm pressure, 400 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure?
 - 200 mL
 - 400 mL
 - 569 mL
 - 621 mL
- Use of hot air balloons in sports and meteorological observations is an application of
 - Boyle's law
 - Newton's law
 - Kelvin's law
 - Charles' law.
- Equal volumes of gases at the same temperature and pressure contain equal number of particles. This statement is direct consequence of
 - perfect gas law
 - partial law of volumes
 - Charles' law
 - ideal gas equation.
- A plot of volume (V) versus temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are shown in the figure. Which of the following order of pressure is correct for this gas?

- (a) $p_1 > p_2 > p_3 > p_4$ (b) $p_1 = p_2 = p_3 = p_4$
 (c) $p_1 < p_2 < p_3 < p_4$ (d) $p_1 < p_2 = p_3 < p_4$

12. When the product of pressure and volume is plotted against pressure for a given amount of gas, the line obtained is

- (a) parallel to x -axis
 (b) parallel to y -axis
 (c) linear with positive slope
 (d) linear with negative slope.

13. Containers A and B have same gases. Pressure, volume and temperature of A are all twice as that of B , then the ratio of number of molecules of A and B are

- (a) 1 : 2 (b) 2 : 1
 (c) 1 : 4 (d) 4 : 1

14. A gas cylinder can withstand a pressure of 15 atm. The pressure of cylinder is measured 12 atm at 27°C . Upto which temperature limit the cylinder will not burst?

- (a) 375°C (b) 102°C
 (c) 33.75°C (d) 240°C

15. Select the correct statement. In the gas equation, $PV = nRT$

- (a) n is the number of molecules of a gas
 (b) n moles of the gas have a volume V
 (c) V denotes volume of one mole of the gas
 (d) P is the pressure of the gas when only one mole of gas is present.

16. Molar volume of CO_2 is maximum at

- (a) NTP (b) 0°C and 2.0 atm
 (c) 127°C and 1 atm (d) 273°C and 2.0 atm.

17. The volume occupied by 1.8 g of water vapour at 374°C and 1 bar pressure will be

[Use $R = 0.083 \text{ bar L K}^{-1}\text{mol}^{-1}$]

- (a) 96.66 L (b) 55.87 L
 (c) 3.10 L (d) 5.37 L

18. Dimension of universal gas constant (R) is

- (a) $[VPT^{-1}n^{-1}]$ (b) $[VP^{-1}Tn^{-1}]$
 (c) $[VPTn^{-1}]$ (d) $[VPT^{-1}n]$

19. The mole fraction of dioxygen in a neon-dioxygen mixture is 0.18. If the total pressure of the mixture is 25 bar, the partial pressure of neon in the mixture would be

- (a) 25.18 bar (b) 25.82 bar
 (c) 4.5 bar (d) 20.5 bar

20. 25 g of each of the following gases are taken at 27°C and 600 mm pressure. Which of these will have the least volume?

- (a) HBr (b) HCl
 (c) HF (d) HI

21. At high pressure, the compressibility factor Z is equal to

- (a) unity (b) $1 - \frac{Pb}{RT}$
 (c) $1 + \frac{Pb}{RT}$ (d) zero.

22. Gas deviates from ideal gas nature because molecules

- (a) are colourless
 (b) attract each other
 (c) contain covalent bond
 (d) show Brownian movement.

23. van der Waals equation of state is obeyed by real gases. For n moles of a real gas, the expression will be

- (a) $\left(\frac{P}{n} + \frac{na}{V^2}\right)\left(\frac{V}{n-b}\right) = RT$
 (b) $\left(P + \frac{a}{V^2}\right)(V-b) = nRT$
 (c) $\left(P + \frac{na}{V^2}\right)(nV-b) = nRT$
 (d) $\left(P + \frac{n^2a}{V^2}\right)(V-nb) = nRT$

24. The van der Waals equation reduces itself to the ideal gas equation at

- (a) high pressure and low temperature
 (b) low pressure and low temperature
 (c) low pressure and high temperature
 (d) high pressure and high temperature.

25. Maximum deviation from ideal gas is expected from

- (a) $\text{CH}_{4(g)}$ (b) $\text{NH}_{3(g)}$
 (c) $\text{H}_{2(g)}$ (d) $\text{N}_{2(g)}$

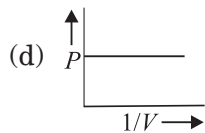
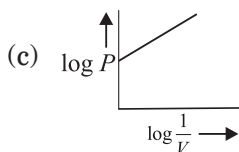
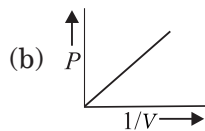
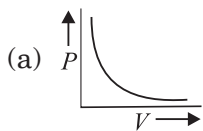
26. A gas such as carbon monoxide would be most likely to obey the ideal gas law at

- (a) low temperatures and high pressures
 (b) high temperatures and high pressures
 (c) low temperatures and low pressures
 (d) high temperatures and low pressures.

27. The correction factor ' a ' to the ideal gas equation corresponds to

- (a) density of the gas molecules
 (b) volume of the gas molecules
 (c) electric field present between the gas molecules
 (d) forces of attraction between the gas molecules.

28. Which of the following plots is not according to Boyle's law?



29. Which of the following expressions does not represent Charles' law?

(a) $V_t = V_0 \left[\frac{273.15 + t^\circ\text{C}}{273.15} \right]$

(b) $V_t = a + bt$

(c) $V_t = \left[\frac{V_0}{273.15 \text{ K}} \right] t$

(d) $V_t = V_0 t$

30. To raise the volume of a gas by four times, the following methods may be adopted. Which of the methods is wrong?

(a) T is doubled and P is also doubled.

(b) Keeping P constant, T is raised four times.

(c) Temperature is doubled and pressure is halved.

(d) Keeping temperature constant, pressure is reduced to $1/4$ of its initial value.

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 31 to 35.

Intermolecular forces are the forces of attraction and repulsion that exist between molecules of a compound. These cause the compound to exist in a certain state of matter – solid, liquid or gas and affect the melting and boiling points of compounds as well as the solubilities of one substance in another. Attractive intermolecular forces are also called van der Waals' forces. These are weak forces.

31. Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is

- (a) more than unit electronic charge
- (b) equal to unit electronic charge
- (c) less than unit electronic charge
- (d) double the unit electronic charge.

32. The nature of inter-particle forces in benzene is

- (a) dipole-dipole interaction
- (b) dispersion force
- (c) ion-dipole interaction
- (d) H-bonding.

33. The interaction energy between two temporary dipoles is proportional to (where r is the distance between the two particles)

- (a) $1/r^4$
- (b) $1/r^2$
- (c) $1/r^5$
- (d) $1/r^6$

34. Attractive intermolecular forces known as van der Waals forces do not include which of the following types of interactions?

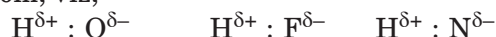
- (a) London forces
- (b) Dipole-dipole forces
- (c) Ion-dipole forces
- (d) Dipole-induced dipole forces

35. In which of the following molecules, the van der Waals forces are likely to be the most important in determining the m.pt. and b.pt?

- (a) CO
- (b) H_2S
- (c) Br_2
- (d) HCl

Case II : Read the passage given below and answer the following questions from 36 to 40.

If a hydrogen atom is bonded to a highly electronegative element such as fluorine, oxygen, nitrogen, then the shared pair of electrons lies more towards the electronegative element. This leads to a polarity in the bond in such a way that a slight positive charge gets developed on H-atom, viz,



Such a bond between the hydrogen atom of one molecule and the more electronegative atom of the same or another molecule is called hydrogen bond.

36. Which of the following compounds can form hydrogen bond?

- (a) CH_4 (b) H_2O
(c) NaCl (d) CHCl_3

37. The boiling point is not affected due to hydrogen bonding in

- (a) water (b) ammonia
(c) methyl alcohol (d) hydrogen chloride.

38. Unusual high b.p. of water is result of

- (a) intermolecular hydrogen bonding
(b) intramolecular hydrogen bonding
(c) both intra and intermolecular hydrogen bonding
(d) high specific heat.

39. Boiling point of hydrogen fluoride is highest amongst HF, HCl, HBr and HI. Which type of intermolecular forces are present in hydrogen fluoride?

- (a) H—F has highest van der Waals forces and dipole moment.
(b) H—F has highest London forces.
(c) H—F has highest dipole moment hence has dipole-dipole, London forces and hydrogen bonding.
(d) H—F has strong intermolecular interactions like dipole-induced dipole.

40. Which of the following statements is not true?

- (a) Intermolecular hydrogen bonds are formed between two different molecules of compounds.
(b) Intramolecular hydrogen bonds are formed between two different molecules of the same compound.
(c) Intramolecular hydrogen bonds are formed within the same molecule.
(d) Hydrogen bonds have strong influence on the physical properties of a compound.

Case III : Read the passage given below and answer the following questions from 41 to 45.

An ideal gas is a gas to which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures.

From Boyle's law we get, $V \propto \frac{1}{P}$
(at constant n and T)

From Charles' law we get, $V \propto T$
(at constant n and P)

From Avogadro's law we get, $V \propto n$ (at constant T and P)

Combining the above three equations we get

$$V \propto \frac{nT}{P} \text{ or, } V = R \frac{nT}{P} \text{ [where } R = \text{ideal gas constant]}$$

$$\text{or } PV = nRT$$

Ideal gas equation is a relation between four variables and it describes the state of any gas. For this reason, it is also called equation of state.

41. At 25°C and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure?

- (a) 365 mL
(b) 449 mL
(c) 569 mL
(d) 621 mL

42. 7.0 g of a gas at 300 K and 1 atm occupies a volume of 4.1 litre. What is the molecular mass of the gas?

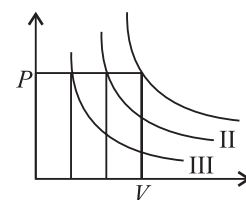
- (a) 42 (b) 38.24
(c) 14.5 (d) 46.5

43. If P is the pressure and ρ is the density of a gas, then P and ρ are related as

- (a) $P \propto \rho$ (b) $P \propto \rho^2$
(c) $P \propto 1/\rho$ (d) $P \propto 1/\rho^2$

44. I, II, III are three isotherms respectively at T_1 , T_2 and T_3 . Temperature will be in order

- (a) $T_1 = T_2 = T_3$
(b) $T_1 < T_2 < T_3$
(c) $T_1 > T_2 > T_3$
(d) $T_1 > T_2 = T_3$



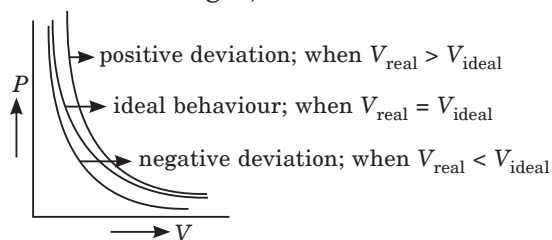
45. If volume of 2 moles of an ideal gas at 540 K is 44.8 litre, then its pressure will be

- (a) 1 atm (b) 3 atm
(c) 2 atm (d) 4 atm

Case IV: Read the passage given below and answer the following questions from 46 to 48.

Real gases do not obey ideal gas equation under all conditions. They nearly obey ideal gas equation at higher temperatures and very low pressures. However, they show deviations from ideality at low temperatures and high pressures.

The isotherms obtained by plotting pressure, P against volume, V for real gases do not coincide with that of ideal gas, as shown :



V_{real} = Volume of the real gas at given pressure.
 V_{ideal} = Volume of the gas calculated by ideal gas equation at given pressure.

The deviation from ideal gas behaviour can also be expressed by compressibility factor, Z .

46. The gas equation $PV = nZRT$ becomes ideal gas equation when

- (a) $Z = 0$
- (b) $Z = 0.5$
- (c) $Z = 1$
- (d) $Z = 2$

47. The units of van der Waals' constants a and b respectively are

- (a) $\text{L atm}^2 \text{ mol}^{-1}$ and mol L^{-1}
- (b) L atm mol^2 and mol L
- (c) $\text{L}^2 \text{ atm mol}^{-2}$ and $\text{mol}^{-1} \text{ L}$
- (d) $\text{L}^{-2} \text{ atm}^{-1} \text{ mol}^{-1}$ and L mol^{-2}

48. The correction factor ' b ' to the ideal gas equation corresponds to

- (a) density of the gas molecules
- (b) excluded volume or covolume
- (c) electric field present between the gas molecules
- (d) forces of attraction between the gas molecules.

➡ Assertion & Reasoning Based MCQs

For question numbers 49-55, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

49. **Assertion :** Three states of matter are the result of balance between intermolecular forces and thermal energy of the molecules.

Reason : Intermolecular forces tend to keep the molecules together but thermal energy of molecules tends to keep them apart.

50. **Assertion :** At constant temperature, PV vs V plot for real gases is not a straight line.

Reason : At high pressure all gases have $Z > 1$ but at intermediate pressure most gases have $Z < 1$.

51. **Assertion :** The plot of volume (V) versus pressure (P) at constant temperature is a hyperbola in the first quadrant.

Reason : $V \propto 1/P$ at constant temperature.

52. **Assertion :** Compressibility factor (Z) for non ideal gases is always greater than 1.

Reason : The gases which have $Z > 1$ are difficult to compress.

53. **Assertion :** van der Waals equation is applicable only to non-ideal gases.

Reason : Ideal gases obey the equation $PV = nRT$.

54. **Assertion :** Vapour pressure of NH_3 is higher than $\text{C}_2\text{H}_5\text{OH}$.

Reason : H-bonding is observed in both the molecules.

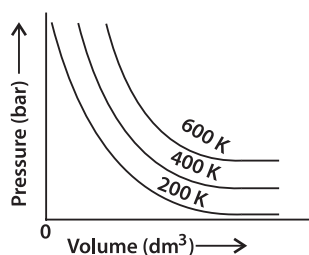
55. **Assertion :** The graph between P vs $1/V$ is a straight line.

Reason : At constant temperature, $P \propto 1/V$.

SUBJECTIVE TYPE QUESTIONS

➡ Very Short Answer Type Questions (VSA)

- Calculate the volume occupied by 4.0 mole of an ideal gas under NTP condition.
- How is the partial pressure of a gas in a mixture related to the total pressure of the gaseous mixture?
- The variation of pressure with volume of the gas at different temperatures can be graphically represented as shown in figure.



On the basis of this graph given, how will the volume of a gas change if its pressure is increased at constant temperature?

- Under which of the following two conditions applied together, a gas deviates most from the ideal behaviour?
- Physical properties of ice, water and steam are very different. What is the chemical composition of water in all the three states.
- Name two intermolecular forces that exist between HF molecules in liquid state.
- Define the partial pressure of gas.
- Define compressibility factor.
- Using the equation of state $PV = nRT$; show that at a given temperature, density of a gas is proportional to gas pressure P .
- Why is boiling point of hydrogen fluoride higher than that of hydrogen chloride?

➡ Short Answer Type Questions (SA-I)

- 40 mL of O_2 was collected at $100^\circ C$ and 1 bar pressure. Calculate its volume (in mL) at 273 K and 1.013 bar.
- 0.068 dm^3 of a sample of nitrogen is collected over water at $20^\circ C$ and 0.92 bar. What will be the volume of dry nitrogen at STP (in mL) (Aqueous tension of water at $20^\circ C = 0.023 \text{ bar}$)?
- Calculate the volume (in m^3) occupied by 2 moles of an ideal gas at $25 \times 10^5 \text{ Nm}^{-2}$ pressure and 300 K temperature.
- At $0^\circ C$, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?
- How much time (in years) would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second?
- Calculate the volume (in litres) occupied by 8.8 g of CO_2 at $31.1^\circ C$ and 1 bar pressure.
- $(R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1})$
- Which type of intermolecular forces exist among the following molecules?
 - He atoms and HCl molecules
 - HF molecules
 - N_2 molecules
 - HCl molecules
- Explain the physical significance of van der Waals' parameters.
- Calculate the total pressure (in bar) in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at $27^\circ C$.
 $R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$
- 1 mole of sulphur dioxide occupies a volume of 350 mL at $27^\circ C$ and $5 \times 10^6 \text{ Pa}$ pressure. Calculate the compressibility factor of the gas. Is it less or more compressible than an ideal gas?

Short Answer Type Questions (SA-II)

21. Describe London forces or dispersion forces with example.

22. The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen (in mL) at 20°C and one bar will be released when 0.15 g of aluminium reacts?

23. On the basis of intermolecular forces and thermal energy explain why substances exist in three different states of matter?

24. Two moles of ammonia gas are enclosed in a vessel of 5 litre capacity at 27°C. Calculate the pressure exerted by the gas, assuming that

(i) the gas behaves like an ideal gas (using ideal gas equation)

(ii) the gas behaves like a real gas (using van der Waals equation)

Given that for ammonia, $a = 4.17 \text{ atm litre}^2 \text{ mol}^{-2}$ and $b = 0.037 \text{ litre mol}^{-1}$.

25. 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of dihydrogen at 17 °C at the same pressure. What is the molar mass of the gas?

26. On the basis of their interaction energy and thermal energy explain why

(i) a solid has high rigidity?

(ii) In gas, molecules are sufficiently apart from one another?

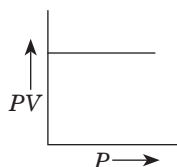
(iii) liquid has no definite shape?

27. Explain the following :

(i) Boyle's law

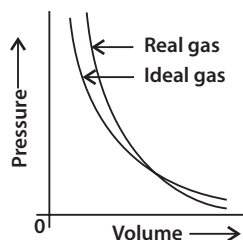
(ii) Avogadro's law

28. (a) Which gas law is shown by the following graph?



(b) At 25°C and 760 mm Hg pressure, a gas occupies 600 mL volume. What will be its pressure (in mmHg) at a height where temperature is 10°C and volume of the gas is 640 mL?

29. Pressure versus volume graph for a real gas and an ideal gas are shown in the figure.



Answer the following questions on the basis of this graph.

(i) Interpret the behaviour of real gas with respect to ideal gas at low pressure.

(ii) Interpret the behaviour of real gas with respect to ideal gas at high pressure.

(iii) Mark the pressure and volume by drawing a line at the point where real gas behaves as an ideal gas.

30. A perfectly elastic spherical balloon of 0.2 m diameter was filled with hydrogen at sea level. What will be its diameter (in m) when it has risen to an altitude where the pressure is 0.65 atm? (Assume no change in temperature and atmospheric pressure at sea level).

31. (i) Out of CO_2 and He, which gas have higher value of van der Waals' constant 'b'?

(ii) At 27°C density of a gaseous substance at 3 bar is same as that of hydrogen at 9 bar. What is molar mass of the substance?

32. What will be the pressure (in bar) of a gas mixture when 0.5 L of H_2 at 0.8 bar and at 2.0 L of oxygen at 0.7 bar are introduced in a 1 L vessel at 27 °C?

33. (a) 22 g of dry ice is placed in an evacuated bottle of 1 litre capacity and tightly stoppered. What would be the pressure inside the bottle in atm, when it is heated to 37°C?

(b) 3.12 g of sulphur is vapourised at 427°C and 760 mm pressure, when the vapours occupy a volume of 700 mL. Find the molecular formula of sulphur. (atomic mass of sulphur = 32).

34. An open beaker at 27°C is heated to 477°C. What percentage of air would have been expelled out?

35. Explain the difficulties faced by the mountaineers with respect to the air present around them. How is this difficulty solved?

Long Answer Type Questions (LA)

36. Payload is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the payload (in kilograms) when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m⁻³ and $R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$)

37. A liquefied petroleum gas (LPG) cylinder weighs 14.8 kg when empty. When full it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27 °C, the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions and the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of 0 °C.

38. At temperature, T and pressure P , two ideal gases A and B are mixed. Show that the density d of the mixture is given by

$d = (X_A M_A + X_B M_B) \times \frac{P}{RT}$ where X_A and X_B are the mole fractions and M_A and M_B are the molecular weights of the gases A and B respectively.

39. The volume of a gas is to be increased by 20% without changing the pressure. To what temperature (in °C) the gas must be heated if the initial temperature of the gas is 27 °C?

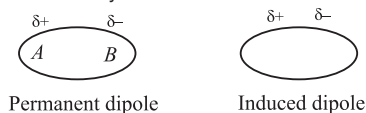
40. Answer the following :

- How are the van der Waals' constants 'a' and 'b' related to the molecular size?
- Using van der Waals' equation, calculate the constant 'a' when two moles of a gas confined in a 4 L flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K. The value of 'b' is 0.05 L mol⁻¹.

ANSWERS

OBJECTIVE TYPE QUESTIONS

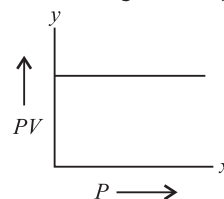
- (d) : Gases are highly compressible.
- (b) : For gaseous state, thermal energy \gg molecular attraction.
- (b) : Solid hydrogen, H₂ is non-polar compound and possesses London dispersion forces. Infact these are the only attractive forces which a non-polar compound can have.
- (c)
- (c) : It is the type of force between the polar molecule and a non-polar molecule. Dipole of polar molecule induces dipole on the electrically neutral molecule.



- (a) : HCl is polar ($\mu \neq 0$) and He is non-polar ($\mu = 0$). Therefore, HCl and He atoms will possess dipole-induced dipole interaction.
- (c) : Boyle's law relates pressure and volume of a gas at constant temperature *i.e.*, $V \propto \frac{1}{P}$ (at constant T).
- (a) : Applying $P_1 V_1 = P_2 V_2$
 $P_1 = 380 \text{ mm}$, $V_1 = 400 \text{ mL}$, $P_2 = 760 \text{ mm}$, $V_2 = ?$

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{380 \times 400}{760} = 200 \text{ mL}$$

- (d) : According to Charles' law $V \propto T$ *i.e.*, air expands on heating, its density decreases. Hence hot air is lighter.
- (d) : Ideal gas equation $PV = nRT$
 If P , V and T are same n will also be same.
- (c) : Since $pV \propto T$ and $p \propto \frac{1}{V}$ hence, volume decreases with pressure. The values of p_1, p_2, p_3, p_4 show decrease in volume. Hence, the order of pressure is $p_1 < p_2 < p_3 < p_4$.
- (a) : $PV = \text{constant}$ (at a given temperature)



- (b) : $P_A V_A = n_A RT_A$ and $P_B V_B = n_B RT_B$

$$\frac{n_A}{n_B} = \frac{\frac{P_A V_A}{RT_A}}{\frac{P_B V_B}{RT_B}} = \frac{2P_B \times 2V_B}{P_B \times V_B} = 2$$

Thus number of molecules are also in the ratio 2 : 1.

14. (b): Cylinder will burst at that temperature when it attains the pressure of 15 atm

$$P_1 = 12 \text{ atm}; T_1 = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}; P_2 = 15 \text{ atm}; T_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow T_2 = \frac{15 \times 300}{12} = 375 \text{ K} = (375 - 273)^\circ\text{C} = 102^\circ\text{C}$$

15. (b): From ideal gas equation, $PV = nRT$, it can be concluded that n moles of a gas occupy the volume V at pressure P and temperature T .

16. (c): We know $V \propto \frac{1}{P}$ and $V \propto T$

\therefore CO_2 has maximum volume at minimum pressure and maximum temperature.

17. (d): $m = 1.8 \text{ g}$

$$n = \frac{m}{M} = \frac{1.8}{18} = 0.1 \text{ mol}$$

$$T = 374^\circ\text{C} = 647 \text{ K}, P = 1 \text{ bar}$$

$$R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$$

$$V = \frac{nRT}{P} = \frac{0.1 \times 0.083 \times 647}{1} = 5.37 \text{ L}$$

18. (a): From the gas equation, $PV = nRT$

$$R = \frac{P \times V}{n \times T} = [VPT^{-1}n^{-1}]$$

19. (d): Given $P_{\text{total}} = 25 \text{ bar}$, $x_{\text{O}_2} = 0.18$

$$\therefore x_{\text{Ne}} = 1 - 0.18 = 0.82$$

$$p_{\text{Ne}} = x_{\text{Ne}} \times P_{\text{total}} = 0.82 \times 25 = 20.5 \text{ bar}$$

20. (d): Ideal gas equation is $PV = nRT$

If pressure and temperature are same for all the gases then

$$V \propto n \text{ (from above equation)}$$

$$n = \text{no. of moles of the gas} = \frac{\text{wt.}}{\text{Mol. wt.}}$$

(here weight of all gases are equal)

$$\therefore V \propto \frac{1}{\text{Mol. wt.}}$$

From the options, HI has more molecular weight than remaining gases, so it has least volume.

$$\mathbf{21. (c):} \left(P + \frac{a}{V^2} \right) (V - b) = RT$$

At high pressure b cannot be neglected in comparison to V . Further though V becomes small, a/V^2 is large but as P is very high, a/V^2 can be neglected in comparison to P . Hence

$$P(V - b) = RT \quad \text{or} \quad PV = RT + Pb$$

$$\text{or} \quad \frac{PV}{RT} = 1 + \frac{Pb}{RT} \quad \text{i.e.} \quad Z = 1 + \frac{Pb}{RT}$$

22. (b): Unlike postulates of kinetic molecular theory, intermolecular forces in a gas are not negligible.

23. (d): van der Waal's equation is

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

24. (c)

25. (b): It is a polar molecule, thus more attractive forces between its molecule.

26. (d): Real gases show ideal gas behaviour at high temperatures and low pressures.

27. (d)

28. (d): $P \propto \frac{1}{V}$, the graph will be a straight line passing through origin.

$$\mathbf{29. (d):} V_t = \frac{V_0}{t_0} \times t$$

30. (a): $\frac{PV}{T} = \text{constant}$, only (a) is wrong.

31. (c): Partial charge is a small charge developed by displacement of electrons. It is less than unit electronic charge and is represented as δ^+ or δ^- .

32. (b): Benzene is non-polar compound and exhibits London or dispersion forces.

33. (d) **34. (c)**

35. (c): In the molecules the van der Waals force are likely to determine the m.pt. and b.pt. Greater the mass of the molecule greater will be its van der Waals force and higher will be its m.pt. and b.pt. Br_2 has highest m.pt.

36. (b): Oxygen has high electronegativity and small size, thus forms H-bond.

37. (d): HCl does not undergo H-bonding and its boiling point is not affected by H-bonding.

38. (a): Due to intermolecular hydrogen bond in H_2O , its molecules are associated with each other which is responsible for unusual high b.p. of water.

39. (c): H—F has dipole-dipole interaction, London forces and hydrogen bonding due to highest electronegativity of F. Hence, boiling point of H—F is highest.

40. (b): Intramolecular hydrogen bonds are formed within the same molecule.

41. (a): Applying $P_1V_1 = P_2V_2$

$$P_1 = 730 \text{ mm}, V_1 = 380 \text{ mL}, P_2 = 760 \text{ mm}, V_2 = ?$$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{730 \times 380}{760} = 365 \text{ mL}$$

42. (a) : Applying, $PV = \frac{m}{M}RT$

$P = 1 \text{ atm}; V = 4.1 \text{ L}; m = 7.0 \text{ g};$

$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}; T = 300 \text{ K}$

$$M = \frac{RT}{PV} \times m = \frac{0.0821 \times 300}{1 \times 4.1} \times 7.0 = 42.05 \approx 42 \text{ g mol}^{-1}$$

43. (a) : $P = \frac{\rho RT}{M}$ i.e., $P \propto \rho$

44. (c) : Draw a line at constant pressure parallel to volume-axis. Take volume corresponding to each temperature.

From volume axis, $V_1 > V_2 > V_3$

Hence $T_1 > T_2 > T_3$.

45. (c) : Number of moles, $n = 2$;

Temperature, $T = 540 \text{ K}$

Volume, $V = 44.8 \text{ L}; P = ?$

[R , gas constant = $0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$]

According to ideal gas equation $PV = nRT$

$$P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 540}{44.8} = 2 \text{ atm}$$

46. (c) : The ideal gas equation is $PV = nRT$

When Z (the compressibility factor) is one, the given equation $PV = nZRT$ becomes ideal gas equation.

47. (c) : a and b are expressed in terms of the units of P and V .

$$\text{Pressure correction} = P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P'V^2}{n^2} = \frac{\text{pressure} \times (\text{volume})^2}{(\text{mole})^2}$$

Unit of $a = \text{atm} \times (\text{L})^2 \text{mol}^{-2}$

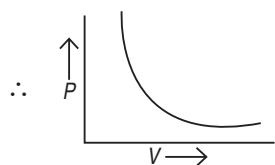
Unit of b is the same as for the volume. i.e., L mol^{-1}

48. (b) : The correction factor 'b' represents excluded volume or covolume.

49. (a)

50. (b) : At constant temperature, plot of PV vs V for real gases is not linear because real gases have intermolecular forces of attraction.

51. (a) : According to Charles's law $V \propto \frac{1}{P}$.



52. (d) : Compressibility factor (Z) can be greater, equal or lesser than 1.

53. (b) : The van der Waals equation is applicable to real gases only, while $PV = nRT$ is applicable to ideal gases.

54. (b) : H - bonding in liquid NH_3 is weaker than $\text{C}_2\text{H}_5\text{OH}$. Thus, escaping tendency is higher and hence, the vapour pressure of NH_3 is also higher.

55. (a)

SUBJECTIVE TYPE QUESTIONS

1. $PV = nRT$

or $V = \frac{nRT}{P} = \frac{4 \times 0.082 \times 273}{1} = 89.54 \text{ L}$

2. Partial pressure of a gas

= Mole fraction of that gas \times Total pressure

3. The volume of a gas decreases if the pressure on the gas is increased keeping the temperature constant.

4. At high pressure and low temperature, the gases deviate from ideal behaviour due to significant intermolecular forces and more than negligible size of the molecules.

5. The chemical composition of water remains same in all the physical states i.e., solid, liquid and gas.

6. Dipole-dipole interactions and hydrogen bonding exist between HF molecules in liquid state.

7. In a mixture of gases, the pressure exerted by the individual gas is called its partial pressure.

8. The extent to which a real gas deviates from ideal behaviour can be conveniently studied in terms of quantity 'Z' called the compressibility factor, which is defined as $Z = \frac{PV}{nRT}$

For an ideal gas, as $PV = nRT$, $Z = 1$

9. $PV = nRT$

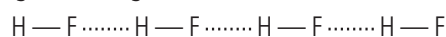
or $P = \frac{wRT}{MV}$ (Since $n = \frac{w}{M}$)

or $P = \frac{dRT}{M}$ (Since $d = \frac{w}{V}$)

or, $P \propto d$

Hence, density (d) of a gas $\propto P$, because R , T and M are constants.

10. Boiling point of HF is higher than HCl due to extensive hydrogen bonding between H — F molecules.



11. Given, $P_1 = 1 \text{ bar}$, $V_1 = 40 \text{ mL} = 0.04 \text{ L} = 0.04 \text{ dm}^3$,
 $T_1 = 373 \text{ K}$, $P_2 = 1.013 \text{ bar}$, $T_2 = 273 \text{ K}$, $V_2 = ?$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{1 \times 0.04 \times 273}{373 \times 1.013} = 0.029 \text{ dm}^3 \text{ or } 29 \text{ mL}$$

12. Given $P_1 = 0.92 - 0.023 = 0.897 \text{ bar}$,
 $V_1 = 0.068 \text{ dm}^3$, $T_1 = 293 \text{ K}$, $P_2 = 1 \text{ bar}$ (Pressure of dry gas),
 $V_2 = ?$, $T_2 = 273 \text{ K}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ or } V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$= \frac{0.897 \times 0.068 \times 273}{1 \times 293} = 0.057 \text{ dm}^3 \text{ or } 57 \text{ mL}$$

13. According to ideal gas equation, $PV = nRT$

$$\text{or } V = \frac{nRT}{P} = \frac{2 \times 8.314 \times 300}{25 \times 10^5} \approx 2 \times 10^{-3} \text{ m}^3$$

$$14. M_{\text{oxide}} = \frac{d_{\text{oxide}} RT}{P_{\text{oxide}}} \quad \dots(1)$$

$$M_{\text{N}_2} = \frac{d_{\text{N}_2} RT}{P_{\text{N}_2}} \quad \dots(2)$$

Dividing equation (1) by equation (2) gives

$$\frac{M_{\text{oxide}}}{M_{\text{N}_2}} = \frac{d_{\text{oxide}} \times P_{\text{N}_2}}{d_{\text{N}_2} \times P_{\text{oxide}}}$$

But $d_{\text{oxide}} = d_{\text{N}_2}$

$$\therefore M_{\text{oxide}} = \frac{5 \text{ bar}}{2 \text{ bar}} \times 28 \text{ g mol}^{-1}$$

$$M_{\text{oxide}} = 70 \text{ g mol}^{-1}$$

15. Time taken to distribute 10^{10} grains = 1 sec.

Time taken to distribute 6.023×10^{23} grains

$$= \frac{1 \times 6.022 \times 10^{23}}{10^{10}} = 6.022 \times 10^{13} \text{ sec}$$

$$= \frac{6.022 \times 10^{13}}{60 \times 60 \times 24 \times 365} = 1.90956 \times 10^6 \text{ years}$$

16. According to ideal gas equation, $PV = nRT$

$$n = \frac{8.8}{44} \text{ moles, } P = 1 \text{ bar,}$$

$$T = 273 + 31.1 = 304.1 \text{ K,}$$

$$V = ?$$

$$R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$$

$$\text{Now, } V = \frac{nRT}{P}$$

$$= \frac{\left(\frac{8.8}{44} \text{ moles}\right) \times (0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}) \times (304.1 \text{ K})}{1 \text{ bar}}$$

$$= 5.05 \text{ L}$$

17. (i) Dipole-induced dipole forces

(ii) Hydrogen bonding

(iii) Dispersion forces

(iv) Dipole-dipole forces

18. 'a' measures the intermolecular forces of attraction. The greater the value of 'a', the more will be intermolecular forces of attraction. 'b' measures volume occupied by molecules of a gas.

19. Partial pressure of oxygen gas,

$$P = \frac{nRT}{V}, n = \frac{8}{32} \text{ mol, } V = 1 \text{ dm}^3, T = 300 \text{ K}$$

$$P_{(\text{O}_2)} = \frac{8 \times 0.083 \times 300}{32 \times 1} = 6.225 \text{ bar}$$

Partial pressure of hydrogen gas,

$$P = \frac{nRT}{V}, n = \frac{4}{2} = 2 \text{ mol}$$

$$P_{(\text{H}_2)} = \frac{2 \times 0.083 \times 300}{1} = 49.8 \text{ bar}$$

$$\text{Total pressure} = P_{(\text{O}_2)} + P_{(\text{H}_2)} = 6.225 + 49.8$$

$$= 56.025 \text{ bar}$$

20. Compressibility factor, $Z = \frac{PV}{nRT}$

$$n = 1 \text{ mol, } P = 5 \times 10^6 \text{ Pa, } V = 350 \text{ mL} = 0.350 \times 10^{-3} \text{ m}^3$$

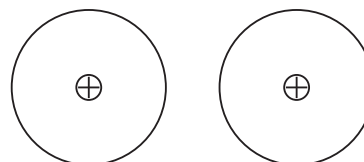
$$R = 8.314 \text{ N m K}^{-1} \text{ mol}^{-1}, T = 27 + 273 = 300 \text{ K}$$

$$\therefore Z = \frac{5 \times 10^6 \times 0.350 \times 10^{-3}}{1.0 \times 8.314 \times 300} = 0.702$$

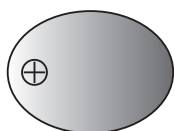
Thus, SO_2 is more compressible than an ideal gas (which has $Z = 1$).

21. London or dispersion forces : This is the weakest intermolecular force. It is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms to form temporary dipoles. This force is sometimes called an *dipole-induced dipole attraction*.

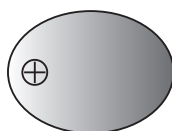
Because of the constant motion of the electrons, an atom or molecule can develop a temporary (instantaneous) dipole when its electrons are distributed unsymmetrically about the nucleus.



Atom A Atom B
 symmetrical distribution of electronic charge cloud
 (a)

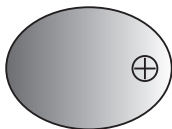


Atom 'A' with instantaneous dipole, more electron density on the right hand side

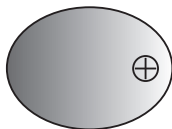


Atom 'B' with induced dipole,

(b)



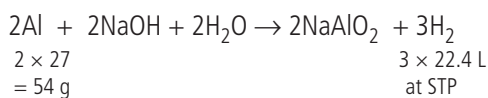
Atom 'A' more electron density on the left hand side



Atom 'B' with induced dipole

(c)

Dispersion forces or London forces between atoms.

22. The reaction between aluminium and caustic soda is \therefore 54 g of Al produces H_2 at S.T.P. = 3×22.4 L0.15 g of Al will produce H_2 at S.T.P.

$$= \frac{3 \times 22.4}{54} \times 0.15 = 0.186 \text{ L}$$

At STP

$P_1 = 1 \text{ atm}$

$V_1 = 0.186 \text{ L}$

$T_1 = 273 \text{ K}$

Given conditions

$P_2 = 1 \text{ bar} = 0.987 \text{ atm}$

$V_2 = ?$

$T_2 = 273 + 20 = 293 \text{ K}$

Applying ideal gas equation, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{1 \times 0.186}{273} = \frac{0.987 \times V_2}{293}$$

$$V_2 = \frac{293}{0.987} \times \frac{1 \times 0.186}{273} = 0.2030 \text{ L} = 203 \text{ mL}$$

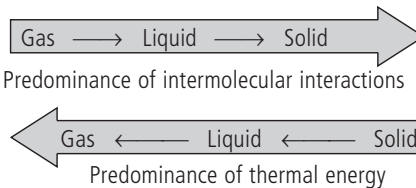
23. The intermolecular forces tend to keep the molecules together but thermal energy tend to keep them apart. Thus, these two compete and the competition between these two (i.e., intermolecular forces and thermal energy) results in three states of matter.

(i) In a solid, the intermolecular forces predominate over the thermal energy and hence, the particles are held together in rigid, highly-oriented and close-packed structure.

(ii) In liquids, the intermolecular forces are no longer strong enough, however, these are still sufficient so that particles remain in each other's environment, hence, liquids have sufficient mobility.

(iii) In gases, the thermal energy dominates the effect of intermolecular forces, thus, the gas molecules acquire the unrestricted and independent mobility in the vapour state.

Predominance of thermal energy and the intermolecular forces in the three state of matter is as follows :

**24.** Given, $n = 2$ moles, $V = 5$ litres, $T = 27^\circ\text{C} = (27 + 273)$ K = 300 K

$a = 4.17 \text{ atm litre}^2 \text{ mol}^{-2}$, $b = 0.037 \text{ litre mol}^{-1}$

Also, we know that $R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$ (i) If the gas behaves like an ideal gas, we have $PV = nRT$

$$\therefore P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300}{5} = 9.85 \text{ atm}$$

(ii) If the gas behaves like a real gas, we apply van der Waals' equation i.e.,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ or } P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$= \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.037} - \frac{4.17 \times (2)^2}{(5)^2} = 9.33 \text{ atm.}$$

25. Case I : Let molar mass of gas be $M \text{ g mol}^{-1}$

Weight of gas = 2.9 g

$$\text{No. of moles} = \frac{\text{Weight}}{\text{Molar mass}} = \frac{2.9}{M}$$

$T = 273 + 95 = 368 \text{ K}$

$$PV = \frac{2.9}{M} \times R \times 368 \qquad \dots(\text{i})$$

Case II : Mass of dihydrogen = 0.184 g

$$\text{No. of moles of } \text{H}_2 = \frac{0.184}{2}$$

$T = 273 + 17 = 290 \text{ K}$

$$PV = \frac{0.184}{2} \times R \times 290 \qquad \dots(\text{ii})$$

From equations (i) and (ii),

$$\frac{2.9}{M} \times 368 = \frac{0.184}{2} \times 290$$

$$M = \frac{2.9 \times 368 \times 2}{0.184 \times 290} = 40 \text{ g mol}^{-1}$$

26. (i) A solid has high rigidity because thermal motion is too weak to overcome the strong intermolecular forces of attraction.

(ii) In a gas, thermal energy is so high that the molecules cannot come close together. Hence, there are large empty spaces between them.

(iii) In a liquid, there is a reasonable balance between the attractive intermolecular forces and thermal energy. Hence, molecules in a liquid exist together, *i.e.*, it is a condensed state of matter but there is no rigidity. That is why they have no definite shape.

27. (i) Boyle's law : According to Boyle's law, at constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure, *i.e.*, if volume increases, the pressure would decrease. This is because as volume increases, the number of molecules striking the walls of a container in a given time decreases leading to decrease in pressure.

$$P \propto \frac{1}{V} ; P = \frac{\text{Constant}}{V}$$

$$\Rightarrow PV = \text{Constant} \Rightarrow P_1V_1 = P_2V_2$$

(ii) Avogadro's law : This law states that equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules.

$$V \propto n(T, P \text{ constant}) = \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

28. (a) Boyle's law

(b) Applying gas equation (combined gas law),

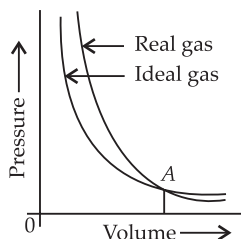
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{760 \times 600}{298} = \frac{P_2 \times 640}{283}$$

$$\text{or } P_2 = 676.6 \text{ mm of Hg}$$

29. (i) At low pressure real gas starts behaving like an ideal gas.

(ii) At high pressure gases deviate from ideal behaviour.

(iii)



At point **A** real gas behaves as an ideal gas.

30. If r_1 is the radius of the balloon at sea level, then, volume

$$\text{of the balloon at sea level} = \frac{4}{3}\pi r_1^3 = \frac{4}{3}\pi(0.1 \text{ m})^3$$

$$\text{i.e., volume of the gas at sea level } (V_1) = \frac{4}{3}\pi(0.1 \text{ m})^3$$

Pressure at the sea level (P_1) = 1 atm

Suppose the radius of the balloon at altitude = r_2

$$\text{Then, volume of the balloon at altitude } (V_2) = \frac{4}{3}\pi r_2^3$$

Pressure at the altitude (P_2) = 0.65 atm (Given)

As temperature remains constant, applying Boyle's law,

$$\begin{array}{ccc} P_1V_1 & = & P_2V_2 \\ \text{(At sea level)} & & \text{(At altitude)} \end{array}$$

$$1 \text{ atm} \times \frac{4}{3}\pi(0.1 \text{ m})^3 = 0.65 \text{ atm} \times \frac{4}{3}\pi r_2^3$$

$$\text{or } r_2^3 = \frac{(0.1 \text{ m})^3}{0.65} = 1.54 \times 10^{-3} \text{ m}^3$$

$$\therefore r_2 = (1.54 \times 10^{-3})^{1/3} \text{ m} = 0.1154 \text{ m}$$

\therefore Diameter of the balloon at altitude

$$= 2 \times 0.1154 \text{ m} = 0.2308 \text{ m}$$

31. (i) Since, CO_2 molecules have larger size than that of He molecules, hence, CO_2 has larger value of van der Waals' constant 'b'.

$$(ii) \quad M_1 = \frac{d_1RT}{P_1} \quad \dots(i)$$

[where,

M_1 = Molecular weight of the substance

d_1 = Density of the substance

P_1 = Pressure of the substance]

$$M_{\text{H}_2} = \frac{d_{\text{H}_2}RT}{P_{\text{H}_2}} \quad \dots(ii)$$

Dividing equation (i) by equation (ii)

$$\frac{M_1}{M_{\text{H}_2}} = \frac{d_1 \times P_{\text{H}_2}}{d_{\text{H}_2} \times P_1} \quad \text{or} \quad \frac{M_1}{M_{\text{H}_2}} = \frac{P_{\text{H}_2}}{P_1} \quad [\text{Given, } d_1 = d_{\text{H}_2}]$$

$$\text{or } M_1 = \frac{M_{\text{H}_2} \times P_{\text{H}_2}}{P_1} = \frac{2 \times 9}{3} = 6$$

32. Partial pressure of H_2 :

$$V_1 = 0.5 \text{ L, } V_2 = 1 \text{ L,}$$

$$P_1 = 0.8 \text{ bar, } P_2 = ?$$

By Boyle's law, $P_1V_1 = P_2V_2$

$$P_2 = \frac{0.8 \times 0.5}{1} = 0.4 \text{ bar}$$

Partial pressure of O_2 :

$$V_1 = 2.0 \text{ L, } V_2 = 1 \text{ L, } P_1 = 0.7 \text{ bar, } P_2 = ?$$

By Boyle's law, $P_1V_1 = P_2V_2$

$$P_2 = \frac{0.7 \times 2.0}{1} = 1.4 \text{ bar}$$

Pressure of the gas mixture,

$$P_{\text{mix}} = p_{\text{H}_2} + p_{\text{O}_2} = 0.4 + 1.4 = 1.8 \text{ bar}$$

33. (a) $W = 22 \text{ g CO}_2$, $V = 1 \text{ L}$, $M = 44$, $T = 37 + 273 = 310 \text{ K}$, $P = ?$

Dry ice is solid CO_2 , which when heated in an evacuated bottle it is converted into gaseous CO_2 .

From ideal gas equation,

$$PV = \frac{WRT}{M} \Rightarrow P = \frac{22 \times 0.082 \times 310}{44 \times 1} = 12.71 \text{ atm.}$$

Now, pressure inside the bottle is 12.71 atm.

(b) For sulphur,

$$W = 3.12 \text{ g, } T = 427 + 273 = 700 \text{ K}$$

$$P = 760 \text{ mm} = 1 \text{ atm.}$$

$$V = 700 \text{ ml} = 0.7 \text{ L.}$$

Now molecular mass of sulphur,

$$M = \frac{WRT}{PV} = \frac{3.12 \times 0.082 \times 700}{1 \times 0.7} = 255.84$$

As atomic mass = 32, so no. of atoms in one molecule of sulphur = $\frac{255.84}{32} = 8$

Hence, molecular formula of sulphur is S_8 .

34. Suppose the number of moles of gas present at 27°C in flask of volume V at pressure P is n_1 , then assuming ideal gas behaviour,

$$PV = n_1 R \times 300 \quad \dots(i)$$

Suppose n_2 = number of moles at 477°C , then

$$PV = n_2 R \times 750 \quad \dots(ii)$$

From equation (i) and equation (ii), we get

$$n_2 = \frac{300}{750} \times n_1 = 0.4 n_1$$

So, $(1 - 0.4) \times 100\%$ i.e. 60% is expelled out.

35. At altitude, the atmospheric pressure is low. Hence, air is less dense. As a result, less oxygen is available for breathing. The person feels uneasiness, headache, etc. This is called altitude sickness. This difficulty is solved by carrying oxygen cylinders with them.

$$\mathbf{36.} \text{ Volume of balloon} = \frac{4}{3} \pi r^3$$

Radius of balloon, $r = 10 \text{ m}$

$$V = \frac{4}{3} \times 3.14 \times (10)^3 = 4186.7 \text{ m}^3$$

$$\begin{aligned} \text{Mass of displaced air} &= 4186.7 \text{ m}^3 \times 1.2 \text{ kg m}^{-3} \\ &= 5024.04 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Moles of gas present} &= \frac{PV}{RT} \\ &= \frac{1.66 \times 4186.7 \times 10^3}{0.083 \times 300} = 279.11 \times 10^3 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{Mass of helium present} &= 279.11 \times 10^3 \times 4 \\ &= 1116.44 \times 10^3 \text{ g} \\ &= 1116.44 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Mass of filled balloon} &= 100 + 1116.44 \\ &= 1216.44 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Payload} &= \text{Mass of displaced air} - \text{Mass of balloon} \\ &= 5024.04 - 1216.44 = 3807.6 \text{ kg} \end{aligned}$$

37. Weight of LPG originally present

$$= 29.0 - 14.8 = 14.2 \text{ kg}$$

Pressure = 2.5 atm

$$\begin{aligned} \text{Weight of LPG present after use} &= 23.2 - 14.8 \\ &= 8.4 \text{ kg} \end{aligned}$$

Since volume of the cylinder is constant, applying

$$\begin{aligned} PV = nRT &\Rightarrow \frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{w_1/M}{w_2/M} = \frac{w_1}{w_2} \\ &\Rightarrow \frac{2.5}{P_2} = \frac{14.2}{8.4} \text{ or } P_2 = \frac{2.5 \times 8.4}{14.2} = 1.48 \text{ atm} \end{aligned}$$

\therefore Weight of used gas = $14.2 - 8.4 = 5.8 \text{ kg}$

$$\text{Moles of gas} = \frac{5.8 \times 10^3}{58} = 100 \text{ mol}$$

Normal conditions : $P = 1 \text{ atm, } T = 273 + 27 = 300 \text{ K}$

Volume of 100 mol of LPG at 1 atm and 300 K

$$V = \frac{nRT}{P} = \frac{100 \times 0.082 \times 300}{1} = 2460 \text{ L} = 2.460 \text{ m}^3$$

38. At temperature T and pressure P , two ideal gases, A and B are mixed.

n_A and n_B are the number of moles of A and B respectively.

n is total moles of A and B present in the mixture.

$$n = n_A + n_B.$$

Let the gas mixture has a volume V .

V_A and V_B are volume of A and B respectively.

From ideal gas equation, $PV = nRT$.

$$\text{For gas } A, PV_A = n_A RT. \therefore V_A = \frac{n_A RT}{P}$$

$$\text{For gas } B, PV_B = n_B RT. \therefore V_B = \frac{n_B RT}{P}$$

M_A and M_B are molecular weights of the gases and X_A and X_B are the mole fractions of the gases A and B respectively.

$$\text{Density of a gas, } d = \frac{\text{mass}}{\text{volume}}$$

$$d = \frac{M}{V} = \frac{\frac{n_A M_A}{P} + \frac{n_B M_B}{P}}{\frac{n_A RT}{P} + \frac{n_B RT}{P}} = \frac{P}{RT} \left[\frac{n_A M_A + n_B M_B}{n_A + n_B} \right]$$

$$= \frac{P}{RT} \left\{ \frac{n_A M_A + n_B M_B}{n} \right\} = \frac{P}{RT} \left\{ \frac{n_A}{n} M_A + \frac{n_B}{n} M_B \right\}$$

$$d = \frac{P}{RT} \{X_A M_A + X_B M_B\}$$

39. Suppose volume of gas at 27°C = $V \text{ cm}^3$

$$\text{Increase in volume desired} = 20\% \text{ of } V = \frac{20}{100} \times V = 0.2 V$$

$$\therefore \text{Final volume} = V + 0.2 V = 1.2 V$$

$$\text{Now, } V_1 = V \text{ cm}^3, T_1 = 300 \text{ K,}$$

$$V_2 = 1.2 V, T_2 = ?$$

At constant P ,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{V}{300} = \frac{1.2 V}{T_2}$$

$$\Rightarrow T_2 = 360 \text{ K} = 360 - 273 = 87^\circ\text{C}$$

40. (a) The van der Waals' constant ' a ' is measure of intermolecular attractions. Therefore, the value of ' a ' reflects the tendency of the gas to liquefy. The gas having larger value of ' a ', will liquefy more easily. The van der Waals' constant ' b ' is a measure of the close-packed molecular volume. Thus the molecule of a gas having greater value of ' b ' has bigger size.

(b) The van der Waals' equation is

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$\text{Given, } n = 2 \text{ mol, } V = 4 \text{ L,}$$

$$P = 11.0 \text{ atm, } T = 300 \text{ K}$$

Substituting the values in the above equation,

$$\left(11.0 \text{ atm} + \left(\frac{2 \text{ mol}}{4 \text{ L}} \right)^2 \cdot a \right) (4 \text{ L} - 2 \text{ mol} \times 0.05 \text{ L mol}^{-1})$$

$$= 2 \text{ mol} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

$$\left(11.0 \text{ atm} + \frac{a}{4} \text{ mol}^2 \text{ L}^{-2} \right) (4 \text{ L} - 0.1 \text{ L}) = 49.2 \text{ L atm}$$

$$\left(11.0 \text{ atm} + \frac{a}{4} \text{ mol}^2 \text{ L}^{-2} \right) (3.9 \text{ L}) = 49.2 \text{ L atm}$$

$$42.9 \text{ L atm} + \frac{3.9a}{4} \text{ mol}^2 \text{ L}^{-1} = 49.2 \text{ L atm}$$

$$\frac{3.9}{4} a \text{ mol}^2 \text{ L}^{-1} = (49.2 \text{ L atm} - 42.9 \text{ L atm})$$

$$= 6.3 \text{ L atm}$$

$$a = \frac{6.3 \text{ L atm} \times 4}{3.9 \text{ mol}^2 \text{ L}^{-1}} = 6.46 \text{ atm L}^2 \text{ mol}^{-2}$$

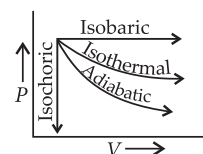


Thermodynamics



Recap Notes

- **Thermodynamics** : It is a branch of science which deals with the study of interconversion of different forms of energies and their quantitative relationships.
- **Some basic terms** :
 - ▶ **System** : It is the part of universe under investigation where energy changes can be regulated and studied.
 - ▶ **Surroundings** : Rest part of the universe which can interact with the system or can influence the properties of the system is called *surroundings*.
 - ▶ **Boundary** : A real or imaginary surface that separates the system from the surroundings is known as *boundary*. A boundary can be rigid or non-rigid (movable), permeable or impermeable, adiabatic (non-conductor of heat) or diathermic (conductor of heat).
- **Types of system** :
 - ▶ **Open system** : A system which can exchange mass as well as energy with the surroundings.
 - ▶ **Closed system** : A system which can exchange energy but not mass with the surroundings.
 - ▶ **Isolated system** : A system which can neither exchange energy nor mass with the surroundings.
 - ▶ **State functions** : Properties which are used to define a particular thermodynamic state and are independent of the path by which the state is attained are called *state functions*. e.g., pressure, mass composition, volume, temperature, internal energy, entropy, Gibbs free energy, etc.
- ▶ **Path functions** : Variables whose values depend upon the path followed by the system in attaining that state, are known as *path functions*.
- **Types of thermodynamic processes** :
 - ▶ **Isothermal process** : Temperature of the system remains constant ($\Delta T = 0$).
 - ▶ **Isobaric process** : Pressure of the system remains constant ($\Delta P = 0$).
 - ▶ **Isochoric process** : Volume of the system remains constant ($\Delta V = 0$).
 - ▶ **Adiabatic process** : The system does not exchange heat with the surroundings (i.e., $q = 0$).
- ▶ **Reversible process** : Direction may be reversed at any stage.
- ▶ **Irreversible process** : Proceeds only in one direction and cannot be reversed.
- ▶ **Cyclic process** : System returns to its original state after a number of steps. For such a process, $\Delta U = 0$ and $\Delta H = 0$.
- ▶ **Exothermic process** : Accompanied by the evolution of heat.
- ▶ **Endothermic process** : Accompanied by the absorption of heat.
- **Internal Energy (U)** : Sum of various forms of energy such as rotational, vibrational, translational, kinetic, coulombic, nuclear, etc. is known as *internal energy*.
 - ▶ It is a state function.
 - ▶ It is extensive property and depends only on temperature.



- **Work (W) :** *Work* is a mode of energy transfer from or to the system to make some net changes in the state of the system. No work is being done when system is in equilibrium. Work = Force \times displacement = $F \times l$
 - ▶ **Electrical work :** It is the work involved in reactions involving ions. Electrical work done = EMF \times quantity of electricity.
 - ▶ **Pressure-volume work :** It is the work done involved in expansion or compression of the gases against external pressure. Work = Pressure \times area $\times l = P_{\text{ext}} \times \Delta V$ where, Force = Pressure \times area; area $\times l$ = volume and ΔV is change in volume *i.e.*, $\Delta V = (V_2 - V_1)$.
- **Heat (q) :** *Heat* is a mode of energy transfer between system and surrounding because of difference in temperature between them. It is measured in terms of calories. SI unit of heat is joule.
- **First law of thermodynamics :** This is the law of conservation of energy which states that energy can neither be created nor be destroyed, although it can be converted from one form to another.
 - ▶ The total energy of the universe remains constant.
 - ▶ ΔE or $\Delta U = q + w$ or $q = \Delta U - w$
 - ▶ q and w are not state functions but $\Delta U = (q + w)$ is a state function.
 - ▶ **Sign convention :**
 - Heat absorbed by the system = +ve
 - Heat evolved by the system = -ve
 - Work done on the system = +ve
 - Work done by the system = -ve
- **Applications :**
 - ▶ **Isothermal reversible expansion of an ideal gas :** Consider a gas enclosed in a cylinder fitted with a frictionless piston. During the expansion volume increases and pressure decreases. In the beginning external pressure P_{ext} is equal to the internal pressure of the gas therefore, the piston does not move. If the external pressure is decreased by dP , the gas expands reversibly and the piston moves through a distance dP . The work done by the gas in an infinitesimal expansion is thus given by

$$dw = -(P_{\text{ext}} - dP)dV$$

but as dP is very small thus, on ignoring $dPdV$, we get $dw = -P_{\text{ext}} dV = -PdV$

- The overall work done in an isothermal reversible expansion of the ideal gas from V_1 to V_2 is as follows :

$$w_{\text{rev}} = - \int_{V_1}^{V_2} PdV$$

From ideal gas equation, $P = RT/V$

Substituting the value of P in the above integral equation,

$$w = -RT \int_{V_1}^{V_2} \frac{dV}{V} = -RT \ln \frac{V_2}{V_1}$$

For n moles, $w = -nRT \ln \frac{V_2}{V_1}$

$$\therefore P_1 V_1 = P_2 V_2$$

$$\therefore w = -nRT \ln \frac{P_1}{P_2} = -2.303nRT \log \frac{P_1}{P_2}$$

- The work done during an isothermal reversible compression can be given as :

$$w = 2.303nRT \log \frac{P_1}{P_2}$$

Thus, opposite to the first case where, work done in isothermal compression has exactly the same value with positive sign.

- ▶ **Free expansion :** Expansion of a gas in vacuum ($P_{\text{ex}} = 0$) is called *free expansion*. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

$$\text{i.e., } \Delta U = q - P_{\text{ex}} \Delta V$$

At constant V , $\Delta U = q_V$

- ▶ **Isothermal and free expansion of an ideal gas :**

- For isothermal expansion of an ideal gas into vacuum; $w = 0$ since, $P_{\text{ex}} = 0$
- For isothermal irreversible change; $q = -w = P_{\text{ex}}(V_f - V_i)$
- For isothermal reversible change;

$$q = -w = 2.303 nRT \log \frac{V_f}{V_i}$$

- For adiabatic change; $q = 0$, $\Delta U = w_{\text{ad}}$

- **Enthalpy (H) :** Total heat content of the system at constant pressure is known as its *enthalpy*.

- ▶ It is an extensive property.
- ▶ It is state function.
- ▶ Its absolute value can not be determined.
- ▶ Mathematically it is given as, $H = U + PV$
- ▶ If H_2 is the enthalpy in final state and H_1 in initial state, then

$$\Delta H = (H_2 - H_1) = \Delta U + P\Delta V$$

- ▶ For exothermic reaction (*i.e.*, heat released during the reaction), ΔH is negative *i.e.*, $\Delta H < 0$. Whereas for endothermic reaction (*i.e.*, heat absorbed during the reaction), ΔH is positive *i.e.*, $\Delta H > 0$.
- ▶ According to first law of thermodynamics, $q = \Delta U - w$; where, w is the pressure-volume work done by the system.

- ▶ $\therefore w = -P\Delta V$

At constant volume ($\Delta V = 0$) then, $w = 0$

$$\therefore q_v = \Delta U$$

- ▶ At constant pressure, ($\Delta P = 0$) then,

$$w = -P\Delta V$$

$$q_p = \Delta U + P\Delta V$$

Comparing this equation with equation of enthalpy change, we get

$$q_p = \Delta H$$

- **Relationship between ΔH and ΔU :**

- ▶ As $P\Delta V = \Delta n_g RT$

where, Δn_g = number of moles of gaseous products – number of moles of gaseous reactants.

$$\therefore \Delta H = \Delta U + \Delta n_g RT \text{ or } q_p = q_v + \Delta n_g RT$$

- When $\Delta n_g = 0$, then $\Delta H = \Delta U$

- When $\Delta n_g > 0$, then $\Delta H > \Delta U$

- When $\Delta n_g < 0$, then $\Delta H < \Delta U$

- For a reaction involving only solids and liquids, $\Delta n_g = 0$, thus, $\Delta H = \Delta U$.

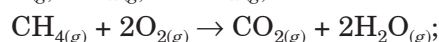
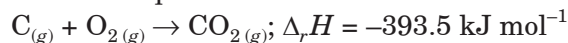
- **Extensive and intensive properties :**

- ▶ **Extensive properties :** The properties which depend upon the amount of matter contained in a system are called *extensive properties*. For example, mass, volume, enthalpy, entropy, free energy, heat capacity, etc.

- ▶ **Intensive properties :** The properties which do not depend upon the amount of

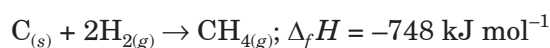
matter present in the system but depend only on the nature of the matter are called *intensive properties*. For example, temperature, pressure, density, refractive index, viscosity, specific heat, freezing point, boiling point, etc.

- **Enthalpy of reaction :** It is defined as the change in enthalpy, or the amount of heat evolved or absorbed when the number of moles of reactants reacts completely to give the products as given by the balanced chemical equation.

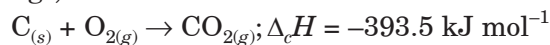


$$\Delta_r H = -890.3 \text{ kJ mol}^{-1}$$

- ▶ **Enthalpy of formation :** It is the change in enthalpy when one mole of a substance is formed directly from its constituent elements, *e.g.*,



- ▶ **Enthalpy of combustion :** It is the change in enthalpy when one mole of a substance is completely burnt in oxygen, *e.g.*,

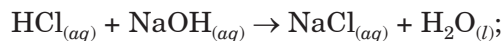


$\Delta_c H$ is always negative as heat is always evolved during combustion.

- ▶ **Enthalpy of solution :** It is the change in enthalpy when one mole of a substance is dissolved in excess of water so that further dilution does not involve any heat change, *e.g.*, $NaCl_{(s)} + aq. \rightarrow NaCl_{(aq)}$;

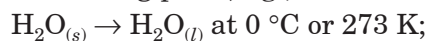
$$\Delta_{\text{soln}} H = +5.0 \text{ kJ mol}^{-1}$$

- ▶ **Enthalpy of neutralisation :** It is the change in enthalpy when one gram equivalent of an acid is completely neutralised by 1 g equivalent of a base in dilute solutions, *e.g.*,



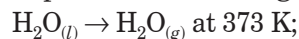
$$\Delta_{\text{neu}} H = -57.1 \text{ kJ mol}^{-1}$$

- ▶ **Enthalpy of fusion :** It is the change in enthalpy when one mole of a solid is completely converted into liquid state at its melting point, *e.g.*,



$$\Delta_{\text{fus}} H = +6.0 \text{ kJ mol}^{-1}$$

- ▶ **Enthalpy of vapourisation** : It is the change in enthalpy when one mole of a liquid is completely converted into its vapours at its boiling point, *e.g.*,



$$\Delta_{\text{vap}}H = +40.6 \text{ kJ mol}^{-1}$$

- ▶ **Enthalpy of sublimation** : It is the change in enthalpy when one mole of a solid is directly converted into vapours, *e.g.*,

$$\Delta_{\text{sub}}H \text{ of iodine is } +62.4 \text{ kJ mol}^{-1}.$$

$$\text{Also, } \Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H$$

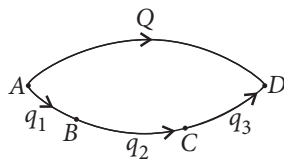
- ▶ **Enthalpy of atomization** : It is the change in enthalpy on breaking one mole of bonds completely to obtain atoms in the gas phase, *e.g.*, $\text{CH}_4(g) \rightarrow \text{C}(g) + 4\text{H}(g)$;

$$\Delta_a H = 1665 \text{ kJ mol}^{-1}$$

- ▶ **Bond enthalpy** : It is the change in enthalpy associated with breaking and making of chemical bonds, *e.g.*,

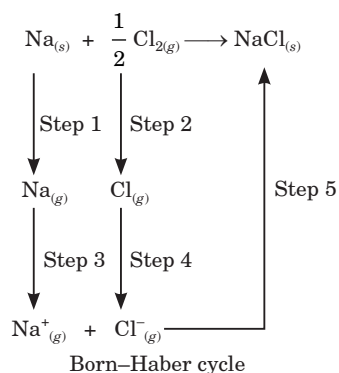


- **Hess's law of constant heat summation** : It states that the total amount of heat change in a chemical reaction is same whether the reaction takes place in one step or in number of steps.

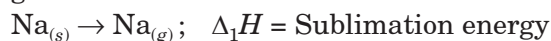


$$Q = q_1 + q_2 + q_3$$

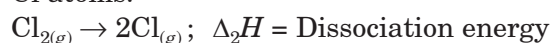
- ▶ **Applications of Hess's law** : The most important application of Hess's law is in the calculation of heat changes for those reactions in which experimental determination is not possible.
- ▶ The thermochemical equations can be treated as algebraic equations which can be added, subtracted, multiplied or divided.
- **Lattice enthalpy** : Hess's law can be used to determine lattice energy which may be defined as the amount of heat liberated when the requisite amounts of ions in the gaseous state combine to produce 1 mole of crystal lattice. For example, lattice energy of NaCl crystal can be determined in the following steps :



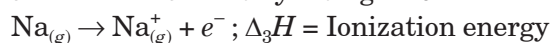
- ▶ **Step 1** : Conversion of Na metal to gaseous atoms.



- ▶ **Step 2** : Dissociation of Cl_2 molecules to Cl atoms.



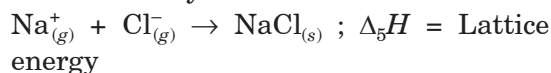
- ▶ **Step 3** : Conversion of gaseous metal atom to metal ions by losing electron.



- ▶ **Step 4** : $\text{Cl}_{(g)}$ atoms gain an electron to form Cl^- ions.



- ▶ **Step 5** : $\text{Na}_{(g)}^+$ and $\text{Cl}_{(g)}^-$ combine together to form the crystal lattice.



Applying Hess's law we get,

$$\Delta_1 H + \frac{1}{2} \Delta_2 H + \Delta_3 H + \Delta_4 H + \Delta_5 H = \Delta_f H \text{ (NaCl)}$$

On putting the various known values, we can calculate the lattice energy.

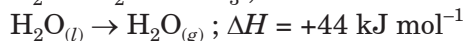
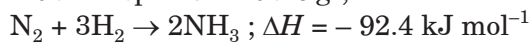
- **Spontaneity** :

- ▶ **Spontaneous process** : The process which takes place by itself or after proper initiation under a given set of conditions is known as *spontaneous process*. All natural processes are spontaneous and cannot be reversed without the help of an external agency. Hence, spontaneous processes are irreversible. *e.g.*, flow of heat from hot reservoir to cold reservoir, flow of water down the hill, dissolution of common salt in water, diffusion of gases from high pressure to low pressure, etc.
- ▶ **Non-spontaneous process** : The process which can neither take place by itself nor by initiation, is called *non-spontaneous process*. *e.g.*, flow of heat from cold

reservoir to hot reservoir, flow of water up the hill, dissolution of sand in water, diffusion of gas from low pressure to high pressure, etc.

● **Factors affecting spontaneity of a reaction :**

► **Energy or enthalpy :** Every system tends to have minimum energy just in order to acquire maximum stability. Thus, the reaction which results in products of lesser energy *i.e.*, exothermic reactions must be spontaneous. *e.g.*,



► **Entropy :** Every system tends to have maximum randomness just in order to acquire maximum stability. An increase in entropy or randomness (*i.e.*, positive ΔS) favours the spontaneity of a reaction. *e.g.*, spreading of a drop of ink in a beaker filled with water is a spontaneous process, where randomness is increasing, *i.e.*, ΔS is positive.

– For a reversible process at equilibrium, $\Delta S = 0$

– For a process to be spontaneous in isolated system, ΔS should be positive.

– For a process in open system, entropy of surrounding should be positive.

$$\therefore \Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}}$$

– For a process to be spontaneous in such condition,

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$$

(i.e., positive)

– For reversible processes,

$$\Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} = 0$$

– For irreversible process,

$$\Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$$

Therefore, it can be said that for all spontaneous processes, ΔS_{Total} must be

positive. Spontaneity of a process is decided by net resultant effect of energy and entropy.

$$\text{If } \Delta S_{\text{System}} = \frac{q_{\text{rev}}}{T}, \text{ then, } \Delta S_{\text{Surrounding}} = -\frac{q_{\text{rev}}}{T}$$

► **Gibbs energy :** Gibbs energy change is given as

$$\Delta G = \Delta H - T\Delta S$$

This expression combines both factors *i.e.*, ΔH and ΔS of spontaneity.

It means, ΔG is resultant of two factors :

– For a reaction to be spontaneous, ΔG must be negative.

– If $\Delta G = 0$, process is in equilibrium.

– If $\Delta G =$ positive, process is non-spontaneous.

► **Gibbs energy change and equilibrium :**

Gibbs energy change, $\Delta_r G$ is related to the equilibrium constant of the reaction as

$$\Delta_r G = -2.303 RT \log K$$

Effect of temperature on spontaneity of reactions

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description*
–	+	–	spontaneous at all temperatures
–	–	– (at low T)	spontaneous at low temperature
–	–	+ (at high T)	non-spontaneous at high temperature
+	+	+ (at low T)	non-spontaneous at low temperature
+	+	– (at high T)	spontaneous at high temperature
+	–	+ (at all T)	non-spontaneous at all temperatures

*The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.



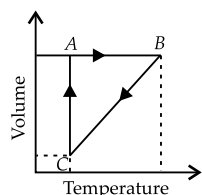
OBJECTIVE TYPE QUESTIONS

➔ Multiple Choice Questions (MCQs)

1. System in which there is no exchange of matter, work or energy from surroundings is

- (a) closed (b) adiabatic
(c) isolated (d) isothermal.

2. Five moles of a gas is put through a series of changes as shown graphically in a cyclic process. The processes $A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow A$ respectively are

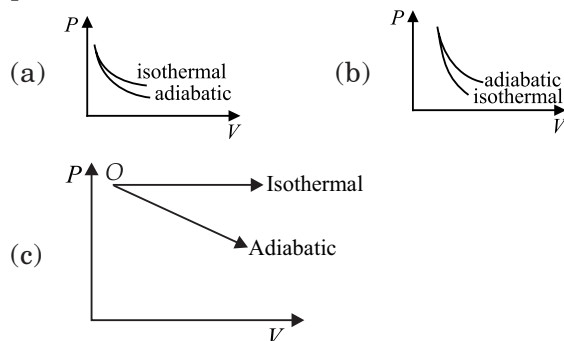


- (a) isochoric, isobaric, isothermal
(b) isobaric, isochoric, isothermal
(c) isothermal, isobaric, isochoric
(d) isochoric, isothermal, isobaric

3. Which one of the following statements is false?

- (a) Work is a state function.
(b) Temperature is a state function.
(c) Change in the state is completely defined when the initial and final states are specified.
(d) Work appears at the boundary of the system.

4. The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is



- (d) none of these.

5. The temperature of the system increases during an

- (a) isothermal expansion
(b) adiabatic compression
(c) adiabatic expansion
(d) isothermal compression.

6. For which of the following reactions will ΔH be equal to ΔU ?

- (a) $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}_{(g)}$
(b) $\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)}$
(c) $2\text{SO}_{3(g)} \rightarrow 2\text{SO}_{2(g)} + \text{O}_{2(g)}$
(d) $2\text{NO}_{2(g)} \rightarrow \text{N}_2\text{O}_{4(g)}$

7. In thermodynamics, which one of the following properties is not an intensive property?

- (a) Pressure (b) Temperature
(c) Volume (d) Density

8. Which of the following reactions corresponds to the definition of enthalpy of formation ?

- (a) $\text{C}_{(g)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$
(b) $\text{C}_{(s)} + \text{O}_{2(l)} \longrightarrow \text{CO}_{2(g)}$
(c) $\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$
(d) $\text{C}_{(l)} + \text{O}_{2(s)} \longrightarrow \text{CO}_{2(g)}$

9. Which of the following statements is correct?

- (a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

10. Enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. What amount of heat will be released upon formation of 35.2 g of CO_2 from carbon and oxygen gas?

- (a) 214.8 kJ (b) 314.8 kJ
(c) 414.8 kJ (d) 514.8 kJ

11. Work done in reversible isothermal process is given by

- (a) $-2.303 nRT \log \frac{V_2}{V_1}$ (b) $\frac{nR}{(\gamma-1)}(T_2 - T_1)$
(c) $-2.303 nRT \log \frac{V_1}{V_2}$ (d) $+2.303 nRT \log \frac{V_2}{V_1}$

12. The standard heat of formation at 298 K for $\text{CCl}_{4(g)}$, $\text{H}_2\text{O}_{(g)}$, $\text{CO}_{2(g)}$ and $\text{HCl}_{(g)}$ are -25.5 , -57.8 , -94.1 and -22.1 kcal per mole respectively. Then ΔH at 298 K for the reaction

- $\text{CCl}_{4(g)} + 2\text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{2(g)} + 4\text{HCl}_{(g)}$ is
(a) -32.9 kcal (b) -41.4 kcal
(c) -99.2 kcal (d) -323.6 kcal

13. In endothermic reactions,

- (a) reactants have more energy than products
(b) reactants have less energy than products
(c) reactants and products have same energy
(d) reactants have lower temperature than products.

14. When 1 M H_2SO_4 is completely neutralised by sodium hydroxide, the heat liberated is 114.64 kJ. What is the enthalpy of neutralisation?

- (a) $+114.64$ kJ (b) -114.64 kJ
(c) -57.32 kJ (d) $+57.32$ kJ

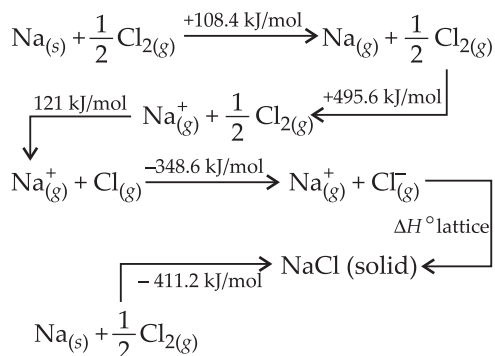
15. In the reaction, $\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{SO}_3 + 2x$ kJ

and $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3 + y$ kJ.

Heat of formation of SO_2 is

- (a) $x + y$ (b) $x - y$
(c) $2x - y$ (d) $2x + y$

16. For one mole of $\text{NaCl}_{(s)}$ the lattice enthalpy is



- (a) -788 kJ/mol (b) $+878$ kJ/mol
(c) $+788$ kJ/mol (d) -878 kJ/mol

17. The heat of neutralization is maximum when

- (a) sodium hydroxide is neutralized by acetic acid
(b) ammonium hydroxide is neutralized by hydrochloric acid
(c) sodium hydroxide is neutralized by formic acid
(d) sodium hydroxide is neutralized by hydrochloric acid.

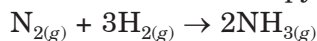
18. Which of the following processes is a non-spontaneous process?

- (a) Dissolution of salt or sugar in water
(b) Mixing of different gases through diffusion
(c) Precipitation of copper when zinc rod is dipped in aqueous solution of copper sulphate
(d) Flow of heat from a cold body to a hot body in contact

19. Bond Bond enthalpy

$\text{N} \equiv \text{N}$	945 kJ mol^{-1}
$\text{H} - \text{H}$	436 kJ mol^{-1}
$\text{N} - \text{H}$	391 kJ mol^{-1}

Calculate the enthalpy change of the reaction,



- (a) -89 kJ mol^{-1} (b) -93 kJ mol^{-1}
(c) -105 kJ mol^{-1} (d) 105 kJ mol^{-1}

20. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

- (a) $q = 0, \Delta T \neq 0, w = 0$ (b) $q \neq 0, \Delta T = 0, w = 0$
(c) $q = 0, \Delta T = 0, w = 0$ (d) $q = 0, \Delta T < 0, w \neq 0$

21. Calculate the resonance energy of N_2O from the following data: ΔH_f of $\text{N}_2\text{O} = 82 \text{ kJ mol}^{-1}$. Bond energies of $\text{N} \equiv \text{N}$, $\text{N} = \text{N}$, $\text{O} = \text{O}$ and $\text{N} = \text{O}$ bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.

- (a) -88 kJ mol^{-1} (b) -170 kJ mol^{-1}
(c) -82 kJ mol^{-1} (d) -258 kJ mol^{-1}

22. The second law of thermodynamics states that

- (a) entropy of the universe is decreasing continuously.
(b) energy can neither be created nor destroyed.
(c) all spontaneous processes are thermodynamically irreversible.
(d) at absolute zero free energy is zero.

23. The heats of neutralization of CH_3COOH , HCOOH , HCN and H_2S are -13.2 , -13.4 , -2.9 and -3.8 kcal per equivalent respectively. The correct increasing order of acid strength is

- (a) $\text{HCOOH} < \text{CH}_3\text{COOH} < \text{H}_2\text{S} < \text{HCN}$
 (b) $\text{HCN} < \text{H}_2\text{S} < \text{CH}_3\text{COOH} < \text{HCOOH}$
 (c) $\text{HCOOH} < \text{CH}_3\text{COOH} < \text{HCN} < \text{H}_2\text{S}$
 (d) $\text{CH}_3\text{COOH} < \text{H}_2\text{S} < \text{HCN} < \text{HCOOH}$

24. One word answer is given for the following definitions. Mark the one which is incorrect.

- (a) The process in which temperature remains constant : Isobaric
 (b) The process in which volume remains constant : Isochoric
 (c) The relation between ΔH and ΔU when all the reactants and products are solid : $\Delta H = \Delta U$
 (d) The relation between ΔG , ΔH and ΔS : $\Delta G = \Delta H - T\Delta S$

25. Choose the reaction with negative ΔS value.

- (a) $2\text{NaHCO}_{3(s)} \longrightarrow \text{Na}_2\text{CO}_{3(s)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(g)}$
 (b) $\text{Cl}_{2(g)} \longrightarrow 2\text{Cl}_{(g)}$
 (c) $2\text{SO}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{SO}_{3(g)}$
 (d) $2\text{KClO}_{3(s)} \longrightarrow 2\text{KCl}_{(s)} + 3\text{O}_{2(g)}$

26. The enthalpies of the elements in their standard states are assumed to be

- (a) zero at 298 K
 (b) unity at 298 K
 (c) zero at all temperatures
 (d) zero at 273 K.

27. According to the 3rd law of thermodynamics, the entropy at 0 K is zero for

- (a) elements in their stable form
 (b) perfectly crystalline solid
 (c) substances at 1 atm and 25 °C
 (d) gaseous substances only.

28. Which of the following condition is not favourable for the feasibility of a reaction?

- (a) $\Delta H = +ve$, $T\Delta S = +ve$ and $T\Delta S > \Delta H$
 (b) $\Delta H = -ve$, $T\Delta S = +ve$
 (c) $\Delta H = -ve$, $T\Delta S = -ve$ and $T\Delta S < \Delta H$
 (d) $\Delta H = +ve$, $T\Delta S = +ve$ and $T\Delta S < \Delta H$

29. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	$\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}$	(i)	$\Delta_{\text{sol}}H$
(B)	$\text{H}_{2(g)} \rightarrow 2\text{H}_{(g)}$	(ii)	$\Delta_{\text{lattice}}H$
(C)	$\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(g)} + \text{Cl}^-_{(g)}$	(iii)	$\Delta_{\text{comb}}H$
(D)	$\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$	(iv)	$\Delta_{\text{disso}}H$

- (a) (A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (i), (D) \rightarrow (ii)
 (b) (A) \rightarrow (ii), (B) \rightarrow (i), (C) \rightarrow (iv), (D) \rightarrow (iii)
 (c) (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)
 (d) (A) \rightarrow (iii), (B) \rightarrow (iv), (C) \rightarrow (ii), (D) \rightarrow (i)

30. In conversion of limestone to lime,



the values of ΔH and ΔS are $+179.1 \text{ kJ mol}^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH and ΔS do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

- (a) 1118 K
 (b) 1008 K
 (c) 1200 K
 (d) 845 K

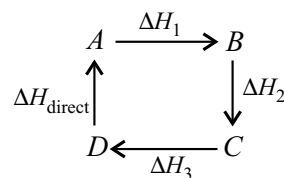
Case Based MCQs

Case I : Read the passage given below and answer the following questions from 31 to 35.

Hess's Law of Constant Heat Summation

This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.

Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.



Total enthalpy change from A to D,

$$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

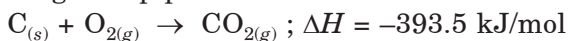
$$\Delta H_{\text{total}} + \Delta H_{\text{direct}} = 0$$

$$\text{i.e., } \Delta H_{\text{total}} = -\Delta H_{\text{direct}}$$

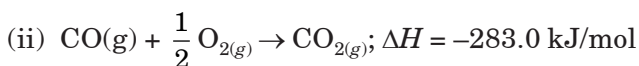
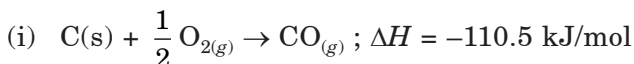
For example, formation of CO_2 from C in two

different manners involves a total heat change of -393.5 kJ/mol

Single step process :

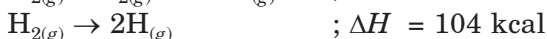
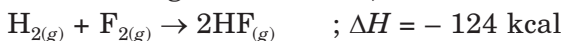


Two step process :



$$\Delta H_{\text{Total}} = -110.5 + (-283.0) = -393.5 \text{ kJ/mol}$$

31. For the given reactions,



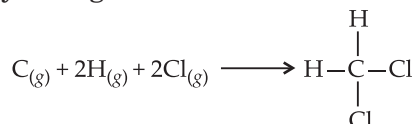
then the value of ΔH for $\text{H}_{(g)} + \text{F}_{(g)} \rightarrow \text{HF}_{(g)}$ is

- (a) 142 kcal (b) -132.9 kcal
(c) 132 kcal (d) 134 kcal.

32. In which of the enlisted cases, Hess's law is not applicable?

- (a) Determination of lattice energy
(b) Determination of resonance energy
(c) Determination of enthalpy of transformation of one allotropic form to another
(d) Determination of entropy

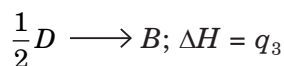
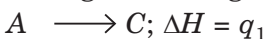
33. Use the bond energy data and calculate the enthalpy change for



The bond energies of C — H and C — Cl are 413 and 328 kJ mol^{-1} respectively.

- (a) -1465 kJ/mol (b) 1465 kJ/mol
(c) -1482 kJ/mol (d) 1482 kJ/mol

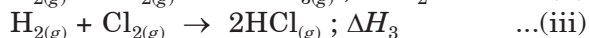
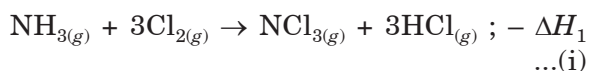
34. A hypothetical reaction, $A \longrightarrow 2B$, proceeds through following sequence of steps :



The heat of reaction is

- (a) $q_1 - q_2 + 2q_3$ (b) $q_1 + q_2 - 2q_3$
(c) $q_1 + q_2 + 2q_3$ (d) $q_1 + 2q_2 - 2q_3$

35. Given :



The heat of formation of $\text{NCl}_{3(g)}$ in the terms of ΔH_1 , ΔH_2 and ΔH_3 is

$$(a) \Delta H_f = -\Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$$

$$(b) \Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$$

$$(c) \Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} + \frac{3}{2}\Delta H_3$$

(d) none of these.

Case II : Read the passage given below and answer the following questions from 36 to 40.

A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together while in a thermodynamically reversible process, the entropy of the system and its surrounding taken together remain unchanged i.e. for reversible process

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

and for irreversible process

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

combining the two we have

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

where 'equal' to sign refers to a reversible process while the 'greater than' sign refers to an irreversible process.

Change in entropy for an ideal gas under different conditions may be calculated as

$$\Delta S = 2.303 nR \log_{10} \frac{V_2}{V_1} = 2.303 nR \log_{10} \frac{P_1}{P_2}$$

(for isothermal process)

$$\Delta S = 2.303 nC_p \log_{10} \frac{T_2}{T_1} = 2.303 nC_p \log_{10} \frac{V_2}{V_1}$$

(for isobaric process)

$$\Delta S = 2.303 nC_v \log_{10} \frac{T_2}{T_1} = 2.303 nC_v \log_{10} \frac{P_2}{P_1}$$

36. Calculate entropy change when 5 moles of an ideal gas expands reversibly and isothermally from an initial volume of 5 litre to 50 litre at 27°C .

- (a) 190.15 JK^{-1} (b) 95.74 JK^{-1}
(c) 87.25 JK^{-1} (d) 90.13 JK^{-1} .

37. The entropy of the universe

- (a) increasing and tending towards maximum value
(b) decreasing and tending to be zero
(c) remains constant
(d) decreasing and increasing with a periodic rate.

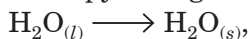
38. The total entropy change for a system and its surroundings increases, if the process is

- (a) reversible (b) irreversible
(c) exothermic (d) endothermic.

39. ΔS is positive for the change

- (a) mixing of two gases (b) boiling of liquid
(c) melting of solid (d) all of these.

40. Entropy changes for the process,



at normal pressure and 274 K are given below

$$\Delta S_{\text{system}} = -22.13, \Delta S_{\text{surr}} = +22.05,$$

the process is non-spontaneous because

(‘surr’ stands for surrounding and ‘u’ stands for universe)

- (a) ΔS_{system} is -ve (b) ΔS_{surr} is +ve
(c) ΔS_{u} is -ve (d) $\Delta S_{\text{system}} \neq \Delta S_{\text{surr}}$

Case III : Read the passage given below and answer the following questions from 41 to 45.

The enthalpy of a system is defined as the sum of the internal energy of the system and the energy that arises due to its pressure and volume. Mathematically, the enthalpy is defined by the equation,

$$H = U + PV$$

Enthalpy change (ΔH) of a system is the heat absorbed or evolved by the system at constant pressure.

$$\Delta H = q_p, \Delta H = \Delta U + P\Delta V$$

41. Which of the following is not correct about enthalpy?

- (a) It is an extensive property.
(b) It is not a state function.
(c) Its absolute value cannot be determined.
(d) Enthalpy of a compound is equal to enthalpy of formation of that compound.

42. In which of the following reactions will ΔU be equal to ΔH ?

- (a) $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)}$
(b) $\text{H}_{2(g)} + \text{I}_{2(g)} \longrightarrow 2\text{HI}_{(g)}$
(c) $\text{N}_2\text{O}_{4(g)} \longrightarrow 2\text{NO}_{2(g)}$
(d) $2\text{SO}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{SO}_{3(g)}$

43. Lattice enthalpies are determined by

- (a) Born-Haber cycle (b) Hess’s law
(c) lattice cycle (d) none of these.

44. In which of the following thermochemical changes ΔH is always negative?

- (a) Enthalpy of solution
(b) Enthalpy of hydrogenation
(c) Enthalpy of reaction
(d) Enthalpy of transition

45. The heat of a chemical reaction is given by the following expression

- (a) $\Delta H = \Sigma H_R - \Sigma H_P$ (b) $\Delta H = \Sigma H_R$
(c) $\Delta H = \Sigma H_P - \Sigma H_R$ (d) $\Delta H = \Sigma H_P$

Case IV : Read the passage given below and answer the following questions from 46 to 50.

In chemical thermodynamics, the type of work involved is mostly pressure-volume work that is the work done when a system (gas) expands or contracts against an external opposing pressure. Hence, work is also defined as the transfer of energy that can be used to change the height of a mass in the surroundings.

Pressure-volume work : The work W , that is done due to the expansion or compression of a gas against an external opposing pressure P is called pressure-volume work.

$$PV = \frac{f}{A} \times V = \frac{f}{d^2} \times d^3 = f \cdot d = W$$

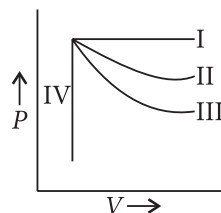
46. Which of the following statement is correct?

- (a) $\Delta U = W_{\text{adiabatic}}$
(b) $W_{ad} = +ve$, when work is done on the system
(c) $W_{ad} = -ve$, when work is done by the system
(d) All of the above.

47. A process in which the system does not exchange heat with the surroundings is known as

- (a) isothermal (b) isobaric
(c) isochoric (d) adiabatic.

48. Which of the following is correct match as far as the thermodynamic processes are involved?



Curve	Thermodynamic Process
1. I	i. Adiabatic
2. II	ii. Isochoric
3. III	iii. Isobaric
4. IV	iv. Isothermal

The correct match is

- | | 1 | 2 | 3 | 4 |
|-----|-----|----|-----|-----|
| (a) | i | ii | iii | iv |
| (b) | iii | iv | i | ii |
| (c) | ii | i | iv | iii |
| (d) | iii | iv | ii | i |

49. 3 moles of an ideal gas are expanded isothermally and reversibly from 10 m^3 to

20 m^3 at 300 K. The work done is ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

- | | |
|---------------|---------------|
| (a) +5.187 kJ | (b) -5.187 kJ |
| (c) -2.175 kJ | (d) +3.750 kJ |

50. A gas expands in vacuum. The work done by the gas is

- | | |
|-------------|--------------------------|
| (a) zero | (b) minimum |
| (c) maximum | (d) cannot be predicted. |

Assertion & Reasoning Based MCQs

For question numbers 51-60, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

51. **Assertion :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Reason : The volume occupied by the molecules of an ideal gas is zero.

52. **Assertion :** U is a state function.

Reason : T is an intensive property.

53. **Assertion :** Sublimation of the solid is non-spontaneous.

Reason : Sublimation is endothermic process.

54. **Assertion :** The sum of $q + w$ is a state function.

Reason : Work and heat are state functions.

55. **Assertion :** Enthalpy of formation of graphite is zero but of diamond it is not zero.

Reason : Enthalpy of formation of the most stable allotrope is taken as zero.

56. **Assertion :** Decrease in free energy causes spontaneous reaction.

Reason : Spontaneous reactions are invariably exothermic reactions.

57. **Assertion :** Heat of neutralisation for both H_2SO_4 and HCl with NaOH is 53.7 kJ mol^{-1} .

Reason : Both HCl and H_2SO_4 are strong acids.

58. **Assertion :** Some salts are sparingly soluble in water at room temperature.

Reason : The entropy increases on dissolving the salts.

59. **Assertion :** Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason : Decrease in enthalpy is a contributory factor for spontaneity.

60. **Assertion :** Entropy of system increases for a spontaneous reaction.

Reason : Enthalpy of reaction always decreases for spontaneous reaction.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

- | | |
|---|---|
| 1. State the difference between adiabatic and isothermal processes. | 3. Define enthalpy of formation. |
| 2. State first law of thermodynamics. | 4. When is bond energy equal to bond dissociation energy? |

- Under what conditions will a reaction be spontaneous if both ΔH and ΔS are negative?
- Give an example of a spontaneous process which is endothermic.
- State the second law of thermodynamics.
- State two ways by which the internal energy

of a system may be changed.

- Give one point of difference : Extensive and intensive properties.

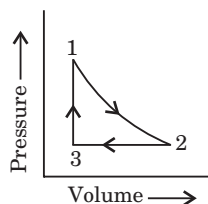
- What will be the sign of ΔS for the following reaction?



➔ Short Answer Type Questions (SA-I)

11. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is $40.79 \text{ kJ mol}^{-1}$. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vaporisation for water?

12. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in figure. What will be the value of ΔH for the cycle as a whole?



13. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

14. The enthalpy of reaction for the reaction : $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(l)}$ is $\Delta_r H = -572 \text{ kJ mol}^{-1}$. What will be standard enthalpy of formation of $\text{H}_2\text{O}_{(l)}$?

15. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from

10 litre to 5 litre. Calculate q , w and ΔU for this process.

($R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, atomic weight of Argon = 40)

16. Calculate the entropy change in surrounding when 1.00 mol of $\text{H}_2\text{O}_{(l)}$ is formed under standard conditions.

$$\Delta_f H = -286 \text{ kJ mol}^{-1}$$

17. Justify the following statements :

- Many thermodynamically feasible reactions do not occur under ordinary conditions.
- At low temperature, enthalpy change dominates the value of ΔG and at high temperature it is the entropy which dominates the value of ΔG .

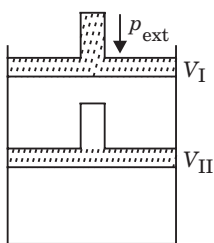
- (a) What is a thermochemical equation?
- (b) Write one application of Hess's law.

19. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

20. Derive the relationship, $\Delta H = \Delta U + \Delta n_g RT$.

➔ Short Answer Type Questions (SA-II)

21. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Figure. Explain graphically.



22. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

23. Comment on the spontaneity of a reaction at constant temperature and pressure in the following cases :

- $\Delta H < 0$ and $\Delta S > 0$
- $\Delta H > 0$ and $\Delta S < 0$
- $\Delta H > 0$ and $\Delta S > 0$

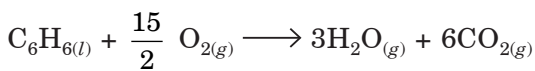
24. (i) Classify the following processes as reversible or irreversible :

- (a) Dissolution of sodium chloride.
 (b) Evaporation of water at 373 K and 1 atm pressure.
 (c) Mixing of two gases by diffusion.
 (d) Melting of ice without rise in temperature.
 (ii) When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why?

25. (i) Explain why the enthalpy changes for the given reactions are not enthalpies of formation of CaCO_3 and HBr .

- (a) $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightarrow \text{CaCO}_{3(s)}$;
 $\Delta_r H = -178.3 \text{ kJ mol}^{-1}$
 (b) $\text{H}_{2(g)} + \text{Br}_{2(g)} \rightarrow 2\text{HBr}_{(g)}$;
 $\Delta_r H = -72.8 \text{ kJ mol}^{-1}$

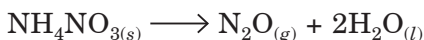
26. Benzene burns in O_2 according to the equation:



If enthalpy of formation of $\text{C}_6\text{H}_{6(l)}$, $\text{H}_2\text{O}_{(g)}$ and $\text{CO}_{2(g)}$ are 11.7, -68.3 , and -94 k cal respectively, calculate the amount of heat liberated by burning 1 kg benzene.

27. The heat of solution of anhydrous CuSO_4 is -15.9 kcal and that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 2.8 kcal . Calculate the heat of hydration of CuSO_4 .

28. The molar heat of formation of $\text{NH}_4\text{NO}_{3(s)}$ is -367.54 kJ and those of $\text{N}_2\text{O}_{(g)}$ and $\text{H}_2\text{O}_{(l)}$ are $+81.46 \text{ kJ}$ and -285.78 kJ respectively at 25°C and 1.0 atmospheric pressure. Calculate ΔH and ΔU for the reaction,

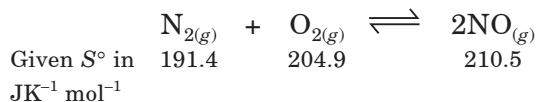


29. A heated copper block at 130°C loses 340 J of heat to the surroundings which are at room temperature of 32°C . Calculate

- (i) the entropy change of the system (copper block)
 (ii) the entropy change in the surroundings
 (iii) the total entropy change in the universe due to this process.

Assume that the temperature of the block and the surroundings remains constant.

30. Assume ΔH° and ΔS° to be independent of temperature, at what temperature will the reaction given below become spontaneous?



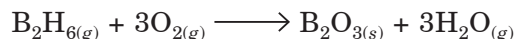
and $\Delta H^\circ = 180.8 \text{ kJ mol}^{-1}$

31. The following data is known about ZnSO_4 : $\Delta H = 7.25 \text{ kJ mol}^{-1}$ and $\Delta S = 7.0 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate its melting point.

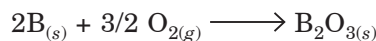
32. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298 K . Given:

- (a) Lattice energy of $\text{NaCl} = 778 \text{ kJ mol}^{-1}$
 (b) Hydration energy of $\text{NaCl} = -774.3 \text{ kJ mol}^{-1}$
 (c) Entropy change at $298 \text{ K} = 43 \text{ J mol}^{-1}$

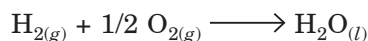
33. Diborane is a potential rocket fuel which undergoes combustion according to the reaction



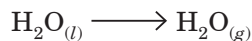
From the following data, calculate the enthalpy change for the combustion of diborane.



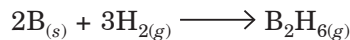
$$\Delta H = -1273 \text{ kJ mol}^{-1}$$



$$\Delta H = -286 \text{ kJ mol}^{-1}$$



$$\Delta H = 44 \text{ kJ mol}^{-1}$$



$$\Delta H = 36 \text{ kJ mol}^{-1}$$

34. The enthalpy change involved in the oxidation of glucose is -2880 kJ/mol . Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after consuming 125 g of glucose?

35. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L . Calculate the value of q , w , ΔU and ΔH .

($R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, at. wt. of $\text{Ar} = 40$)

➔ Long Answer Type Questions (LA)

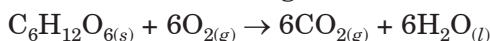
36. Answer the following :

- Why does entropy of a solid increases on fusion?
- State the thermodynamic conditions of spontaneous occurrence of a process.
- Why a non-spontaneous reaction becomes spontaneous when coupled with a suitable spontaneous reaction?
- For an isolated system, $\Delta U = 0$, what will be ΔS ?

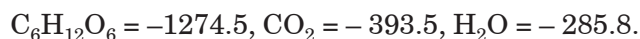
37. (a) The melting point of ice is 273 K. At this temperature the enthalpy of fusion of ice is 6.025 kJ mol⁻¹. Calculate the entropy change for melting of 1 mole of ice. State giving reason whether the entropy change for vaporization of one mole of water will be more or less than entropy change per mole for fusion of ice.

(b) Calculate the entropy change involved in the conversion of one mole of liquid water at 373 K to vapour at the same temperature (Latent heat of vaporization, $\Delta H_{\text{vap}} = 2.257$ kJ/g).

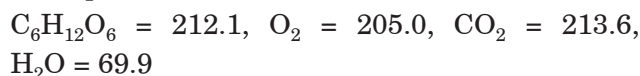
38. Calculate the standard Gibbs energy change for the combustion of α -D glucose at 298 K



Given that standard enthalpies of formation (kJ mol⁻¹)



Entropies (J K⁻¹ mol⁻¹)



39. A gas absorbs 120 J of heat and expands against the external pressure of 1.10 atm from a volume of 0.5 L to 2.0 L. What is the change in internal energy? (1 L atm = 101.3 J)

40. Whenever an acid is neutralised by a base, the net reaction is



Calculate the heat evolved for the following experiments:

- 0.50 mole of HCl solution is neutralised by 0.50 mole of NaOH solution.
- 0.50 mole of HNO₃ solution is mixed with 0.30 mole of KOH solution.
- 100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M NaOH solution.
- 400 mL of 0.2 M H₂SO₄ is mixed with 600 mL of 0.1 M KOH solution.

ANSWERS

OBJECTIVE TYPE QUESTIONS

- (c) : In isolated system, work, energy or heat are not exchanged with the surroundings.
- (a) : Process $A \rightarrow B$ is isochoric, i.e., volume remains constant.
Process $B \rightarrow C$ is isobaric, i.e., pressure remains constant.
Process $C \rightarrow A$ is isothermal, i.e., temperature remains constant.
- (a) : Work is not a state function.
- (a) : Slope of adiabatic curve is steeper than isothermal curve.
- (b) : $\Delta U = q + w$ if $q = 0$ for adiabatic process, then $\Delta U = w$, i.e., work done on the system or work of compression brings in an increase in temperature.
- (a) : $\Delta H = \Delta U + \Delta n_g RT \Rightarrow \Delta H = \Delta U$ if $\Delta n_g = 0$
For $\text{H}_{2(\text{g})} + \text{I}_{2(\text{g})} \rightarrow 2\text{HI}_{(\text{g})}$; $\Delta n_g = 0$

- (c) : Volume is an extensive property.
- (a) : Enthalpy of formation is the heat change when 1 mole of a substance is formed from its constituent elements in gaseous state.
- (c) : In a closed system there is no exchange of matter but exchange of energy is possible. A closed vessel made of copper can exchange heat with the surroundings.
- (b) : $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$; $\Delta_c H = -393.5$ kJ mol⁻¹
For the formation of 44 g of CO₂, 393.5 kJ mol⁻¹ of heat is released.
So, heat released for the formation of 35.2 g of CO₂
 $= \frac{393.5}{44} \times 35.2 = 314.8$ kJ
- (a)
- (b) : $\text{CCl}_{4(\text{g})} + 2\text{H}_2\text{O}_{(\text{g})} \rightarrow \text{CO}_{2(\text{g})} + 4\text{HCl}_{(\text{g})}$
 $\Delta H_f^\circ (\text{kcal}) \quad -25.5 \quad 2 \times -57.8 \quad -94.1 \quad 4 \times -22.1$

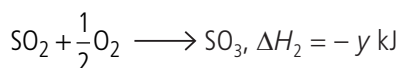
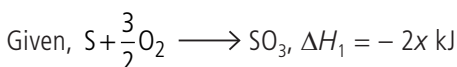
$$\begin{aligned}\Delta H_{\text{Reaction}}^{\circ} &= \Delta H_{\text{f}}^{\circ}(\text{Products}) - \Delta H_{\text{f}}^{\circ}(\text{Reactants}) \\ &= -94.1 + 4(-22.1) - [-25.5 + 2(-57.8)] \\ &= -182.5 + 141.1 = -41.4 \text{ kcal}\end{aligned}$$

13. (b) : For endothermic reactions, $H_R < H_P$.

14. (c) : 1 M $\text{H}_2\text{SO}_4 = 2 \text{ N H}_2\text{SO}_4$

As heat of neutralisation is heat evolved for 1 mole of H^+ ions, therefore enthalpy of neutralisation = $-114.64/2 = -57.32 \text{ kJ}$

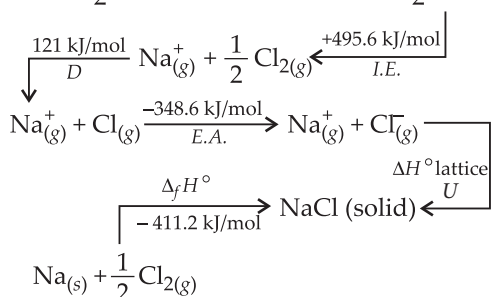
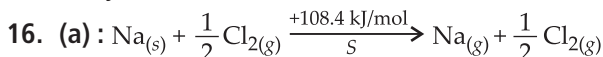
15. (c) : After applying Hess's law on the given reactions, we can get the value of heat of formation of SO_2 . Hess's law states that the amount of heat evolved or absorbed in chemical change is same whether the process takes place in one step or multiple steps.



From Hess's law

$$\Delta H_3 + \Delta H_2 = \Delta H_1 \Rightarrow -z - y = -2x$$

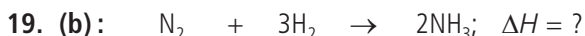
$$z = 2x - y$$



$$\begin{aligned}\Delta_f H &= S + D + I.E. + E.A. + U \\ -411.2 &= 108.4 + 121 + 495.6 - 348.6 + U \\ U &= -787.6 \text{ kJ/mol} \approx -788 \text{ kJ/mol}\end{aligned}$$

17. (d) : Heat of neutralization is maximum for neutralization of a strong acid with strong base.

18. (d)



B.E.:	$\text{N}\equiv\text{N}$	$3\text{H}-\text{H}$	$6\text{N}-\text{H}$
kJ	945	3×436	6×391

$$\begin{aligned}\Delta H &= \Sigma B.E.(\text{Reactants}) - \Sigma B.E.(\text{Products}) \\ &= 945 + 3(436) - 6(391) = -93 \text{ kJ mol}^{-1}\end{aligned}$$

20. (c) : For free expansion $w = 0$ and for adiabatic process $q = 0$

$\Delta U = q + w = 0$ this means that internal energy remains constant.

Therefore, $\Delta T = 0$

21. (a) : $\text{N}\equiv\text{N} + 1/2 \text{O}=\text{O} \longrightarrow \text{N}=\text{N}=\text{O}$

$$\begin{aligned}\Delta H^{\circ}_f &= \Sigma B.E. \text{ of reactants} - \Sigma B.E. \text{ of products} \\ &= [B.E. (\text{N}\equiv\text{N}) + 1/2 B.E. (\text{O}=\text{O})] - \\ &\quad [B.E. (\text{N}=\text{N}) + B.E. (\text{N}=\text{O})] \\ &= (946 + 1/2 \times 498) - (418 + 607) = 170 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\text{Resonance energy} &= \Delta H^{\circ}_f (\text{observed}) - \Delta H^{\circ}_f (\text{calculated}) \\ &= 82 - 170 = -88 \text{ kJ mol}^{-1}\end{aligned}$$

22. (c)

23. (b) : Stronger the acid, more will be heat of neutralization. Negative sign signifies evolution of heat.

24. (a) : In isothermal process, temperature remains constant.

25. (c) : ΔS has negative value if $\Delta n_g = -ve$ i.e. number of gaseous moles decreasing during a reaction.

$$\text{For (a), } \Delta n_g = 2 - 0 = 2$$

$$\text{For (b), } \Delta n_g = 2 - 1 = 1$$

$$\text{For (c), } \Delta n_g = 2 - 3 = -1 \quad (\Delta S \text{ negative})$$

$$\text{For (d), } \Delta n_g = 3 - 0 = 3$$

26. (a) : The enthalpies of all elements in their standard state at 25°C or 298 K are zero.

27. (b)

28. (d) : For a reaction to be feasible; its free energy must be negative ;

$$\Delta G = \Delta H - T\Delta S = -ve$$

In all three cases (a, b, c), ΔG is negative but in option (d), ΔG is positive which is not favourable for the feasibility of the reaction.

29. (d) : (A) : $\text{CH}_{4(\text{g})} + 2\text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})} + 2\text{H}_2\text{O}$ shows combustion reaction

(B) : $\text{H}_{2(\text{g})} \rightarrow 2\text{H}_{(\text{g})}$ shows bond dissociation

(C) : $\text{NaCl}_{(\text{s})} \rightarrow \text{Na}_{(\text{g})}^+ + \text{Cl}_{(\text{g})}^-$ shows dissociation of NaCl

(D) : $\text{NaCl}_{(\text{s})} \rightarrow \text{Na}_{(\text{aq})}^+ + \text{Cl}_{(\text{aq})}^-$ shows dissolution of NaCl

30. (a) : $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

For a spontaneous process, $\Delta G^{\circ} < 0$

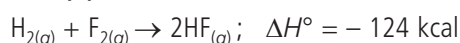
$$\text{i.e. } \Delta H^{\circ} - T\Delta S^{\circ} < 0$$

$$\text{or } \Delta H^{\circ} < T\Delta S^{\circ} \quad \text{or, } T\Delta S^{\circ} > \Delta H^{\circ}$$

$$\text{or } T > \frac{\Delta H}{\Delta S} \quad \text{i.e. } T > \frac{179.1 \times 1000}{160.2}$$

$$\text{or } T > 1117.9 \text{ K} \approx 1118 \text{ K}$$

31. (b) : For the reaction,



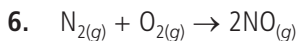
$$\Delta H^{\circ} = \Sigma B.E. (\text{reactants}) - \Sigma B.E. (\text{products})$$

$$\begin{aligned}\text{or } -124 &= \Delta H_{\text{H-H}} + \Delta H_{\text{F-F}} - 2\Delta H_{\text{H-F}} \\ &= 104 + 37.8 - 2\Delta H_{\text{H-F}}\end{aligned}$$

$$5. \quad \Delta G = \Delta H - T\Delta S$$

Given, $\Delta H = -ve$ and $\Delta S = -ve$

For a reaction to be spontaneous, ΔG should be negative, reaction takes place spontaneously only at lower temperature.



It is endothermic as well as spontaneous.

7. Whenever a spontaneous process takes place, it is always accompanied by an increase in total entropy of the universe.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

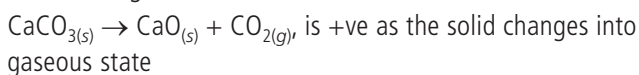
8. (i) If the work is done by or on the system.

(ii) Heat is absorbed by the system or heat is evolved from the system.

9. Extensive properties: Properties that depend on the quantity of matter contained in the system, e.g., mass, volume, etc.

Intensive properties: Properties which depend on the nature of the substance and not on the amount of substance, e.g., viscosity, etc.

10. The sign of ΔS for the reaction,



11. Enthalpy of a reaction is the energy change per mole for the process.

18 g of $H_2O = 1$ mole ($\Delta H_{vap} = 40.79 \text{ kJ mol}^{-1}$)

For 2 moles of H_2O , enthalpy of vaporisation = 2×40.79
= 81.58 kJ

$$\Delta H_{vap}^\circ = 40.79 \text{ kJ mol}^{-1}$$

12. For a cyclic process $\Delta H = 0$

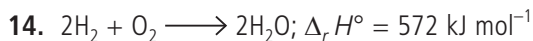
13. Molar enthalpy change for graphite (ΔH)

= enthalpy change for 1 g \times molar mass of C

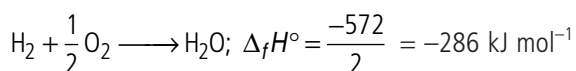
$$= -20.7 \times 12$$

$$= -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

Since the sign of $\Delta H = -ve$, it is an exothermic reaction.



$\Delta_f H^\circ$ will be half of the enthalpy of the given equation as enthalpy of formation is the enthalpy change of the reaction when 1 mole of the compound is formed from its elements.



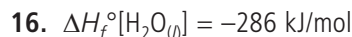
$$15. \quad W_{iso, rev} = -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{5}{10}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log \frac{5}{10} = 103.9 \text{ cal}$$

For isothermal process $\Delta U = 0$

From 1st law of thermodynamics, $\Delta U = q + W$

$$\therefore q = -W = -103.9 \text{ cal}$$



$$\therefore q_{surroundings} = +286 \text{ kJ/mol}$$

$$\Delta S_{(surr)} = \frac{q}{298} = \frac{286 \times 1000}{298} \text{ JK}^{-1} \text{ mol}^{-1} = 959.73 \text{ JK}^{-1} \text{ mol}^{-1}$$

17. (a) Under ordinary conditions, the average energy of the reactants may be less than the threshold energy. They require some activation energy to initiate the reaction.

$$(b) \quad \Delta G = \Delta H - T\Delta S$$

At lower temperature, if value of ΔH is negative ΔG will be $-ve$ and if ΔH is positive, ΔG will be positive. While at higher temperature $-T\Delta S$ will be high, thus, sign of ΔS will decide whether ΔG will be positive or negative.

18. (a) The balanced chemical equation which includes the amount of heat evolved or absorbed during the reaction is called a thermochemical equation.

(b) Hess's law is found very useful in calculating the enthalpy change for the reaction for which experimental determination is not possible.

19. Heat absorbed by the system (q) = 701 J

Work done by the system (w) = -394 J

According to first law of thermodynamics,

$$\Delta U = q + w = 701 + (-394) = 701 - 394 = 307 \text{ J}$$

20. The enthalpy H can be written as :

$$H = U + pV \quad \dots(i)$$

For finite changes at constant pressure, we can write equation (i) as

$$\Delta H = \Delta U + \Delta(pV)$$

Since p is constant, we can write

$$\Delta H = \Delta U + p\Delta V \quad \dots(ii)$$

Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT$$

$$\text{and } pV_B = n_B RT$$

$$\text{Thus, } pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A) RT$$

$$\text{or } p(V_B - V_A) = (n_B - n_A) RT$$

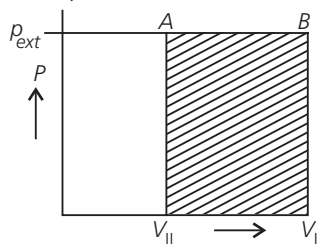
$$\text{or } p\Delta V = \Delta n_g RT \quad \dots(iii)$$

where, $\Delta n_g = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$

Substituting the value of $p\Delta V$ from equation (iii) in equation (ii), we get

$$\Delta H = \Delta U + \Delta n_g RT$$

21. Work done is equal to the shaded area ABV_1V_{II}



22. $q = \Delta U + (-w)$

$$-w = p\Delta V$$

$$\therefore q = \Delta U + p\Delta V$$

At constant volumes $\Delta V = 0$

$$\text{Hence, } q_V = \Delta U + 0 = \Delta U$$

At constant pressure,

$$q_p = \Delta U + p\Delta V$$

$$\text{Since } \Delta U + p\Delta V = \Delta H$$

$$\Rightarrow q_p = \Delta H$$

Hence, at constant volume and at constant pressure heat change is a state function because it is equal to ΔU and ΔH respectively which are state functions.

23. (i) Both energy factor and randomness factor favour the process. Hence, reaction will always be spontaneous.

(ii) Both factor opposes the process. Hence, reaction would always be non-spontaneous.

(iii) Energy factor opposes but randomness factor favours. For spontaneity, $T\Delta S > \Delta H$. Hence, reaction is spontaneous at high temperature and non-spontaneous at low temperature.

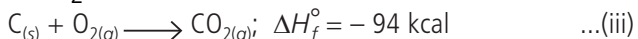
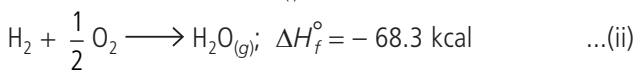
24. (i) (a) Reversible (b) Reversible

(c) Irreversible (d) Reversible.

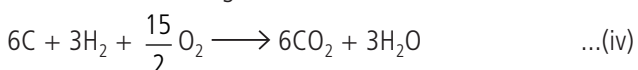
(ii) In an ideal gas, there are no intermolecular forces of attraction. Hence, no energy is required to overcome these forces. Moreover, when a gas expands against vacuum, work done is zero as $P_{\text{ext}} = 0$. Hence, internal energy of the system does not change *i.e.*, there is no absorption or evolution of heat.

25. (i) (a) Given enthalpy change is not enthalpy of formation of CaCO_3 because it is not being formed from constituting elements.

(b) Given enthalpy change is not enthalpy of formation of HBr because 2 moles of HBr are being formed.

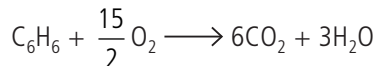


To get required equation, multiply eq. (ii) by 3 and eq. (iii) by 6 and then add; we get:



$$\Delta H^\circ = -768.9 \text{ kcal}$$

Subtract eq. (i) from (iv), we get:



$$\Delta H^\circ = -780.6 \text{ kcal}$$

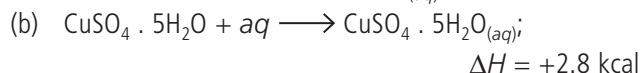
78 g C_6H_6 gives heat = 780.6 kcal

$$\therefore 1000 \text{ g } \text{C}_6\text{H}_6 \text{ will give heat} = \frac{780.6 \times 1000}{78}$$

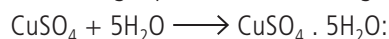
$$= 10067.7 \text{ kcal/mol}$$

Heat liberated by burning 1 kg benzene = 10067.7 k cal/mole

27. Given:

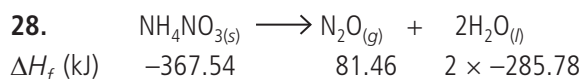


subtracting eqn. (b) from (a), we get:



$$\Delta H = -15.9 - 2.8 = -18.7 \text{ kcal}$$

Heat of hydration of $\text{CuSO}_4 = -18.7 \text{ kcal}$



$$\Delta H_f \text{ (kJ)} \quad -367.54 \quad 81.46 \quad 2 \times -285.78$$

$$\Delta H = \Delta H_f \text{ (Products)} - \Delta H_f \text{ (Reactants)}$$

$$= [2 \times (-285.78) + 81.46] - (-367.54)$$

$$= -122.56 \text{ kJ} = -122.56 \times 10^3 \text{ J}$$

$$\Delta n_g = n_p - n_r = 1 - 0 = 1$$

$$\Delta H = \Delta U + \Delta n_g RT \longrightarrow \Delta U = \Delta H - \Delta n_g RT$$

$$\Delta U = -122.56 \times 10^3 - 1 \times 8.314 \times 298$$

$$= -125.04 \times 10^3 \text{ J} = -125.04 \text{ kJ}$$

$$29. T_{\text{system}} = 130^\circ\text{C} = 130 + 273 \text{ K} = 403 \text{ K},$$

$$T_{\text{surr}} = 32^\circ\text{C} = 32 + 273 \text{ K} = 305 \text{ K}$$

$$q_{\text{system}} = -340 \text{ J}, q_{\text{surr}} = +340 \text{ J}$$

$$(i) \Delta S_{\text{system}} = \frac{q_{\text{system}}}{T_{\text{system}}} = \frac{-340 \text{ J}}{403 \text{ K}} = -0.84 \text{ J K}^{-1}$$

$$(ii) \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{+340 \text{ J}}{305 \text{ K}} = +1.11 \text{ J K}^{-1}$$

$$(iii) \Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\ = -0.84 + (+1.11) \text{ J K}^{-1} = 0.27 \text{ J K}^{-1}$$

30. As $\Delta S^\circ = S^\circ_{\text{Product}} - S^\circ_{\text{Reactant}}$

$$\Delta S^\circ = (2S^\circ_{\text{NO}}) - (S^\circ_{\text{N}_2} + S^\circ_{\text{O}_2})$$

$$= 2 \times 210.5 - (191.4 + 204.9)$$

$$= 24.7 \text{ J K}^{-1} \text{ mol}^{-1} = 24.7 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = 180.8 - (T \times 24.7 \times 10^{-3}) \text{ kJ mol}^{-1}$$

for a spontaneous process ΔG° should be -ve which is possible if

$$T\Delta S^\circ > \Delta H^\circ; T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{180.8 \times 10^3}{24.7} = 7319 \text{ K}$$

The reaction becomes spontaneous above the temperature of 7320 K.

$$31. \Delta S_{(\text{fus})} = \frac{\Delta H_{(\text{fus})}}{T_f} \text{ or } T_f = \frac{\Delta H_{(\text{fus})}}{\Delta S_{(\text{fus})}}$$

$$\Delta H_{(\text{fus})} = 7.25 \text{ kJ mol}^{-1} = 7.25 \times 1000 = 7250 \text{ J mol}^{-1}$$

$$\Delta S_{(\text{fus})} = 7.0 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\therefore T_f = \frac{(7250 \text{ J mol}^{-1})}{(7.0 \text{ JK}^{-1} \text{ mol}^{-1})} = 1035.7 \text{ K}$$

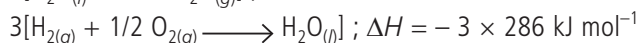
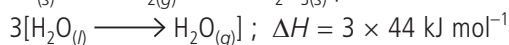
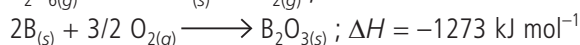
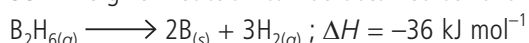
$$32. \Delta H_{\text{dissolution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}} = 778 - 774.3 \\ = 3.7 \text{ kJ mol}^{-1} = 3700 \text{ J mol}^{-1}$$

$$\Delta S_{\text{dissolution}} = 43 \text{ J mol}^{-1}$$

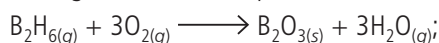
$$\therefore \Delta G_{\text{dissolution}} = \Delta H - T\Delta S \\ = 3700 - 298 \times 43 = -9114 \text{ J}$$

$$\text{or } \Delta G_{\text{dissolution}} = -9.114 \text{ kJ}$$

33. The given reaction can be obtained as follows:



Adding all the above equations,



$$\Delta H = -2035 \text{ kJ mol}^{-1}$$

34. Energy available for muscular work from

$$1 \text{ mole of glucose} = \frac{2880 \times 25}{100} = 720 \text{ kJ/mole}$$

Thus 180 g of glucose (mol. wt. of glucose) supplies 720 kJ energy.

$$125 \text{ g of glucose will supply} = \frac{720}{180} \times 125 = 500 \text{ kJ}$$

100 kJ is needed to walk 1 km

$$500 \text{ kJ is needed to walk } \frac{1}{100} \times 500 = 5.0 \text{ km}$$

$$35. w = -2.303nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \times \log \frac{5}{10}$$

$$w = 103.991 \text{ cal}$$

$$\Delta U = 0, q = \Delta U - w$$

$$\therefore q = -w = -103.991 \text{ cal}$$

When temperature is constant,

$$P_1V_1 = P_2V_2 \text{ or } PV = \text{constant}$$

$$\Delta H = \Delta U + \Delta(PV) = 0 + 0 = 0.$$

36. (i) In a solid, the constituent particles are fixed. On melting, they fall apart and are free to move, i.e., their randomness increases.

(ii) For spontaneous occurrence, ΔG of the process must be < 0 , i.e., -ve. This can be so under the following conditions :

(a) ΔH is negative and ΔS is positive (at any temperature).

(b) If ΔH and ΔS both are positive, then T should be so high that $T\Delta S < \Delta H$.

(c) If both ΔH and ΔS are negative, then T should be so low that $T\Delta S < \Delta H$.

(iii) The overall free energy change of the coupled reaction is negative.

(iv) When energy factor has no role to play, for the process to be spontaneous ΔS must be +ve i.e., $\Delta S > 0$.

$$37. (a) \Delta S_{(\text{fusion})} = \frac{\Delta H_{(\text{fusion})}}{T} = \frac{6025}{273} = 22.07 \text{ J K}^{-1} \text{ mol}^{-1}.$$

The entropy change for the conversion of 1 mole of liquid water to steam at the boiling point will be more as compared to the value at the freezing point, because in the vaporisation randomness increases (due to the conversion of liquid into vapour) much more than in fusion.

$$(b) \text{ Latent heat of vaporisation per mole} \\ = 2.257 \times 10^3 \times 18 = 40,626 \text{ J mol}^{-1}$$

$$\Delta S_{(\text{vap})} = \frac{\Delta H_{(\text{vap})}}{T} = \frac{40626}{373} = 108.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

38. As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta H^\circ_f = \Delta H^\circ_{f(\text{product})} - \Delta H^\circ_{f(\text{reactant})}$$

$$\therefore \Delta H^\circ = [6\Delta H^\circ_f(\text{CO}_2) + 6\Delta H^\circ_f(\text{H}_2\text{O})] \\ - [\Delta H^\circ_f(\text{C}_6\text{H}_{12}\text{O}_6) + 6\Delta H^\circ_f(\text{O}_2)] \\ = [6 \times (-393.5) + 6 \times (-285.8)] - [(-1274.5) + 6 \times 0] \\ [\Delta H^\circ_f(\text{O}_2) = 0] \\ = -2361.0 - 1714.8 + 1274.5 = -2801.3 \text{ kJ mol}^{-1}$$

$$\text{Similarly } \Delta S^\circ = S^\circ_{(\text{product})} - S^\circ_{(\text{reactant})}$$

$$\Delta S^\circ = [6S^\circ(\text{CO}_2) + 6S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + S^\circ(\text{O}_2)] \\ = [6 \times (213.6) + 6 \times (69.9)] - [(212.1) + 6 \times (205.0)] \\ = [1281.6 + 419.4] - [212.1 + 1230] \\ = 258.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = -2801.3 \text{ kJ} = 2801300 \text{ J mol}^{-1}$$

$$\Delta S^\circ = 258.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\therefore \Delta G^\circ = -2801300 - 298 \times (258.9) \\ = -2878.4 \text{ kJ mol}^{-1}$$

39. Work of expansion,

$$W = -P\Delta V$$

$$P\Delta V = -1.10 \times (2.0 - 0.5) = -1.10 \times 1.5$$

$$= -1.650 \text{ L atm}$$

$$= -1.650 \times 101.3 \text{ J} \quad (1 \text{ L atm} = 101.3 \text{ J})$$

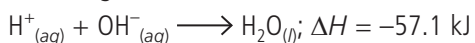
$$= -167.1 \text{ J}$$

Since work is done by the system, $w = -167.1 \text{ J}$

Heat absorbed by the system = 120 J or $q = +120 \text{ J}$

Now, $\Delta E = q + w = 120 + (-167.1) = -47.1 \text{ J}$

40. According to reaction :



When 1 mole of H^+ ions and 1 mole of OH^- ions are neutralised, 1 mole of water is formed and 57.1 kJ of energy is released.

(i) 0.50 mole HCl \equiv 0.50 mole H^+ ions

0.50 mole NaOH \equiv 0.50 mole OH^- ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water

$$= 57.1 \times 0.5 = 28.55 \text{ kJ}$$

(ii) 0.50 mole $\text{HNO}_3 \equiv$ 0.50 mole H^+ ions

0.30 mole KOH \equiv 0.30 mole OH^- ions

i.e., 0.30 mole of H^+ ions react with 0.30 mole of OH^- ions to form 0.30 mole of water molecules.

Heat evolved in the formation of 0.3 mole of water

$$= 57.1 \times 0.3 = 17.13 \text{ kJ}$$

(iii) 100 mL of 0.2 M HCl will give

$$100 \times \frac{0.2}{1000} = 0.02 \text{ mole of } \text{H}^+ \text{ ions and 100 mL of 0.3 M}$$

$$\text{NaOH will give } \frac{0.3}{1000} \times 100 = 0.03 \text{ mole of } \text{OH}^- \text{ ions}$$

i.e., 0.02 mole of H^+ ions react with 0.02 mole of OH^- ions to form 0.02 mole of water molecules.

Heat evolved in the formation of 0.02 mole of water

$$= 0.02 \times 57.1 = 1.142 \text{ kJ}$$

(iv) 400 mL of 0.2M H_2SO_4 will give $\frac{400 \times 0.2}{1000} = 0.08$ mole of H^+ ions

and 600 mL of 0.1M KOH will give $\frac{600 \times 0.1}{1000} = 0.06$ mole of OH^- ions

i.e., 0.06 mole of H^+ ions react with 0.06 mole of OH^- ions to form 0.06 mole of water molecules.

Heat evolved in the formation of 0.06 mole of water

$$= 0.06 \times 57.1 = 3.426 \text{ kJ.}$$



Equilibrium



Recap Notes

- **Physical equilibrium** : It is the process which involves physical changes only, like equilibrium between different states of substances at a particular temperature.
 - ▶ Solid \rightleftharpoons Liquid : ice \rightleftharpoons water at 0°C
rate of melting = rate of freezing
 - ▶ Liquid \rightleftharpoons Gas (vapour) :
water (liquid) \rightleftharpoons water (vapours) at 100°C
rate of evaporation = rate of condensation
 - ▶ Solid \rightleftharpoons Gas (vapour) :
CO₂ (solid) \rightleftharpoons CO₂ (vapours)
rate of sublimation = rate of condensation
 - ▶ Solid \rightleftharpoons Saturated solution of solid in liquid
rate of dissolution = rate of precipitation
 - ▶ Gas \rightleftharpoons Saturated solution of gas in liquid is always exothermic and spontaneous.
 - ▶ **Freezing point/melting point** : The temperature at which the solid-liquid equilibrium is reached for a pure substance under one atmospheric pressure is called normal *melting point* or normal *freezing point* of the substance.
 - ▶ **Boiling point** : The temperature at which liquid-gas equilibrium is attained for a pure substance under one atmospheric pressure is called normal *boiling point* of the substance.
- **General characteristics of physical equilibria** :
 - ▶ Equilibrium can be established only in case of closed system, *i.e.*, the system should neither gain matter from the surroundings nor lose matter to the surroundings.

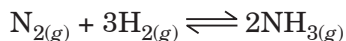
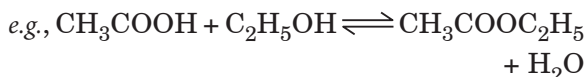
- ▶ The equilibrium is always dynamic in nature. This means that the process does not stop but the changes take place in the forward and backward directions with the same speed.
- ▶ The measurable properties of the system become constant at equilibrium. This is so because the concentration of the substances become constant.
- ▶ At equilibrium, there exists an expression involving concentration of reacting substances which becomes constant at a given temperature. For example, for the equilibrium,
 $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ the pressure of water becomes constant.
- ▶ The magnitude of the constant value of the concentration related expression (called *equilibrium constant*) gives an indication of the extent to which the reaction proceeds before acquiring equilibrium.
- ▶ **Some features of physical equilibrium**

	Process	Conclusion
1.	$\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ [liquid \rightleftharpoons vapour]	$P_{\text{H}_2\text{O}}$ is constant at given temperature.
2.	$\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ [solid \rightleftharpoons liquid]	Melting point is constant at a given pressure.
3.	$\text{Sugar}_{(s)} \rightleftharpoons \text{Sugar}_{(aq)}$ (solution) [Solute _(s) \rightleftharpoons Solute _(aq)] (solution)	Concentration of sugar (solute) in solution is constant at a given temperature.

4.	$\text{CO}_{2(g)} \rightleftharpoons \text{CO}_{2(aq)}$ $[\text{gas}_{(g)}] \rightleftharpoons [\text{gas}_{(aq)}]$	$\frac{[\text{CO}_{2(aq)}]}{[\text{CO}_{2(g)}]}$ $\left(\text{i.e., } \frac{[\text{gas}_{(aq)}]}{[\text{gas}_{(g)}]} \right)$ <p>is constant at a given temperature.</p>
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- **Chemical equilibrium** : If the process involves only chemical change, the equilibrium is called *chemical equilibrium*.

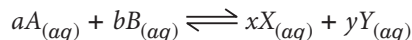
► **Reversible reaction** : A reaction in which the reactants are formed back by the reaction of products with each other at the given conditions of the reaction. These reactions if carried out in a closed vessel do not go to completion.



- **Irreversible reaction** : These are the reactions in which products do not react back to give the reactants, *i.e.*, reaction cannot be retraced at any point.
- **State of equilibrium** : Chemical equilibrium is that state of a reaction at which the rate of forward reaction becomes equal to rate of backward reaction.
- **Dynamic nature of equilibrium** : In dynamic equilibrium, changes occur but in opposite directions and at constant rate *i.e.*, forward and backward reactions take place even after the equilibrium is attained but at equal speeds.
- **General characteristics of chemical equilibrium** :
 - It is dynamic in nature.
 - The observable properties of the system become constant at equilibrium and remain unchanged thereafter.
 - The equilibrium can be approached from either directions.
 - The equilibrium can be attained only if the system is a closed one.
 - The free energy change at constant pressure and temperature is zero.
 - Addition of a catalyst does not change the equilibrium state, it only helps in attaining the equilibrium faster.

- **Law of chemical equilibrium** :

► For the reversible reaction,



At equilibrium, $\frac{[X]^x[Y]^y}{[A]^a[B]^b} = K_c$, K_c is called

equilibrium constant which is constant for a reaction at constant temperature.

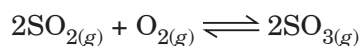
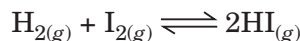
► Relations between equilibrium constants for a general reaction and its multiples.

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K
$cC + dD \rightleftharpoons aA + bB$	$K'_c = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K''_c = (K_c^n)$

- **Types of equilibrium** :

► **Homogeneous equilibrium** :

Equilibrium is said to be homogeneous if reactants and products are in same phase, *e.g.*,



► **Relationship between K_p and K_c** :

For reaction : $aA + bB \rightleftharpoons xX + yY$

$$K_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b} \text{ and } K_p = \frac{P_X'^x P_Y'^y}{P_A'^a P_B'^b}$$

(for gaseous reaction)

For ideal gases $PV = nRT$

$$\text{or } \frac{P}{RT} = \frac{n}{V} \text{ (concentration in mole L}^{-1}\text{)}$$

$$\therefore \text{Concentration of A, } [A] = \frac{n_A}{V} = \frac{P_A'}{RT}$$

$$\text{Similarly, } [B] = \frac{n_B}{V} = \frac{P_B'}{RT}$$

Substituting these values :

$$K_c = \frac{\left(\frac{P_X'}{RT}\right)^x \left(\frac{P_Y'}{RT}\right)^y}{\left(\frac{P_A'}{RT}\right)^a \left(\frac{P_B'}{RT}\right)^b}$$

$$= \frac{P_X'^x \cdot P_Y'^y}{P_A'^a \cdot P_B'^b} \times \frac{\left(\frac{1}{RT}\right)^x \left(\frac{1}{RT}\right)^y}{\left(\frac{1}{RT}\right)^a \left(\frac{1}{RT}\right)^b} = K_p \left(\frac{1}{RT}\right)^{(x+y)-(a+b)}$$

$(x + y) - (a + b) = \Delta n_g$ (difference in number of moles of gaseous products and reactants)

$$\therefore K_c = K_p \left(\frac{1}{RT} \right)^{\Delta n_g}$$

or $K_p = K_c (RT)^{\Delta n_g}$

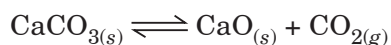
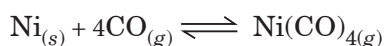
If $\Delta n_g = 0$, $K_p = K_c$

If $\Delta n_g = +ve$, $K_p > K_c$

If $\Delta n_g = -ve$, $K_p < K_c$

► **Heterogeneous equilibrium :**

Equilibrium is said to be heterogeneous if reactants and products are in different phases, e.g.,



► **Units of equilibrium constant :**

Concentration of a substance is measured in terms of moles/litre, therefore, unit of K_c is $(\text{mol L}^{-1})^{\Delta n_g}$. Similarly, partial pressure is measured in terms of atmosphere, hence, unit of K_p is $(\text{atm})^{\Delta n_g}$

- If $\Delta n = 0$, both K_c and K_p have no units

- If $\Delta n > 0$, unit of $K_c = (\text{mol L}^{-1})^{\Delta n_g}$, unit of $K_p = (\text{atm})^{\Delta n_g}$

- If $\Delta n < 0$, unit of $K_c = (\text{L mol}^{-1})^{\Delta n_g}$, unit of $K_p = (\text{atm}^{-1})^{\Delta n_g}$

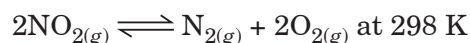
► Equilibrium constants can also be expressed as dimensionless quantities if the standard states of reactants and products are specified.

• **Applications of equilibrium constant :**

► **Predicting the extent of a reaction :**

The magnitude of equilibrium constant K indicates the extent to which a reaction can go. In other words, it is a measure of the completion of a reversible reaction. Larger the value of K , greater will be the equilibrium concentration of the components on the right hand side of reaction relative to those on the left hand side, i.e., the reaction proceeds to a greater extent.

For example, consider the reaction :



$$K = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2} = 6.7 \times 10^{-16}$$

The value of K is very small which means that the forward reaction has proceeded to

small extent only. Thus we can say that NO_2 is quite stable and decomposes only slightly.

► **Predicting the direction of a reaction :**

The equilibrium constant helps in predicting the direction in which a reaction can proceed at any stage. By substituting the concentration of substances that exist in a reaction mixture we can calculate the reaction quotient, Q and comparing the value of Q with the equilibrium constant, K , we can predict whether the reaction will proceed towards products or towards reactants.

Case I : If $Q < K$, the reaction will proceed in the forward direction.

Case II : If $Q > K$, the reaction will proceed in the backward direction.

Case III : If $Q = K$, the reaction mixture is already at equilibrium.

• **Relation between equilibrium constant (K) and ΔG° :**

► Free energy change (ΔG) is related to ΔG° as follows, $\Delta G = \Delta G^\circ + 2.303 RT \log Q$

But at equilibrium, $Q = K$ and $\Delta G = 0$

$$\therefore \Delta G = -2.303 RT \log K$$

If $K > 1$, then $\Delta G = -ve$, i.e., reaction is spontaneous in forward direction.

If $K < 1$, then $\Delta G = +ve$, i.e., reaction is spontaneous in backward direction.

► **Le Chatelier's principle :** The law states that if any kind of change in concentration, temperature or pressure is imposed on the system in equilibrium, then equilibrium shifts in a direction that tends to undo the effect of the change imposed.

► **Effect of change in concentration :** In a reaction at equilibrium, if concentration of any reactant or product is increased, the equilibrium shifts in a direction where it will be consumed or if concentration of any reactant or product is decreased, the equilibrium will shift in a direction where it will be produced.

► **Effect of change in temperature :** In a reaction at equilibrium if temperature is increased, reaction will proceed in the direction in which some heat can be destroyed i.e., absorbed so that

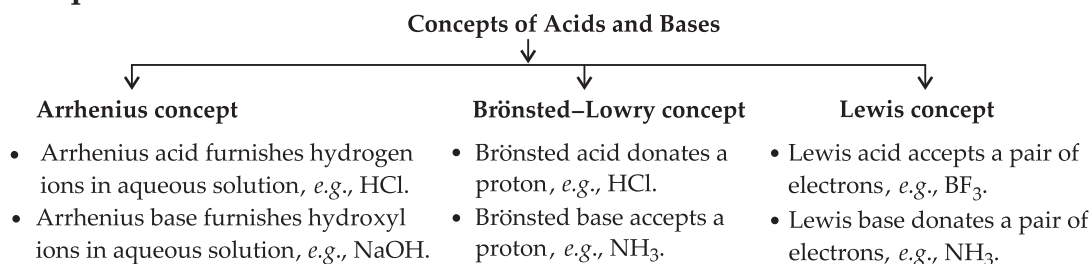
temperature of the system remains constant. It means increase in temperature supports the endothermic reaction, where heat is absorbed. Decrease in temperature favours exothermic reaction in which heat is liberated.

- ▶ **Effect of change in pressure :** In a reaction at equilibrium if pressure is increased, then according to Le Chatelier's principle, the equilibrium will shift in a direction in which the pressure decreases. This implies that equilibrium will shift in a direction which produces smaller number of moles, since pressure is directly proportional to the number of moles. On the other hand we can say that if the pressure on the system in equilibrium is decreased, the equilibrium will shift in the direction in which it is accompanied by increase in total number of moles.
- ▶ **Effect of catalyst :** Catalyst increases the speed of forward as well as backward reaction to the same extent. Therefore, it does not affect the equilibrium position. It only helps in attaining the equilibrium state quickly without shifting it in any direction.
- ▶ **Effect of adding inert gas :**
 - If inert gas is added at constant volume to the reaction at equilibrium, the equilibrium will not be changed/ disturbed, because at constant volume addition of an inert gas will not change the molar concentration of the reactants and products.
 - If inert gas is added at constant pressure to the reaction at equilibrium, the volume of reaction mixture increases and equilibrium will shift in the direction in which there is increase in the number of moles of the gas. If

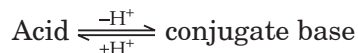
number of moles on either side of equilibrium are same, there will be no effect of adding an inert gas on the state of equilibrium.

- **Application of Le Chatelier's principle to chemical equilibria :**
 - For reaction, $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$; $\Delta H = +ve$
 - **Effect of change in temperature :** The dissociation of PCl_5 is endothermic. Hence increase of temperature increases the rate of formation of PCl_3 and Cl_2 .
 - **Effect of change in pressure :** Increase of pressure will favour the backward direction, with decrease in the number of gaseous moles.
 - **Effect of change in concentration :** Addition of PCl_3 or Cl_2 or removal of PCl_5 will shift the equilibrium in backward direction.
 - **Effect of adding an inert gas :** In above reaction, $n_p > n_r$, addition of an inert gas has no effect at constant volume but, at constant pressure, the equilibrium shifts in the forward direction.
 - For reaction, $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$; $\Delta H = +ve$
 - **Effect of change in temperature :** The dissociation of HI is an endothermic reaction hence increase of temperature favours the formation of H_2 and I_2 .
 - **Effect of change in pressure :** As the number of reactant molecules is equal to the number of product molecules, hence pressure has no effect on the equilibrium.
 - **Effect of change in concentration :** Addition of HI or removal of H_2 or I_2 favours the forward reaction.

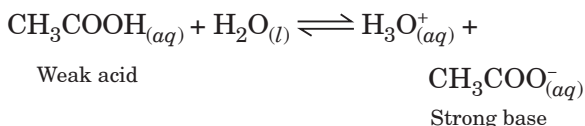
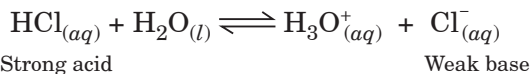
● Ionic Equilibrium :



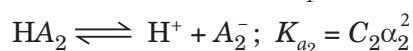
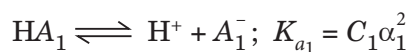
- **Conjugate acid - base pairs :** These are pairs of acids and bases which differ by a proton, *e.g.*,



- Relative strengths of conjugate acids or bases depend upon their tendency to donate a proton or to accept a proton.
- Stronger the acid, weaker is its conjugate base and vice-versa, *e.g.*,



- **Relative strength of acids and bases :** This is the ratio of strengths of acids. *e.g.*, for acids HA_1 and HA_2 :



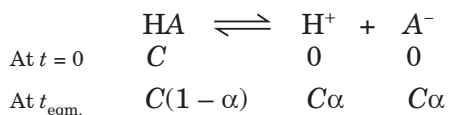
Relative strength

$$\begin{aligned} &= \frac{[\text{H}^+] \text{ furnished by HA}_1}{[\text{H}^+] \text{ furnished by HA}_2} = \frac{C_1\alpha_1}{C_2\alpha_2} \\ & \quad (\because \alpha = \sqrt{K_a/C}) \\ &= \frac{C_1\sqrt{K_{a1}/C_1}}{C_2\sqrt{K_{a2}/C_2}} = \sqrt{(K_{a1}C_1)/(K_{a2}C_2)} \end{aligned}$$

If concentrations of acids are same, then

$$\text{Relative strength} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

- **Dissociation constant of weak acids and weak bases :** Let us consider the dissociation of a weak acid HA as,



Dissociation constant of acid,

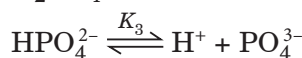
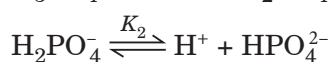
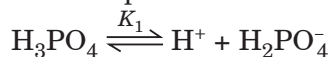
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

Similarly, for the dissociation of a weak base BOH as $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$

Dissociation constant of base,

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{C\alpha^2}{(1 - \alpha)}$$

- **Dissociation constant for polyprotic acids and bases :** These acids involve number of steps to ionise completely, where number of steps is equal to the number of replaceable hydrogen atoms. The value of ionisation constant of each step is definite and constant *e.g.*,



The overall dissociation constant (K) is given as $K = K_1 \times K_2 \times K_3$ where $K_1 > K_2 > K_3$.

- **pH and pH-scale :** pH of a solution is defined as the negative logarithm of hydrogen ion concentration.

$$\text{pH} = -\log [\text{H}^+] \text{ or } \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{or } \text{pH} = \log \frac{1}{[\text{H}^+]}$$

Similarly, negative logarithm of hydroxyl ion concentration is called pOH.

$$\text{pOH} = -\log [\text{OH}^-] \text{ or } \text{pOH} = \log \frac{1}{[\text{OH}^-]}$$

- **pH-scale :** A solution is classified as acidic, basic or neutral based on its pH value.

- If $\text{pH} = \text{pOH} = 7$, then solution will be neutral.
- If $\text{pH} < 7$ or $\text{pOH} > 7$, then solution will be acidic.
- If $\text{pH} > 7$ or $\text{pOH} < 7$, then solution will be basic.
- pH scale varies from 0 to 14.

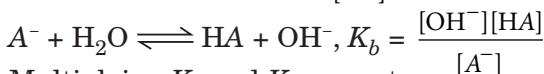
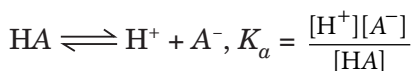
- **Relationship between pH and pOH**

$$\text{pH} + \text{pOH} = 14 \text{ and } \text{pH} + \text{pOH} = \text{p}K_w$$

- **Relation between K_a and K_b :** If K_a and K_b are the dissociation constants of weak acid and weak base respectively then,

$$\text{p}K_a = -\log K_a \text{ and } \text{p}K_b = -\log K_b$$

Consider a weak acid, HA



Multiplying K_a and K_b , we get

$$K_a \times K_b = [\text{H}^+][\text{OH}^-]$$

But $[H^+][OH^-] = K_w$

$$\therefore K_a \times K_b = K_w$$

Taking log on both sides, we get

$$\log K_a + \log K_b = \log K_w$$

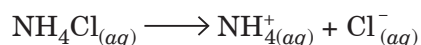
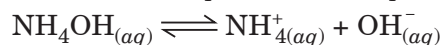
$$\text{or } -\log K_a - \log K_b = -\log K_w$$

$$pK_a + pK_b = pK_w$$

- **Common ion effect in the ionisation of acids and bases :** There exists a dynamic equilibrium between unionised molecule and ions of a weak electrolyte : $AB \rightleftharpoons A^+ + B^-$

► To this equilibrium if a solution of a strong electrolyte (AX or YB) is mixed, due to the presence of a common ion, either A^+ or B^- , the degree of dissociation is suppressed in both the cases.

► The decrease in dissociation is much more in case of weak electrolytes, e.g., if a solution of NH_4OH some NH_4Cl is added,



NH_4Cl ionises almost completely leading to a high concentration of NH_4^+ (common ion).

According to Le Chatelier's principle, the dissociation of NH_4OH is suppressed.

- Thus, *common ion effect* can be defined as the suppression of the degree of ionisation of a weak electrolyte by the addition of a strong electrolyte having an ion common with the weak electrolyte.

- **Buffer solutions :** *Buffer solution* is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for a long time.

Buffers are classified into two categories :

- **Simple buffers :** These are the solutions of salt of weak acid and weak base. For example, CH_3COONH_4 (ammonium acetate).
- **Mixed buffers :** These are the mixture of two solutions. These are further of two types :

- **Acidic buffers :** These are the solutions of a mixture of weak acid and salt of this weak acid with strong base.
- For example, $CH_3COOH + CH_3COONa$. They have pH value lesser than 7.
- **Basic buffers :** These are the solutions of mixture of a weak base and salt of this weak base with strong acid. For example, $NH_4OH + NH_4Cl$. They have the pH value more than 7.

- **Solubility product :** *Solubility product* of an electrolyte at a specified temperature may be defined on the product of the molar concentrations of its ions in a saturated solution, each concentration raised to the power equal to the number of ion produced on dissociation of one molecule of electrolyte.

Salt type	Relation between K_{sp} and S	Examples
AB_2	$K_{sp} = (S)(2S)^2 = 4S^3$	$PbCl_2, HgCl_2$
A_2B	$K_{sp} = (2S)^2(S) = 4S^3$	$Ag_2CrO_4,$ $Ag_2C_2O_4,$ Ag_2SO_4
AB_3	$K_{sp} = (S)(3S)^3 = 27S^4$	$Fe(OH)_3,$ $Al(OH)_3,$ $Cr(OH)_3$
A_3B_2	$K_{sp} = (3S)^3(2S)^2$ $= 108S^5$	$Ca_3(PO_4)_2,$ $Zn_3(PO_4)_2$
AB	$K_{sp} = (S)(S) = S^2$	$AlPO_4, AgCl,$ $AgBr, PbSO_4,$ $BaSO_4, ZnS$

- **Effect of common ion on solubility :** Addition of a common ion lowers the solubility of a sparingly soluble salt. Let S be the solubility of a salt $AgCl$ in pure water and suppose x g equivalent of $NaCl$ is added to a litre of the saturated solution. Suppose the solubility of $AgCl$ becomes S' .

$$K_{sp} = [Ag^+][Cl^-] = S'(S' + x)$$

When the addition of a common ion or an inert salt leads to a considerable increase in the solubility of a salt, then it can be concluded that a complex ion has been formed.



OBJECTIVE TYPE QUESTIONS

➔ Multiple Choice Questions (MCQs)

- For the following three reactions (i), (ii) and (iii), equilibrium constants are given
 (i) $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_2_{(g)}$; K_1
 (ii) $\text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{(g)} + 3\text{H}_{2(g)}$; K_2
 (iii) $\text{CH}_{4(g)} + 2\text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + 4\text{H}_{2(g)}$; K_3
 Which of the following relations is correct?
 (a) $K_3 K_2^3 = K_1^2$ (b) $K_1 \sqrt{K_2} = K_3$
 (c) $K_2 K_3 = K_1$ (d) $K_3 = K_1 K_2$
- If K_1 and K_2 are the respective equilibrium constants for the two reactions,
 $\text{XeF}_{6(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{XeOF}_{4(g)} + 2\text{HF}_{(g)}$
 $\text{XeO}_{4(g)} + \text{XeF}_{6(g)} \rightleftharpoons \text{XeOF}_{4(g)} + \text{XeO}_3\text{F}_{2(g)}$
 The equilibrium constant for the reaction,
 $\text{XeO}_{4(g)} + 2\text{HF}_{(g)} \rightleftharpoons \text{XeO}_3\text{F}_{2(g)} + \text{H}_2\text{O}_{(g)}$ is
 (a) $K_1 K_2$ (b) K_1 / K_2^2
 (c) K_2 / K_1 (d) K_1 / K_2
- For the reversible reaction,
 $\text{A}_{(s)} + \text{B}_{(g)} \rightleftharpoons \text{C}_{(g)} + \text{D}_{(g)}$, $\Delta G^\circ = -350 \text{ kJ}$,
 which one of the following statements is true?
 (a) The reaction is thermodynamically nonfeasible.
 (b) The entropy change is negative.
 (c) Equilibrium constant is greater than one.
 (d) The reaction should be instantaneous.
- In a chemical equilibrium the rate constant of backward reaction is 3.2×10^{-2} and the equilibrium constant is 2^{-5} . The rate constant of forward reaction is
 (a) 1×10^{-3} (b) 2×10^{-2}
 (c) 8×10^{-2} (d) 4×10^{-2}
- It is not possible to attain equilibrium in
 (a) closed system (b) isolated system
 (c) open system (d) none of these.
- Conjugate base for Bronsted acids H_2O and HF are
 (a) H_3O^+ and H_2F^+ , respectively
 (b) OH^- and H_2F^+ , respectively
 (c) H_3O^+ and F^- , respectively
 (d) OH^- and F^- , respectively.
- For the reaction $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$ at 300 K, the value of ΔG is $-690.9 R$. The equilibrium constant value for the reaction at that temperature is (R is gas constant)
 (a) 10 atm^{-1} (b) 10 atm
 (c) 10 (d) 1
- The solubility product of aluminium sulphate is given by the expression
 (a) $4s^3$ (b) $6912s^7$
 (c) s^2 (d) $108s^5$
- In a reversible chemical reaction at equilibrium, if the concentration of any one of the reactants is doubled, then the equilibrium constant will
 (a) also be doubled (b) be halved
 (c) remain the same (d) become one-fourth.
- Identify a species which is 'NOT' a Bronsted acid but a Lewis acid.
 (a) BF_3 (b) H_3O^+
 (c) NH_3 (d) HCl
- For the system $3\text{A} + 2\text{B} \rightleftharpoons \text{C}$, the expression for equilibrium constant K is
 (a) $\frac{[3\text{A}] \times [2\text{B}]}{[\text{C}]}$ (b) $\frac{[\text{A}]^3 \times [\text{B}]}{[\text{C}]}$
 (c) $\frac{\text{C}}{[\text{A}]^3 \times [\text{B}]^2}$ (d) $\frac{[\text{C}]}{[3\text{A}] \times [2\text{B}]}$
- Among the following, the one which can act as both Bronsted acid as well as Bronsted base is
 (a) H_3PO_4 (b) AlCl_3
 (c) CH_3COO^- (d) H_2O
- The solubility of $\text{Ca}_3(\text{PO}_4)_2$ in water is y moles/litre. Its solubility product is
 (a) $6y^4$ (b) $36y^4$
 (c) $64y^5$ (d) $108y^5$
- Which of the following is not a characteristic of equilibrium?
 (a) Rate is equal in both directions.
 (b) Measurable quantities are constant at equilibrium.

- (c) Equilibrium occurs in reversible condition.
 (d) Equilibrium occurs only in an open vessel at constant temperature

15. When the rate of formation of reactants is equal to the rate of formation of products, this is known as,

- (a) chemical reaction
 (b) chemical equilibrium
 (c) chemical kinetics
 (d) none of these.

16. Which of the following options will be correct for the stage of half completion of the reaction $X \rightleftharpoons Y$.

- (a) $\Delta G^\circ = 0$ (b) $\Delta G^\circ > 0$
 (c) $\Delta G^\circ < 0$ (d) $\Delta G^\circ = -RT \ln 2$

17. In Bronsted–Lowry concept of acid-base, H^+ donor is a/an

- (a) acid
 (b) basic
 (c) exclusively amphoteric substance
 (d) hydroxide acceptor.

18. In HS^- , I^- , $R - NH_2$, NH_3 order of proton accepting tendency will be

- (a) $I^- > NH_3 > R - NH_2 > HS^-$
 (b) $NH_3 > R - NH_2 > HS^- > I^-$
 (c) $R - NH_2 > NH_3 > HS^- > I^-$
 (d) $HS^- > R - NH_2 > NH_3 > I^-$

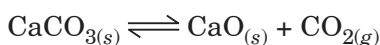
19. Equilibrium constants are given for the following reactions. Out of the following, which is farthest towards completion?

- (a) $K = 100$ (b) $K = 0.1$
 (c) $K = 0.01$ (d) $K = 1$

20. Of the following the incorrect relation is

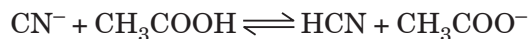
- (a) $\Delta G = \Delta G^\circ + RT \ln K$ (b) $\Delta G^\circ = -RT \ln K$
 (c) $\Delta G^\circ = \Delta G + RT \ln K$ (d) $K = e^{-\Delta G / RT}$

21. Calculate K_c for the reversible process given below if $K_p = 167$ and $T = 800^\circ C$.



- (a) 1.95 (b) 1.85
 (c) 1.89 (d) 1.60

22. The dissociation constants for acetic acid and HCN at $25^\circ C$ are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium,



would be

- (a) 3.0×10^{-5} (b) 3.0×10^{-4}
 (c) 3.0×10^4 (d) 3.0×10^5

23. What will be the solubility product of AX_3 ?

- (a) $27S^4$ (b) $4S^3$
 (c) $36S^4$ (d) $9S^3$

24. Which of the following is a characteristic of reversible reaction?

- (a) It never proceeds to completion.
 (b) It can be influenced by a catalyst.
 (c) It proceeds only in the forward direction.
 (d) Number of moles of reactants and products are equal.

25. For the reaction, $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$,

if $K_p = K_c(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality)

- (a) 1 (b) -1
 (c) $-\frac{1}{2}$ (d) $\frac{1}{2}$

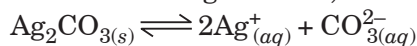
26. Which of these is least likely to act as a Lewis base?

- (a) BF_3 (b) PF_3
 (c) CO (d) F^-

27. Which of the following solutions will have pH close to 1.0?

- (a) 100 mL of M/10 HCl + 100 mL of M/10 NaOH
 (b) 55 mL of M/10 HCl + 45 mL of M/10 NaOH
 (c) 10 mL of M/10 HCl + 90 mL of M/10 NaOH
 (d) 75 mL of M/10 HCl + 25 mL of M/10 NaOH

28. Using the Gibbs' energy change, $\Delta G = +63.3$ kJ, for the following reaction,

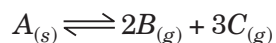


the K_{sp} of $Ag_2CO_{3(s)}$ in water at $25^\circ C$ is

$$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

- (a) 3.2×10^{-26} (b) 8.0×10^{-12}
 (c) 2.9×10^{-3} (d) 7.9×10^{-2}

29. Consider the general hypothetical reaction,



If the concentration of C at equilibrium is doubled, then after the equilibrium is re-established, the concentration of B will be

- (a) two times the original value
 (b) one half of its original value
 (c) $1/2\sqrt{2}$ times the original value
 (d) $2\sqrt{2}$ times the original value.

30. The pH of 10^{-4} M KOH solution will be

- (a) 4 (b) 11
(c) 10.5 (d) 10

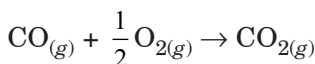
31. If the pH increases from 5 to 7, then acidic strength decreases _____ times.

- (a) 2 (b) 20
(c) 10 (d) 100

32. The reaction quotient, Q_c is useful in predicting the direction of the reaction. Which of the following is incorrect?

- (a) If $Q_c > K_c$, net reaction goes from right to left.
(b) If $Q_c < K_c$, net reaction goes from left to right.
(c) If $Q_c = K_c$, no net reaction occurs.
(d) If $Q_c > K_c$, net reaction goes from left to right.

33. $\frac{K_p}{K_c}$ for following reaction will be



- (a) RT (b) $\frac{1}{RT}$
(c) $\frac{1}{\sqrt{RT}}$ (d) $\frac{RT}{2}$

34. Buffer solutions have constant acidity and alkalinity because

- (a) these give unionised acid or base on reaction with added acid or alkali
(b) acids and alkalies in these solutions are shielded from attack by other ions
(c) they have large excess of H^+ or OH^- ions
(d) they have fixed value of pH.

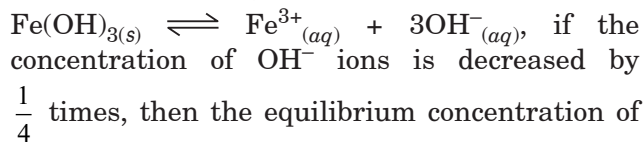
35. The equilibrium constant, K_p for the reaction,



The pressure at which PCl_5 will be 50% dissociated at 200°C is

- (a) 3.2 atm (b) 4.8 atm
(c) 2.4 atm (d) 6.4 atm

36. In the reaction;



- (a) 8 times (b) 16 times
(c) 64 times (d) 4 times.

37. The value of ΔH for the reaction



Formation of $\text{XY}_{4(g)}$ will be favoured at

- (a) high temperature and high pressure
(b) low pressure and low temperature
(c) high temperature and low pressure
(d) high pressure and low temperature.

38. In which of the following equilibrium K_c and K_p are not equal?

- (a) $2\text{NO}_{(g)} \rightleftharpoons \text{N}_{2(g)} + \text{O}_{2(g)}$
(b) $\text{SO}_{2(g)} + \text{NO}_{2(g)} \rightleftharpoons \text{SO}_{3(g)} + \text{NO}_{(g)}$
(c) $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$
(d) $2\text{C}_{(s)} + \text{O}_{2(g)} \rightleftharpoons 2\text{CO}_{2(g)}$

39. Which will make basic buffer?

- (a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
(b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
(c) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
(d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH

40. 4 moles of A are mixed with 4 moles of B, when 2 moles of C and D are formed at equilibrium according to the reaction,



the value of equilibrium constant is

- (a) 4 (b) 1
(c) 1/2 (d) 1/4



Case Based MCQs

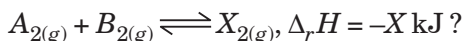
Case I : Read the passage given below and answer the following questions from 41 to 45.

Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of change on a system at chemical equilibrium.

This principle states that equilibrium adjust the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factor like concentration, pressure, temperature, inert gas that affect

equilibrium are changed, the equilibrium will shift in that direction where the effects that caused by these changes are nullified. This principle is also used to manipulate reversible reaction in order to obtain suitable outcomes.

41. Which one of the following conditions will favour maximum formation of the product in the reaction

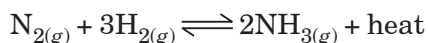


- Low temperature and high pressure
- Low temperature and low pressure
- High temperature and high pressure
- High temperature and low pressure

42. In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?

- $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
- $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
- $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

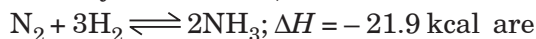
43. For the reversible reaction,



The equilibrium shifts in forward direction

- by increasing the concentration of $NH_{3(g)}$
- by decreasing the pressure
- by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$
- by increasing pressure and decreasing temperature.

44. Favourable conditions for manufacture of ammonia by the reaction,



- low temperature, low pressure and catalyst
- low temperature, high pressure and catalyst
- high temperature, low pressure and catalyst
- high temperature, high pressure and catalyst.

45. $X + Y \rightleftharpoons P + Q$

For the above equilibrium, the reactant concentration is doubled, what would happen then to equilibrium constant?

- Remains constant
- Be doubled
- Be halved
- Cannot be predicted

Case II : Read the passage given below and answer the following questions from 46 to 50.

Reactants and products coexist at equilibrium, so that the conversion of reactant to products is always less than 100%. Equilibrium reaction may involve the decomposition of a covalent (non-polar) reactant or ionization of ionic compound into their ions in polar solvents. Ostwald dilution law is the application of the law of mass action to the weak electrolytes in solution.

A binary electrolyte AB which dissociates into A^+ and B^- ions i.e.



for every weak electrolyte, Since $\alpha \ll 1$

$$(1 - \alpha) = 1$$

$$K = C \alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha = \sqrt{KV}.$$

46. A monobasic weak acid solution has a molarity of 0.005M and pH of 5. What is its percentage ionization in this solution?

- 2.0
- 0.2
- 0.5
- 0.25

47. Calculate ionisation constant for pyridinium hydrogen chloride. (Given that H^+ ion concentration is 3.6×10^{-4} M and its concentration is 0.02 M.)

- 6.48×10^{-2}
- 6×10^{-6}
- 1.5×10^{-9}
- 12×10^{-8}

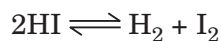
48. The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is

- 9.525×10^{-8} M
- 1.0×10^{-8} M
- 1.0×10^{-6} M
- 1.0525×10^{-7} M

49. Ostwald dilution law is applicable to

- weak electrolytes
- non-electrolyte
- strong electrolyte
- all type of electrolyte.

50. If α is the fraction of HI dissociated at equilibrium in the reaction :



then starting with 2 mol of HI, the total number of moles of reactants and products at equilibrium are

- 1
- 2
- $1 + \alpha$
- $2 + 2\alpha$

➡ Assertion & Reasoning Based MCQs

For question numbers 51-60, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

51. Assertion : At 25°C the pH of 10⁻⁷ M HCl is 6.69.

Reason : pH of acidic solution is always below 7 at 25°C.

52. Assertion : The value of K_w at 25°C is $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$.

Reason : K_w of water changes with change in temperature.

53. Assertion : K_p can be equal to, less than or greater than the value of K_c .

Reason : $K_p = K_c(RT)^{\Delta n}$ where Δn is the change in the number of moles of gaseous reactants and products.

54. Assertion : The active mass of pure solid is taken unity.

Reason : The active mass of pure solids depends on density and molecular mass. The density and molecular mass of pure solids are constant.

55. Assertion : H₃PO₄ is a stronger acid than H₂PO₄⁻

Reason : pK_{a_1} is greater than pK_{a_2} for H₃PO₄.

56. Assertion : For the equilibrium mixture $\text{CO}_{(g)} + 3\text{H}_{2(g)} \rightleftharpoons \text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)}$ if the volume is decreased, reaction proceeds in the forward direction.

Reason : For the methanation reaction (above), decrease in volume causes $Q_c > K_c$.

57. Assertion : At constant temperature, the pressure of the gas is proportional to its concentration.

Reason : $K_p = K_c$ for all reactions.

58. Assertion : For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason : Equilibrium constant is independent of temperature.

59. Assertion : On dilution, the solubility of BaSO₄ increases.

Reason : On dilution, K_{sp} increases.

60. Assertion : The equilibrium constant does not change on addition of catalyst.

Reason : A catalyst provides an alternative path of lower activation energy for conversion of reactants to products.

SUBJECTIVE TYPE QUESTIONS

➡ Very Short Answer Type Questions (VSA)

1. A mixture of 1.57 mol of N₂, 1.92 mol of H₂ and 8.13 mol of NH₃ is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$ is 1.7×10^2 . Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

2. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression.

3. Conjugate acid of a weak base is always stronger. What will be the decreasing order of

basic strength of the following conjugate bases?

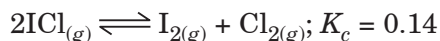


4. Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base : (a) OH⁻ (b) F⁻ (c) H⁺ (d) BCl₃.

5. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

6. Give two important characteristics of chemical equilibrium.

7. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?



8. Give relation between $[A]$ and $[B]$ for

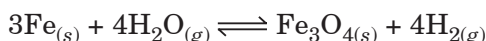
the stage of half completion of the reaction $A \rightleftharpoons B$.

9. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ions in it.

Short Answer Type Questions (SA-I)

10. Equilibrium constant for a reaction is 10. What will be the equilibrium constant for the reverse reaction?

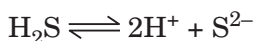
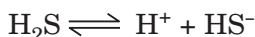
11. Write the expression for the equilibrium constant K_c for the following equilibrium :



12. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant K is?

13. Differentiate between homogeneous and heterogeneous equilibrium giving examples.

14. K_{a_1} , K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.



The correct relationship between K_{a_1} , K_{a_2} and K_{a_3} is

15. Write expressions for K_p and K_c for the decomposition reaction of calcium carbonate.

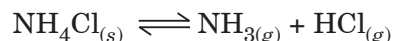
16. The ionization constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4} , 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

17. Write the relation between Q_c and K_c for reverse reaction.

18. We know that the relationship between K_c and K_p is

$$K_p = K_c(RT)^{\Delta n}$$

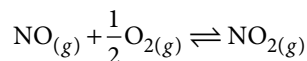
What would be the value of Δn for the reaction



19. What will be the conjugate bases for the Bronsted acids: HF, H_2SO_4 and HCO_3^- ?

Short Answer Type Questions (SA-II)

20. Calculate (a) ΔG and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K.



$$\text{where } \Delta_f G^\circ(\text{NO}_2) = 52.0 \text{ kJ mol}^{-1},$$

$$\Delta_f G^\circ(\text{NO}) = 87.0 \text{ kJ mol}^{-1},$$

$$\Delta_f G^\circ(\text{O}_2) = 0 \text{ kJ mol}^{-1}$$

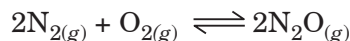
21. What will be the correct order of vapour pressure of water, acetone and ether at 30°C? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

22. In 1 L saturated solution of AgCl

$$[K_{sp} = 1.6 \times 10^{10}], 0.1 \text{ mol of CuCl}$$

$[K_{sp} = 1.0 \times 10^{-6}]$ is added. Find out the resultant concentration of Ag^+ in the solution.

23. Reaction between N_2 and O_2 takes place as follows :



If a mixture of 0.482 mol of N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

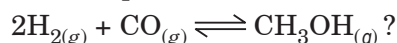
24. Equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? (For copper iodate, $K_{sp} = 7.4 \times 10^{-8}$)

25. Define Le-Chatelier's Principle. What is the effect of :

(i) addition of H_2

(ii) removal of CO

on the equilibrium :



26. The value of ΔG° for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K.

27. For the reaction,



predict the direction of the reaction when

- pressure is doubled
- temperature is doubled.

28. What is the effect of increase of temperature on the pH of a buffer solution?

29. Equilibrium constant, K_c for the reaction,



At a particular time, the analysis shows that composition of the reaction mixture is $3.0 \text{ mol L}^{-1} \text{ N}_2$, $2.0 \text{ mol L}^{-1} \text{ H}_2$ and $0.5 \text{ mol L}^{-1} \text{ NH}_3$. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

30. (i) Define Lewis acids and bases with example.

(ii) The value of K_{sp} of two sparingly soluble salts $\text{Ni}(\text{OH})_2$ and AgCN are 2×10^{-15} and 6×10^{-17} . Which salt is more soluble and why?

31. Which of the following combinations would result in the formation of a buffer solution?

- $\text{NH}_4\text{Cl} + \text{NH}_3$
- $\text{CH}_3\text{COOH} + \text{HCl}$

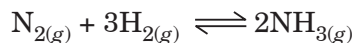
(iii) $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$

(iv) $\text{NH}_3 + \text{HCl}$ in the molar ratio of 2 : 1

(v) $\text{HCl} + \text{NaOH}$

32. A sparingly soluble salt having general formula $A_x^{p+}B_y^{q-}$ and molar solubility S is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

33. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.



What will be the effect on K_c if the total pressure at which the equilibrium is established, is increased without changing the temperature?

34. The solubility product of AgCl is 1.5×10^{-10} . Predict whether there will be any precipitation by mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M AgNO_3 solution.

35. What is the pH of 0.001 M aniline solution? The ionisation constant of aniline is 4.27×10^{-10} . Calculate the degree of ionisation of aniline in the solution. Also calculate the ionisation constant of the conjugate acid of aniline.

➡ Long Answer Type Questions (LA)

36. (i) Point out the differences between ionic product and solubility product.

(ii) The solubility of AgCl in water at 298 K is 1.06×10^{-5} mole per litre. Calculate its solubility product at this temperature.

37. (i) Derive the relationship between $\text{p}K_w$, pH and pOH starting from ionisation constant of water, K_w . What is the numerical value of $\text{p}K_w$ at 298 K?

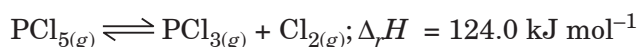
(ii) If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of K^+ and OH^- . What is its pH? (Give atomic masses $\text{K} = 39$, $\text{O} = 16$, $\text{H} = 1$)

38. (i) What is common ion effect?

(ii) Write the K_{sp} expressions for Ag_2CrO_4 and zirconium phosphate.

(iii) Calculate the pH of 0.005 M HCl solution.

39. At 473 K, equilibrium constant, K_c for decomposition of PCl_5 is 8.3×10^{-3} . If decomposition is depicted as :



(a) Write an expression for K_c for the reaction.

(b) What is the value of K_c for the reverse reaction at same temperature?

(c) What would be the effect on K_c if

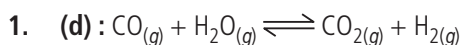
- the pressure is increased
- the temperature is increased?

40. One mole of N_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 227°C . The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction

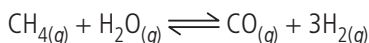


ANSWERS

OBJECTIVE TYPE QUESTIONS



$$K_1 = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} \quad \dots(\text{i})$$

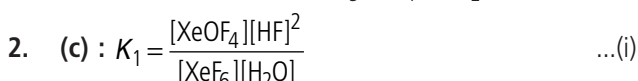


$$K_2 = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} \quad \dots(\text{ii})$$



$$K_3 = \frac{[\text{CO}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{O}]^2} \quad \dots(\text{iii})$$

From equations (i), (ii) and (iii) ; $K_3 = K_1 \times K_2$

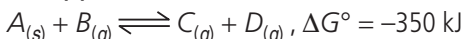


$$K_2 = \frac{[\text{XeOF}_4][\text{XeO}_3\text{F}_2]}{[\text{XeO}_4][\text{XeF}_6]} \quad \dots(\text{ii})$$

Dividing Eq. (ii) by (i) we have,

$$\frac{K_2}{K_1} = \frac{[\text{XeO}_3\text{F}_2][\text{H}_2\text{O}]}{[\text{XeO}_4][\text{HF}]^2} = K'$$

3. (c) : For a reversible reaction,



Standard free energy change can be thermodynamically calculated as,

when $\Delta G^\circ < 0$, i.e., negative, then $K_c > 1$. In this case forward reaction is feasible. The reaction is spontaneous reaction.

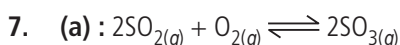
4. (a) : In a chemical equilibrium
Equilibrium constant,

$$K = \frac{\text{Rate constant of forward reaction, } k_f}{\text{Rate constant of backward reaction, } k_b}$$

$$\therefore k_f = k_b \times K = 3.2 \times 10^{-2} \times 2^{-5} = \frac{3.2 \times 10^{-2}}{32} = 1 \times 10^{-3}$$

5. (c) : In open system equilibrium cannot be attained.

6. (d) : Bronsted acid Conjugate base

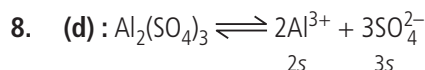


$$\Delta G = -RT \ln K \Rightarrow -690.9 R = -RT \ln K \text{ or } \frac{690.9}{300} = \ln K$$

$$2.303 = \ln K \Rightarrow 2.303 = 2.303 \log K, K = 10^1$$

$$K_p = \frac{p_{\text{SO}_3}^2}{p_{\text{SO}_2}^2 \times p_{\text{O}_2}} \times \frac{\text{atm}^2}{\text{atm}^3} = \text{atm}^{-1}$$

$$\therefore K_p = 10 \text{ atm}^{-1}$$



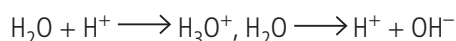
$$K_{sp} = (2s)^2 (3s)^3 = 4 \times 27s^5 = 108s^5$$

9. (c) : Equilibrium constant depends only on temperature.

10. (a) : Molecules having a central atom with incomplete octet, act as a Lewis acid not Brønsted acid (proton donor). In BF_3 , B is having six electrons.

11. (c) : $K = \frac{[\text{C}]}{[\text{A}]^3[\text{B}]^2}$

12. (d) : H_2O can accept or give a proton hence, it acts both as Bronsted acid as well as Bronsted base.



13. (d) : $\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$
Concentrations of various species at equilibrium

$$\text{Ca}^{2+} = 3y, \text{PO}_4^{3-} = 2y$$

$$\text{Solubility product} = (3y)^3 (2y)^2 = 27y^3 \times 4y^2 = 108y^5$$

14. (d) : Equilibrium state can only be achieved if a reversible reaction is carried out in a closed vessel.

15. (b) : At equilibrium, rate of forward reaction is equal to rate of backward reaction.



$$\Delta G^\circ = -RT \ln K$$

At the stage of half completion of reaction $[X] = [Y]$.

Therefore, $K = 1$. Thus, $\Delta G^\circ = 0$.

17. (a)

18. (c) : Proton accepting tendency is known as the strength of basicity.

In $R-\ddot{\text{N}}\text{H}_2$, N has lone pair of electrons which intensify due to electron releasing R group and increase the tendency to donate lone pair of electrons to H^+ .

Secondly, as the size of the ion increases there is less attraction for H^+ to form weaker bonds with H – atom and are less basic. The order of the given series is: $\text{RNH}_2 > \text{NH}_3 > \text{HS}^- > \text{I}^-$.

19. (a) : Higher the value of equilibrium constant, the reaction is farther towards completion.

20. (c) : $\Delta G = \Delta G^\circ + RT \ln K$

at equilibrium $\Delta G = 0$

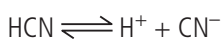
$$\Delta G^\circ = -RT \ln K \text{ and } K = e^{-\Delta G^\circ/RT}$$

21. (c) : $K_p = K_c(RT)^{\Delta n}$; $\Delta n = n_p - n_r = 1$

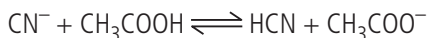
$$K_p = K_c(0.0821 \times 1073) \Rightarrow K_c = \frac{167}{0.0821 \times 1073} = 1.891$$



$$K_1 = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1.5 \times 10^{-5}$$

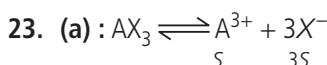


$$K_2 = \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = 4.5 \times 10^{-10}$$



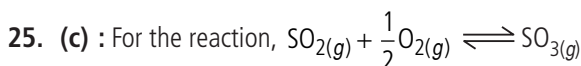
$$K = \frac{[\text{HCN}][\text{CH}_3\text{COO}^-]}{[\text{CN}^-][\text{CH}_3\text{COOH}]}$$

$$K = \frac{K_1}{K_2} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} \approx 0.3 \times 10^5 \text{ or } K = 3 \times 10^4$$



$$K_{sp} = [\text{A}^{3+}][\text{X}^-]^3 = (S) \cdot (3S)^3 = 27S^4$$

24. (a) : Reversible reaction never goes to completion, rather attains an equilibrium point.



Using formula, $K_p = K_c(RT)^{\Delta n_g}$

where, $\Delta n_g = \text{no. of products}_{(\text{g})} - \text{no. of reactants}_{(\text{g})}$

$$= 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2} = x$$

26. (a) : BF_3 is Lewis acid (electron pair acceptor).

27. (d) : (a) is exact neutralisation. Hence $\text{pH} = 7$

(b) After neutralisation, M/10 HCl left = 10 mL

Total volume = 100 mL

Dilution = 10 times. $\therefore [\text{H}^+] = 10^{-2}$ or $\text{pH} = 2$

(c) After neutralisation, M/10 NaOH left = 80 mL

Total volume = 100 mL, $\text{pH} > 7$

(d) After neutralisation, M/10 HCl left = 50 mL

Total volume = 100 mL

Dilution = 2 times

$$\therefore [\text{H}^+] = \frac{1}{2 \times 10} = \frac{10^{-1}}{2} \text{ M or } \text{pH} = 1.3$$

28. (b) : $\Delta G^\circ = -2.303RT \log K_{sp}$

$$63.3 \times 10^3 \text{ J} = -2.303 \times 8.314 \times 298 \log K_{sp}$$

$$63.3 \times 10^3 \text{ J} = -5705.84 \log K_{sp}$$

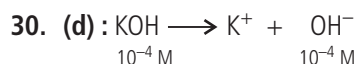
$$\log K_{sp} = -\frac{63.3 \times 10^3}{5705.84} = -11.09$$

$$K_{sp} = \text{antilog}(-11.09) = 8.128 \times 10^{-12}$$

29. (c) : $K = [\text{B}_{(\text{g})}]^2[\text{C}_{(\text{g})}]^3 = x^2 y^3$.

If $[\text{C}_{(\text{g})}]$ is doubled i.e. = $2y$, suppose $[\text{B}_{(\text{g})}]$ is z , then

$$K = z^2(2y)^3 = x^2 y^3 \text{ or } z^2 = \frac{1}{8} x^2 \text{ or } z = \frac{1}{\sqrt{8}} x = \frac{1}{2\sqrt{2}} x$$



$$10^{-4} \text{ M} \quad 10^{-4} \text{ M}$$

$$\therefore [\text{OH}^-] = 10^{-4} \text{ M}$$

$$\therefore \text{pOH} = -\log_{10} [\text{OH}^-] = -\log_{10}(10^{-4}) = 4$$

$$\therefore \text{pH} = 14 - 4 = 10$$

31. (d) : $\text{pH} = 5 \Rightarrow [\text{H}^+] = 10^{-5}$

$$\text{pH} = 7 \Rightarrow [\text{H}^+] = 10^{-7}$$

\therefore Acidic strength decreases 10^2 or 100 times.

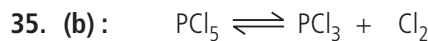
32. (d)

33. (c) : $\Delta n_g = n_p - n_r = 1 - \frac{3}{2}$

$$\Delta n_g = \frac{-1}{2}. \text{ Hence } K_p = K_c(RT)^{-1/2}$$

$$\frac{K_p}{K_c} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{RT}}$$

34. (a)



Initial moles 1 0 0

Moles at eqm. 0.5 0.5 0.5

Total moles at equilibrium = 1.5

Partial pressures $\frac{0.5}{1.5}P$ $\frac{0.5}{1.5}P$ $\frac{0.5}{1.5}P$

(where P is the total pressure.)

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} \text{ or } 1.6 = \frac{\left(\frac{0.5}{1.5}P\right)\left(\frac{0.5}{1.5}P\right)}{\left(\frac{0.5}{1.5}P\right)}$$

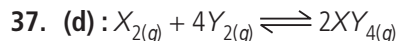
$$\text{or } \frac{1}{3}P = 1.6 \text{ (Given) or } P = 4.8 \text{ atm}$$

36. (c) : $K_c = [x][3x]^3 \dots(i)$

When concentration of OH^- ions is decreased by $\frac{1}{4}$ times,

$$K_c = [x']\left[\frac{3x}{4}\right]^3 \dots(ii)$$

$$\text{Equating eq. (i) and (ii), } x \times (3x)^3 = x' \left(\frac{3x}{4}\right)^3 \Rightarrow 64x = x'$$



$\Delta n_g = -ve$ and $\Delta H = -ve$

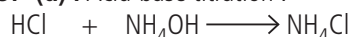
The reaction is favoured in forward direction at low temperature and high pressure

38. (d) : K_p and K_c are related by the equation,

$K_p = K_c(RT)^{\Delta n_g}$ where, $\Delta n_g = \text{difference in the number of moles of products and reactants in the gaseous state.}$

$$\text{For } 2\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{CO}_{2(\text{g})}, \Delta n_g = 2 - (1) = 1 \neq 0$$

39. (d) : Acid-base titration :



10 mmol 20 mmol

\therefore HCl is the limiting reagent.

Solution contains NH_4OH (weak base) and NH_4Cl (salt of strong acid and weak base). Therefore, a basic buffer will be formed.

40. (b)

41. (a) : On increasing the pressure and decreasing the temperature, equilibrium will shift in forward direction.

42. (b) : An increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller no. of gaseous moles. Thus, only in the reaction, $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$ there are smaller no. of gaseous moles on left hand side.

43. (d) : As the forward reaction is exothermic and leads to lowering of pressure (produces lesser number of gaseous moles) hence, according to Le Chatelier's principle, at high pressure and low temperature, the given reversible reaction will shift in forward direction to form more product.

44. (b) : The formation of ammonia is favoured by high pressure which would shift the reaction in the forward direction. The reaction shifts in forward direction at low temperature and more product formation occurs.

Fe acts as a positive catalyst and also shifts the reaction in forward reaction.

45. (a) : Value of equilibrium constant is independent of initial concentration of reactants.

46. (b) : $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}, \quad \text{pH} = -\log[\text{H}^+]$$

$$[\text{H}^+] = 10^{-5}; \quad [\text{H}^+] = [\text{A}^-]$$

$$K_a = \frac{10^{-5} \times 10^{-5}}{0.005} = 2 \times 10^{-8}; \quad \alpha = \sqrt{\frac{K_a}{C}} = 2 \times 10^{-3}$$

Percentage ionization = 0.2

47. (c) : Pyridinium hydrochloride is a salt of weak base and strong acid.

$$\text{pH} = -\log[\text{H}^+] = -\log(3.6 \times 10^{-4}) = 3.44$$

$$\text{Now, } \text{pH} = -\frac{1}{2}[\log K_w - \log K_a + \log C]$$

$$\Rightarrow 3.44 = -\frac{1}{2}[-14 - \log K_a + \log(2 \times 10^{-2})]$$

$$\Rightarrow 6.88 = 14 + \log K_a + 1.70 \Rightarrow \log K_a = -8.82$$

$$\Rightarrow K_a = \text{antilog}(-8.82) = 1.5 \times 10^{-9}$$

48. (d) : $10^{-8} \text{ M HCl} = 10^{-8} \text{ M H}^+$

Also from water, $[\text{H}^+] = 10^{-7} \text{ M}$

$$\therefore \text{Total } [\text{H}^+] = 10^{-7} + 0.10 \times 10^{-7} = 1.1 \times 10^{-7} \text{ M}$$

49. (a)

50. (b) : $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$

Initial moles	2	0	0
At eqm.	$2(1 - \alpha)$	α	α

$$\text{Total number of moles} = 2(1 - \alpha) + \alpha + \alpha = 2$$

51. (a) : Since HCl is a strong acid therefore, its pH should be less than 7. In this case we should also consider the $[\text{H}^+]$ which comes from water i.e.

$$[\text{H}^+] = 10^{-7} \text{ M from } \text{H}_2\text{O} + [\text{Acid}]$$

$$= 10^{-7} + 10^{-7} = 2 \times 10^{-7}$$

$$\text{pH} = -\log [\text{H}^+] = -\log(2 \times 10^{-7}) = 6.69$$

52. (b) : The value of K_w at 25°C is about $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Since in pure water, the concentration of H^+ and OH^- ions must be equal to one another i.e., $1.0 \times 10^{-7} \text{ mol dm}^{-3}$.

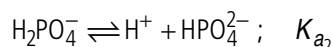
53. (a) : If $\Delta n = +ve$, $K_p > K_c$

$$\Delta n = -ve, K_p < K_c$$

$$\Delta n = 0, K_p = K_c$$

54. (a)

55. (c) : $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-; K_{a_1}$



H^+ and H_2PO_4^- are having stronger ion-pair attraction.

Hence, $K_{a_2} < K_{a_1}$ and $\text{p}K_{a_2} > \text{p}K_{a_1}$.

56. (c) : Volume is decreased, reaction proceeds in the forward direction because decrease in volume increases the number of moles per unit volume. In order to undo the effect the reaction shifts towards the direction which produces lesser number of moles. Concentration increases, Q_c must be lesser than K_c . Suppose volume is decreased to half, concentration becomes 2 times.

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

$$\text{after decreasing } Q_c = \frac{[2\text{CH}_4] \cdot [2\text{H}_2\text{O}]}{[2\text{CO}][2\text{H}_2]^3}$$

$$Q_c = \frac{K_c}{4}$$

57. (c) : $K_p \neq K_c$ for all reactions.

$$K_p = K_c (\text{RT})^{\Delta n}$$

Δn = number of moles of gaseous products – number of moles of gaseous reactants in the balanced chemical equation.

So, if for a reaction $\Delta n = 0$, then $K_p = K_c$.

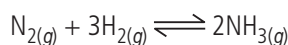
58. (c) : Equilibrium constant is temperature dependent.

59. (c) : K_{sp} remains constant at a particular temperature.

60. (b): A catalyst increases the rate of forward and backward reactions by same factor hence, does not change the equilibrium constant.

SUBJECTIVE TYPE QUESTIONS

1. The reaction is :



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$= \frac{\left(\frac{8.13}{20} \text{ mol L}^{-1}\right)^2}{\left(\frac{1.57}{20} \text{ mol L}^{-1}\right)\left(\frac{1.92}{20} \text{ mol L}^{-1}\right)^3} = 2.38 \times 10^3$$

As $Q_c \neq K_c$, the reaction mixture is not in equilibrium.

As $Q_c > K_c$, the net reaction will be in the backward direction.

2. For the concentration of pure solid or pure liquid,

$$\text{Molar conc.} = \frac{\text{Moles of the substance}}{\text{Volume of the substance}}$$

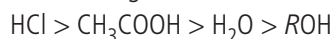
$$= \frac{\text{Mass/Molar mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Molar mass}}$$

$$= \frac{\text{Density}}{\text{Molar mass}}$$

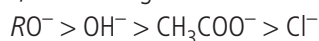
Since density of pure solid or liquid is constant at constant temperature and molar mass is also constant therefore, their molar concentrations are constant and are included in the equilibrium constant.

3. Conjugate acids of given bases are H_2O , ROH , CH_3COOH , HCl .

Their acidic strength is in the order



Hence, basic strength is in the order



4. (a) OH^- : OH^- is a Lewis base because it can donate lone pair of electrons.

(b) F^- : F^- is a Lewis base because it can donate lone pair of electrons.

(c) H^+ : H^+ is a Lewis acid because it can accept lone pair of electrons.

(d) BCl_3 : BCl_3 is a Lewis acid because it is electron deficient and can accept a lone pair of electrons.

5. pH of solution A = 6

$$[\text{H}^+] = 10^{-6} \text{ mol L}^{-1}$$

pH of solution B = 4

$$[\text{H}^+] = 10^{-4} \text{ mol L}^{-1}$$

On mixing one litre of each solution

$$\text{Total volume} = 1 \text{ L} + 1 \text{ L} = 2 \text{ L}$$

Total amount of H^+ in 2 L solution formed by mixing solutions A and B = $10^{-6} + 10^{-4} \text{ mol}$

$$\text{Total } [\text{H}^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01 \times 10^{-4}}{2}$$

$$= 5 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(5 \times 10^{-5})$$

$$= -\log 5 - (-5\log 10) = -\log 5 + 5$$

$$= 5 - \log 5 = 5 - 0.6990 = 4.3010 = 4.3$$

6. Characteristics of chemical equilibrium are as follows :

(i) Chemical equilibrium is dynamic in nature.

(ii) A catalyst does not alter the state of equilibrium.

7. $2\text{ICl}_{(g)} \rightleftharpoons \text{I}_{2(g)} + \text{Cl}_{2(g)}$; $K_c = 0.14$

Initial molar conc.	0.78	0	0
Eqm. molar conc.	$0.78 - 2x$	x	x

Applying law of chemical equilibrium,

$$K_c = \frac{[\text{I}_2][\text{Cl}_2]}{[\text{ICl}]^2} \Rightarrow 0.14 = \frac{x \cdot x}{(0.78 - 2x)^2}$$

$$x^2 = 0.14(0.78 - 2x)^2$$

$$\text{or } \frac{x}{0.78 - 2x} = \sqrt{0.14} = 0.374$$

$$\text{or } x = 0.292 - 0.748x$$

$$\text{or } 1.748x = 0.292 \text{ or } x = 0.167$$

Hence at equilibrium, $[\text{I}_2] = [\text{Cl}_2] = 0.167 \text{ M}$

$$[\text{ICl}] = 0.78 - 2 \times 0.167 = 0.446 \text{ M}$$

8. $A \rightleftharpoons B$

At the stage of half completion of reaction $[\text{A}] = [\text{B}]$.

9. We know that $\text{pH} = -\log[\text{H}^+]$

$$\therefore [\text{H}^+] = \text{antilog}[-\text{pH}] = \text{antilog}(-3.76)$$

$$= 1.738 \times 10^{-4} \text{ M}$$

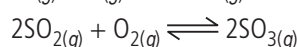
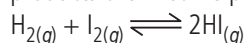
$$10. K'_c = \frac{1}{K_c} = \frac{1}{10} = 0.1$$

$$11. K_c = \frac{[\text{H}_2(g)]^4 [\text{Fe}_3\text{O}_4(s)]}{[\text{Fe}(s)]^3 [\text{H}_2\text{O}(g)]^4} = \frac{[\text{H}_2(g)]^4}{[\text{H}_2\text{O}(g)]^4}$$

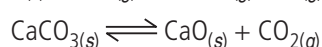
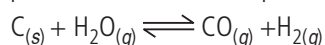
(\therefore concentration of solids is taken as unity)

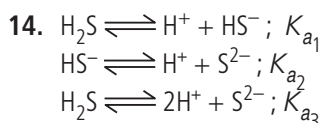
$$12. K = \frac{[\text{C}]}{[\text{A}]^3 [\text{B}]^2}$$

13. Equilibrium is said to be homogeneous if reactants and products are in same phase, e.g.,

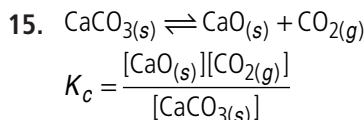


Equilibrium is said to be heterogeneous if reactants and products are in different phases, e.g.,



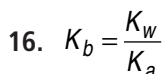


The correct relationship between K_{a_1} , K_{a_2} and K_{a_3} is
 $K_{a_3} = K_{a_1} \times K_{a_2}$.



Taking active masses of solids to be unity,

$$K_c = [\text{CO}_2(\text{g})], K_p = p_{\text{CO}_2}$$



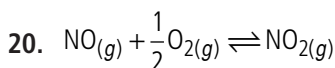
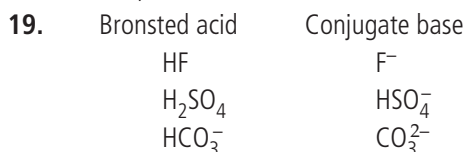
$$\text{For } \text{F}^-, K_b = \frac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

$$\text{For } \text{HCOO}^-, K_b = \frac{10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

$$\text{For } \text{CN}^-, K_b = \frac{10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

17. $Q_c > K_c$, for reverse reaction.

$$18. \Delta n = n_p - n_r = 2 - 0 = 2$$



$$\Delta G^\circ = \Delta_f G^\circ(\text{NO}_2) - [\Delta_f G^\circ(\text{NO}) + \frac{1}{2}\Delta_f G^\circ(\text{O}_2)]$$

$$= 52.0 - 87.0 - \frac{1}{2} \times 0 = -35 \text{ kJ mol}^{-1}$$

$$\text{Now, } \log K = -\frac{\Delta G^\circ}{2.303 RT}$$

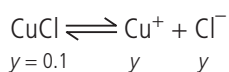
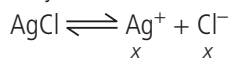
$$= -\frac{-35 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 6.314$$

$$\text{or } K = 2.06 \times 10^6$$

21. Higher the boiling point, lesser the vapour pressure hence the order of V.P. is

water < acetone < ether

22. Let the concentration of AgCl be x mol/litre and that of CuCl be y mol/litre



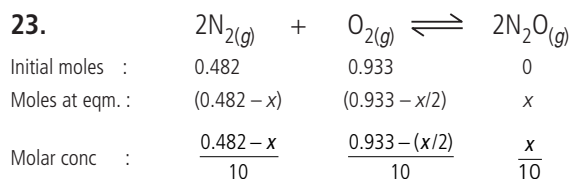
$$K_{sp} \text{ of AgCl} = [\text{Ag}^+][\text{Cl}^-] = x(x+y) \quad \dots(i)$$

$$K_{sp} \text{ of CuCl} = [\text{Cu}^+][\text{Cl}^-] = y(x+y) \quad \dots(ii)$$

On solving (i) and (ii), we get

$$\frac{K_{sp} \text{ of AgCl}}{K_{sp} \text{ of CuCl}} = \frac{x}{y} \Rightarrow \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-6}} = \frac{x}{0.1}$$

$$\Rightarrow x = 1.6 \times 10^{-5} \text{ mol/litre}$$



As $K_c = 2.0 \times 10^{-37}$ is very small, this means that the amount of N_2 and O_2 reacted (x) is very small. Hence, at equilibrium, we have

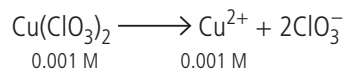
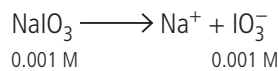
$$[\text{N}_2] = 0.0482 \text{ mol L}^{-1}, [\text{O}_2] = 0.0933 \text{ mol L}^{-1}, [\text{N}_2\text{O}] = 0.1x \text{ mol L}^{-1}$$

$$\therefore K_c = \frac{(0.1x)^2}{(0.0482)^2(0.0933)} = 2.0 \times 10^{-37} \text{ (given)}$$

On solving this we get, $x \approx 6.6 \times 10^{-20}$

$$\therefore [\text{N}_2\text{O}] = 0.1x = 6.6 \times 10^{-21} \text{ mol L}^{-1}$$

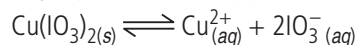
24. When equal volumes of sodium iodate and copper chlorate are mixed, the molar concentrations of both the solutes would be reduce to half i.e., 0.001 M.



\therefore After mixing, $[\text{IO}_3^-] = [\text{NaIO}_3] = 0.001 \text{ M}$

$$[\text{Cu}^{2+}] = [\text{Cu}(\text{IO}_3)_2] = 0.001 \text{ M}$$

Solubility equilibrium for copper iodate may be written as,



Ionic product of copper iodate

$$= [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (0.001)(0.001)^2 = 1 \times 10^{-9}$$

Since ionic product (1×10^{-9}) is less than $K_{sp}(7.4 \times 10^{-8})$, therefore, no precipitation will take place.

25. When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

(i) When H_2 is added, the rate of forward reaction will increase.

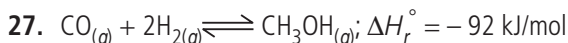
(ii) Addition of CH_3OH will lead to increase in rate of backward reaction

$$26. \Delta G^\circ = -RT \ln K_c$$

$$-13.8 \times 10^3 = 8.314 \times 298 \times \ln K_c$$

$$\therefore \ln K_c = -5.569$$

$$K_c = e^{-5.569} \Rightarrow K_c = 3.81 \times 10^{-3}$$



(i) When pressure is doubled, equilibrium will shift in the direction where pressure decreases *i.e.*, forward direction.

(ii) As this is an exothermic reaction, so the equilibrium will shift in backward direction when the temperature is doubled.

28. pH of a buffer changes with temperature because concentration of H^+ ions increases, thus pH decreases with increase of temperature.

$$29. Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

Given, $K_c = 0.061$

As $Q_c \neq K_c$, reaction is not in equilibrium.

As $Q_c < K_c$, reaction will proceed in the forward direction.

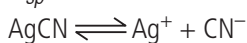
30. (i) Lewis acids are those which can accept a pair of electrons or negatively charged ions *e.g.*, BCl_3 . Lewis bases can donate a pair of electrons or negatively charged ions *e.g.*, NH_3 .

(ii) Given, K_{sp} of $\text{Ni}(\text{OH})_2 = 2 \times 10^{-15}$

$$K_{sp} \text{ of } \text{AgCN} = 6 \times 10^{-17}$$

i.e., $\text{Ni}(\text{OH})_2 \rightleftharpoons \text{Ni}^{2+} + 2\text{OH}^-$

$$K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-15}$$



$$K_{sp} = [\text{Ag}^+][\text{CN}^-] = 6 \times 10^{-17}$$

Suppose $[\text{Ag}^+] = [\text{CN}^-] = s_1$ and $[\text{Ni}^{2+}] = s_2$

Hence, $[\text{OH}^-] = 2s_2$

$$\text{Since, } s_1^2 = 6 \times 10^{-17} \Rightarrow s_1 = \sqrt{60 \times 10^{-18}}$$

$$\Rightarrow s_1 = 7.7 \times 10^{-9} \text{ M}$$

$$\text{Since, } s_2 \times (2s_2)^2 = 2 \times 10^{-15} \Rightarrow 4s_2^3 = 2 \times 10^{-15}$$

$$\Rightarrow s_2^3 = 0.5 \times 10^{-15} \Rightarrow s_2^3 = 5 \times 10^{-16}$$

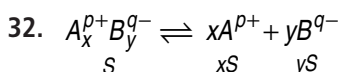
$$\Rightarrow s_2^3 = 500 \times 10^{-18}$$

$$\Rightarrow s_2 = \sqrt[3]{500 \times 10^{-18}} = 7.9 \times 10^{-6} \text{ M}$$

$$s_2 = 7.9 \times 10^{-6} \text{ M}$$

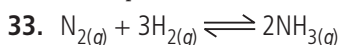
Since $s_2 > s_1$, therefore $\text{Ni}(\text{OH})_2$ is more soluble than AgCN .

31. (i), (iii), (iv) would result in the formation of a buffer solution.



$$K_{sp} = [A^{p+}]^x [B^{q-}]^y = (xS)^x (yS)^y = x^x \cdot y^y \cdot S^{(x+y)}$$

$$S^{(x+y)} = K_{sp} / x^x \cdot y^y$$



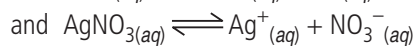
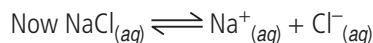
According to Le Chatelier's principle, at constant temperature, the equilibrium composition will change but K will remain same.

34. On mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M AgNO_3 the total volume becomes 100 mL.

Therefore,

$$\text{Conc. of NaCl in 100 mL} = \frac{0.01 \times 50}{100} = 0.005 \text{ M}$$

$$\text{Conc. of AgNO}_3 \text{ in 100 mL} = \frac{0.01 \times 50}{100} = 0.005 \text{ M}$$

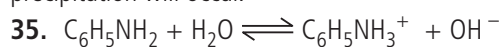


$$[\text{Cl}^-] = [\text{NaCl}] = 0.005 \text{ M}$$

$$[\text{Ag}^+] = [\text{AgNO}_3] = 0.005 \text{ M}$$

$$\therefore \text{Ionic product of } [\text{Ag}^+][\text{Cl}^-] = 0.005 \times 0.005 = 2.5 \times 10^{-5}$$

Since, ionic product is greater than its solubility product, precipitation will occur.



$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{[\text{OH}^-]^2}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

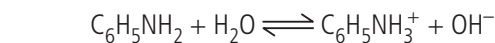
$$[\text{OH}^-] = \sqrt{K_b [\text{C}_6\text{H}_5\text{NH}_2]}$$

$$= \sqrt{(4.27 \times 10^{-10})(10^{-3})}$$

$$= 6.534 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log(6.534 \times 10^{-7}) = 6.18$$

$$\therefore \text{pH} = 14 - 6.18 = 7.82$$



$$\text{Initial : } \quad \quad \quad \text{C} \quad \quad \quad 0 \quad \quad \quad 0$$

$$\text{At. eqm. : } \quad \text{C} - \text{C}\alpha \quad \quad \quad \text{C}\alpha \quad \quad \quad \text{C}\alpha$$

$$K_b = \frac{\text{C}\alpha \cdot \text{C}\alpha}{\text{C}(1-\alpha)} = \frac{\text{C}\alpha^2}{(1-\alpha)} = \text{C}\alpha^2 \quad (\because 1 \gg \alpha)$$

$$\therefore \alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{4.27 \times 10^{-10}}{10^{-3}}} = 6.53 \times 10^{-4}$$

$$\text{p}K_b = -\log(4.27 \times 10^{-10}) = 9.37$$

$$\text{p}K_a + \text{p}K_b = 14$$

(for a pair of conjugate acid and base)

$$\therefore \text{p}K_a = 14 - 9.37 = 4.63$$

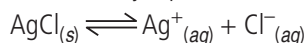
$$\text{i.e., } -\log K_a = 4.63 \text{ or, } \log K_a = -4.63$$

$$\text{or, } K_a = \text{antilog}(-4.63) = 2.34 \times 10^{-5}$$

36. (i) The term ionic product has a broad meaning since it is applicable to all types of solution, may be unsaturated or saturated. On the other hand, the solubility product has restricted meaning since it applies only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in solution. Thus, the solubility product is, in fact the ionic product for a saturated solution.

The solubility product of a salt is constant at constant temperature whereas ionic product depends upon the concentrations of ions in the solution.

(ii) The solubility equilibrium in the saturated solution is



The solubility of AgCl is 1.06×10^{-5} mole per litre.

$$[\text{Ag}^+_{(aq)}] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{Cl}^-_{(aq)}] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned} K_{sp} &= [\text{Ag}^+_{(aq)}] [\text{Cl}^-_{(aq)}] \\ &= (1.06 \times 10^{-5} \text{ mol L}^{-1}) \times (1.06 \times 10^{-5} \text{ mol L}^{-1}) \\ &= 1.12 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2} \end{aligned}$$

37. (i) Sorensen (1909) defined pH of a solution as negative logarithm of the hydrogen ion concentration of the solution.

$$\text{Thus, } \text{pH} = -\log[\text{H}^+] = \log \frac{1}{[\text{H}^+]} \text{ or } [\text{H}^+] = 10^{-\text{pH}}$$

Likewise, pOH of a solution

$$\text{pOH} = -\log[\text{OH}^-] = \log \frac{1}{[\text{OH}^-]} \text{ or } [\text{OH}^-] = 10^{-\text{pOH}}$$

$$K_w = [\text{H}^+][\text{OH}^-] = \text{Ionic product of water} = 10^{-14} \text{ (mol/L)}^2$$

$$\text{p}K_w = -\log K_w$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

$$\text{(ii) } \text{KOH} = \frac{0.561}{56} \times \frac{1000}{200} = 0.05 \text{ M}$$



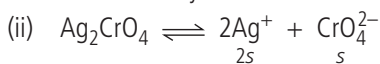
$$[\text{K}^+] = [\text{OH}^-] = 0.05 \text{ M}$$

$$[\text{H}^+] = K_w / [\text{OH}^-] = 10^{-14} / 0.05$$

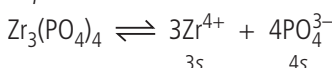
$$= 10^{-14} / (5 \times 10^{-2}) = 2.0 \times 10^{-13} \text{ m}$$

$$\text{pH} = -\log 2 \times 10^{-13} = 13 - \log 2 = 12.69$$

38. (i) Common ion effect can be defined as the suppression of the degree of ionisation of a weak electrolyte by the addition of a strong electrolyte having an ion common with the weak electrolyte.



$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2s)^2 \times s = 4s^3$$



$$K_{sp} = [\text{Zr}^{4+}]^3 [\text{PO}_4^{3-}]^4 = (3s)^3 \times (4s)^4 = 6912s^7$$

$$\text{(iii) } \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.005) = 2.30$$

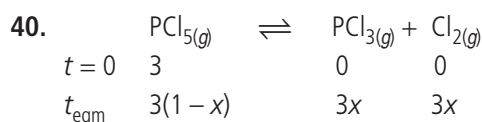
39. $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$; $\Delta_r H^\circ = 124.0 \text{ kJ mol}^{-1}$

$$\text{(a) } K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 8.3 \times 10^{-3}$$

$$\begin{aligned} \text{(b) } K_c \text{ for the reverse reaction} \\ &= \frac{1}{K_c \text{ for the forward reaction}} \\ &= \frac{1}{8.3 \times 10^{-3}} = 120.48 \end{aligned}$$

(c) (i) When pressure increases, K_c remains unchanged.

(ii) K_c increases with increase in temperature because the reaction is endothermic.



where x = degree of dissociation of $\text{PCl}_{5(g)}$ at 227°C

Total no. of moles at equilibrium = $[(3 - 3x) + 3x + 3x + 1 \text{ (molar concentration of } \text{N}_2)] = 4 + 3x$.

From gas equation : $PV = nRT$

$$\begin{aligned} \text{Total pressure (P)} &= \frac{(4 + 3x)}{100} \times 0.082 \times 500 \text{ atm} \\ &= 2.05 \text{ atm (given)} \end{aligned}$$

$$\text{Thus, } 4 + 3x = 5.0$$

$$\text{or } 3x = 1.0$$

$$\text{Hence, } x = \frac{1.0}{3} = 0.33$$

Percentage dissociation = 33%

$$p_{\text{PCl}_5} = \frac{3 - 3x}{4 + 3x} \times P = \frac{(3 - 0.99) \times 2.05}{4 + 0.33 \times 3} = \frac{2.01 \times 2.05}{4.99} = 0.825$$

$$p_{\text{PCl}_3} = \frac{3x}{4 + 3x} \times P = \frac{3 \times 0.33 \times 2.05}{4.99} = \frac{2.03}{4.99} = 0.4067$$

$$p_{\text{Cl}_2} = \frac{3x}{4 + 3x} \times P = \frac{3 \times 0.33 \times 2.05}{4.99} = \frac{2.03}{4.99} = 0.4067$$

$$\text{Hence, } K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{0.4067 \times 0.4067}{0.825} = 0.200 \text{ atm.}$$



The s-Block Elements



Recap Notes

GROUP 1 ELEMENTS (ALKALI METALS)

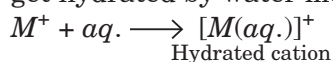
- **General characteristics :**
 - ▶ **Electronic configuration :** Alkali metals are s-block elements. These contain only one electron in the s-orbital of the valence shell outside the noble gas core and hence their valence shell electronic configuration is ns^1 .
 - ▶ **Atomic and ionic radii :** Alkali metal atoms are largest in their corresponding period in periodic table. Atomic as well as ionic size increases from Li to Fr due to the presence of an extra shell of electrons. Atomic volume (At.wt./density) also increases in moving down from Li to Cs.

Element	Atomic radii (pm)	Ionic radii (pm)	Atomic volume (mL/mol)
Li	152	76	13.0
Na	186	102	23.7
K	227	138	44.4
Rb	248	152	55.8
Cs	265	167	69.3

- ▶ **Ionization energy :** Alkali metals have the lowest ionization energy in their

corresponding period in periodic table because they have large size which results in a large distance between the nucleus and the outermost electron. Ionization energy of alkali metals decreases from Li to Cs due to increase in atomic size.

- ▶ **Hydration of ions :** The salts of alkali metals are ionic and soluble in water. The solubility is due to the fact that cations get hydrated by water molecules.



The smaller the cation, the greater is the degree of its hydration. Thus, the degree of hydration of M^+ ions decreases from Li^+ to Cs^+ . Consequently, the radii of the hydrated ion decreases from Li^+ to Cs^+ .

- **Physical properties :**
 - ▶ **Flame colouration :** Alkali metals and their salts, when introduced into the flame impart characteristic colour to the flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Pale violet	Red violet	Blue

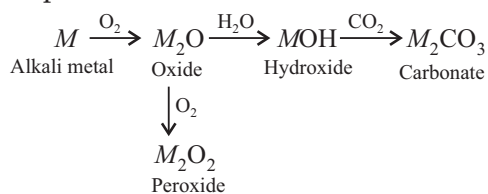
Atomic and physical properties of the alkali metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol ⁻¹)	6.94	22.99	39.10	85.47	132.91	223
Electronic configuration	[He] 2s ¹	[Ne] 3s ¹	[Ar] 4s ¹	[Kr] 5s ¹	[Xe] 6s ¹	[Rn] 7s ¹

Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/ kJ mol^{-1}	-506	-406	-330	-310	-276	-
Metallic radius / pm	152	186	227	248	265	-
Ionic radius (M^+) / pm	76	102	138	152	167	180
Melting point / K	454	371	336	312	302	-
Boiling point / K	1615	1156	1032	961	944	-
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	-
Standard potential E°/V for (M^+ / M)	-3.04	-2.714	-2.925	-2.930	-2.927	-

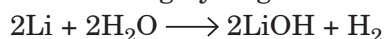
- **Chemical properties :**

- ▶ **Action with air :** On exposure to moist air, all alkali metals except lithium tarnish quickly. The effect of atmosphere increases from Li to Cs. These are, therefore, always kept under kerosene oil to protect them from air.



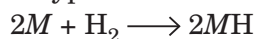
- ▶ Lithium forms lithium oxides, sodium forms sodium oxide and peroxide. Potassium, rubidium and caesium form oxides, peroxides and superoxides due to increase in the size of cations on moving down the group.

- ▶ **Action of water :** The alkali metals react readily with water forming hydroxides and evolving hydrogen. For example,



- The reactivity with water increases down the group from lithium to caesium. The basic nature of hydroxides increases down the group.

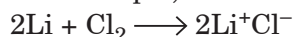
- ▶ **Action with hydrogen :** Alkali metals react with hydrogen to form ionic hydrides of type M^+H^- .



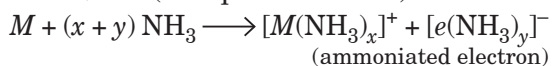
- The electrolysis of the fused hydride (LiH) yields hydrogen at anode.

- The ionic character of the bonds in these hydrides increases from LiH to CsH and their stability decreases in the same order. They are powerful reducing agents especially at high temperatures.

- ▶ **Action with halogens :** The alkali metals combine readily with halogens forming the halides. These are ionic compounds and are represented as M^+X^- . For example,



- ▶ **Solubility in liquid NH_3 :** The alkali metals dissolve in liquid ammonia without the evolution of hydrogen. The colour of the dilute solutions is blue. The metal atom loses electron and it combines with ammonia molecule.

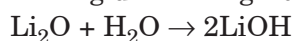


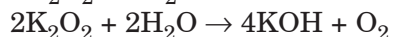
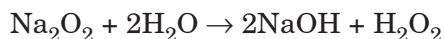
- On heating its blue colour changes to bronze.

- It is ammoniated electron which is responsible for colour.

- **General characteristics of the compounds of the alkali metals :**

- ▶ **Nature of alkali metal oxides :** Alkali metal oxides are basic in nature and their basic character increases gradually on moving down the group.





► **Nature of alkali metal hydroxides:**

Alkali metal hydroxides, form the strongest bases. The basic character of the alkali metal hydroxides increases from LiOH to CsOH.



This can be explained on the basis of increase in internuclear distances between the oxygen of the OH group and the metal ion, which increases with the increase in the cation size (Li⁺ to Cs⁺). The thermal stability, solubility, reactivity, m.pt. and b.pt. of hydroxides also increases on moving from Li to Cs.

► **Nature of alkali metal halides :** Alkali metals halides are ionic compounds except LiBr and LiI. All alkali halides are freely soluble in water except LiF. LiF is soluble in non-polar solvents. The insolubility of LiF in water is attributed to high lattice energy as Li⁺ and F⁻ ions have small size and large charge. The CsI has also low solubility due to smaller hydration energy of its two ions.

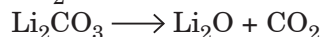
– Melting point and boiling point of halides of a particular alkali metal follow the order :



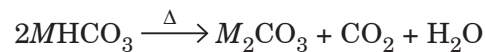
► **Salts of oxoacids :** Alkali metal hydroxides being basic in nature react with oxoacids (such as H₂CO₃, H₃PO₄, HNO₃, HNO₂, H₂SO₄, etc.) to form different salts such as metal carbonates, bicarbonates, sulphates, nitrates, etc.

► **Nature of carbonates and bicarbonates :** Alkali metal carbonates and bicarbonates are highly stable towards heat and their stability increases down the group, since electropositive character increases from Li to Cs. However Li₂CO₃ is less stable and readily decomposes to form oxide because Li⁺ ion exerts a strong polarising action and distorts the electron cloud of the nearby oxygen atom of CO₃²⁻ ion. This result in the weakening of the C—O bond and strengthening of

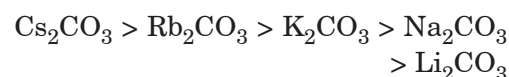
Li—O bond. This ultimately facilitate the decomposition of Li₂CO₃ into Li₂O and CO₂.



– Alkali metal bicarbonates on heating decompose to give respective carbonates.



– All carbonates and bicarbonates are water soluble. Their solubility and stability decreases in the following order :



► **Anomalous behaviour of Li :** Due to very small size, comparatively high ionization enthalpy, non-availability of *d*-orbitals and high polarizing power of Li⁺.

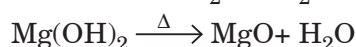
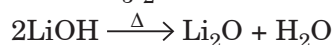
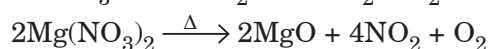
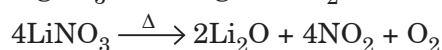
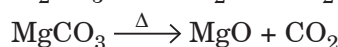
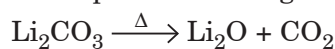
All alkali metals	Except
Do not react directly with N ₂ or C.	Li which forms Li ₃ N or Li ₂ C ₂
Form amide (MNH ₂) with ammonia.	Li which forms Li ₂ NH
Nitrates are thermally stable.	LiNO ₃
Carbonates are thermally stable.	Li ₂ CO ₃
Form double salts (alums) from their sulphates.	Li ₂ SO ₄
Form acetylides with acetylene.	Li

• **Diagonal relationship of Li with Mg :**

Lithium resembles magnesium mainly due to the similarity in sizes of their atoms.

► Both Li and Mg are quite hard. They are harder and have high m.pt. than other elements in their respective groups.

► Carbonates, nitrates and hydroxides decompose on heating :



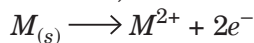
- ▶ Combine directly with N_2 :
 $6Li + N_2 \longrightarrow 2Li_3N$
 $3Mg + N_2 \longrightarrow Mg_3N_2$
- ▶ Combine with carbon on heating :
 $2Li + 2C \longrightarrow Li_2C_2$
 $Mg + 2C \longrightarrow MgC_2$
- ▶ Form monoxide on heating with oxygen :
 $4Li + O_2 \longrightarrow 2Li_2O$
 $2Mg + O_2 \longrightarrow 2MgO$
- ▶ Their periodic properties like atomic radii, ionic radii, atomic volume are quite comparable.
- ▶ $MgSO_4$ like Li_2SO_4 does not form alums.
- ▶ $LiHCO_3$ and $Mg(HCO_3)_2$ do not exist in solid state, they exist in solution only.

- **Biological importance of sodium and potassium** : Sodium and potassium are present in biological fluids. The most remarkable feature of Na^+ and K^+ ions is the development and functional features of nerve cells. In the resting state, a nerve cell shows a potential corresponding to the potassium ion concentration across the membrane. During activation of nerve cells, a chemical, acetyl-choline is released near its end plate and the membrane potential is discharged. This discharge is transmitted through the length of the nerve cell by an electric pulse. This action illustrates the importance of Na^+ and K^+ ions.

GROUP 2 ELEMENTS (ALKALINE EARTH METALS)

- **General characteristics** :
 - ▶ **Electronic configuration** : The electronic configuration of alkaline earth metals are ns^2 .
 - ▶ **Atomic and ionic radii** : The atoms and ions are large but are smaller than the corresponding group 1 elements since the extra charge on the nucleus draws the valence electrons. The size of atom increases gradually from Be to Ra.
 - ▶ **Ionisation energies and electropositive character** : With increasing size, the ionization energy decreases from Be to Ra. Although the second ionization energy of these atoms to produce M^{2+} ions is greater than the

first to produce M^+ ions, the extra energy to remove second electron is offset by the lattice energy in crystals or the solvation energy in solutions. The electropositive character increases from Be to Ra. The oxidation potentials corresponding to the reaction,



are relatively high which indicate that in solutions these elements are good reducing agents.

- ▶ **Hydration of ions and hydration energy** : The ions are hydrated in aqueous solutions. The extent of hydration of the ions decreases with increase in atomic number as shown by their heats of hydration (ΔH) in kJ mol^{-1} .

Be ²⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
-2406	-1929	-1632	-1485	-1276

- ▶ **Flame test** : In flame the electrons are excited to higher energy states, and when these drop back to the original state, extra energy is emitted in the form of visible light. This accounts for the characteristic colours given by Ca, Sr, and Ba in the flame test.

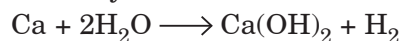
Calcium—brick red, Strontium—crimson red

Barium—apple green, Radium—crimson red

- **Chemical properties** :

- ▶ **Action of air** : Alkaline earth metals being less electropositive than the alkali metals, are less reactive. These are only slowly oxidised on exposure to air. Their activity increases down the group from Be to Ra.

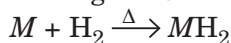
- ▶ **Action of water** : With the exception of beryllium and magnesium, the alkaline earth metals react vigorously with cold water to form hydrogen and corresponding metal hydroxide.



The alkaline earth metal hydroxides are less basic than the alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature, whereas the basic

character of other hydroxides increases down the group.

- ▶ **Action of hydrogen** : All the alkaline earth metals except Be, combine with H_2 directly on heating to form metal hydrides of the general formula, MH_2 .



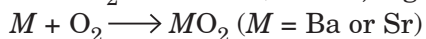
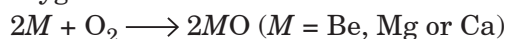
(where, $M = Mg, Ca, Sr$ or Ba)

BeH_2 can, however be prepared by reducing $BeCl_2$ with $LiAlH_4$.



BeH_2 is covalent, MgH_2 is partly ionic but the hydrides of $Ca, Sr,$ and Ba are ionic solids. Further, BeH_2 and MgH_2 are polymeric while others are monomeric.

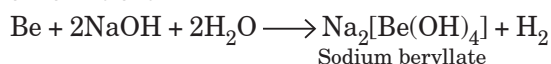
- ▶ **Reaction with oxygen** : The alkaline earth metals burn in oxygen to form oxides or peroxides. Beryllium, magnesium and calcium form oxides, strontium and barium form peroxides with excess of oxygen.



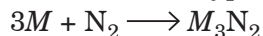
The reactivity of the alkaline earth metals towards oxygen increases down the group.

- ▶ **Action of halogens** : Alkaline earth metals combine with halogens at high temperatures to form halides, MX_2 . Beryllium halides are covalent, hygroscopic and fumes, in air due to hydrolysis. The other halides are electrovalent and readily soluble in water.

- ▶ **Action of acids** : All of them easily dissolve in acids with the liberation of hydrogen. Beryllium differs from other members of its group in being soluble in alkalis also.



- ▶ **Action with nitrogen** : All the alkaline earth metals burn in nitrogen to form nitrides of the type M_3N_2 .

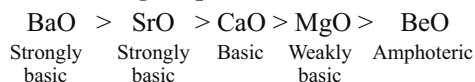


The ease of formation of nitrides decreases from Be to Ba .

- **Characteristics of compounds of the alkaline earth metal :**

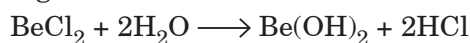
- ▶ **Nature of oxides and peroxides** : Oxides of group 2 elements are basic in

nature. Their basic strength increases down the group.



- ▶ **Nature of hydroxides** : $Be(OH)_2$ is amphoteric, but the hydroxides of Mg, Ca, Sr and Ba are basic. The basic strength increases from Mg to Ba .

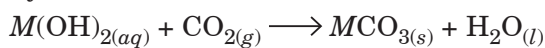
- ▶ **Nature of halides** : Due to small size and high charge density, all beryllium halides are essentially covalent and are soluble in organic solvents.



The halides of all other alkaline earth metals are ionic. Their ionic character, however, increases as the size of the metal ion increases.

They are hygroscopic, and fume in air due to hydrolysis. On hydrolysis, they produce acidic solution.

- ▶ **Carbonates and bicarbonates** : Carbonates of alkaline earth metals can be produced by passing CO_2 through their hydroxides.



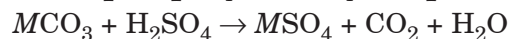
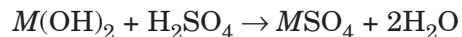
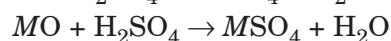
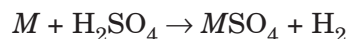
Alkaline earth metal carbonates are ionic but beryllium carbonate is prone to hydrolysis. It contains the hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+} . The solubility of carbonates decreases down the group from Be to Ba .

Bicarbonates of alkaline earth metals exist in solution only. On heating, bicarbonates decompose to carbonates with evolution of CO_2 .

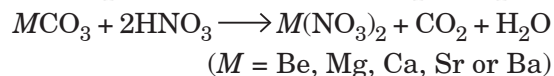
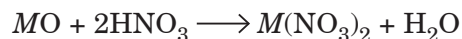


Bicarbonates of Ca and Mg cause temporary hardness of water whereas their chlorides and sulphates are responsible for permanent hardness of water.

- ▶ **Sulphates** : The sulphates of alkaline earth metals (MSO_4) are prepared by the action of sulphuric acid on metals, metal oxides, hydroxides and carbonates.



- **Nitrates** : Alkaline earth metal nitrates are prepared in solution and can be crystallized as hydrated salts by the action of HNO_3 on oxides, hydroxides and carbonates.



Magnesium nitrate crystallizes as $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ while $\text{Ba}(\text{NO}_3)_2$ crystallises as anhydrous salt.

- **Anomalous behaviour of Be** : It is due to small size, high ionization enthalpy, absence of d -orbitals.

All alkaline earth metals	Except
Form ionic non volatile nitrides.	Be_3N_2 is covalent and volatile.
Form ionic carbonates.	BeCO_3 is unstable.
Form basic oxides.	BeO is amphoteric.

- **Diagonal relationship of beryllium and aluminium** : Both have same electronegativity, polarising power and charge / radius ratio of their ions.
 - Both have tendency to form covalent compounds.
 - Both BeCl_2 and AlCl_3 have chlorine bridged structure in vapour phase.
 - Both the metals dissolve in strong alkalies.



OBJECTIVE TYPE QUESTIONS

➔ Multiple Choice Questions (MCQs)

- Which of the following alkali metals gives hydrated salts?
(a) Li (b) Na (c) K (d) Cs
- Which of the following order is correct for the thermal stability of alkali metal carbonates?
(a) $\text{Li}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3$
(b) $\text{Cs}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{Li}_2\text{CO}_3$
(c) $\text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3 < \text{Li}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3$
(d) $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
- The reducing power of a metal depends on various factors. Suggest the factor which makes Li, the strongest reducing agent in aqueous solution.
(a) Sublimation enthalpy
(b) Ionisation enthalpy
(c) Hydration enthalpy
(d) Electron-gain enthalpy
- Strongest reducing agent in the aqueous solution is
(a) Na (b) Rb (c) Ca (d) Li
- Which of the following statements is false regarding alkali metals?
(a) Alkali metals are soft and can be cut with the help of knife.
(b) Alkali metals do not occur in free state in nature.
(c) Alkali metals are highly electropositive elements.
(d) Alkali metal hydrides are covalent in character.
- Which of the following does not illustrate the anomalous properties of Li?
(a) The m.pt. and b.pt. of Li are comparatively high.
(b) Li forms a nitride Li_3N unlike group 1 metals.
(c) Li is much softer than the other group 1 metals.
(d) Li^+ ion and its compounds are more heavily hydrated than those of the rest of the group.
- The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to
(a) ionic nature of lithium fluoride
(b) high lattice enthalpy
(c) high hydration enthalpy for lithium ion
(d) low ionisation enthalpy of lithium atom.
- Which of the following does not show diagonal relationship between beryllium and aluminium?
(a) Both BeO and Al_2O_3 are amphoteric in nature.
(b) Both beryllium and aluminium form polymeric covalent hydrides.
(c) Both beryllium and aluminium form nitrides with nitrogen which evolve NH_3 with water.
(d) Both metal carbonates are highly stable.
- The formula of nitre is
(a) KNO_3 (b) NaNO_2 (c) BaCl_2 (d) Na_2CO_3
- Amphoteric hydroxides react with both alkalies and acids. Which of the following group 2 metal hydroxides is soluble in sodium hydroxide?
(a) $\text{Be}(\text{OH})_2$ (b) $\text{Mg}(\text{OH})_2$
(c) $\text{Ca}(\text{OH})_2$ (d) $\text{Ba}(\text{OH})_2$
- Match the elements given in Column I with the properties mentioned in Column II.

Column I	Column II
(i) Li	(A) Insoluble sulphate
(ii) Na	(B) Strongest monoacidic base
(iii) Ca	(C) Most negative E° value among alkali metals
(iv) Ba	(D) Insoluble oxalate
	(E) $6s^2$ outer electronic configuration

- (a) (i) → (C, D), (ii) → (B), (iii) → (D), (iv) → (A, E)
 (b) (i) → (C), (ii) → (A), (iii) → (B), (iv) → (D, E)
 (c) (i) → (A), (ii) → (D), (iii) → (E), (iv) → (B, C)
 (d) (i) → (B, C), (ii) → (A), (iii) → (E), (iv) → (D)

12. If Na^+ ion is larger than Mg^{2+} ion and S^{2-} ion is larger than Cl^- ion, which of the following will be least soluble in water?

- (a) Sodium chloride (b) Sodium sulphide
 (c) Magnesium chloride
 (d) Magnesium sulphide

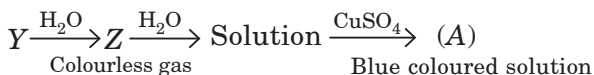
13. Alkali metals form hydrated compounds. The hydration enthalpies of alkali metals is in the sequence

- (a) $\text{Rb}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$
 (b) $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
 (c) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
 (d) $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Rb}^+ > \text{Cs}^+$

14. The alkali metals have low melting points. Which of the following alkali metals is expected to melt if the room temperature rises to 30°C ?

- (a) Na (b) K
 (c) Rb (d) Cs

15. $\text{Mg} \xrightarrow[\text{Heat}]{\text{Air}} \text{X} + \text{Y}$



Substances X, Y, Z and A are respectively

- (a) Mg_3N_2 , MgO, NH_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (b) $\text{Mg}(\text{NO}_3)_2$, MgO, H_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) MgO, Mg_3N_2 , NH_3 , $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (d) $\text{Mg}(\text{NO}_3)_2$, MgO, H_2O_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

16. Fill up the blanks with appropriate choices.

Lithium and magnesium react slowly with water. Their hydroxides are (i) soluble in water. Carbonates of Li and Mg (ii) easily on heating. Both LiCl and MgCl_2 are (iii) in ethanol and are (iv). They crystallise from their aqueous solutions as (v).

- | | | | | | |
|-----|------------------|------------------|--------------|--------------|----------|
| | (i) | (ii) | (iii) | (iv) | (v) |
| (a) | more | do not decompose | soluble | hygroscopic | hydrates |
| (b) | less | decompose | soluble | deliquescent | hydrates |
| (c) | freely sublime | insoluble | deliquescent | anhydrous | |
| (d) | freely decompose | soluble | hygroscopic | crystals | |

17. Which of the following has correct increasing basic strength?

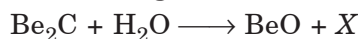
- (a) $\text{MgO} < \text{BeO} < \text{CaO} < \text{BaO}$
 (b) $\text{BeO} < \text{MgO} < \text{CaO} < \text{BaO}$
 (c) $\text{BaO} < \text{CaO} < \text{MgO} < \text{BeO}$
 (d) $\text{CaO} < \text{BaO} < \text{BeO} < \text{MgO}$

18. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	Li	(i)	Violet flame
(B)	K	(ii)	Golden yellow flame
(C)	Na	(iii)	Photoelectric cell
(D)	Cs	(iv)	Carbonate decomposes on heating

- (a) (A) → (iv), (B) → (i), (C) → (iii), (D) → (ii)
 (b) (A) → (i), (B) → (iii), (C) → (ii), (D) → (iv)
 (c) (A) → (iii), (B) → (ii), (C) → (i), (D) → (iv)
 (d) (A) → (iv), (B) → (i), (C) → (ii), (D) → (iii)

19. In the given reactions,



X, Y and Z are respectively

- (a) CH_4 , C_2H_2 , C_3H_8 (b) CH_4 , C_2H_6 , C_3H_8
 (c) CH_4 , C_2H_2 , C_3H_4 (d) C_2H_2 , C_2H_6 , C_3H_4

20. Which of the following statements are wrong?

- Barium is more reducing than magnesium.
 - $\text{Ba}(\text{OH})_2$ is more basic than $\text{Be}(\text{OH})_2$.
 - Mg^{2+} is precipitated as MgCO_3 by ammonium carbonate in presence of ammonium chloride.
 - MgCl_2 gives colouration in flame test.
- (a) 1 and 2 (b) 3 and 4
 (c) 1 and 3 (d) 1, 2 and 3

21. Lattice energies of BeF_2 , MgF_2 , CaF_2 and BaF_2 are -2906 , -2610 , -2459 and -2367 kJ mol^{-1} respectively. Hydration energies of Be^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} and F^- are -2494 , -1921 , -1577 , -1305 and -457 kJ mol^{-1} respectively. Which of the fluorides is soluble in water?

- (a) BeF_2 (b) MgF_2
 (c) CaF_2 (d) BaF_2

22. The element A burns in nitrogen to give an ionic compound B. The compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide. What is the nature of compound D?

- (a) Acidic (b) Basic
(c) Amphoteric (d) Neutral

23. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequence represents the increasing order of the polarizing power of the cationic species, K^+ , Ca^{2+} , Mg^{2+} , Be^{2+} ?

- (a) Mg^{2+} , Be^{2+} , K^+ , Ca^{2+}
(b) Be^{2+} , K^+ , Ca^{2+} , Mg^{2+}
(c) K^+ , Ca^{2+} , Mg^{2+} , Be^{2+}
(d) Ca^{2+} , Mg^{2+} , Be^{2+} , K^+

24. Metals form basic hydroxides. Which of the following metal hydroxide is the least basic?

- (a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Sr(OH)_2$ (d) $Ba(OH)_2$

25. Which of the following is incorrect?

- (a) Both $BeCl_2$ and $AlCl_3$ have bridged chloride structure.
(b) Both $BeCl_2$ and $AlCl_3$ are strong Lewis acids.
(c) Both $BeCl_2$ and $AlCl_3$ are covalent compounds.
(d) $BeCl_2$ is weak Lewis acid while $AlCl_3$ is strong Lewis acid.

26. Some of the group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is

- (a) $BeCl_2$ (b) $MgCl_2$
(c) $CaCl_2$ (d) $SrCl_2$

27. The hydroxide, which is best soluble in water, is

- (a) $Sr(OH)_2$ (b) $Ba(OH)_2$
(c) $Ca(OH)_2$ (d) $Mg(OH)_2$

28. The activity of alkaline earth metals as reducing agents

- (a) decreases from Be to Ba
(b) increases from Be to Ba
(c) increases from Be to Ca and decreases from Ca to Ba
(d) decreases from Be to Ca and increases from Ca to Ba.

29. For alkali metals, which one of the following trends is incorrect?

- (a) Hydration energy : $Li > Na > K > Rb$
(b) Ionization energy : $Li > Na > K > Rb$
(c) Density : $Li < Na < K < Rb$
(d) Atomic size : $Li < Na < K < Rb$

30. The first ionization energies of alkaline earth metals are higher than those of the alkali metals. This is because

- (a) there is an increase in the nuclear charge of the alkaline earth metals
(b) there is a decrease in the nuclear charge of the alkaline earth metals
(c) there is no change in the nuclear charge
(d) none of the above.

31. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	Na	(i)	Crimson red
(B)	K	(ii)	Yellow
(C)	Sr	(iii)	Apple green
(D)	Ba	(iv)	Violet

- (a) (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)
(b) (A) \rightarrow (ii), (B) \rightarrow (iv), (C) \rightarrow (i), (D) \rightarrow (iii)
(c) (A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (i)
(d) (A) \rightarrow (iii), (B) \rightarrow (iv), (C) \rightarrow (i), (D) \rightarrow (ii)

32. Group 2 elements form compounds in +2 oxidation state though total energy required to produce M^{2+} ions of these elements is quite high. This is because

- (a) these elements predominantly form ionic compounds
(b) lattice enthalpy of bivalent compounds of group 2 elements more than compensates the energy requirement for the formation of +2 ions
(c) their hydration energy is quite high
(d) none of these.

33. Which of the following is true for magnesium?

- (a) It is more electropositive than sodium.
(b) It is manufactured by electrolysis of aqueous magnesium chloride.
(c) It is a strong reducing agent.
(d) It resembles, in chemical properties, with its diagonally placed element boron in group 13 of the periodic table.

34. Choose the incorrect statement in the following.

- (a) BeO is almost insoluble but $BeSO_4$ is soluble in water.
(b) BaO is soluble but $BaSO_4$ is insoluble in water.
(c) LiI is more soluble than KI in ethanol.
(d) Both Li and Mg form solid hydrogen carbonates.

35. A metal salt solution forms a yellow precipitate with potassium chromate in acetic acid, a white precipitate with dilute sulphuric acid but does not give precipitate with sodium chloride or iodide. The white precipitate obtained when sodium carbonate is added to the metal salt solution will consist of

- (a) lead carbonate (b) basic lead carbonate
(c) barium carbonate
(d) strontium carbonate.

36. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in

- (a) maximum covalency in compounds
(b) exhibiting amphoteric nature in their oxides
(c) forming covalent halides
(d) forming polymeric hydrides.

37. Halides of alkaline earth metals form hydrates such as $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot 2H_2O$. This shows that halides of group 2 elements

- (a) are hygroscopic in nature
(b) act as dehydrating agents

- (c) can absorb moisture from air
(d) all of the above.

38. Magnesium reacts with an element (X) to form an ionic compound. If the ground state electronic configuration of (X) is $1s^2 2s^2 2p^3$, the simplest formula for this compound is

- (a) Mg_2X_3 (b) MgX_2
(c) Mg_2X (d) Mg_3X_2

39. The correct order of solubility of the sulphates of alkaline earth metals in water is $Be > Mg > Ca > Sr > Ba$. This is due to

- (a) decreasing lattice energy
(b) high heat of solvation for smaller ions like Be^{2+}
(c) increase in melting points
(d) increasing molecular weight.

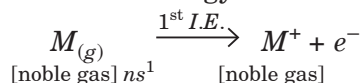
40. Magnesium forms Mg^{2+} and not Mg^+ because

- (a) magnesium(II) carbonate is insoluble in water
(b) generally higher oxidation states are preferred by metals
(c) ionic radius of $Mg(II)$ is smaller than of $Mg(I)$
(d) hydration energy of divalent magnesium ion is higher.

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 41 to 43.

Alkali metals have the lowest ionization energy in their corresponding period in periodic table because they have large size which results in a large distance between the nucleus and the outermost electron. Ionization energy of alkali metals decreases from Li to Cs due to increase in atomic size. First ionization energy of alkali metals is very low but they have very high value of second ionization energy.



Metal	Ionization Energy (kJ mol^{-1})	
	IE_1	IE_2
Li	520.1	7296
Na	495.7	4563
K	418.6	3051
Rb	402.9	2633
Cs	375.6	2230

41. Alkali metals are characterised by
- (a) good conductors of heat and electricity
(b) high melting points
(c) low oxidation potentials
(d) high ionisation potentials.

42. Metals dissolve in liquid ammonia giving coloured solutions which are conducting in nature. The colour of the solution and reason of its conductance is

- (a) yellow, NH_4^+
(b) blue, ammoniated metals
(c) orange, $[M(NH_3)_x]^+$
(d) blue, ammoniated electron.

43. Alkali metals displace hydrogen from water forming bases due to the reason that

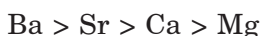
- (a) they are far above the hydrogen in electrochemical series based on oxidation potential
(b) they are far below the hydrogen in electrochemical series based on oxidation potential

- (c) their ionization potential is less than that of other elements.
 (d) they contain only one electron in their outermost shell.

Case II : Read the passage given below and answer the following questions from 44 to 46.

Alkaline earth metals are less reactive with water as compared to alkali metals. Their reactivity with water increases down the group. Be does not react with water at all, magnesium reacts only with hot water while other metals Ca, Sr and Ba react with cold water.

Order of the reactivity with water :



$\text{Be}(\text{OH})_2$ is amphoteric, but the hydroxides of Mg, Ca, Sr and Ba are basic. The basic strength increases from Mg to Ba.

$\text{Be}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	$\text{Sr}(\text{OH})_2$	$\text{Ba}(\text{OH})_2$
Amphoteric	Weakly basic	Basic	Strongly basic	Strongly basic

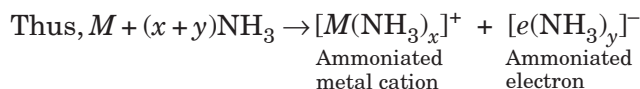
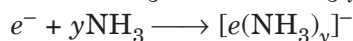
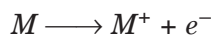
44. Which of the following statements is false?
 (a) Strontium decomposes water readily than beryllium.
 (b) Barium carbonate melts at a higher temperature than calcium carbonate.
 (c) Barium hydroxide is more soluble in water than magnesium hydroxide.
 (d) Beryllium hydroxide is more basic than barium hydroxide.
45. Chemical compound 'A' is used as flocculant in water and sewage treatment. It reacts with Na_2CO_3 to generate caustic soda. When CO_2 is bubbled through 'A', it turns cloudy. What is the chemical formula of 'A' ?
 (a) CaCO_3 (b) CaO
 (c) $\text{Ca}(\text{OH})_2$ (d) $\text{Ca}(\text{HCO}_3)_2$
46. What is X in the following reaction?

$$\text{MgCl}_2 + 2\text{H}_2\text{O} \longrightarrow X + 2\text{HCl} + \text{H}_2\text{O}$$
 (a) MgO
 (b) Mg
 (c) $\text{Mg}(\text{OH})_2$
 (d) $\text{Mg}(\text{OH})\text{Cl}$

Case III : Read the passage given below and answer the following questions from 47 to 50.

All alkali metals dissolve and form blue solution in liquid ammonia. When alkali metals

are dissolved in liquid ammonia, there is a considerable expansion in total volume hence such solutions are called expanded metals. The blue solution of an alkali metal in ammonia shows certain characteristic properties which are explained on the basis of formation of ammoniated (solvated) metal cations and ammoniated electrons in the metal ammonia solution in the following way :



The blue solution is paramagnetic and has high electrical conductivity due to the presence of unpaired electron in the cavities in ammoniacal solution.

47. A metal M reacts with N_2 to give a compound 'A' ($M_3\text{N}$). 'A' on heating at high temperature gives back 'M' and 'A' on reacting with H_2O gives a gas 'B'. 'B' intensifies colour of CuSO_4 solution when passes through it. M and B can be
 (a) Mg and NH_3
 (b) Na and NH_3
 (c) Li and NH_3
 (d) Al and NH_3
48. Sodium dissolves in liquid NH_3 to give a deep blue solution. This is due to
 (a) ammoniated Na^+
 (b) ammoniated Na^-
 (c) formation of Na^+/Na^- pair
 (d) ammoniated electrons.
49. The increasing order of the density of alkali metals is
 (a) $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{Cs}$
 (b) $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$
 (c) $\text{Cs} < \text{Rb} < \text{Na} < \text{K} < \text{Li}$
 (d) $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$
50. The reaction between sodium and water can be made less vigorous by
 (a) lowering the temperature
 (b) adding a little alcohol
 (c) amalgamating sodium
 (d) adding a little acetic acid.

➔ Assertion & Reasoning Based MCQs

For question numbers 51-60, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

51. Assertion : The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2 .

Reason : Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2 .

52. Assertion : Generally alkali and alkaline earth metals form superoxides.

Reason : There is a single bond between O and O in superoxides.

53. Assertion : BeSO_4 is soluble in water while BaSO_4 is not.

Reason : Hydration energy decreases down the group from Be to Ba and lattice energy remains almost constant.

54. Assertion : Lithium salts are hydrated.

Reason : Lithium has higher polarising power than other alkali metal group members.

55. Assertion : Beryllium carbonate is kept in the atmosphere of carbon dioxide.

Reason : Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide.

56. Assertion : *s*-block elements are highly electropositive.

Reason : The valence electrons present in *s*-orbital are loosely held.

57. Assertion : The ionization enthalpies of alkali metals increase progressively as we move down the group from Li to Cs.

Reason : The ionic radii increase as we move down the group from Li to Cs.

58. Assertion : The solubility of the alkaline earth metal hydroxides in water increases with increase in atomic number down the group.

Reason : The alkaline earth metal hydroxides are basic in character. The only exception is $\text{Be}(\text{OH})_2$ which is amphoteric.

59. Assertion : Electrode potential is a measure of the tendency of an element to lose electrons in the aqueous solution. So, the reducing property can be correlated in terms of electrode potentials (E°) of alkali metals.

Reason : More negative is the electrode potential, higher is the tendency of the element to lose electrons and hence, stronger is the reducing agent.

60. Assertion : The first element (Li) of group I differs considerably from the rest of the elements of the same group.

Reason : Lithium has small ionic and atomic radii, high electronegativity and ionization enthalpy, high polarising power of its cation and absence of *d*-electrons in its valence shell compared to rest of the elements of the same group.

SUBJECTIVE TYPE QUESTIONS

➔ Very Short Answer Type Questions (VSA)

- Which has a higher melting point, sodium or potassium?
- Why are the first ionization enthalpies of group 1 elements low?
- Why are group 2 elements harder than group 1 elements?
- BeCl_2 in aqueous solution exists as $[\text{Be}(\text{OH})_4]^{2+}$. Explain.

- Find out the oxidation state of sodium in Na_2O_2 .
- Halides of Be dissolve in organic solvents while those of Ba do not. Why is it so?
- What will be formed when lithium nitrate is heated?
- Why are lithium salts commonly hydrated and those of the other alkali ions are usually anhydrous?
- Explain why Cs is used in photoelectric cell?
- Potassium carbonate cannot be prepared by Solvay process. Why ?

➡ Short Answer Type Questions (SA-I)

- On combustion Li forms Li_2O ; sodium gives the peroxide, Na_2O_2 ; and potassium, rubidium and caesium give superoxides, MO_2 . Why Li does not form a peroxide?
- Complete the reactions :
 - $\text{Be}(\text{OH})_2 + 2\text{OH}^- \longrightarrow$
 - $\text{BaO} + \text{H}_2\text{O} \longrightarrow$
- (i) Why are alkali metal used in photoelectric cells?
(ii) What happens when K burns in air? Write equation.
- What happens when :
 - sodium metal is dropped in water?
 - sodium metal is dissolved in liquid ammonia?
- Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?
- What happens when :
 - sodium peroxide dissolved in hot water?
 - sodium metal is heated in free supply of air?
- Draw the structure of (i) BeCl_2 (vapour) (ii) BeCl_2 (solid).
- (i) Name the chief factors responsible for the anomalous behaviour of lithium.
(ii) Complete the following reactions :
 - $4\text{LiNO}_3 \xrightarrow{\Delta}$
 - $2\text{NaNO}_3 \xrightarrow{\Delta}$
- Account for the following:
 - Magnesium does not show any flame colouration.
 - Group 1 elements have low melting and boiling points.
- Alkaline earth metals always form divalent cations even though their second ionization enthalpies are almost double than their first ionization enthalpies. Explain.

➡ Short Answer Type Questions (SA-II)

- Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals.
 - Nitrates
 - Carbonates
 - Sulphates
- (a) Write balanced equations for the reactions:
 - alkali metal and water
 - alkali metal and dihydrogen.

(b) The E for Cl_2/Cl^- is +1.36, for I_2/I^- is +0.53, for Ag^+/Ag is +0.79, for Na^+/Na is -2.71 and for Li^+/Li is -3.04. Arrange the following ionic species in decreasing order of reducing strength:
 I^- , Ag , Cl^- , Li , Na
- Compare the alkali metals and alkaline earth metals with respect to (i) ionisation enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides.
- Give reason :
 - Alkali metals are strong reducing agents
 - Alkali metals are soft metals
 - Alkali metals tarnish in air easily.
- Complete the reactions:
 - $\text{Na} + \text{O}_2 \longrightarrow$
 - $\text{BeCl}_2 + \text{LiAlH}_4 \longrightarrow$
 - $\text{NaNO}_3 \xrightarrow{\Delta}$
- Explain term Diagonal Relationship in context of Be and Al. Give two points of similarities between them.
- Give reason:
 - Sodium is less reactive than potassium.
 - Be and Mg do not give colour to the flame whereas other alkaline earth metals do so.
 - Sodium is stored under kerosene oil.

28. An element of group 2 forms covalent oxide which is amphoteric in nature and dissolves in water to give an amphoteric hydroxide. Identify the element and write chemical reactions of the hydroxide of the element with an alkali and an acid.
29. In what ways lithium shows similarities to magnesium in its chemical behaviour?
30. Arrange the following in order of property mentioned against each :
- BeCl_2 , MgCl_2 , CaCl_2 , BaCl_2 [Increasing ionic character]
 - $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$ [Increasing solubility in water]
31. Given reason:
- Alkali metals impart colours to Bunsen Burner flame.
 - KO_2 is paramagnetic.
- Alkaline earth metals give blue solutions, when dissolved in liquid ammonia.
32. (a) Among the given alkali metals, which has least melting point? Na, K, Rb, Cs
(b) Which one of the following alkali metals gives hydrated salts? Li, Na, K, Cs
33. How would you explain the following observations?
- BeO is almost insoluble but BeSO_4 is soluble in water,
 - LiI is more soluble than KI in ethanol.
34. Comment on the following observations :
- Why are alkali metals not found in nature?
 - The mobilities of the alkali metal ions in aqueous solution are $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$
35. Discuss the general characteristics and gradation in properties of alkaline earth metals.

Long Answer Type Questions (LA)

36. Present a comparative account of the alkali and alkaline earth metals with respect to the following characteristics :
- Tendency to form ionic/ covalent compounds
 - Nature of oxides and their solubility in water
 - Formation of oxosalts
 - Solubility of oxosalts
 - Thermal stability of oxosalts
37. (a) (i) What are the products formed when alkali metal oxide (M_2O), peroxide (M_2O_2) and superoxide (MO_2) hydrolysed by water?
(ii) Why sodium forms peroxide but potassium forms superoxide?
- (b) (i) Can we store sodium in water or not? Why.
(ii) Write balanced equations for the reactions between :
- Na_2O_2 and H_2O
 - KO_2 and H_2O .
38. (a) Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods.
(b) Explain the following :
- Be and Mg do not impart any colour to the flame.
 - What happens when Mg is burnt in air?
 - Account for the following:
 - Magnesium does not show any flame colouration.
 - Group 1 elements have low melting and boiling points.
39. The s-block elements are characterised by their larger atomic sizes, lower ionisation enthalpies, invariable +1 oxidation state and solubilities of their oxosalts. In the light of these features describe the nature of their oxides, halides and oxosalts.
40. (a) When a metal of group 1 was dissolved in liquid ammonia, the following observations were obtained:
- Blue solution was obtained initially.
 - On concentrating the solution, blue colour changed to bronze colour.
- How do you account for the blue colour of the solution? Give the name of the product formed on keeping the solution for some time.
- (b) The stability of peroxide and superoxide of alkali metals increase as we go down the group. Explain giving reason.

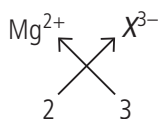
- 23. (c) :** Polarizing power $\propto \frac{\text{charge on ion}}{\text{size of cation}}$
- 24. (a) :** Mg(OH)_2 is least basic since basic character of hydroxides increases from Mg(OH)_2 to Ba(OH)_2 .
- 25. (d) :** Both BeCl_2 and AlCl_3 are strong Lewis acids.
- 26. (a) :** BeCl_2 is a covalent compound due to small size of Be^{2+} (Fajan's rule) hence, soluble in ethanol.
- 27. (b) :** The hydroxides of alkaline earth metals are less soluble. The solubility increases with increase in size of the metal and this is due to decrease in their lattice energy and increase in hydration energy.
- 28. (b) :** As the reduction potential values decreases down a group, the reducing character increases down the group.
- 29. (c) :** Density gradually increases on moving down from Li to Cs. Potassium is, however, lighter than sodium. The abnormal value of potassium is due to unusual increase in atomic size, *i.e.*, atomic volume.
- 30. (a) :** 1st ionisation energy of alkaline earth metals is higher than those of alkali metals due to increased nuclear charge.

31. (b)

32. (b)

- 33. (c) :** Magnesium is a strong reducing agent.
- 34. (d) :** Lithium does not form solid bicarbonate though it does exist in solution. Bicarbonates of alkaline earth metals are stable only in solution and have not isolated in the pure state.
- 35. (c) :** Pb and Ba both give yellow ppt. with K_2CrO_4 in acetic acid and white precipitate with dil. H_2SO_4 . But lead salts give precipitate with sodium chloride or iodide also whereas barium does not. It means given salt is barium salt and with sodium carbonate it gives white precipitate of barium carbonate.
- 36. (a) :** Be exhibits maximum covalency of four whereas Al shows maximum covalency of six.
- 37. (d) :** Halides of alkaline earth metals are hygroscopic in nature, act as dehydrating agent and can absorb moisture from air.
- 38. (d) :** Electronic configuration of X is $1s^2, 2s^2, 2p^3$. So, valency of X will be 3.

Magnesium ion = Mg^{2+}



Formula : Mg_3X_2

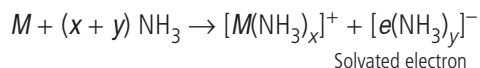
- 39. (b) :** As we move down the group from BeSO_4 to BaSO_4 , the enthalpy of hydration of the cations become smaller due

to increase in ionic size. Salts of heavier metal ions are less soluble than those of lighter ions.

40. (d) : Hydration energy for $\text{Mg}^{2+} >$ hydration energy for Mg^+ , hence Mg forms dipositive ion.

41. (a) : Alkali metals are good conductors of heat and electricity but have low melting points and ionisation potentials.

42. (d) : The metal atom loses electron and combines with ammonia molecule.

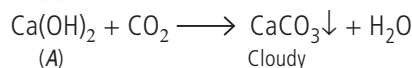
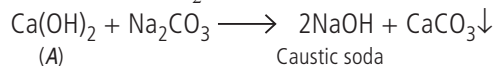


These ammoniated electrons are responsible for blue colour and conductivity of the solution.

43. (b) : In electrochemical series based on oxidation potential alkali metals are far below hydrogen, thus they displace hydrogen from water.

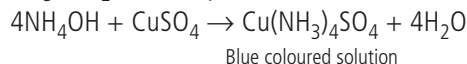
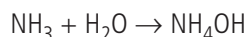
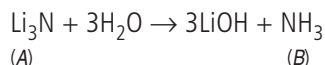
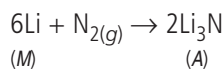
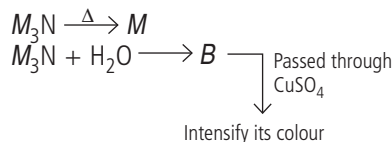
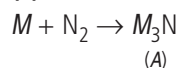
44. (d) : Basic strength of alkali metal hydroxides increases down the group. Hence Ba(OH)_2 is more basic than Be(OH)_2 .

45. (c) : Ca(OH)_2 is used as flocculant.



46. (a) : $\text{MgCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{MgO} + 2\text{HCl} + \text{H}_2\text{O}$

47. (c) : Reaction can be summarized as :



48. (d) : $M + (x + y)\text{NH}_3 \rightarrow [M(\text{NH}_3)_x]^+ + [e(\text{NH}_3)_y]^-$

The deep blue colour of the solution is due to the ammoniated electrons which absorbs energy in the visible region of light and thus imparts blue colour to the solution.

49. (a) : Density gradually increases in moving down from Li to Cs. K is, however, lighter than Na.

Densities of alkali metals are as follows :

Element	Li	Na	K	Rb	Cs
Density (g/mL)	0.54	0.97	0.86	1.53	1.90

i.e., $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{Cs}$

50. (c)

51. (a)

52. (c) : Only K, Rb and Cs from alkali metals form superoxides and superoxides possess three electron bond ($:\ddot{\text{O}} \text{---} \ddot{\text{O}}:\text{)}^-$.

53. (a)

54. (c) : Li^+ has maximum degree of hydration due to its small size and for this reason lithium salts are mostly hydrated.

55. (a)

56. (a) : The loosely held s -electron in the outermost valence shell of these elements makes them the most electropositive metals which readily give ions, M^+ or M^{2+} .

57. (d) : The ionization enthalpies of alkali metals decrease progressively as we move down the group from Li to Cs.

58. (b) : The solubility of the alkaline earth metal hydroxides in H_2O increases with increase in atomic number down the group. This is due to the reason that both lattice energy and hydration energy decrease down the group as the size of the cation increases but lattice energy decreases more rapidly than the hydration energy and hence, their solubility increases down the group.

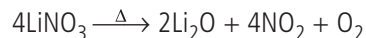
59. (a)

60. (a)

SUBJECTIVE TYPE QUESTIONS

- Sodium has higher melting point than potassium because of stronger metallic bonding.
- The ionization enthalpy, is the energy required to completely remove an electron from an isolated gaseous atom or ion. The closer and more tightly an electron is bound to its nucleus, the more difficult it will be to remove the electron and higher will be the ionization enthalpy. Group 1 elements have low first ionization enthalpies because the loss of an electron takes place readily to form a stable octet.
- This is because the smaller atomic size causes the electrons to be packed more closely, thereby forming strong metallic bonds.
- Due to small size and high ionisation enthalpy, Be forms coordination compound.
- Let oxidation state of Na = x
The oxidation state of O = -1 (present as peroxide)
 $\therefore 2x + 2(-1) = 0 \Rightarrow 2x - 2 = 0$
 $\Rightarrow 2x = 2 \Rightarrow x = +1$
 \therefore Oxidation state of Na in Na_2O_2 is $+1$.
- This is because halides of Be are covalent while those of Ba are ionic.

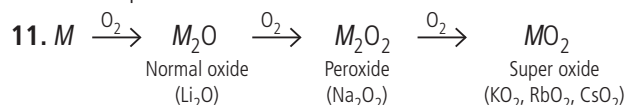
7. Lithium nitrate on heating decomposes to give Li_2O , NO_2 and O_2



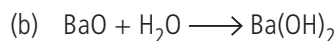
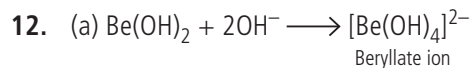
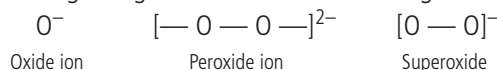
8. Because of smallest size among alkali metals, Li^+ can polarise water molecules more easily than the other alkali metal ions and hence get attached to lithium salts as water of crystallisation. For example, lithium chloride crystallises as $\text{LiCl} \cdot 2\text{H}_2\text{O}$ but sodium chloride as NaCl .

9. Calcium is used in photoelectric cell due to low value of ionization potential.

10. Solvay process cannot be extended to the manufacture of K_2CO_3 because KHCO_3 is too soluble to be precipitated by the addition of ammonium hydrogen carbonate to a saturated solution of potassium chloride.

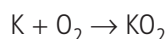


The normal oxides contain O^{2-} ion, the peroxides contain O_2^{2-} ion and superoxides contain O_2^- ion. The peroxides and superoxides become more stable with increase in atomic number of the alkali metal. The formation and stability of these oxides can be explained on the basis of lattice energy effects. Li^+ ion being a small ion has a strong positive field around it and can stabilise only a small anion, O^{2-} whereas Na^+ being a large cation can stabilise a large ion and so on.

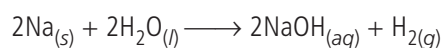


13. (i) Alkali metals are used in photoelectric cells and because of their low ionization energies they lose electrons very easily on irradiation.

(ii) Potassium reacts with oxygen to form superoxide.



14. (a) Sodium hydroxide and hydrogen gas will be formed which will catch fire.



(b) Sodium metal dissolves in liquid ammonia and gives deep blue solution which is conducting in nature.

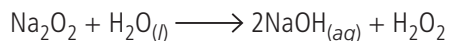


The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution.

15. Li_2CO_3 decomposes on heating because the Li^+ ion exerts a strong polarising action and distorts the electron cloud of the nearby oxygen atom of the large CO_3^{2-} ion. This results in the weakening of the C—O bond and strengthening of the Li—O bond. This ultimately facilitates the decomposition

of Li_2CO_3 into Li_2O and CO_2 . The lattice energy of Li_2O is higher than the lattice energy of Li_2CO_3 . This also favours decomposition of Li_2CO_3 . Na^+ ion being bigger in size, the lattice energy of Na_2O is less stable than that of Na_2CO_3 . Therefore, Na_2CO_3 does not decompose on heating.

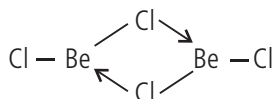
16. (i) Sodium hydroxide and hydrogen peroxide will be formed.



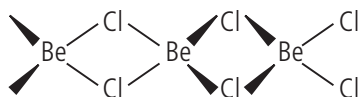
(ii) Sodium peroxide is formed.



17. (i) BeCl_2 exists as a dimer in vapour phase, which dissolves into the linear monomer $\text{Cl}-\text{Be}-\text{Cl}$ at 1200 K.

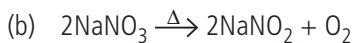
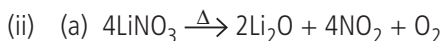


(ii) BeCl_2 (solid): Beryllium chloride has a chain structure in solid state :



18. (i) Chief factors responsible for the anomalous behaviour of lithium are :

- (I) its very small size
- (II) high electronegativity
- (III) high ionization enthalpy and
- (IV) absence of vacant *d*-atomic orbital in the valence shell.

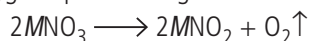


19. (i) In Mg, the electrons are tightly held and excitation by mere flame is rather difficult, thus, Mg does not show flame colouration.

(ii) As group 1 elements have large size, the intermetallic bonds in them are quite weak. Hence they have low melting and boiling points.

20. In the solid state, higher enthalpy of lattice formation by M^{2+} ions (as compared to M^+ ions) more than compensates the higher second ionization enthalpies of metals and in aqueous solution, higher enthalpy of hydration of M^{2+} ions (as compared to M^+ ions) more than compensate at the higher second ionization enthalpy of metals.

21. (a) **Nitrates** : Nitrates of alkali metals are of the type $M\text{NO}_3$, they are soluble in water and do not undergo hydrolysis. Except LiNO_3 , other nitrates of this group decompose to nitrites and oxygen upon heating.



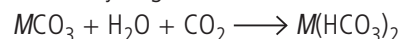
Nitrates of alkaline earth metals are of the type $M(\text{NO}_3)_2$. They are soluble in water and upon heating they decompose into their corresponding oxides with evolution of a mixture of NO_2 and oxygen.



(b) **Carbonates** : All alkali metals form carbonates of the type $M_2\text{CO}_3$. Their carbonates are highly stable towards heat and readily soluble in water. The stability and solubility of the carbonates increases in the same order:



Li_2CO_3 decomposes on heating and is insoluble in water. Carbonates of alkaline earth metals ($M\text{CO}_3$) are insoluble in water, they dissolve in water only in presence of CO_2 due to the formation of a hydrogen carbonate.



Solubility of carbonates decreases as we descend the group and stability increases due to increase in electropositive character of the metal.

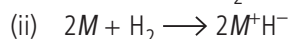
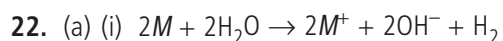
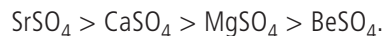
(c) **Sulphates** : Alkali metal sulphates are of the type $M_2\text{SO}_4$. Except Li_2SO_4 , all other sulphates are soluble in water. Alkaline earth metal sulphates are of the type $M\text{SO}_4$. The solubility of sulphates decreases on moving down the group. CaSO_4 is sparingly soluble, SrSO_4 , BaSO_4 and RaSO_4 are almost insoluble. The solubilities of BeSO_4 and MgSO_4 are due to high energy of solvation of smaller Be^{2+} and Mg^{2+} ions. The order of solubility is :



The sulphates decompose on heating to give the corresponding oxide (MO).



The stability increases as the basic nature of the metal increases.



(b) The order is : $\text{Li} > \text{Na} > \text{I}^- > \text{Ag} > \text{Cl}^-$

23. (i) **Ionisation Enthalpy** : The ionisation energies of alkaline earth elements are higher than those of alkali metals due to higher nuclear charge and smaller radii.

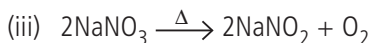
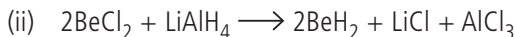
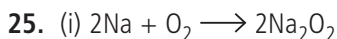
(ii) **Basicity of oxides** : Oxides of alkali metals are stronger bases as compared to those of alkaline earth metals present in the same period. e.g., when Na_2O is dissolved in water, NaOH formed is a stronger base than when MgO is dissolved in water to form $\text{Mg}(\text{OH})_2$. This is due to higher ionisation energies of alkaline earth metals.

(iii) **Solubility of hydroxides** : Alkali metal hydroxides are more soluble in water as compared to the hydroxides of alkaline earth metals present in the same period. This is due to higher lattice energy of the hydroxides of alkaline earth elements as compared to those of alkali metals.

24. (i) The alkali metals have only one electron in their valence shell which they lose easily, owing to their low ionization enthalpies, hence they are strong reducing agents.

(ii) Due to the presence of weak metallic bonding, alkali metals are soft and can be cut with a knife.

(iii) Lithium, sodium and potassium are all soft metals that are easily cut with a knife. The freshly cut surface is a shiny, silver colour, but this tarnishes quickly to a dull grey as the metal reacts with oxygen and water present in the air.



26. The charge/radius ratio of Be^{2+} is nearly the same as that of Al^{3+} ion. Hence, beryllium resembles aluminium. This is known as diagonal relationship.

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

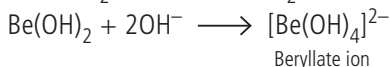
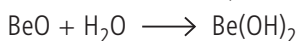
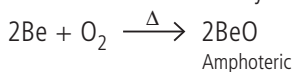
(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[\text{Be}(\text{OH})_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[\text{Al}(\text{OH})_4]^-$.

27. (a) This is mainly due to high ionisation enthalpy of sodium as compared to potassium. Therefore, potassium is more electropositive, reactive and a stronger reducing agent than sodium.

(b) In Be and Mg, the electrons are tightly held and excitation by mere flame is rather difficult, thus, they do not show flame colouration.

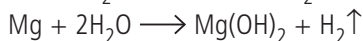
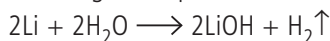
(c) Sodium is stored in kerosene oil because in air, sodium is easily oxidised to oxide which may dissolve in the moisture to form hydroxide.

28. The element is beryllium.

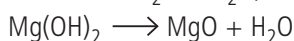


29. (a) Both Li and Mg are harder and lighter than the other metals in their respective groups.

(b) Li like Mg decomposes water slowly to liberate hydrogen.



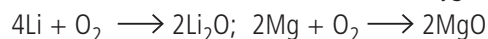
The hydroxides so formed are weak bases and decompose on heating.



(c) Both form nitrides upon direct combination with nitrogen gas.

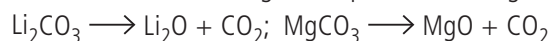


(d) Both form monoxides when heated in oxygen.

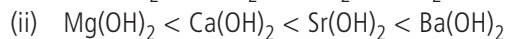


The oxides do not combine with excess oxygen to give superoxides.

(e) Carbonates of Li and Mg decompose on heating.



(f) Both LiCl and MgCl_2 are soluble in ethanol, they are deliquescent and crystallise from aqueous solution as hydrates, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.



31. (i) Alkali metals and their salts impart colour to flame. It is because their loosely held valence electrons get excited to higher energy level. When they return back they release visible light of characteristic colour to flame.

(ii) In KO_2 , superoxide ion O_2^- is present. O_2^- ion has one unpaired electron in its antibonding molecular orbital. Hence, it is paramagnetic in nature.

(iii) Like alkali metals the alkaline earth metals dissolve in liquid ammonia to give deep blue black solution forming ammoniated ions.



32. (a) Atomic size increases as we move down the group. As a result, the strength of metallic bonding decreases on moving down a group in the periodic table. This causes a decrease in the melting point. Among the given metals, the size of Cs is the largest and thus it has the least melting point.

(b) Smaller the size of an ion, the more highly it is hydrated. Among alkali metal ions, Li^+ ion is smallest in size. Also, it has the highest charge density and highest polarizing power. Hence, it attracts water molecules more strongly than the other alkali metal ions. As a result, it forms hydrated salts such as $\text{LiCl} \cdot 2\text{H}_2\text{O}$. The other alkali metal ions are larger in size than Li^+ and have weaker charge densities. Hence, they usually do not form hydrated salts.

33. (i) BeO is almost insoluble in water as it is covalent in nature and tightly held together in the solid state while BeSO_4 is highly soluble in water due to high energy of solvation of smaller Be^{2+} ion.

(ii) LiI having much more covalent character than KI because of small size of Li^+ as compared to K^+ . Hence, LiI is more soluble in ethanol.

34. (a) All the alkali metals have one valence electron, ns^1 , outside the noble gas core. The loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose an electron to give monovalent M^+ ions. Thus, due to the reason cited above, alkali metals are never found free in nature but are always found in combined state.

(b) This is attributed to the hydration of the cation in water. As a result, size of the cation increases and its mobility decreases. Due to the smallest size, Li^+ ion is hydrated to the maximum and has least mobility while Cs^+ ion due to least hydration has maximum mobility.

35. (i) Electronic configuration : The valence electronic configuration of atoms of the group II A elements is ns^2 , where 'n' is the period number.

(ii) **Atomic and ionic sizes :** The size of the atom increases gradually from Be to Ra. Their ions are also large and size of the ion increases from Be^{2+} to Ra^{2+} .

(iii) **Ionisation enthalpy :** The 1st and 2nd ionisation energies of these metals decrease from Be to Ba as size increases.

36. (i) Tendency to form ionic/covalent compounds :

(a) All common compounds of alkali metals are generally ionic in nature. Halides and oxides are ionic in nature with exception of lithium compounds which are generally covalent in nature.

(b) Alkaline earth metals form ionic oxides and halides except Be which forms covalent compounds.

(ii) Nature of oxides and their solubility in water :

(a) Alkali metals form oxides, peroxides and superoxides. These oxides are basic in nature and basic character increases down the group. Oxides dissolve in water to give hydroxides. These hydroxides are strong bases.

(b) Alkaline earth metal oxides are basic in nature but less basic than alkali metal oxides. BeO is amphoteric while other oxides are basic and form sparingly soluble hydroxides.

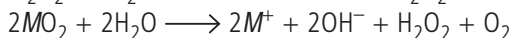
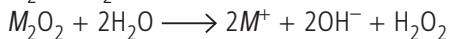
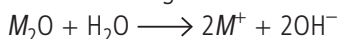
(iii) Formation of oxosalts :

(a) Alkali metals form sulphates, carbonates and bicarbonates. (b) Alkaline earth metals form sulphates, carbonates and nitrates.

(iv) Solubility of oxosalts : (a) Alkali metal oxosalts are generally soluble in water. Solubility increases down the group. (b) Carbonates and sulphates of alkaline earth metals become insoluble as we move down the group.

(v) Thermal stability of oxosalts : (a) Alkali metal oxosalts are thermally stable and stability increases down the group. Li_2CO_3 and Li_2SO_4 decompose on heating. (b) Alkaline earth metals carbonates decompose on heating while their thermal stability increases down the group.

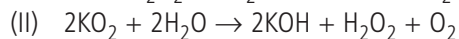
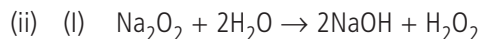
37. (a) (i) Alkali metal oxide, peroxide and superoxide are easily hydrolysed by water to form the hydroxides according to the following reactions:



(ii) Sodium ion is larger in size and has comparatively weaker +ve field around it which can not prevent oxide ion to combine with another oxygen atom to form peroxide ion.

While K^+ is larger than Na^+ and has still weaker +ve field which can not prevent even peroxide ion to combine with another oxygen atom to form superoxide.

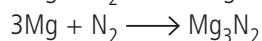
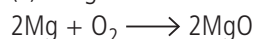
(b) (i) Sodium will react with water to form sodium hydroxide and hydrogen gas which will catch fire. For this reason, sodium cannot be stored in water.



38. (a) Alkali metals cannot be extracted by the reduction of their oxides and other compounds as they are strong reducing agents themselves and no such reducing agents are there which can reduce them to get pure metal.

(b) (i) In Be and Mg, the electrons are tightly held and excitation by mere flame is rather difficult, thus, they do not show flame colouration.

(ii) Mg burns in air to form MgO and Mg_3N_2 .



(c) (i) In Mg, the electrons are tightly held and excitation by mere flame is rather difficult, thus, Mg does not show flame colouration.

(ii) As group 1 elements have large size, the intermetallic bonds in them are quite weak. Hence they have low melting and boiling points.

39. (i) Nature of oxides – Alkali metals form M_2O , M_2O_2 and MO_2 types of oxides. The stability of the peroxide or superoxide increases as the size of metal cation increases, this is due to stabilisation of large anions by larger cations.

(ii) Nature of halides – Alkali metal halides have general formula MX . All halides are soluble in water. LiF is very less soluble in water due to its high lattice energy. Their m.pt. and b.pt. follow the trend – fluoride > chloride > bromide > iodide due to increase in size of halide ion, the lattice energy increases.

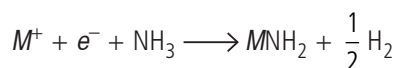
(iii) Oxosalts – Oxosalts of alkali metals are generally soluble in water and thermally stable. As electropositive character increases down the group, stability of carbonates and bicarbonates increases.

40. (a) (i) Alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.



Blue colour is due to ammoniated electron.

(ii) On standing, hydrogen is slowly liberated and amide is formed. The colour changes to bronze. On keeping for sometime.



(b) The increase in stability of peroxides and superoxides of alkali metals from Li to Cs can be explained by stabilisation of larger anions by larger cations through higher lattice energy.



The *p*-Block Elements (Group 13 and 14)



Recap Notes

- The elements in which the last electron enters into any of the outermost *p*-orbitals are called *p-block elements*.
 - The general outer electronic configuration of the *p*-block elements is ns^2np^{1-6} .
 - The elements belonging to the group 13 to 18 of the long form of periodic table are *p-block elements*. The *p*-block elements include *metals*, *non-metals* and *metalloids*.
 - The *p*-block elements enter into chemical combination by losing, gaining or sharing the valence electrons.
 - Nature of compounds** : The *p*-block elements mostly form covalent compounds. The halogens, however, form ionic compounds with alkali and alkaline earth metals.
 - Oxidation states** : The highest oxidation state shown by a *p*-block element is equal to the total number of valence electrons.
 - The first element of a group differs from the heavier elements in their ability to form $p\pi-p\pi$ bonds.
- Electronegativity** : First decreases from B to Al and then increases.
- Metallic or electropositive character** : First increases from B to Al and then decreases.
- Density** : Increases down the group.
- Melting and boiling points** : Melting points decreases sharply on moving down the group from B to Ga and then increases from Ga to Tl while boiling points decreases from B to Tl.
- Reducing character** : $\text{Al} > \text{Ga} > \text{In} > \text{Tl}$.

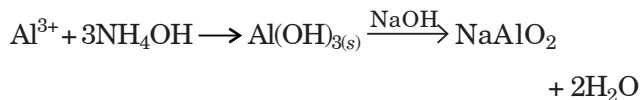
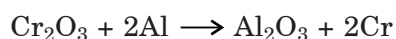
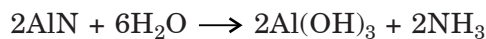
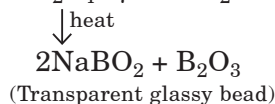
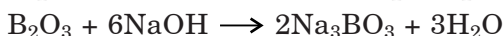
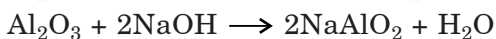
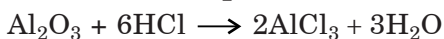
GROUP 13 ELEMENTS (BORON FAMILY)

- Group 13 of periodic table consists of following elements : ${}^5\text{B}$, ${}_{13}\text{Al}$, ${}_{31}\text{Ga}$, ${}_{49}\text{In}$, ${}_{81}\text{Tl}$ and ${}_{113}\text{Nh}$.
- Physical properties** :
 - Physical state** : All are solids, B is non-metallic, Al, Ga, In and Tl are silvery white metals.
 - Atomic and ionic radii** : Increases from B to Al then decreases from Al to Ga and then again increases.
 - Ionisation enthalpy** : Less than the corresponding members of alkaline earth metals and shows no regular trend down the group : $\text{B} > \text{Tl} > \text{Ga} > \text{Al} > \text{In}$

Chemical properties :

Hydrides (MH_3)	$\text{MH}_3 + \text{H}^- \rightarrow [\text{MH}_4]^-$ Electron acceptor Electron donor Anionic complex (where $M = \text{B, Al and Ga}$) Thermal stability : $\text{BH}_3 > \text{AlH}_3 > \text{GaH}_3 > \text{InH}_3 > \text{TlH}_3$
Oxides (M_2O_3) and Hydroxides $\text{M}(\text{OH})_3$	Basic strength : $\text{B}_2\text{O}_3 < \text{Al}_2\text{O}_3 < \text{Ga}_2\text{O}_3 < \text{In}_2\text{O}_3 < \text{Tl}_2\text{O}_3$ $\text{B}(\text{OH})_3 < \text{Al}(\text{OH})_3 < \text{Ga}(\text{OH})_3$ Acidic Amphoteric Basic Basic $< \text{In}(\text{OH})_3 < \text{Tl}(\text{OH})_3$
Halides (MX_3)	$2\text{M} + 3\text{X}_2 \rightarrow 2\text{MX}_3$ (where, $M = \text{B, Al, Ga, In and X} = \text{F, Cl, Br, I}$) Lewis acid strength of boron trihalides : $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ Lewis acid strength of trihalides of group 13 elements : $\text{BX}_3 > \text{AlX}_3 > \text{GaX}_3 > \text{InX}_3$ Tl does not form trihalides.

► **Some important chemical reactions :**



● **Preparation, properties and uses of boron:**

Preparation	Physical properties	Chemical properties	Uses
$\text{B}_2\text{O}_3 + 3\text{Mg} \xrightarrow{\text{Heat}} 3\text{MgO} + 2\text{B}_{(s)}$	<ul style="list-style-type: none"> It is extremely hard and black coloured solid. 	$2\text{B} + 3\text{X}_2 \longrightarrow 2\text{BX}_3$	<ul style="list-style-type: none"> In making filaments which are used in making light composite materials for aircraft.
$2\text{BX}_3 + 2\text{H}_2 \xrightarrow[\text{Ta or W}]{1270^\circ\text{C}} 2\text{B} + 6\text{HX}$	<ul style="list-style-type: none"> It has low electrical conductivity and is non-metallic. 	$\text{B} + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{BO}_3 + 3\text{NO}_2\uparrow$ (conc.)	<ul style="list-style-type: none"> As semiconductor in making electronic devices.
$\text{KBF}_4 \xrightarrow{\text{Electrolysis}} \text{K}^+ + \text{B}^{3+} + 4\text{F}^-$	<ul style="list-style-type: none"> It has two allotropes : <ul style="list-style-type: none"> Crystalline boron : Black and chemically inert. It is very hard in nature. Amorphous boron: Brown and chemically active. The transition between these forms is extremely slow process. 	$2\text{B} + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}_3\text{BO}_3 + 3\text{SO}_2\uparrow$ (conc.)	<ul style="list-style-type: none"> In preparation of metal borides which are used as protective shields and control rods in nuclear reactors because $^{10}_5\text{B}$ has high ability to absorb neutrons.
$\text{B}_2\text{H}_6 \xrightarrow[1773\text{ K}]{\text{Heat}} 2\text{B} + 3\text{H}_2$	<ul style="list-style-type: none"> It is poor conductor of heat and electricity. It has two isotopes : $^{10}_5\text{B}$(20%) and $^{11}_5\text{B}$(80%). 	$4\text{B} + 3\text{O}_2 \longrightarrow 2\text{B}_2\text{O}_3$ $2\text{B} + \text{N}_{2(g)} \longrightarrow 2\text{BN}_{(s)}$ $2\text{B} + 6\text{NaOH} \xrightarrow{>773\text{ K}} 2\text{Na}_3\text{BO}_3 + 3\text{H}_2$ $2\text{B} + 3\text{H}_2\text{O} \longrightarrow \text{B}_2\text{O}_3 + 3\text{H}_2$ (Red (Steam) hot)	<ul style="list-style-type: none"> In steel industry for increasing the hardness of steel.

● **Anomalous behaviour of boron :**

Property	Boron	Other elements of group 13
Metallic behaviour	Non-metal	Metals
Maximum covalency	4	6
Allotropy	Exhibits	Do not exhibit
Oxidation states	Only +3	+1, +3
Compounds	Only covalent	Both ionic and covalent
Halides	Monomeric	Polymeric
Aqueous solution	No ionisation	Form cations
Oxides and hydroxides	Acidic	Mainly basic
Action of non-oxidising acids	No action	React
Combination with metals	Forms boride	Do not combine (form alloy)

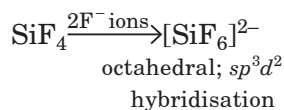
GROUP 14 ELEMENTS (CARBON FAMILY)

- Group 14 of periodic table consists of following elements : ${}_6\text{C}$, ${}_{14}\text{Si}$, ${}_{32}\text{Ge}$, ${}_{50}\text{Sn}$, ${}_{82}\text{Pb}$ and ${}_{114}\text{Fl}$.

Property	C	Si	Ge	Sn	Pb	Fl
Atomic number(Z)	6	14	32	50	82	114
Covalent radius (pm)	77	118	122	140	144	180
Electro-negativity	2.5	1.8	1.8	1.8	1.8	–
Oxidation states	+4	+4	+2, +4	+2, +4	+2, +4	0, +1, +2, +4, +6

● **General characteristics and properties :**

- ▶ The variable oxidation states are seen due to *inert pair effect*.
- ▶ C and Si → non-metals, Ge → metalloid, Sn and Pb → metals. Metallic character increases down the group.
- ▶ The covalent nature in the compounds of Sn^{4+} and Pb^{4+} ions is due to high polarisation produced by them.
- ▶ As we move down the group, stability of lower oxidation state increases due to inert pair effect.
- ▶ Except C, all other elements form complexes due to presence of vacant *d*-orbitals in them *i.e.*, these behave as Lewis acids *e.g.*,

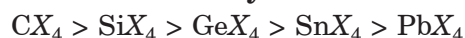


- ▶ Semiconductor grade Si is prepared by the reduction of highly pure $\text{SiCl}_4/\text{SiHCl}_3$ with H_2 or by the pyrolysis of SiH_4 mainly.

▶ **Nature of oxides :**

Oxides	Nature
CO , CO_2 , SiO_2	acidic
GeO , GeO_2 , SnO , SnO_2 , Pb_3O_4	amphoteric
PbO , PbO_2	basic

▶ **Thermal stability of tetrahalides :**



- ▶ Elements in this group are relatively unreactive but reactivity increases down the group. Pb often appears more noble than expected due to a surface coating of oxide and partly due to high over potential for the reduction of H^+ to H_2 at a lead surface.

▶ **Reactivity of the elements of group 14 :**

Reagent	Reactivity
H_2O	C, Si, Ge, Pb are unaffected by H_2O .
	$\text{Sn} + 2\text{H}_2\text{O} \longrightarrow \text{SnO}_2 + 2\text{H}_2$ (steam)
Dilute acids	C, Si, Ge are unaffected by dilute acids.
	Pb does not dissolve in dilute H_2SO_4 due to formation of PbSO_4 coating.
Concentrated acids	Diamond is unaffected by concentrated acids, but graphite is oxidised by concentrated HNO_3 to give graphitic acid ($\text{C}_{11}\text{H}_4\text{O}_5$) which is an insoluble yellowish green substance and to graphite oxide with hot concentrated HF/HNO_3 .
	Si is oxidised and changes to SiF_4 by hot concentrated HNO_3/HF .
	Pb does not dissolve in concentrated HCl due to formation of PbCl_2 coating.

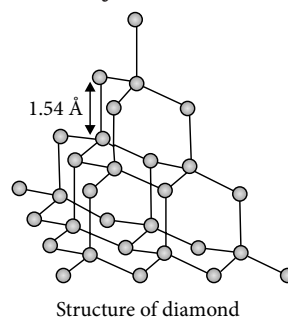
Alkalies	Carbon is unaffected by alkalies.
	Sn and Pb are slowly attacked by cold alkali, and rapidly by hot alkali, giving stannates $\text{Na}_2[\text{Sn}(\text{OH})_6]$ and plumbates $\text{Na}_2[\text{Pb}(\text{OH})_6]$.
Complex formation	Si, Ge, Sn and Pb can show coordination number more than 4. <i>e.g.</i> , : Si, Ge (6), Sn, Pb (8)
Halogens	Diamond is unreactive, but graphite reacts forming $(\text{CF})_n$.
	Si and Ge form volatile SiX_4 and GeX_4 respectively.
	Sn and Pb are less reactive. Sn reacts with Cl_2 and Br_2 in cold, and with F_2 and I_2 on warming. Lead reacts with F_2 in cold and with Cl_2 on heating forming PbX_2 .

● **Anomalous behaviour of carbon :**

Property	Carbon	Other elements
Hardness	hardest	less hard
M.pt. and B.pt.	high	low
Maximum covalency	4	6
Multiple bonds	$p\pi-p\pi$ (high extent)	$p\pi-d\pi$ (low extent)
Catenation	very high tendency	very low
Tetrahalides	does not undergo hydrolysis	undergo hydrolysis

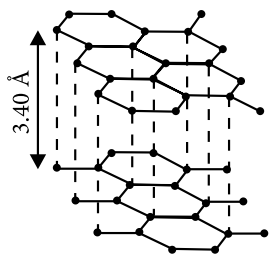
- ▶ **Multiple bonding:** C has strong tendency to form $p\pi-p\pi$ multiple bonds either with itself ($\text{C}=\text{C}$, $\text{C}\equiv\text{C}$) or with atoms like N, O ($\text{C}\equiv\text{N}$, $\text{C}=\text{O}$). Carbon does not have d -orbitals and never forms $d\pi-p\pi$ or $d\pi-d\pi$ bonds. Silicon on the other hand forms $d\pi-d\pi$ bonds.
- ▶ In case of $\text{N}(\text{CH}_3)_3$, geometry is pyramidal but in case of $\text{N}(\text{SiH}_3)_3$ it is planar because the lone pair on N-atom is transferred to the empty d -orbitals of silicon. ($p\pi-d\pi$ overlapping).

- **Allotropes of carbon :**
 - ▶ **Crystalline form :** It includes diamond, graphite and fullerene.
 - ▶ **Amorphous form :** It includes coal, charcoal, lampblack, etc.
- **Diamond**
 - ▶ It is a transparent, crystalline substance with very high refractive index.
 - ▶ It is the purest form of carbon found naturally and can also be made artificially.
 - ▶ Diamond is the hardest natural substance known and is a bad conductor of heat and electricity.
 - ▶ **Structure :**
 - All important properties of diamond are attributed to its structure.
 - Each carbon atom of diamond is bonded to four other carbon atoms, through sp^3 hybridised orbitals, situated at the corners of a regular tetrahedron, with C–C bond length 1.54 Å and bond angle of 109.5°.
 - This gives diamond a three-dimensional network structure which explains its hardness and poor conductivity due to absence of any free electron.



- **Graphite**
 - ▶ It is a dark grey, crystalline solid which is soft and greasy to touch. It possesses a metallic lustre.
 - ▶ It is also known as '*plumbago*' (black lead) as it leaves a black mark on paper.
 - ▶ It is a good conductor of electricity and its conductivity increases with rise in temperature.
 - ▶ **Structure :**
 - It has a two dimensional sheet like structure with each carbon atom being covalently bonded to three carbon atoms through sp^2 hybridised orbitals, forming a planar hexagonal structure.

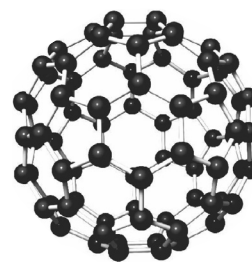
- The fourth electron of each carbon forms a pi(π) bond with partial overlap with that of the neighbouring carbon.
- The C – C bond length is 1.42 Å, shorter than that in diamond. The π -electrons are free to move (mobile electrons) and account for the electrical conductivity.
- The adjacent hexagonal layers (sheets) are held by weak van der Waals' forces thus, making it easy for the layers to slide over one another, accounting for its soft and greasy texture.



Structure of graphite

● Fullerenes

- ▶ Fullerenes are made by heating graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called Buckminsterfullerene.
- ▶ It contains twenty, six-membered rings and twelve, five-membered rings. A six membered ring is fused with six or five membered ring but a five membered ring can only be fused with six membered ring. All the carbon atoms are equal and they undergo sp^2 hybridisation. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm, respectively. Spherical fullerenes are also called *bucky balls* in short.



Structure of Buckminsterfullerene

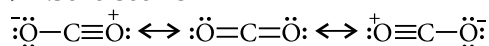
▶ Uses of carbon :

- Diamond is used as previous decorative stones in jewellery because of its unusual brilliant shine.
- Graphite is used as a lubricant at higher temperature and as a refractory material in making crucibles and electrodes for high temperature work.
- Coal and charcoal are used as fuel.
- Coal is used for manufacturing producer gas and water gas.
- Coke is used as a reducing agent in metallurgical operations.

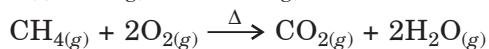
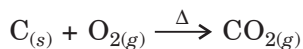
● Some important compounds of carbon and silicon :

● Carbon dioxide (CO₂)

▶ Structure :



▶ Preparation :



▶ Properties :

- It is an acidic oxide, and reacts with bases, forming salts.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

$$CO_2 + K_2CO_3 + H_2O \rightarrow KHCO_3$$
- Solid CO₂ is called 'dry ice' and is used to freeze foods and ice-cream.
- It is consumed during photosynthesis.



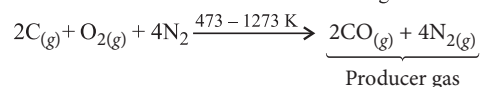
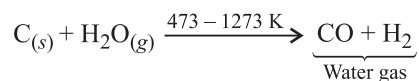
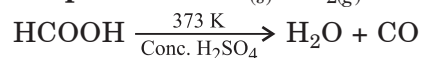
▶ Uses :

- In aerated water, e.g., in soda water, etc.
- In extinguishing fire.
- Solid carbon dioxide (dry ice) is used as refrigerant.
- As *carbogen* [mixture of O₂ + CO₂ (5-10%)] in artificial respiration especially for pneumonia patients and victims of CO poisoning.

- **Carbon monoxide (CO)**

- ▶ **Structure** : $\text{C}=\ddot{\text{O}}:$ \leftrightarrow $\text{:C}\equiv\overset{+}{\text{O}}:$ or $\text{:C}\equiv\text{O:}$

- ▶ **Preparation** : $2\text{C}_{(s)} + \text{O}_{2(g)} \xrightarrow{\Delta} 2\text{CO}_{(g)}$



- ▶ **Properties :**

- Highly poisonous due to the ability to form a complex with haemoglobin (Hb)

which is 300 times more stable than O_2 -Hb complex thus, prevents Hb in the RBCs from carrying O_2 around the body.

- It is a powerful reducing agent and reduces many metal oxides to the metal.
- CO molecule acts as a donor and reacts with metals to form metal carbonyls.

- ▶ **Uses :**

- As an important constituent of two industrial fuels, *i.e.*, water gas and producer gas.
- In Mond's process for the purification of nickel.



OBJECTIVE TYPE QUESTIONS

➔ Multiple Choice Questions (MCQs)

- The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence
 - Al < Ga < In < Tl
 - Tl < In < Ga < Al
 - In < Tl < Ga < Al
 - Ga < In < Al < Tl
- In group 13, electronegativity first decreases from B to Al and then increases marginally down the group. This is because of
 - non-metallic nature of B
 - discrepancies in atomic size of elements
 - ability of B and Al to form $p\pi - p\pi$ multiple bonds
 - irregular trend in electronegativity throughout the periodic table.
- Choose the correct statement.
 - Non-metals have higher ionisation enthalpies and higher electronegativities than the metals.
 - Non-metals and metalloids exist only in the p -block of the periodic table.
 - Change of non-metallic to metallic character can be illustrated by the nature of oxides they form.
 - All are correct.
- What is the hybridisation of B in BCl_3 ?
 - sp^3
 - sp^2
 - sp
 - dsp^2
- Elements of group 14
 - exhibit oxidation state of +4 only
 - exhibit oxidation state of +2 and +4 only
 - form M^{2-} and M^{4+} ions
 - form M^{2+} and M^{4-} ions.
- Carbon-60 contains
 - 20 pentagons and 12 hexagons
 - 12 pentagons and 20 hexagons
 - 30 pentagons and 30 hexagons
 - 24 pentagons and 36 hexagons.
- Al and Ga have nearly the same covalent radii because of
 - greater shielding effect of s -electrons of Ga atom
 - poor shielding effect of s -electrons of Ga atom
 - poor shielding effect of d -electrons of Ga atom
 - greater shielding effect of d -electrons of Ga atom.
- Which of the following structures correctly represents the boron trifluoride molecule?
 -
 -
 -
 -
- Boron is unable to form BF_6^{3-} because of
 - high electronegativity of boron
 - high electronegativity of fluorine
 - lack of d -orbitals in boron
 - less difference in electronegativity between B and F.
- Which of the following bonds has the most polar character?
 - C – O
 - C – Br
 - C – S
 - C – F

11. In graphite, electrons are
- localised on every third C-atom
 - present in anti-bonding orbital
 - localised in each C-atom
 - spread out between the structure.

12. Amongst the halides

- | | |
|---------------------|---------------------|
| (1) BCl_3 | (2) AlCl_3 |
| (3) GaCl_3 | (4) InCl_3 |

the order of decreasing Lewis acid character is

- | | |
|----------------|----------------|
| (a) 1, 2, 3, 4 | (b) 4, 3, 2, 1 |
| (c) 3, 4, 2, 1 | (d) 2, 3, 4, 1 |

13. The +1 oxidation state of thallium is more stable than its +3 oxidation state because of

- its atomic size
- its ionisation potential
- inert pair effect
- diagonal relationship.

14. Ionisation enthalpy ($\Delta_i H_1$ kJ mol⁻¹) for the elements of Group 13 follows the order

- $\text{B} > \text{Al} > \text{Ga} > \text{In} > \text{Tl}$
- $\text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Tl}$
- $\text{B} < \text{Al} > \text{Ga} < \text{In} > \text{Tl}$
- $\text{B} > \text{Al} < \text{Ga} > \text{In} < \text{Tl}$

15. Which of the following conceivable structures for CCl_4 will have a zero dipole moment?

- Square planar
- Square pyramid (carbon at apex)
- Irregular tetrahedron
- Regular tetrahedron

16. The wrong statement about fullerene is

- it has 5-membered carbon ring
- it has 6-membered carbon ring
- it has sp^2 hybridization
- it has 5-membered rings more than 6-membered rings.

17. Fluorine is more electronegative than either boron or phosphorus. What conclusion can be drawn from the fact that BF_3 has no dipole moment but PF_3 does?

- BF_3 is not spherically symmetrical, but PF_3 is.
- BF_3 molecule must be linear.
- The atomic radius of P is larger than the atomic radius of B.
- The BF_3 molecule must be planar triangular.

18. Which of the following statements is correct?

- Graphite is thermodynamically more stable than diamond.
- Diamond is thermodynamically more stable than graphite.
- Graphite has such a high thermodynamical stability that diamond spontaneously changes into graphite in ordinary conditions.
- Graphite and diamond have equal thermodynamic stability.

19. In the carbon family, the elements other than carbon do not form $p\pi-p\pi$ bonds because the atomic orbitals are too

- small and diffused to undergo effective lateral overlap
- large and diffused to undergo effective lateral overlap
- large and far, too less diffused to overlap linearly
- small to overlap both laterally and linearly.

20. Which among CH_4 , SiH_4 , GeH_4 and SnH_4 is most volatile?

- | | |
|--------------------|--------------------|
| (a) CH_4 | (b) SiH_4 |
| (c) GeH_4 | (d) SnH_4 |

21. Which of the following does not have a tetrahedral structure?

- | | |
|---------------------|---------------------|
| (a) BH_3 | (b) NH_4^+ |
| (c) BH_4^- | (d) CH_4 |

22. Which is least stable compound?

- | | |
|---------------------|---------------------|
| (a) BCl_3 | (b) GaCl_3 |
| (c) InCl_3 | (d) TlCl_3 |

23. Which of the following acts as an oxidising agent?

- | | |
|----------------------|----------------------|
| (a) B^{3+} | (b) Al^{3+} |
| (c) Tl^{3+} | (d) None of these |

24. Match the species given in Column I with the properties mentioned in Column II.

Column I	Column II
(i) BF_4^-	(A) Oxidation state of central atom is +4
(ii) AlCl_3	(B) Strong oxidising agent
(iii) SnO	(C) Lewis acid
(iv) PbO_2	(D) Can be further oxidised
	(E) Tetrahedral shape

- (a) (i) → (E), (ii) → (B), (iii) → (D), (iv) → (A, C)
 (b) (i) → (E), (ii) → (C), (iii) → (D), (iv) → (A, B)
 (c) (i) → (B), (ii) → (E), (iii) → (D), (iv) → (A, C)
 (d) (i) → (D), (ii) → (E), (iii) → (B), (iv) → (A, C)
25. Which element does not exhibit allotropy?
 (a) C (b) Sn
 (c) Si (d) Pb
26. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-} ?
 (a) B (b) Al
 (c) Ga (d) In
27. Aluminium vessels should not be washed with materials containing washing soda since
 (a) washing soda is expensive
 (b) washing soda is easily decomposed
 (c) washing soda reacts with Al to form insoluble aluminium oxide
 (d) washing soda reacts with Al to form insoluble aluminate.
28. Carbon forms a large number of compounds because it has
 (a) fixed valency
 (b) non-metallic nature
 (c) high ionization potential
 (d) property of catenation.
29. Thallium shows different oxidation states because
 (a) of its high reactivity
 (b) of inert pair of electrons
 (c) of its amphoteric nature
 (d) it is a transition metal.
30. Aluminium is more reactive than iron but aluminium is less easily corroded than iron because
 (a) aluminium is a noble metal
 (b) iron undergoes reaction easily with water
 (c) aluminium with oxygen forms a protective oxide layer
 (d) iron forms mono and divalent ions.
31. The shape and hybridisation of $Si(CH_3)_4$ is
 (a) bent, sp (b) trigonal, sp^2
 (c) tetrahedral, sp^3 (d) octahedral, sp^3d^2
32. The element with smallest atomic radius and lowest melting point out of the following is
 (a) Al (b) Ga
 (c) In (d) Tl

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 33 to 38.

The heavier members of 13 and 14 groups besides the group oxidation state also show another oxidation state which is two units less than the group oxidation state. Down the group (\downarrow), the stability of higher oxidation state decreases and that of lower oxidation state increases. This concept which is commonly called inert pair effect has been used to explain many physical and chemical properties of the element of these groups.

33. Heavier members of groups 13 exhibit oxidation state
 (a) +3 only (b) +1 only
 (c) +1 and +3 both (d) +1, +2, +3
34. Which among the following is the strongest oxidising agent?
 (a) SiO_2 (b) GeO_2
 (c) SnO_2 (d) PbO_2
35. Which among the following is the strongest reducing agent?
 (a) $GaCl$ (b) $InCl$
 (c) BCl_3 (d) $TlCl$
36. The strongest reductant among the following is
 (a) $SnCl_2$ (b) $SnCl_4$
 (c) $PbCl_2$ (d) $GeCl_2$
37. Which of the following statement is wrong?
 (a) Tl(III) salt undergo disproportionation.
 (b) CO is used as a reducing agent.
 (c) CO_2 is a greenhouse gas.
 (d) SiO_2 is a covalent solid.
38. Which of the following act as the strongest acid?
 (a) Tl_2O_3 (b) SnO_2
 (c) PbO_2 (d) CO_2

Case II : Read the passage given below and answer the following questions from 39 to 43.

Allotropy : The phenomenon of existence of the same substance (element or compound) in two or more forms, in the same physical state, having different properties. Different forms are called allotropes or allotropic modifications.

Except lead, all other elements of group 14 show allotropy.

Element	Allotropic form
C	Crystalline : graphite and diamond Amorphous : coal, coke and charcoal
Si	Crystalline and amorphous
Ge	Two crystalline forms
Sn	Three forms : grey tin, white tin, rhombic tin

39. Wood charcoal is used in gas masks because it

- (a) is poisonous
- (b) liquefies gases
- (c) is porous
- (d) adsorbs poisonous gases.

40. Which of the following is not sp^2 hybridised?

- (a) Graphite
- (b) Graphene
- (c) Fullerene
- (d) Dry ice

41. Fullerene with formula C_{60} has a structure where every carbon atom is

- (a) sp -hybridized
- (b) sp^2 -hybridized
- (c) sp^3 -hybridized
- (d) not hybridized.

42. Thermodynamically the most stable form of carbon is

- (a) diamond
- (b) graphite
- (c) fullerene
- (d) coal.

43. The element that does not show catenation among the following p -block elements is

- (a) carbon
- (b) silicon
- (c) germanium
- (d) lead.

Case III : Read the passage given below and answer the following questions from 44 to 47.

The high charge and small size of Al^{3+} ion gives it a high charge density which is responsible for its tendency to show

- (a) covalency in its compounds in the gaseous state
- (b) high hydration enthalpy which stabilizes its compounds in solution, and

- (c) high lattice enthalpy of its compounds in the solid state.

Hence, aluminium can form both covalent and ionic bond. Like halides of boron, halides of aluminium do not show backbonding because of increase in size of aluminium. In fact, aluminium atoms complete their octets by forming dimers. Thus, chloride and bromide of aluminium exist as dimers. Thus, chloride and bromide of aluminium exist as dimers, both in the vapor state and in polar solvents like benzene, while the corresponding boron halides exist as monomer. In boron trihalides, the extent of back bonding decreases with increase in size of halogens and thus Lewis acid character increases. All BX_3 are hydrolysed by water but BF_3 shows as different behavior.

44. Which of the following statements about anhydrous aluminium chloride is correct?

- (a) It exists as Al_2Cl_6 dimer in vapour form.
- (b) It is not easily hydrolysed.
- (c) It sublimes at $100^\circ C$ under vacuum.
- (d) It is a strong Lewis base.

45. Which one of the following statements is correct?

- (a) All boron trihalides form back bonding.
- (b) Anhydrous aluminium chloride is an ionic compound.
- (c) Aluminium bromide make up the electron deficiency by bridging with other aluminium bromide.
- (d) None of these.

46. The dimeric structure of aluminium chloride disappear when

- (a) it dissolves in water
- (b) it reacts with donor molecules like R_3N
- (c) it dissolves in benzene
- (d) both (a) and (b).

47. Which of the following reaction is incorrect?

- (a) $BF_{3(g)} + F^-_{(aq)} \longrightarrow BF_4^-$
- (b) $BF_{3(g)} + 2H_2O \longrightarrow [BF_3OH]^- + H_3O^+$
- (c) $BCl_{3(g)} + 3C_2H_5OH_{(l)} \longrightarrow B(OC_2H_5)_{3(l)} + 3HCl$
- (d) $BCl_{3(g)} + 2C_5H_5N_{(l)} \longrightarrow Cl_3B(C_5H_5N)_{2(s)}$

➔ Assertion & Reasoning Based MCQs

For question numbers 48-55, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

48. Assertion : Compounds formed by non-metals with metals are covalent in nature.

Reason : Compounds formed between non-metals themselves are largely covalent.

49. Assertion : Anhydrous AlCl_3 is covalent but hydrated AlCl_3 is ionic.

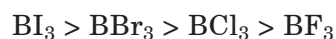
Reason : In water, Al_2Cl_6 dissociates into hydrated Al^{3+} and Cl^- ions due to high heat of hydration of these ions.

50. Assertion : The tetrahalides of carbon are not hydrolysed by water under normal conditions.

Reason : Carbon cannot expand its coordination number beyond 4 because of the absence of *d*-orbitals.

51. Assertion : All the trihalides of boron act as Lewis acids.

Reason : The relative strength of boron trihalides is of the order



52. Assertion : Al forms $[\text{AlF}_6]^{3-}$ but B does not form $[\text{BF}_6]^{3-}$.

Reason : B does not react with F_2 .

53. Assertion : The tendency for catenation decreases in the order $\text{C} > \text{Si} > \text{Ge} > \text{Sn}$.

Reason : The catenation depends on the strength of the element-element bond.

54. Assertion : Boron differs from aluminium and other members of group 13 in a number of properties.

Reason : Boron shows anomalous behaviour.

55. Assertion : In carbon dioxide, the carbon is sp^3 hybridized.

Reason : CO is a linear monomeric covalent compound.

SUBJECTIVE TYPE QUESTIONS

➔ Very Short Answer Type Questions (VSA)

- Why does graphite act as a good lubricant?
- What is inert pair effect?
- Write reactions to justify amphoteric nature of aluminium.
- Describe the shapes of BF_3 and BH_4^- . Assign the hybridisation of boron in these species.
- How would you explain the lower atomic radius of Ga as compared to Al?
- Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon?
- Suggest reasons why the B—F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.
- What are electron deficient compounds? Are BCl_3 and SiCl_4 electron deficient species? Explain.
- What are fullerenes? How are they prepared?
- If B—Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

➡ Short Answer Type Questions (SA-I)

11. What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?
12. Draw the structures of $\text{BCl}_3 \cdot \text{NH}_3$ and AlCl_3 (dimer).
13. Explain why the following compounds behave as Lewis acids?
(i) BCl_3 (ii) AlCl_3
14. Describe the general trends in the metallic character of the elements in groups 13 and 14.
15. The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.
16. What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?
17. Carbon and silicon both belong to the group 14, but in spite of the stoichiometric similarity, the dioxides, (*i.e.*, carbon dioxide and silicon dioxide), differ in their structures. Comment.
18. Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than BCl_3 . Comment.
19. Explain, why CO_2 is a gas whereas SiO_2 is a solid?
20. Give reason why CCl_4 is immiscible in water, whereas SiCl_4 is easily hydrolysed.

➡ Short Answer Type Questions (SA-II)

21. (a) Classify following oxides as neutral, acidic, basic or amphoteric:
 CO , B_2O_3 , SiO_2 , CO_2 , Al_2O_3 , PbO_2 , Tl_2O_3
(b) Write suitable chemical equations to show their nature.
22. Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known. Explain.
23. Arrange the following in increasing order of the property indicated :
(a) SiCl_2 , GeCl_2 , SnCl_2 and PbCl_2 (stability)
(b) CO , SiO , SnO , GeO , PbO (basicity)
(c) SiF_4 , SiCl_4 , SiI_4 , SiBr_4 (stability)
24. Explain the difference in properties of diamond and graphite on the basis of their structures.
25. Describe the general trends in the following properties of the elements in Groups 13 and 14.
(i) Oxidation states
(ii) Atomic size
(iii) Nature of halide
26. Explain the following :
(i) Boron does not exist as B^{3+} ion.
(ii) Discuss the Lewis acid nature of boron halides.
27. How does AlCl_3 act as a Lewis acid?
28. Explain the following :
(a) Electron gain enthalpy of chlorine is more negative as compared to fluorine.
(b) Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.
29. BCl_3 exists as monomer whereas AlCl_3 is dimerised through halogen bridging. Give reason. Explain the structure of the dimer of AlCl_3 also.
30. Complete the following chemical equations and identify X, Y and Z.
$$\text{Z} + 3 \text{LiAlH}_4 \longrightarrow \text{X} + 3\text{LiF} + 3\text{AlF}_3$$
$$\text{X} + 6\text{H}_2\text{O} \longrightarrow \text{Y} + 6\text{H}_2$$
$$\text{X} + 3\text{O}_2 \xrightarrow{\Delta} \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$$

➡ Long Answer Type Questions (LA)

31. (a) Boron fluoride exists as BF_3 but boron hydride doesn't exist as BH_3 . Give reason. In which form does it exist? Explain its structure.
- (b) A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is

obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element and write formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

32. Explain the following :

- Carbon shows catenation property but lead does not.
- Lead does not form PbI_4 .
- Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.

33. Explain the following:

- Why PbO_2 is a stronger oxidising agent than SnO_2 ?
- Why ionisation enthalpy of Ga is higher than that of Al?

(iii) Thallous compounds (Tl^+) are more stable than thallic (Tl^{3+}) compounds. Why?

34. Three pairs of compounds are given below. Identify that compound in each of the pairs which has group 13 element in more stable oxidation state. Give reason for your choice. State the nature of bonding also.

- $TlCl_3$, $TlCl$ (ii) $AlCl_3$, $AlCl$
- $InCl_3$, $InCl$

35. Describe the general trends in the following properties of the elements of groups 13.

- Atomic size
- Ionisation enthalpy
- Metallic character
- Oxidation states
- Nature of halides.

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (a) : In group 13 elements, stability of +3 oxidation state decreases down the group while that of +1 oxidation state increases due to inert pair effect.

Hence, stability of +1 oxidation state increases in the sequence : $Al < Ga < In < Tl$.

2. (b) : There is a large size difference between B and Al.

3. (d)

4. (b) : In BCl_3 , B is sp^2 hybridised.

5. (b) : General electronic configuration of Group-14 elements is ns^2np^2 . Thus, they can exhibit +2 oxidation state by losing $2p$ -electron or +4 oxidation state by losing all 4 valence electrons.

6. (b) : C-60 contains 12 pentagons and 20-hexagons folded into a sphere.

7. (c) : Due to poor shielding effect of d -electrons of Ga, the outer electrons experience more attraction by the nucleus.

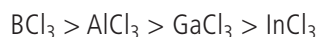
8. (a) : BF_3 molecule involves extensive back bonding from fluorine to boron.

9. (c)

10. (d) : C – F bond has maximum electronegativity difference, hence most polar.

11. (d) : In graphite, electrons are spread out between the structure.

12. (a) : Lewis acid strength of group 13 halides follows the order :



13. (c)

14. (d) : *I.E.* has the order $B > Al < Ga > In < Tl$

Decrease from B to Al is associated with increase in size. Discontinuity between Al and Ga and between In and Tl are due to poor shielding of d and f electrons.

15. (d) : CCl_4 has regular tetrahedral structure where dipole moment of all four C–Cl bonds are cancelled out by each other and CCl_4 as a molecule remains non-polar.

16. (d) : Fullerene consists of 12 five-membered rings and 20 six-membered rings. So, it has five-membered rings less than six-membered rings.

17. (d) : In BF_3 , B is sp^2 hybridised and compound is planar triangular so that BF_3 is non-polar.

18. (a) : Graphite is thermodynamically more stable than diamond.

19. (b) : In carbon family, elements other than carbon do not form $p\pi-p\pi$ bonds because the atomic orbitals are too large and diffused to undergo effective lateral overlap.

20. (a) : CH_4 is most volatile due to lower molecular mass.

21. (a) : BH_3 is trigonal planar where B is sp^2 hybridised.

22. (d) : All the given compounds belong to group 13 of the periodic table. In this group, the +3 oxidation state becomes less stable on moving down the group due to inert pair effect. Hence, BCl_3 is most stable and TlCl_3 is least stable.

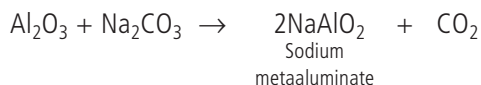
23. (c) : Due to inert pair effect Tl^{3+} is unstable and is reduced to more stable Tl^+ thus behaving as an oxidising agent.

24. (b) : (i) \rightarrow (E), (ii) \rightarrow (C), (iii) \rightarrow (D), (iv) \rightarrow (A, B)

25. (d) : Lead (Pb) does not show allotropy.

26. (a) : Boron can not expand its coordination number from 4 due to absence of d -orbitals.

27. (d) : Aluminium vessel has an upper layer of aluminium oxide. When this vessel is washed with material containing washing soda then insoluble sodium metaaluminate is formed.



28. (d) : Carbon has high tendency to catenate thus forms large number of compounds.

29. (b) : Tl^+ ions are more stable than Tl^{3+} due to inert pair effect which results in reluctance of s -electrons to unpair to show higher oxidation state.

30. (c) : Al forms a protective oxide layer, on reaction with oxygen which is hard and impervious.

31. (c)

32. (b) : Element with smallest atomic radius (135 pm) and lowest melting point (303 K) is Ga.

33. (c) : In heavier members due to inert pair effect both +1, +3 oxidation state are possible.

34. (d)

35. (c) : +1, +3 oxidation state are possible in Ga.

Ga^{3+} is more stable than Ga^{1+} hence. GaCl act as reducing agent.

36. (d) : GeCl_2 is the strongest reductant because Ge in +4 oxidation state is more stable than Ge in +2 oxidation state.

37. (a) : Tl(III) salt doesn't undergo disproportionation reaction because +3 oxidation state of Tl is more stable due to inert pair effect.

38. (d) : CO_2 is most acidic as acidic character of oxide decrease down the group.

39. (d) : Wood charcoal adsorbs large volume of poisonous gases from atmosphere.

40. (d) : Solid CO_2 is dry ice in which carbon atom undergoes sp -hybridisation.

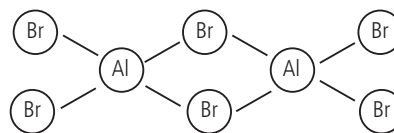
41. (b) : In fullerene with formula C_{60} , all the carbon atoms are equal and they undergo sp^2 hybridisation.

42. (b)

43. (d)

44. (a) : Anhydrous AlCl_3 dimerise to form Al_2Cl_6 in vapour form.

45. (c) : AlX_3 ($X = \text{Cl, Br, I}$) make up the electron deficiency by forming the dimer Al_2X_6



46. (a) : $\text{AlCl}_3 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3$

47. (b) : $\text{BF}_3 + \text{H}_2\text{O} \rightarrow \text{BF}_4^-$

48. (d) : Compounds formed by non-metals with metals are generally ionic in view of larger differences in their electronegativities. Compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities.

49. (a)

50. (a)

51. (b) : BF_3 is weakest Lewis acid.

52. (c) : B does not have vacant d -orbitals as for B, second shell is the outermost shell.

53. (a) : As we move down the group 14, the element-element bond energies decrease rapidly, viz. C-C (355 kJ mol^{-1}), Si-Si (222 kJ mol^{-1}), Ge-Ge (167 kJ mol^{-1}) and Sn-Sn (155 kJ mol^{-1}), so the tendency for catenation decreases in the order $\text{C} > \text{Si} > \text{Ge} > \text{Sn}$.

54. (b) : This is due to small atomic size, high electronegativity, high ionization energy and absence of d -orbital of B.

55. (d) : In CO_2 , C is sp hybridized. It forms two σ bonds with two oxygen atoms and two $p\pi-p\pi$ multiple bonds. So CO_2 is a linear, monomeric and covalent compound.

SUBJECTIVE TYPE QUESTIONS

1. Graphite has sheet like structure and it is slippery so, it can act as lubricant.

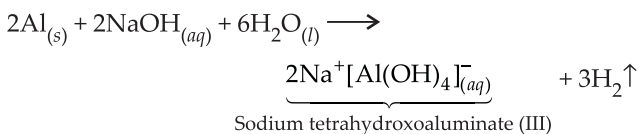
2. The tendency of s -electrons of the valence shell to participate in bond formation decreases down the group. This

reluctance of the *s*-electrons to participate in bond formation is called inert pair effect.

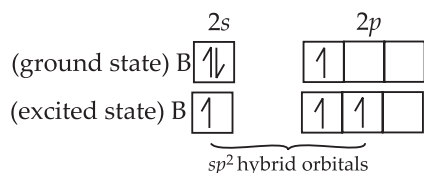
3. Amphoteric substances are those that can react with both acids and bases. Aluminium reacts with HCl to liberate H₂ gas as :



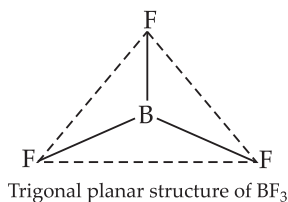
Aluminium can react with aqueous alkali and liberate hydrogen gas.



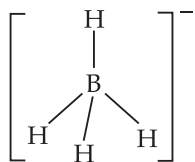
4. BF₃ has a planar triangular structure which arises from the *sp*² hybrid orbitals.



These three *sp*² hybrid orbitals are directed towards the corners of triangle and BF₃ has a trigonal structure.



BH₄⁻ may be assumed to be made of a central B atom, 3H atoms and one hydride ion H⁻.



In order to accommodate the 3H atoms and one H⁻ ion, B undergoes *sp*³ hybridisation yielding four orbitals, 3 of which contain one e⁻ each and one is empty. The fourth, empty orbital accommodates the H⁻ ion. Thus, the structure of BH₄⁻ is tetrahedral.

5. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect for the outer electron from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

6. Large decrease in ionisation potential from C to Si is due to increase in size of the atom and shielding effect.

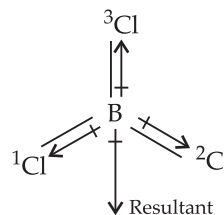
7. The bond length in any compound is dependent on the hybridisation of the central atom. Boron in BF₃ is *sp*² hybridised which means that the *s*-character is 33% and therefore, the bond length is shorter. Also due to similar size of both atoms and vacant *p*-orbital of B, a *pπ-pπ* back bonding from F to B occurs causes partial double bond character. This further decreases the bond length of B — F. In BF₄⁻, the hybridisation of B is *sp*³ which means that the *s*-character is 25% and therefore, a longer bond length.

8. Electron deficient compounds are those where the central atom has less than 8 electrons in its outermost shell. Out of BCl₃ and SiCl₄, the former is an electron deficient compound since it has only 6 electrons in the outermost shell. SiCl₄ is not an electron deficient compound.

However, it can accept electrons by expanding its octet due to presence of empty *d*-orbitals. Thus, it may form species like SiCl₆²⁻.

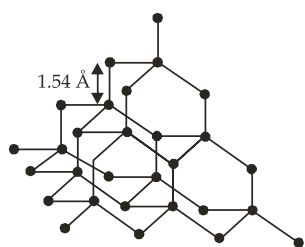
9. Fullerenes are the purest form of carbon, consisting of mainly C₆₀ units. C₆₀ unit has a shape of football, called Buckminsterfullerene. Fullerenes are prepared by heating graphite in an electric arc in the presence of inert gas such as helium or argon.

10. The dipole moment of any molecule is the vector sum total of each of the dipole moments. In BCl₃ molecule, although the B—Cl bonds individually are polar, the resultant dipole moment becomes zero.

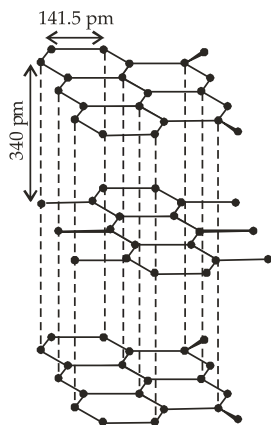


We can see that the dipole moments of B—¹Cl and B—²Cl produce a resultant which is equal in magnitude but opposite in direction to B—³Cl and hence cancels it out. That is why the net dipole moment of BCl₃ is zero.

11. The property due to which an element exists in two or more forms which differ in their physical and some of the chemical properties is known as allotropy and the various forms are called allotropes or allotropic modifications. Carbon exists in two allotropic forms crystalline and amorphous. The crystalline forms are diamond and graphite.



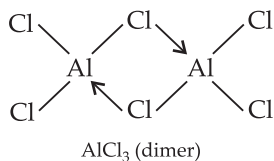
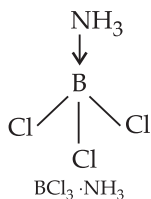
Structure of diamond



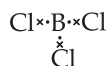
Structure of graphite

Diamond due to extended covalent bonding is the hardest natural substance on the earth. Graphite has layer of sheets which are held by weak van der Waals' forces thus, it can be cleaved easily between layers which makes it soft and slippery.

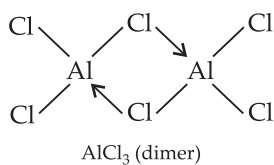
12.



13. (i) BCl_3 – Boron has 6 electrons in its outermost orbital and has a vacant p -orbital. Thus, it is an electron deficient compound hence acts as Lewis acid and accepts a lone pair of electrons.



(ii) AlCl_3 is also an electron deficient compound and acts as Lewis acid. It generally forms a dimer to achieve stability.



14. Metallic character : Metallic character increases from boron to aluminium then decreases down the group for group

13 elements. Due to smaller size group 14 elements are less metallic. Metallic character increases gradually down the group. C (non-metal), Si, Ge (metalloid) Sn, Pb (metals).

15. In group 13 and 14, as we move down the group, the tendency of s -electrons of the valence shell to participate in bond formation decreases. This is due to ineffective shielding of ns^1 and ns^2 electrons of the valence shell by intervening d - and f -electrons. This is called inert pair effect.

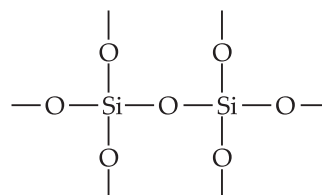
Due to this, ns^1 and ns^2 electrons of valence shell of group 13 and 14 are unable to participate in bonding. Hence, +1 and +2 oxidation states become more stable with increasing atomic number.

16. (a) Inert pair effect : The reluctance of ns^2 pair in p -block elements having higher atomic number to take part in bond formation is called inert pair effect.

(b) Allotropy : The existence of an element in more than one form having different physical properties but same or slightly different chemical properties is called allotropy.

(c) Catenation : The property by virtue of which a large number of atoms of the same element get linked together through covalent bonds resulting in the formation of long chains, branched chains and rings of different sizes is called catenation.

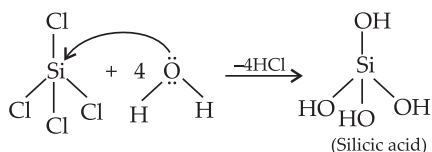
17. Due to absence of d -orbitals multiple $p\pi-p\pi$ bonding is present in carbon dioxide hence CO_2 is linear ($\text{O}=\text{C}=\text{O}$) with sp hybridisation. SiO_2 has discrete single bonded structure in a tetrahedral manner.



18. Due to back bonding in $\text{B}-\text{F}$, electron deficiency is compensated which makes it a weaker Lewis acid than BCl_3 . However, in $\text{B}-\text{Cl}$, back bonding is not significant due to much bigger size of $3p$ -orbital of Cl than vacant $2p$ -orbital of B.

19. Silicon dioxide is a covalent three dimensional network solid due to absence of $p\pi-p\pi$ bonding in SiO_2 and very high $\text{Si}-\text{O}$ bond enthalpy but in CO_2 due to $p\pi-p\pi$ bonding gives discrete molecules unlike SiO_2 . Thus, CO_2 is a gas.

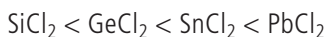
20. CCl_4 cannot be hydrolysed by water because carbon atom can not accommodate lone pair of electrons from oxygen atom of water due to absence of d -orbital. SiCl_4 can be hydrolysed to give $\text{Si}(\text{OH})_4$ due to presence of d -orbitals.



21. (a) Neutral oxides : CO
 Acidic oxides : B₂O₃, SiO₂, CO₂
 Basic oxides : Tl₂O₃
 Amphoteric oxides : Al₂O₃, PbO₂
- (b) (i) CO Neutral to litmus [Neutral]
 (ii) B₂O₃ reacts with basic (metallic) oxides forming meta-borates.
 $B_2O_3 + CuO \longrightarrow Cu(BO_2)_2$ [Acidic]
 (iii) $SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$ [Acidic]
 (iv) $CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$ [Acidic]
 (v) $Tl_2O_3 + 3H_2SO_4 \longrightarrow Tl_2(SO_4)_3 + 3H_2O$ [Basic]
 (vi) $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$
 $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$ } [Amphoteric]
 (vii) $PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$
 $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$ } [Amphoteric]

22. SiF₆²⁻ ion exists because of presence of *d*-orbitals. Silicon expands its octet to give *sp*³*d*² hybridisation and forms complexes or ions by accepting electron pairs from donor species like SiF₆²⁻. Carbon cannot exceed its covalency more than 4. Thus, CF₆²⁻ is not known.

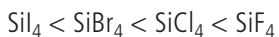
23. (a) The stability of dihalides increases down the group because divalent state becomes more and more stable as we move down the group.



(b) Basicity of oxides increases down the group as metallic character increases.



(c) Si—X bond strength decreases as the size of the halogen increases. The correct order is



24.

Criterion	Diamond	Graphite
Hybridisation	<i>sp</i> ³	<i>sp</i> ²
Structure	Tetrahedral carbon which gives rise to a 3-dimensional structure.	Planar trigonal which gives rise to a 2-dimensional sheet like structure of carbon.
C — C	154 pm	141.5 pm

Hardness	Due to 3-D structure, diamond is the hardest natural element on the earth.	It is made up of 2-D sheets of carbon which slip over each other. This gives graphite a slippery surface.
Electrical Conductivity	Diamond is an insulator.	Graphite is a good conductor of electricity due to presence of delocalised π -electrons.

25. (i) Oxidation states : For group 13 both +1 and +3 oxidation state are observed. +1 oxidation state becomes more stable as we move down the group due to inert pair effect. Boron does not show +3 oxidation state.

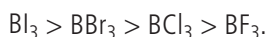
For group 14 common oxidation state are +4 and +2. Tendency to show +2 oxidation state increases down the group.

(ii) Atomic size : Atomic radii of group 13 elements increases down the group with exception Ga < Al due to presence of 10 *d*-electrons which offer poor screening effect. In group 14, there is a considerable increase in radius from C to Si, thereafter from Si → Pb a small increase is seen due to presence of completely filled *d* and *f*-orbitals.

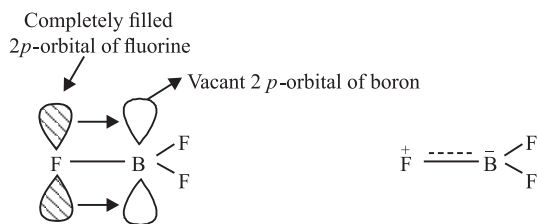
(iii) Nature of halides : Group 13 elements form trihalides (except TlI₃). Due to electron deficient nature BCl₃ accepts electrons and forms adducts. AlCl₃ achieves stability by forming a dimer. Group 14 elements form halides with formula MX₂ and MX₄. Except CCl₄ other halides are easily hydrolysed. Stability of dihalides increases down the group.

26. (i) Due to small size of boron, the sum of its first three ionisation enthalpies is very high, hence, it does not exist in +3 form.

(ii) The Lewis acid character of boron trihalides follows the order :



The above order is just the reverse of the expected order on the basis of relative electronegativities of the halogens. This can be explained on the basis of the tendency of the halogen atom to back-donate its electrons to the boron atoms resulting in the formation of an additional *pπ*–*pπ* bond. This type of bond formation is known as dative or back bonding.



Formation of back bonding between boron and fluorine in BF_3 molecule.

As a result of back donation of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and therefore, the Lewis acid character of BF_3 decreases.

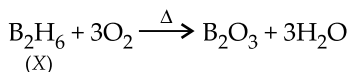
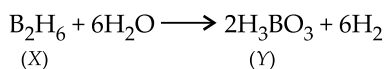
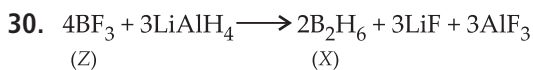
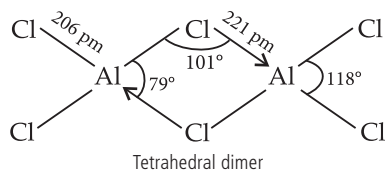
The tendency to form $p\pi-p\pi$ bond is maximum in the case of BF_3 and falls rapidly as we move to BCl_3 and BBR_3

27. AlCl_3 is a Lewis acid since it is an electron deficient halide. It has only six electrons in its outermost shell therefore, to complete its octet it accepts a lone pair of electrons and acts as a Lewis acid.

28. (a) Due to small size of fluorine there is inter-electronic repulsion which reduces its tendency to accept electron.

(b) Pb^{4+} acts as oxidising agent because it has a tendency to exist in Pb^{2+} form which is more stable. Sn^{2+} is a reducing agent due to tendency to form Sn^{4+} compounds.

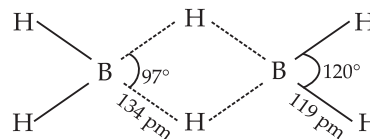
29. Due to absence of d -orbitals in boron, it exists as an electron deficient monomer and achieves stability through accepting electrons from a base like NH_3 . It cannot exist as dimer due to small size of B which cannot accommodate bigger size 4 Cl atoms around it. AlCl_3 achieves stability by forming a dimer.



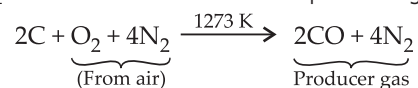
31. (a) Due to non-availability of d -orbitals, boron is unable to expand its octet hence, it exists as BF_3 and is electron deficient compound. Due to back bonding, electron deficiency of BF_3 is compensated. But in boron hydride, hydrogen atoms does not have lone pairs for back bonding thus, to compensate electron deficiency it exists in the form of diborane.

In the structure of diborane, four terminal hydrogen

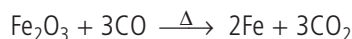
atoms and two boron atoms are in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B — H bonds are regular two centre two electron bonds while the two bridge B — H — B bonds are different and are three centre — two electron bonds.



(b) The tetravalent element is carbon which forms CO and CO_2 . When heated in air it forms producer gas.



CO is a powerful reducing agent and reduces ferric oxide to iron.



32. (a) Property of catenation is maximum in carbon because C — C bonds are very strong due to smaller size. The tendency of catenation decreases down the group due to increase in size and decrease in electronegativity.

(b) $\text{Pb} + 2\text{I}_2 \not\rightarrow \text{PbI}_4$

I^- is a good reducing agent and therefore, reduces Pb (IV) to Pb (II) easily. That is why, PbI_4 does not exist.

(c) Pb^{4+} acts as an oxidising agent because it has a tendency to exist in Pb^{2+} form which is more stable. Sn^{2+} is a reducing agent due to tendency to form Sn^{4+} compounds.

33. (i) Lead compounds in +2 oxidation state are more stable than +4 oxidation state hence are stronger oxidising agents. Due to stronger inert pair effect Pb^{2+} is more stable than Sn^{2+} .

(ii) As we move from Al to Ga, due to poor shielding of the nucleus by $3d$ -electrons, the effective nuclear charge acting on Ga is slightly higher than that on Al. As a result, ionisation enthalpy of Ga is higher than that of Al.

(ii) TlCl is more stable than TlCl_3 due to inert pair effect.

34. (i) TlCl_3 , $\text{TlCl} - \text{TlCl}$ is in more stable oxidation state (+1 O.S. more stable). It is ionic in nature.

(ii) AlCl_3 , $\text{AlCl} - \text{AlCl}_3$ is more stable (+3 oxidation state). It is covalent in nature.

(iii) InCl_3 , $\text{InCl} - \text{InCl}_3$ is relatively more stable than InCl due to higher stability of +3 oxidation state. It is covalent in nature.

35. (i) Atomic size : Atomic radii of group 13 elements increase down the group with the exception that atomic radius of Ga is less than that of Al due to the presence of 10 *d*-electrons which offer poor screening effect for the outer electrons from the increased nuclear charge in Ga.

(ii) Ionisation enthalpy : For group 13 elements, the trend of ionisation enthalpy is

$B > Al < Ga > In < Tl$. This is due to increase in size and low screening effect of *d*- and *f*- electrons.

(iii) Metallic character : Metallic character increases from boron to aluminium then decreases down the group.

(iv) Oxidation states : For group 13 elements, both +1 and +3 oxidation states are observed. The +1 oxidation state becomes more stable as we move down the group due to inert pair effect. Boron does not show +3 oxidation state.

(v) Nature of halides : Group 13 elements form trihalides (except TlI_3). Due to electron deficient nature, BCl_3 accepts electrons and forms adducts. $AlCl_3$ achieves stability by forming a dimer.

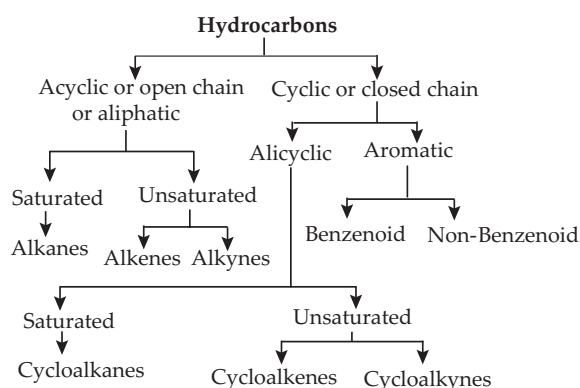


Hydrocarbons



Recap Notes

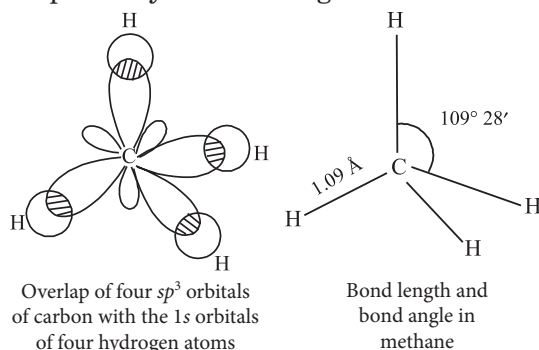
Classification of Hydrocarbons :



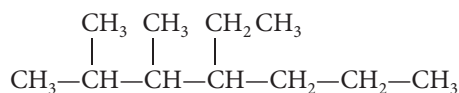
Alkanes	Alkenes	Alkynes
Saturated means that each carbon is bonded to four other atoms through single covalent bonds. Hydrogen atoms usually occupy all available bonding positions after the carbons have bonded to each other.	Unsaturated hydrocarbons contain either double or triple bonds. Since the compound is unsaturated with respect to hydrogen atoms, the extra electrons are shared between two carbon atoms forming double or triple bonds.	
Paraffins which is derived from a Latin word, meaning "little affinity", and means that the compounds are very unreactive.	Alkenes are also called Olefins because they form oily product (<i>i.e.</i> , ethylene chloride) on reaction with chlorine gas.	Alkynes are also generally known as Acetylenes from the first compound in the series.

- Alkanes:** Alkanes are saturated hydrocarbons with general formula C_nH_{2n+2} , where, n is equal to 1, 2, 3.... *e.g* ; CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), etc.

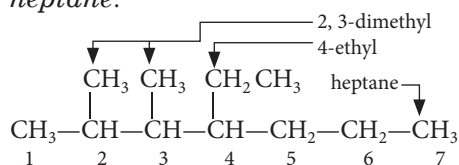
- Structure :** Each carbon atom of alkanes is in sp^3 state of hybridization with its four bonding orbitals directed towards the four corners of a regular tetrahedron. All the C—C and C—H bonds are strong sigma (σ) bonds. Every C—C and C—H bond has a length of 1.54 Å and 1.09 Å respectively. All bond angles are of $109^\circ 28'$.



- Nomenclature :** Use the following procedure step-by-step to write the IUPAC names from the structural formulae. Consider the following structural formula :



- Step 1. Identify the longest chain :** In the given example, longest chain has seven carbons. The seven carbon chain is named as *heptane*.

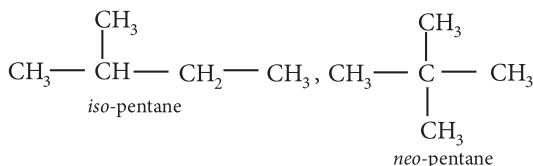
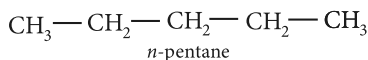
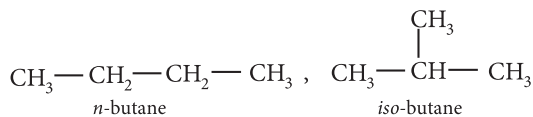


Step 2. Number the chain : The chain is numbered from left to right. This gives lowest numbers to the attached alkyl group.

Step 3. Identify the alkyl group : There are two methyl groups at C-2 and C-3, there is one ethyl group of C-4.

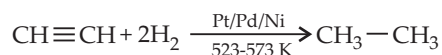
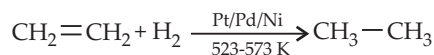
Step 4. Write the IUPAC name : In this case, the IUPAC name is 4-ethyl-2,3-dimethyl heptane. Always keep in mind

- Numbers are separated from each other by commas.
- Numbers are separated from names by hyphens.
- Prefixes di, tri are not taken into account in alphabetising substituent names.
- **Isomerism :** Alkanes exhibit chain isomerism. Although the first three members (methane, ethane and propane) do not exhibit isomerism, the number of isomers in other alkanes increases with the increase in the number of carbon atoms. Thus, butane has two isomers, pentane has three, hexane has five, heptane has nine, octane has eighteen, and decane as many as seventy five isomers.

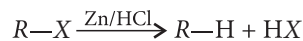


► **Preparation :**

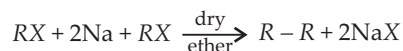
- **By hydrogenation of unsaturated hydrocarbons (Sabatier-Senderens reaction or reduction) :**



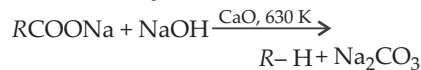
- **Reduction of alkyl halides :**



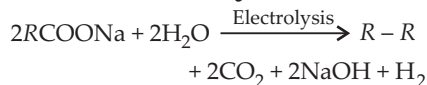
- **Wurtz reaction :**



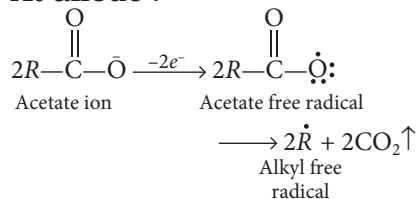
- **Decarboxylation :**



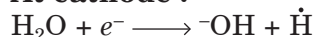
- **Kolbe's electrolysis :**



At anode :



At cathode :

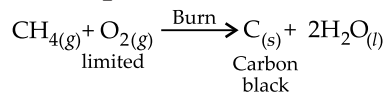


Methane cannot be prepared by this method.

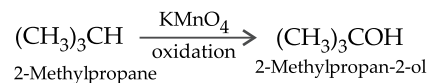
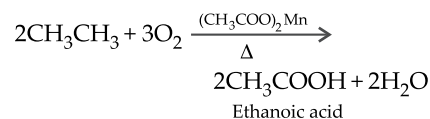
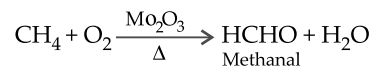
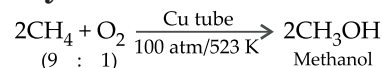
- **Physical properties :**

- Due to presence of weak van der Waals' forces, the first four members, C₁ to C₄ are gases, C₅ to C₁₇ are liquids and C₁₈ and above are solids at 298 K.
- All alkanes are colourless, odourless and insoluble in water but dissolve in non-polar solvents.
- The boiling point of alkanes increases with increase in molecular mass and for the same alkane the boiling point decreases with branching.
- Alkanes with even number of carbon atoms have higher melting points than those with odd number of carbon atoms due to symmetry.

- **Incomplete combustion :**

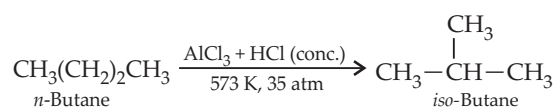


- **Catalytic oxidation :**

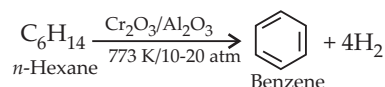


(For alkanes having 3° H-atoms)

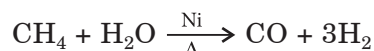
– **Isomerisation :**



– **Aromatisation :**



– **Reaction with steam :**



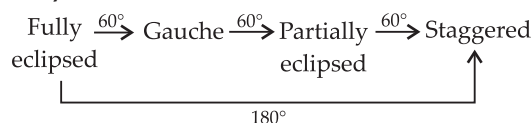
► **Conformational isomerism :** The different arrangements of atoms in space that results from the free rotation of groups about C — C bond axis are called *conformational isomers* or *rotational isomers* and the phenomenon is called *conformational* or *rotational isomerism*.

– **Torsional strain** is a weak repulsive interaction between the adjacent bonds due to which rotation around a C—C single bond is not free completely.

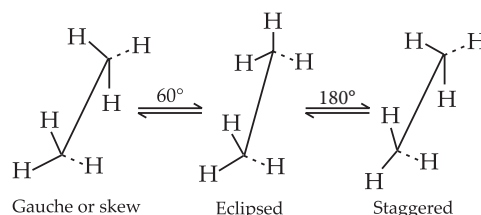
– **Fully eclipsed conformation :** In this form, the bigger atoms are nearest to each other. These conformers have maximum energy and minimum stability.

– **Staggered conformation :** In this form, the bigger atoms are farthest from each other. These conformers have minimum energy and maximum stability.

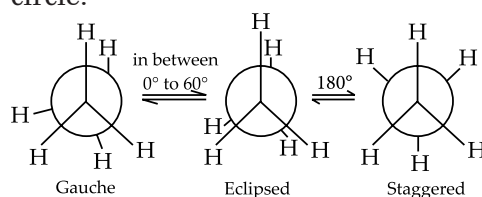
– **Gauche or skew conformation :** Rotation between 0 to 60 generates one of the many arrangements in between staggered and eclipsed forms. These arrangements are called *Gauche* or *skew conformation*.



► **Sawhorse projection :** It is a view of molecule down a particular C — C bond and groups connected to both the front and back carbons are drawn using sticks at 120° angle. The left-hand bottom end of this locates atoms nearer to the observer and right-hand top end locates atom further away.



► **Newman projection :** In Newman projection, the two carbon atoms forming the σ -bond are represented by two circles, one behind the other, so that only front carbon is seen. The atoms attached to the front carbon are shown by the bonds from the centre of the circle while the atoms attached to the back carbon are shown by the bonds from the circumference of the circle.



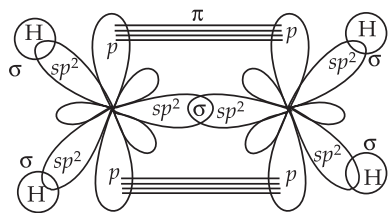
– The order of stability of different conformations of ethane is

Staggered > skew or Gauche > Eclipsed

► The potential energy difference among these conformations of ethane is about 3 kcal/mol (or 12.5 kJ mol⁻¹), called torsional strain (or energy barrier). Due to small difference in energy the two conformations are readily interconvertible and that is why not possible to separate the two conformations of ethane.

• **Alkenes :** Those unsaturated hydrocarbons which have general formula 'C_nH_{2n}' are called '*alkenes*'. They contain double bond (C = C) which is considered as a functional group. e.g., C₂H₄ (ethene or ethylene), C₃H₆ (propene or propylene).

► **Structure :** In ethylene molecule, one of the sp²-hybridised orbitals of one carbon atom overlaps axially with one of the sp²-orbitals of another carbon atom. Two of the sp²-hybridised orbitals of each carbon atom overlap separately and along the axes with the 1s orbitals of the hydrogen atoms. The pure p-orbital on each of the two carbon atoms overlap each other laterally (sideways) and thus, a new type of bond (π) is formed between the two carbon atoms.



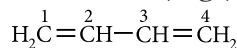
Formation of ethylene molecule

- **Nomenclature** : The IUPAC names of simple alkenes are derived from the IUPAC names of the corresponding alkanes by replacing the ending *-ane* by *-ene*; while the names of higher alkenes are obtained according to some rules.

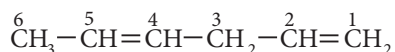
Alkene	Common name	IUPAC name
$\text{CH}_2 = \text{CH}_2$	Ethylene	Ethene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C} = \text{CH}_2 \end{array}$	Isobutylene	2-Methylpropene
$\text{CH}_2 = \text{CHCH}_2\text{CH}_3$	α -Butylene	1-Butene
$\text{CH}_3\text{CH} = \text{CHCH}_3$	β -Butylene	2-Butene

- In a case where the olefin contains two or more double bonds, the ending *ane* of alkanes is replaced by *adiene* or *atriene*, etc., to get the name of the olefin.

- Positions of double bonds are indicated by the number of carbon atoms carrying the double bond, e.g.,



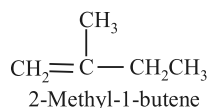
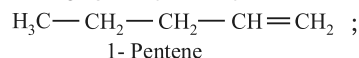
1,3-Butadiene



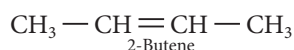
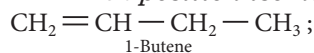
1,4-Hexadiene

- **Isomerism** : Alkenes show following types of isomerism :

- **Chain isomerism** : This type of isomerism is shown by all alkenes having four or more carbon atoms, e.g., pentene has following two chain isomers.

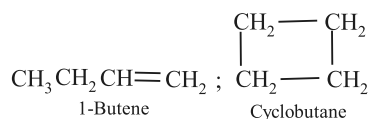
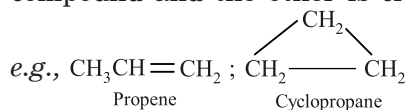


- **Position isomerism** : The two isomers differ in the position of double bond, known as *position isomers*. e.g.,



- **Ring chain isomerism** : In this type of isomerism, one isomer is open-chain

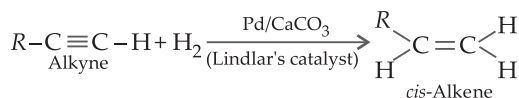
compound and the other is closed chain.



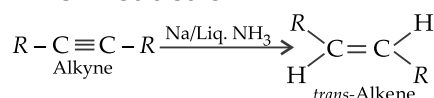
- **Geometrical isomerism** : A carbon-carbon double bond is made up of one σ -bond and one π -bond. The presence of π -bond prevents free rotation about the double bond with the result of the type $ab\text{C} = \text{Cab}$ can exist in two different geometrical isomeric forms, i.e., *cis*-form and *trans*-form.

- **Preparation** :

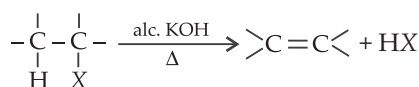
- **Partial hydrogenation of alkynes** :



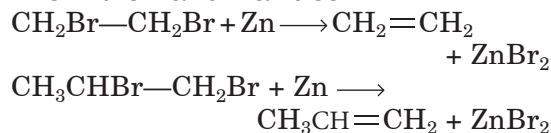
- **Birch reduction** :



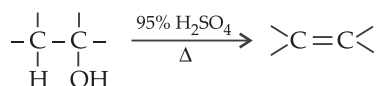
- **By dehydrohalogenation of alkyl halides** :



- **From vicinal dihalides** :



- **By dehydration of alcohols** :



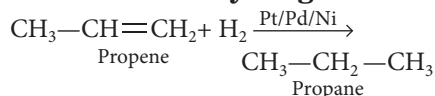
Saytzeff rule : If a single starting compound can yield two or more isomers then more substituted alkene is formed in greater amount.

- **Physical properties** :

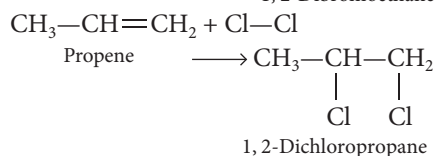
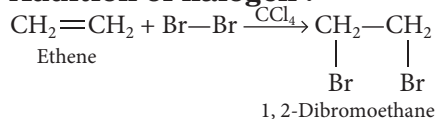
- The first three members are gases, the next fourteen are liquids and the higher ones are solids.
- All alkenes are colourless and odourless except ethene which has faint sweet smell.
- All alkenes are insoluble in water but fairly soluble in non polar solvents.
- Boiling points of alkenes increase regularly with increase in size and straight chain alkenes have higher boiling points than isomeric branched chain compounds.

► **Chemical properties :**

- **Addition of dihydrogen :**



- **Addition of halogen :**

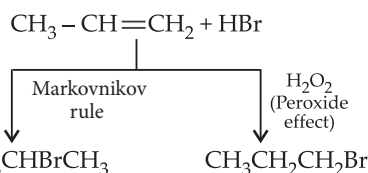


- **Addition of hydrogen halides :**

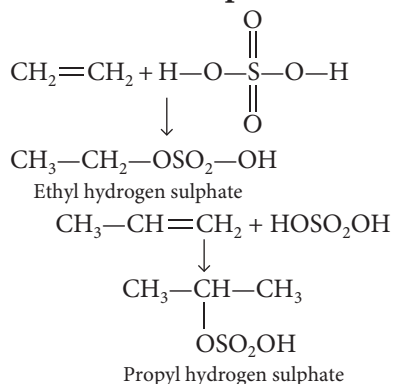
Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl.

- **Markovnikov rule :** The negative part of unsymmetrical reagent adds to less hydrogenated carbon atom of double bond.

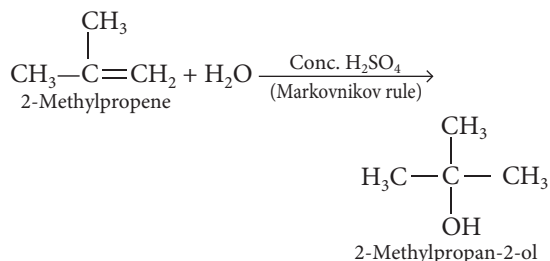
- **Peroxide effect :** Addition of HBr in presence of peroxide gives products opposite to Markovnikov rule.



- **Addition of sulphuric acid :**

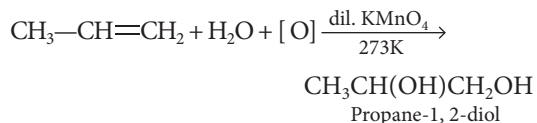
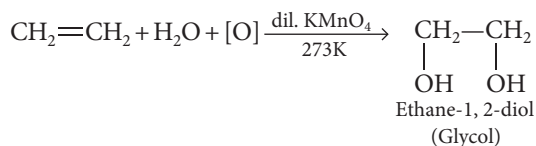


- **Addition of water :**

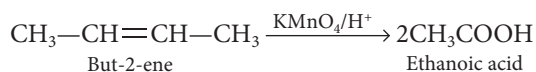
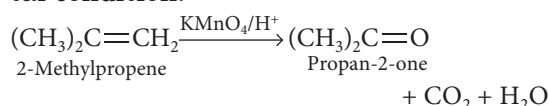


- **Oxidation :** Alkenes on reaction with cold dilute, aqueous solution of potassium

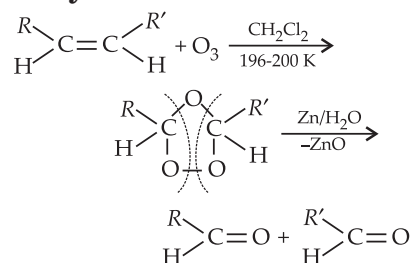
permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of KMnO₄ solution is used as a test for unsaturation.



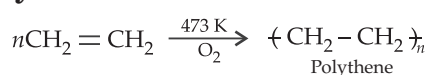
Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental condition.



- **Ozonolysis :**



- **Polymerisation :**



• **Alkynes :** Those unsaturated hydrocarbons which have molecular formula C_nH_{2n-2} are called *alkynes*.

► They contain triple bond. e.g., C₂H₂ (HC ≡ CH) called *acetylene* or *ethyne* and HC ≡ CCH₃ called *propyne* (or *methyl acetylene*).

► They are more acidic than alkenes and alkanes because they have sp-hybridised carbon atom which is more electronegative.

► **Nomenclature :** Alkynes may be named either by the common name or by the IUPAC name. The only common name used in practice is acetylene for the first member. Other members are usually named according to IUPAC system in which the suffix *ane*, of the corresponding alkane is replaced by the suffix *yne*.

In case of alkynes the derived system of nomenclature is already adopted in practice according to which alkynes are regarded as the derivatives of the first member, *i.e.*, acetylene.

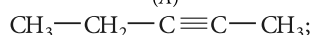
Common name	IUPAC name
Acetylene	Ethyne
Methyl acetylene	Propyne
Ethyl acetylene	1-Butyne
Dimethyl acetylene	2-Butyne

► **Isomerism :**

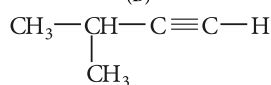
- Ethyne does not show any type of isomerism.
- Alkynes form chain, position, functional and metamers.



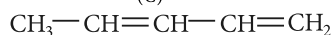
1-Pentyne
(A)



2-Pentyne
(B)



3-Methyl-1-butyne
(C)

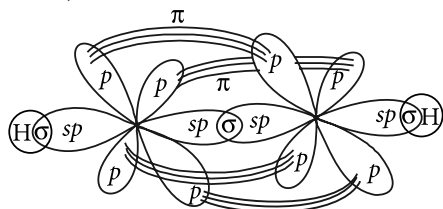


1,3-Pentadiene
(D)

A and B are position isomers; A and C are chain isomers; A and D are functional isomers.

$\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_3$ and $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_3$ are also said to be metamers.

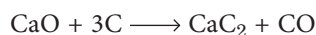
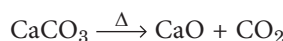
- **Structure :** In acetylene molecule, one of the *sp*-hybridised orbitals of one carbon atom overlaps axially with one of the *sp*-hybridised orbitals of the other carbon atom; thus a C — C σ -bond is formed. Second *sp* hybridised orbitals of each carbon atom overlaps axially and separately with the 1s orbitals of the two hydrogen atoms and thus two C — H σ -bonds are formed. The remaining two pure *p*-orbitals of one carbon atom overlaps sideways with the corresponding *p*-orbitals of the other carbon atom and thus, two C — C π -bonds are formed.



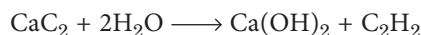
Formation of acetylene molecule

► **Preparation :**

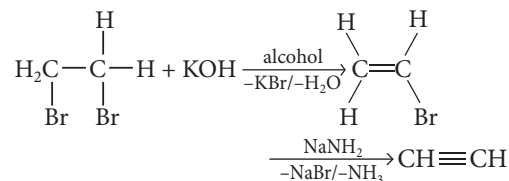
- **From calcium carbide :**



Calcium carbide



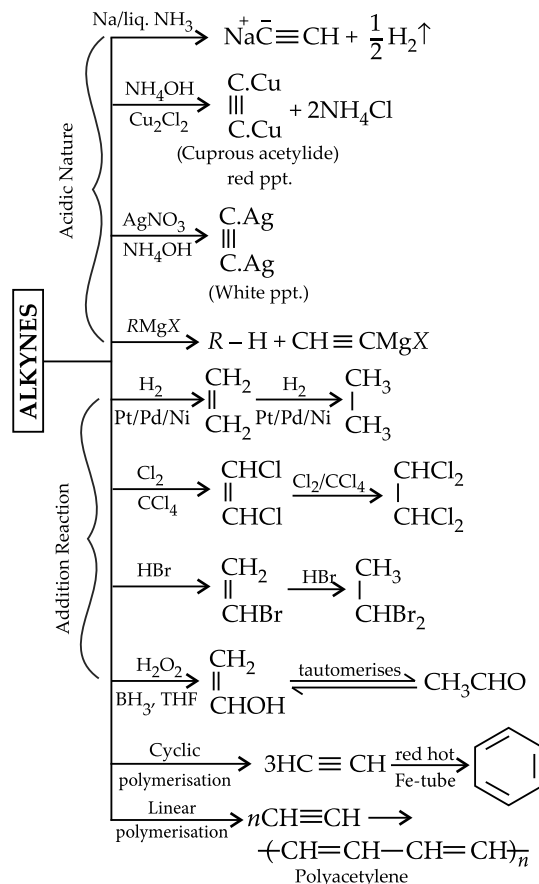
- **From vicinal dihalides :**



► **Physical properties :**

- First three members are gases, the next eight are liquids and the higher ones are solids.
- All alkynes are colourless and odourless except ethyne which has characteristic odour.
- All alkynes are insoluble in water but soluble in non polar solvents.
- Melting points, boiling points and density increase with increase in molar mass.

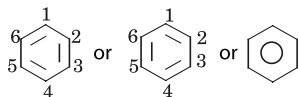
► **Chemical properties :**



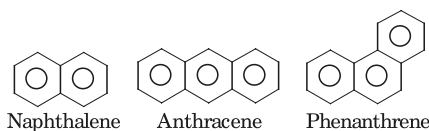
- **Aromatic hydrocarbons** : Those hydrocarbons which contain benzene ring are called *aromatic hydrocarbons* or *arenes*.

► **Nomenclature :**

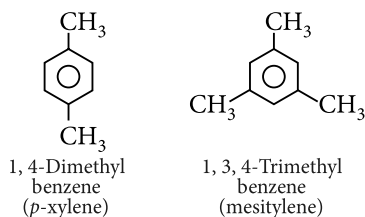
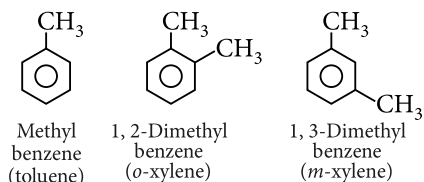
- Aromatic compounds contain at least one benzenoid ring. The simplest aromatic hydrocarbon is benzene which has a planar, hexagonal ring with alternate double bonds.



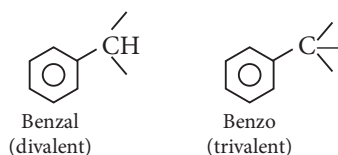
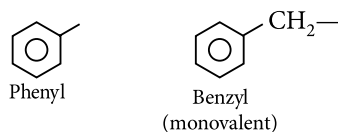
- **Hydrocarbons with more than one ring:**



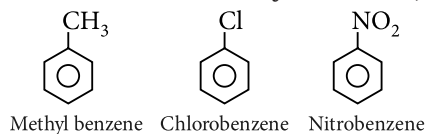
- **Alkyl benzenes** : Common names are given in brackets



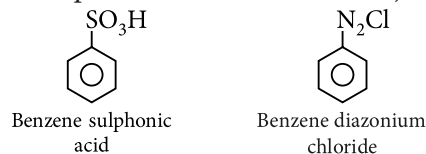
- **Aryl groups :**



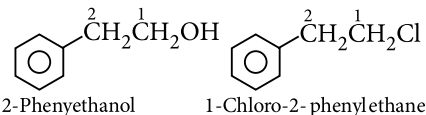
- Mono-substituted derivatives are named by prefixing the name of the substituent before the name of hydrocarbon, e.g.,



Exceptions to the above rule, e.g.,

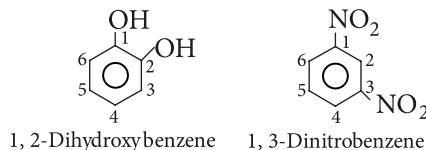


- **Side chain substituted compounds:** When side chain attached to benzene nucleus is substituted, compound is named as *phenyl derivative of aliphatic compounds* e.g.,

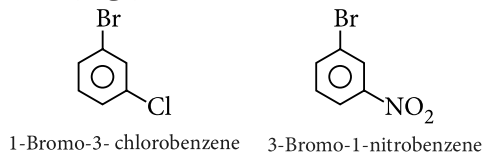


- **Disubstituted compounds :**

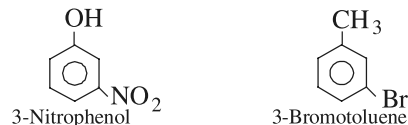
- If the substituents are same then the positions are given and prefix 'di' is added before the name of the substituent, e.g.,



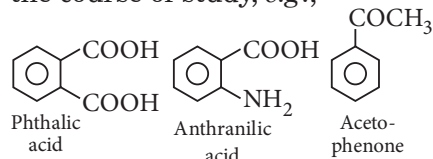
- If the two substituents are different then they are named successively in alphabetical order, e.g.,



- If one of the substituents gives a special name to the compound then the molecule is named as a derivative of that compound with position 1 given to that functional group, e.g.,

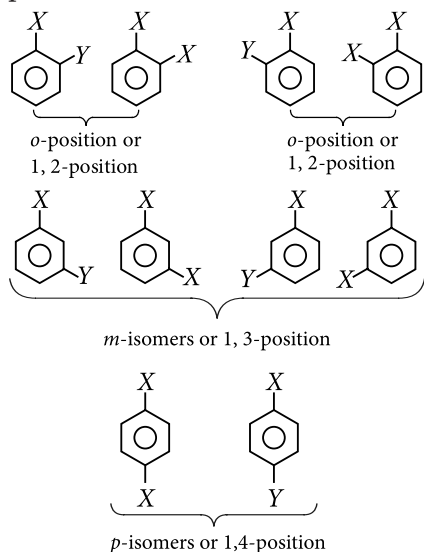


- There are many aromatic compounds which are generally still having special names. These names will be used during the course of study, e.g.,

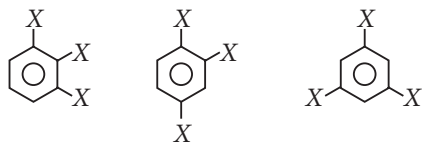


- **Isomerism** : All six hydrogen atoms in benzene are equivalent hence, only one mono-substituted derivative is possible.

- **Position isomerism** : When two substituents are present (either same or different), three position isomers are possible.

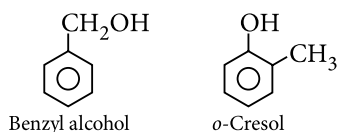


- When three substituents present are identical, only three position isomers are possible.



- When two substituents are same and one is different, six isomers are possible and if all three groups are different, ten isomers are possible.

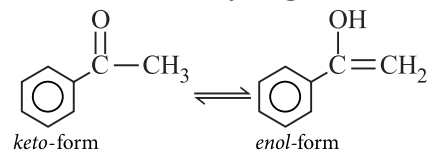
- **Functional isomerism** : This can be seen in phenyl alcohols and phenols, e.g.,



Molecular formula = C_7H_8O

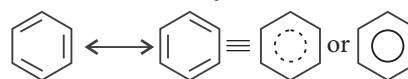
In the two compounds the properties of the $-OH$ group are different.

- **Tautomerism** : *Keto-enol isomerism* is also found to exist in acetophenone due to the presence of mobile α -hydrogen atoms. e.g.,



► **Structure** :

- In benzene, each carbon is sp^2 hybridised. Two of the hybrid orbitals on each carbon are used for the formation of σ -bonds with two adjacent carbon atoms whereas the third sp^2 hybrid orbital overlaps with the σ -orbital of H-atom to form a σ -bond. All these lie in the same plane. The unhybridised orbital of each C-atom overlaps equally with unhybridized p -orbital of both the adjacent C-atoms to which it is bonded.
- It has high degree of unsaturation and has unusual stability due to resonance.



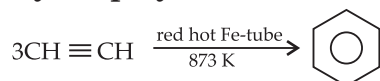
► **Aromaticity or Hückel rule** : A compound is said to be *aromatic*, if it meets all of the following criteria :

- Aromatic compounds contain one or more rings that have a cyclic arrangement of p -orbitals.
- Aromatic rings are planar.
- Aromatic systems are conjugated cyclic systems.
- Aromatic systems must contain $(4n + 2)\pi$ electrons used in delocalisation, where $n = \text{integer } (0, 1, 2, \dots)$.

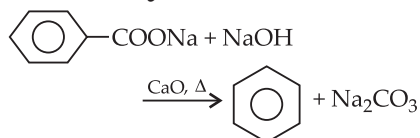
Aromatic	Anti-aromatic	Non-aromatic
<ul style="list-style-type: none"> • Cyclic, planar molecule • Complete delocalisation of π-electrons • Follow Huckel's rule $(4n + 2)\pi$ electrons • e.g., cycloheptatrienyl cation (tropylium ion), cyclopropenyl cation, benzene, etc. <p>Cyclopropenyl cation (Aromatic)</p>	<ul style="list-style-type: none"> • Cyclic, planar molecule • Complete delocalisation of π-electrons • Follow $4n\pi$ electrons • e.g., cyclopropenyl anion, cyclopentadienyl cation, etc. <p>Cyclopentadienyl cation (Anti-aromatic) Cyclopropenyl anion (Anti-aromatic)</p>	<ul style="list-style-type: none"> • Either non-cyclic, non-planar • No delocalisation of π-electrons. • May or may not follow Huckel's rule. • e.g., cyclooctatetraene (tub-shaped), etc. <p>(Non-aromatic)</p>

Preparation :

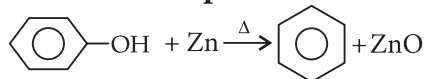
- **Cyclic polymerisation of ethyne :**



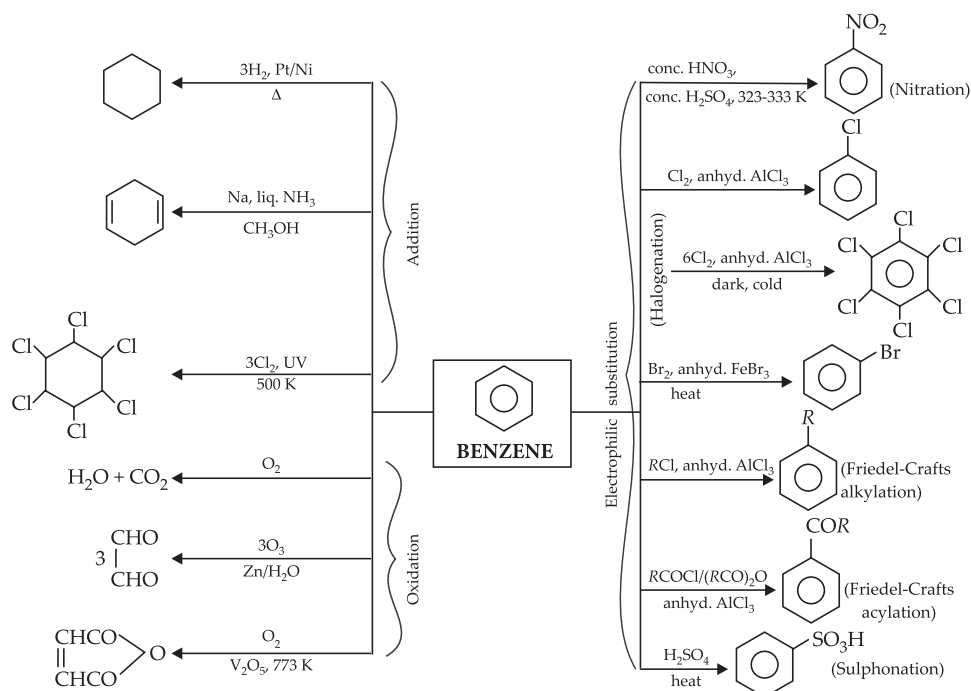
- **Decarboxylation of aromatic acids :**



- **Reduction of phenol :**

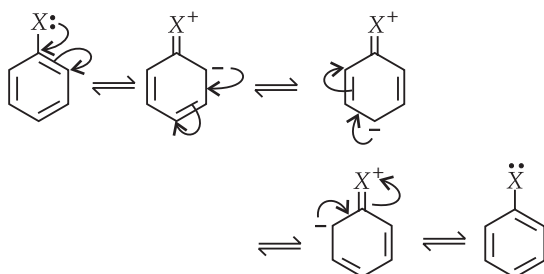


► **Chemical properties :**



► **Directive influence :**

- Groups with positive mesomeric effect (+M) increases electron density at *o*- and *p*-positions due to delocalisation.



(Here, X may be $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NHR}$, NHCOCH_3 , $-\text{OH}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$.)

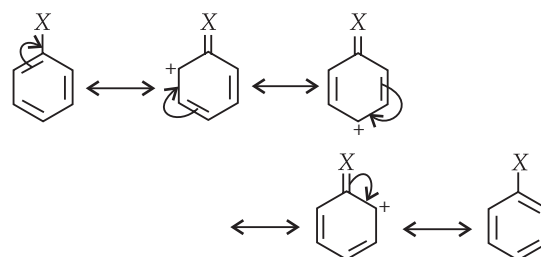
Thus, electrophile attacks on *o*- and *p*-

► **Physical properties :**

- These are colourless liquids or solids with characteristic aroma. These are immiscible with water but miscible in organic solvents and burn with sooty flame.
- Boiling point of arenes increases with increase in the molecular size due to increase in van der Waals' forces of attraction. Melting point depends on molecular size and symmetry. Among *o*-, *m*- and *p*-xylenes, *p*-isomer has highest melting point.

positions because these are electron rich positions.

- Groups with negative mesomeric effect ($-M$) decreases electron density on *o*- and *p*-positions, so electrophile will attack on *m*-position.



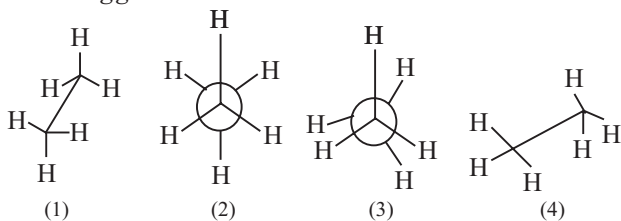
(Here, X may be $-\text{NO}_2$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, $-\text{CN}$.)



OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. In the following structures, which two forms are staggered conformation of ethane?

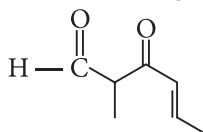


- (a) 1 and 4
(b) 2 and 3
(c) 1 and 2
(d) 1 and 3

2. Which of the following molecules represents the order of hybridisation sp^2 , sp^2 , sp , sp from left to right atoms?

- (a) $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$
(b) $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$
(c) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
(d) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$

3. The IUPAC name of the given compound is

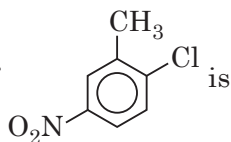


- (a) 5-formylhex-2-en-3-one
(b) 5-methyl-4-oxohex-2-en-5-al
(c) 3-keto-2-methylhex-5-enal
(d) 3-keto-2-methylhex-4-enal

4. Arrange the following in decreasing order of their boiling points.

- (I) *n*-Butane
(II) 2-Methylbutane
(III) *n*-Pentane
(IV) 2,2-Dimethylpropane
- (a) I > II > III > IV
(b) II > III > IV > I
(c) IV > III > II > I
(d) III > II > IV > I

5. IUPAC name of



- (a) 1-chloro-2-methyl-4-nitrobenzene
(b) 2-chloro-1-methyl-5-nitrobenzene
(c) 1-nitro-1-methyl-4-nitrobenzene
(d) 2-methyl-1-chloro-4-nitrobenzene.

6. The alkene that exhibits geometrical isomerism is

- (a) propene
(b) 2-methylpropene
(c) 2-butene
(d) 2-methyl-2-butene.

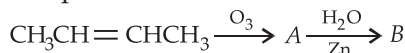
7. During ozonolysis of $\text{CH}_2 = \text{CH}_2$ if hydrolysis is made in absence of Zn dust the products formed are

- (a) HCHO
(b) HCOOH
(c) $\text{CH}_2\text{OHCH}_2\text{OH}$
(d) CH_3OH

8. Among the three conformations of ethane, the order of stability follows the sequence :

- (a) eclipsed > gauche > staggered
(b) eclipsed > staggered > gauche
(c) staggered > gauche > eclipsed
(d) gauche > staggered > eclipsed

9. In the following sequence of reactions, the compound B is



- (a) CH_3CHO
(b) $\text{CH}_3\text{CH}_2\text{CHO}$
(c) CH_3COCH_3
(d) $\text{CH}_3\text{CH}_2\text{COCH}_3$

10. Which of the following is Baeyer's reagent?

- (a) alkaline KMnO_4
(b) acidic $\text{K}_2\text{Cr}_2\text{O}_7$
(c) alkaline $\text{Na}_2\text{Cr}_2\text{O}_7$
(d) MnO_2

11. The function of anhydrous AlCl_3 in Friedel-Crafts reaction is

- (a) to absorb water
(b) to absorb HCl
(c) to produce attacking electrophile
(d) to produce nucleophile.

12. *Meta*-directing and deactivating group in aromatic electrophilic substitution is

- (a) $-\text{CH}_3$
(b) $-\text{OH}$
(c) $-\text{NO}_2$
(d) $-\text{Cl}$

13. The numbers of σ and π -bonds present in 1, 3-butadiene are respectively
 (a) 9 and 2 (b) 8 and 2
 (c) 9 and 3 (d) 9 and 1
14. Which of the following reaction is not correct?
 (a) Propene + HCl \rightarrow 2-chloropropane
 (b) Propene + HBr $\xrightarrow{\text{peroxide}}$ 1-bromopropane
 (c) Propene + HCl $\xrightarrow{\text{peroxide}}$ 2-chloropropane
 (d) Propene + HBr \rightarrow 1-bromopropane
15. Which of the following species is most stable?
 (a) $p\text{-O}_2\text{N} - \text{C}_6\text{H}_4 - \overset{+}{\text{C}}\text{H}_2$
 (b) $\text{C}_6\text{H}_5 - \overset{+}{\text{C}}\text{H}_2$
 (c) $p\text{-Cl} - \text{C}_6\text{H}_4 - \overset{+}{\text{C}}\text{H}_2$
 (d) $p\text{-CH}_3\text{O} - \text{C}_6\text{H}_4 - \overset{+}{\text{C}}\text{H}_2$
16. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.
 (a) HCl > HBr > HI (b) HBr > HI > HCl
 (c) HI > HBr > HCl (d) HCl > HI > HBr
17. The IUPAC name of the compound having the formula $\text{CH} \equiv \text{C} - \text{CH} = \text{CH}_2$ is
 (a) 1-butyne-2-ene (b) but-1-yn-3-ene
 (c) 1-buten-3-yne (d) 3-buten-1-yne
18. Which of the following reactions of methane is incomplete combustion?
 (a) $2\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Cu}/523\text{K}/100\text{ atm}} 2\text{CH}_3\text{OH}$
 (b) $\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Mo}_2\text{O}_3} \text{HCHO} + \text{H}_2\text{O}$
 (c) $\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_{(s)} + 2\text{H}_2\text{O}_{(l)}$
 (d) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
19. Benzene is obtained when
 (a) acetylene is passed through red hot iron tube
 (b) benzenesulphonic acid is treated with superheated steam
 (c) both (a) and (b)
 (d) none of these.
20. The molecule having net dipole moment is
 (a) 2,2-dimethylpropane
 (b) *trans*-pent-2-ene
 (c) *trans*-but-2-ene
 (d) 2, 2, 3, 3-tetramethylbutane.
21. In which of the following compounds only primary carbon atoms are present?
 (a) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_3$ (b) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$
 (c) $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_3$ (d) $\text{CH}_3 - \text{CH}_3$
22. The dihedral angle HCH in staggered conformation of C_2H_6 is
 (a) 120° (b) 60° (c) 0° (d) 90°
23. The reaction, $\text{RC} \equiv \text{CR} \xrightarrow[\text{Lindlar's catalyst}]{\text{H}_2}$ gives the main product as
 (a) *cis*-alkene (b) *trans*-alkene
 (c) alkane (d) none of these.
24. Anti-Markownikoff addition of HBr is not observed in
 (a) propene (b) 1-butene
 (c) 2-butene (d) 2-pentene
25. Mark the correct decreasing order of stability.
 (a) Aromatic > non-aromatic > anti-aromatic
 (b) Aromatic > anti-aromatic > non-aromatic
 (c) Non-aromatic > anti-aromatic > aromatic
 (d) Anti-aromatic > non-aromatic > aromatic
26. Which among the following is very strong *o*-, *p*-directing group?
 (a) $-\text{Cl}$ (b) $-\text{OR}$ (c) $-\text{NH}_2$ (d) $-\text{NHR}$
27. Electrolysis of an aqueous solution of sodium ethanoate gives
 (a) methane (b) ethane
 (c) butane (d) methyl ethanoate.
28. Which of the following compounds reacts with sodium to liberate hydrogen gas?
 (a) Ethane (b) Propene
 (c) Acetylene (d) Benzene
29. The correct order of reactivity towards electrophilic substitution is
 (a) phenol > benzene > chlorobenzene > benzoic acid
 (b) benzoic acid > chlorobenzene > benzene > phenol
 (c) phenol > chlorobenzene > benzene > benzoic acid
 (d) benzoic acid > phenol > benzene > chlorobenzene
30. Which is the correct IUPAC name of the following compound?

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\underset{\text{CH}_2}{\text{CH}} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

$$\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

- (a) 5-(2', 2'-Dimethylpropyl)decane
 (b) 4-Butyl-2,2-dimethylnonane
 (c) 2,2-Dimethyl- 4-pentyloctane
 (d) 2,2-Dimethyl- 4-butylnonane

31. An alkene on ozonolysis gave 2-pentanone and acetaldehyde. The alkene was

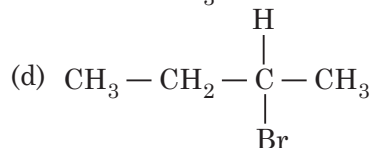
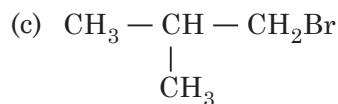
- (a) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—C}(\text{CH}_3)=\text{CH—CH}_3$
 (b) $\text{CH}_3\text{—CH}_2\text{—CH}=\text{C}(\text{CH}_3)\text{—CH}_2\text{—CH}_3$
 (c) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—C}(\text{CH}_2)=\text{CH}_2\text{—CH}_3$
 (d) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}(\text{CH}_3)\text{—CH}=\text{CH}_2$

32. Which of the following compounds will not undergo Friedal-Crafts reaction easily?

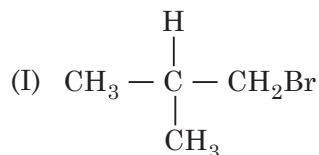
- (a) Nitrobenzene (b) Toluene
 (c) Cumene (d) Xylene

33. The reaction of HBr with $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}_2$ in the presence of peroxide will give

- (a) $\text{CH}_3\text{—C}(\text{CH}_3)(\text{Br})\text{—CH}_3$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—Br}$



34. Arrange the following alkyl halides in decreasing order of the rate of β -elimination reaction with alcoholic KOH.



- (a) I > II > III (b) III > II > I
 (c) II > III > I (d) I > III > II

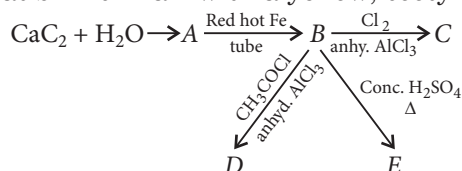
35. Benzene easily shows

- (a) ring fission reactions since it is unstable
 (b) addition reactions since it is unsaturated
 (c) electrophilic substitution reactions due to stable ring and high π electron density
 (d) nucleophilic substitution reactions due to stable ring and minimum electron density.

Case Based MCQs

Case I : Read the following and answer the questions from 36 to 40 given below.

Compound (A) is an important industrial feed stocks, but it's largest use as the fuel for the oxyacetylene torch. It is a colourless, foul smelling gas that burns in air with a yellow, sooty flame.



36. Identify the product A.
 (a) ethane (b) ethyne
 (c) ethene (d) methane
37. The compound (B) formed is
 (a) cyclohexane (b) benzene
 (c) hexane (d) cyclopentane.
38. The reaction $\text{B} \xrightarrow[\text{Anhy. AlCl}_3]{\text{Cl}_2} \text{C}$ follows
 (a) nucleophilic substitution mechanism

- (b) electrophilic addition mechanism
 (c) electrophilic substitution mechanism
 (d) elimination reaction mechanism.

39. The product E is

- (a) nitrobenzene
 (b) benzene sulphonic acid
 (c) both (a) and b (d) none of these.

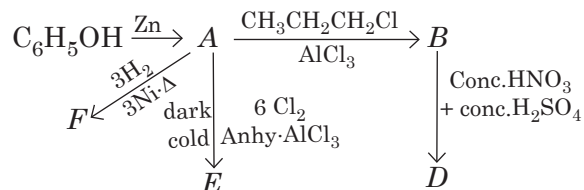
40. Identify the product 'D'.

- (a) Chlorobenzene (b) Bromobenzene
 (c) Toluene (d) Acetophenone

Case II : Read the following and answer the questions from 41 to 45 given below.

Compound 'A' is the simplest and ideal aromatic compound. It is also one of the most basic petrochemicals which is mainly used to prepare a number of important chemicals such as toluene, phenol, aniline, biphenyl etc, which are used in manufacture of dyes, detergents, drugs, explosives, pesticides etc. But it is carcinogenic.

In the given sequence of reaction, compound A undergoes a number of changes



41. The name of compound A is

- (a) cyclohexane
 (b) benzene
 (c) cyclohexene
 (d) none of these.

42. The reaction $\text{A} \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}} \text{B}$ is an example of

- (a) elimination reaction
 (b) addition reaction
 (c) electrophilic substitution reaction
 (d) nucleophilic substitutional reaction.

43. The name of product F is

- (a) benzene (b) cyclohexene
 (c) cyclohexane (d) cyclohex-1,4-diene

44. The major product when 'A' reacts with propyl chloride in the presence of AlCl₃ is

- (a) propyl benzene
 (b) isopropyl benzene
 (c) chloro benzene
 (d) ethyl benzene.

45. The major product 'D' in the given series of reaction is

- (a) 4-nitro isopropyl benzene
 (b) 2-nitro isopropyl benzene
 (c) 3-nitro propyl benzene
 (d) none of these.

➡ Assertion & Reasoning Based MCQs

For question numbers 46-55, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

46. **Assertion :** Boiling point of alkanes increases with increase in molecular weight.

Reason : van der Waal's forces increase with increase in molecular weight.

47. **Assertion :** Acetylene is acidic in nature.

Reason : Acetylene is sp hybridised.

48. **Assertion :** *Trans*-pent-2-ene is polar but *trans*-but-2-ene is non-polar.

Reason : The polarity of cis-isomer is more than trans which are either non-polar or less polar.

49. **Assertion :** Benzene on heating with conc. H₂SO₄ gives benzenesulphonic acid which when heated with superheated steam under pressure gives benzene.

Reason : Sulphonation is a reversible process.

50. **Assertion :** Sodium acetate on Kolbe's electrolysis gives methane.

Reason : Methyl free radical is formed at anode.

51. **Assertion :** HC≡C⁻ is more stable than H₂C=CH⁻.

Reason : HC≡C⁻ has more s-character than H₂C=CH⁻.

52. **Assertion :** All the hydrogen atoms in CH₂=C=CH₂ are attached to sp² hybridised carbon atom.

Reason : All the carbon atoms in its are sp² hybridized.

53. **Assertion :** Methane cannot be obtained by Wurtz reaction.

Reason : Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.

54. **Assertion :** Saturated hydrocarbons are chemically less reactive.

Reason : All isomeric paraffins have same parent name.

55. **Assertion :** Nitrobenzene does not undergo Friedel Crafts reaction.

Reason : Nitrobenzene is a *m*-director.

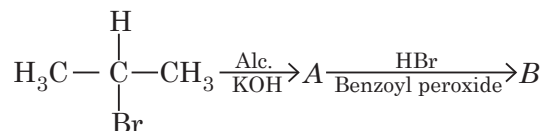
SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

- When alkyne is treated with bromine water then what will be the colour of product?
- What product would you get from acid catalysed hydration of 1-methylcyclohexene? Explain.
- Explain why the branching of an alkane chain lowers its boiling point.
- Give a brief account for the following statement :
CH₄ cannot be synthesized by Wurtz reaction.
- Acetylene is acidic but it does not react with NaOH or KOH. Give reason.
- Complete the following reaction :

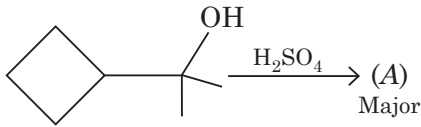


- Write structures of A and B in the following reaction :



- Name the chain isomer of C₅H₁₂ which has a tertiary hydrogen atom.
- Explain why dry ether is used as a solvent in Wurtz reaction.
- Draw the Newmann projection formula for staggered and eclipsed conformation of ethane.


Short Answer Type Questions (SA-I)

- 

Identify A
- How will you convert methyl bromide to ethane?
- Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms?
- Ethyne reacts with dil. H₂SO₄ in presence of mercury salt to give acetaldehyde but with dil. HCl under similar conditions, it gives vinyl chloride. Explain why.
- Which alkyne would you start with and what reagents would you use to prepare :
(i) *cis*-but-2-ene (ii) *trans*-pent-2-ene

- What do the following compounds produce when passed through Cr₂O₃ supported over alumina at 600°C?

- n*-Hexane
- n*-Heptane

- What will  produce on ozonolysis?

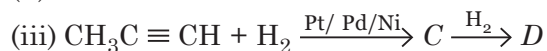
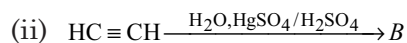
- Ph-CH₂-C≡CH $\xrightleftharpoons[Y]{X}$ Ph-C≡C-CH₃

Identify X and Y .

- Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also, give reason for this behaviour.
- Explain Friedel-Crafts alkylation reaction with chemical equation.

Short Answer Type Questions (SA-II)

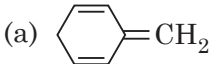
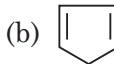
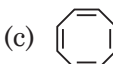

- An alkyne (X) has molecular formula C₅H₈. It reacts neither with sodamide nor with ammoniacal cuprous chloride. Identify X.
- Complete the following reactions :
(i) HC≡CH $\xrightarrow{\text{NaNH}_2, \text{CH}_3\text{Br}}$ A



- An alkene 'A' contains three C—C, eight C—H σ bonds and one C—C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.

24. (a) Explain the order of stability of carbocations giving reason.
 (b) Addition of HBr to propene in the presence of benzoyl peroxide yields 1-bromopropane. Explain with suitable mechanism.
25. (a) Write chemical reactions to illustrate the Kolbe's reaction
 (b) Name the compound that will be required to obtain butane using Kolbe's electrolysis process.
26. Why *cis*-but-2-ene has higher boiling point than *trans*-but-2-ene?
27. Despite their $-I$ effect, halogens are *o*- and *p*-directing in haloarenes. Explain.
28. An organic compound *A* with molecular formula C_3H_8O reacts with conc. H_2SO_4 to give *B*, which on reaction with HCl gives *C*. Compound *C* reacts with metallic sodium to give *D*. Identify compounds *A*, *B*, *C* and *D*.
29. Explain *ortho*- and *para*-directing influence of monosubstituted benzene giving suitable example.
30. Draw the Newman projections of the eclipsed and staggered conformers of ethane. Which of the two is stable and why?
31. Explain anti-Markovnikov addition or peroxide effect or Kharash effect with example.
32. What does ozonolysis of benzene yield?
33. Give two reactions to show acidic character of alkynes.
34. Identify a reagent which can easily distinguish between 1-butyne and 2-butyne.
35. A hydrocarbon (*Z*) has molecular formula C_8H_{10} . It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers *A*, *B* and *C*. Write the structures of *Z*, *A*, *B* and *C*.

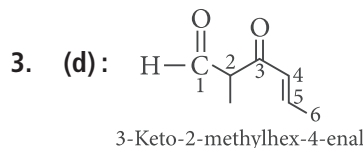
➡ Long Answer Type Questions (LA)

36. An alkyl halide $C_5H_{11}Br$ (*A*) reacts with ethanolic KOH to give an alkene '*B*', which reacts with Br_2 to give a compound '*C*', which on dehydrobromination gives an alkyne '*D*'. On treatment with sodium metal in liquid ammonia one mole of '*D*' gives one mole of the sodium salt of '*D*' and half a mole of hydrogen gas. Complete hydrogenation of '*D*' yields a straight chain alkane. Identify *A*, *B*, *C* and *D*. Give the reactions involved.
37. A hydrocarbon '*Y*' decolourises bromine water. On ozonolysis it gives 3-methylbutanal and formaldehyde. Give the name of the compound. Identify *Y*.
38. Explain why the following systems are not aromatic.
- (a)  (b) 
- (c) 
39. Draw the resonating structure of C_6H_5OH (phenol) and C_6H_5CHO (benzaldehyde).
40. Give mechanism for the following reaction.
-  + $Cl_2 \xrightarrow{\text{Anhy. } AlCl_3}$

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (c) : In staggered conformation, the rotation about the C – C bond is such that the hydrogen atoms attached tetrahedrally to the two carbon atoms are completely staggered *i.e.* they are at maximum distance apart in space.
2. (b) : $CH_2 \overset{sp^2}{=} CH - C \overset{sp}{\equiv} CH$

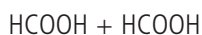
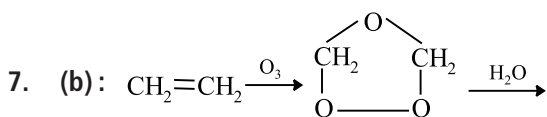
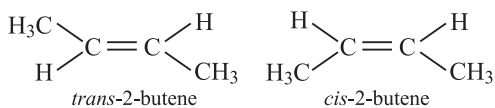


4. (d) : Boiling point increases with increase in molecular mass. Straight chain hydrocarbons have higher boiling points than branched chain hydrocarbons of comparable molecular mass.

5. (a)

6. (c) : When two groups attached to a double bonded carbon atom are same, the compound does not exhibit geometrical isomerism.

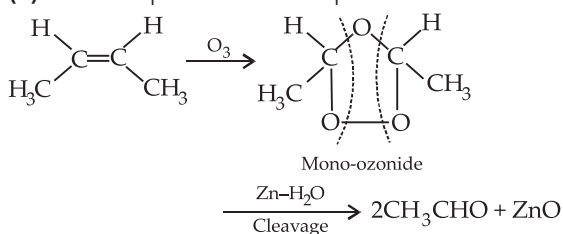
Compounds in which the two groups attached to a double bonded carbon are different, exhibit geometrical isomerism, thus, only 2-butene exhibits *cis-trans* isomerism.



Reductive hydrolysis of ozonide with Zn dust gives carbonyl compound whereas oxidative hydrolysis yields carboxylic acid.

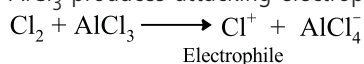
8. (c) : The eclipsed conformation is least stable because the hydrogens and bonding pairs of electrons on adjacent carbon atoms are as close to one another as possible. This causes maximum repulsion and least stability. Staggered conformation is most stable because of minimum repulsion. Gauche conformation lie between these two in stability. Thus, order of stability is : staggered > gauche > eclipsed.

9. (a) : The complete reaction sequence is as follows:

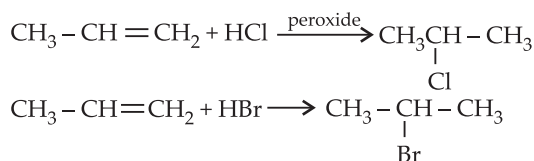
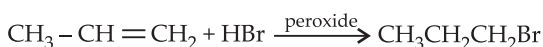
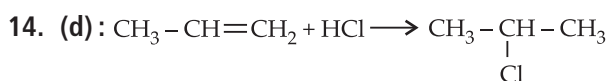
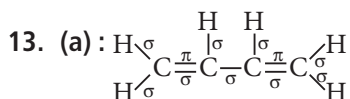


10. (a) : Baeyer's reagent is alkaline solution of cold potassium permanganate (KMnO_4).

11. (c) : AlCl_3 produces attacking electrophile.

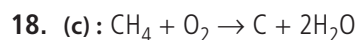
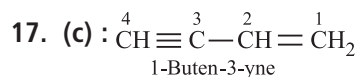


12. (c) : $-\text{CH}_3$: Activating and *o, p*-directing
 $-\text{OH}$: Activating and *o, p*-directing
 $-\text{NO}_2$: Deactivating and *m*-directing
 $-\text{Cl}$: Deactivating and *o, p*-directing



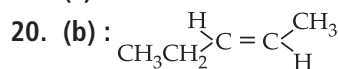
15. (d) : $\text{H}_3\text{CO} \rightarrow \text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$. Electron donating group stabilizes the cation.

16. (c) : The decreasing order of reactivity of halo acids with propene is $\text{HI} > \text{HBr} > \text{HCl}$. As the size of halogen increases, the strength of $\text{H}-\text{X}$ bond decreases and hence, reactivity increases.



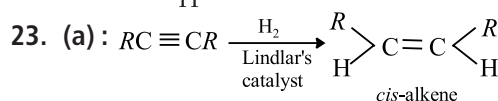
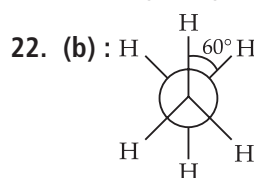
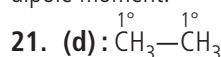
Complete combustion will give CO_2 and H_2O .

19. (c)



trans-pent-2-ene is unsymmetrical, therefore, show net dipole moment.

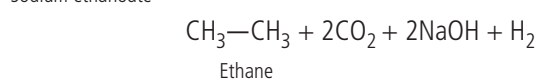
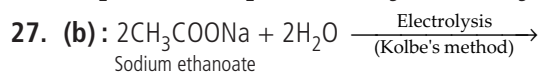
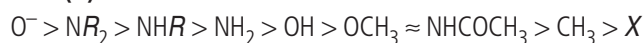
While 2,2-dimethylpropane, *trans*-but-2-ene and 2,2,3,3-tetramethylbutane are symmetrical, therefore do not show net dipole moment.



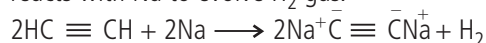
24. (c) : Anti-Markownikoff addition of HBr is observed only with unsymmetrical alkenes *i.e.*, propene, 1-butene, 2-pentene. As, 2-butene is symmetrical so in its case anti-Markownikoff addition will not be observed.

25. (a) : Aromatic are most stable followed by non-aromatic and anti-aromatics are least stable.

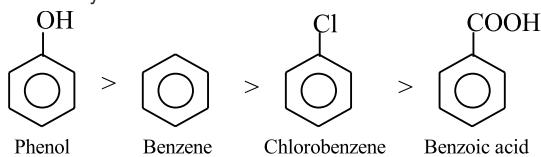
26. (d) : The directive influence order is



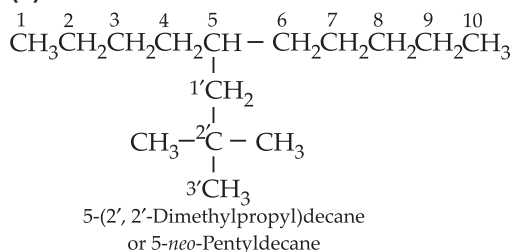
28. (c) : Only acetylene has acidic hydrogens and hence reacts with Na to evolve H_2 gas.



29. (a) : In general electron-releasing groups activate and electron withdrawing groups deactivate the benzene ring towards electrophilic substitutions. Thus order of reactivity is:



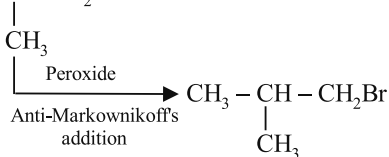
30. (a) :



31. (a)

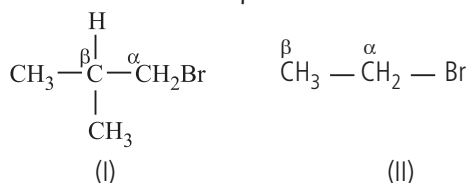
32. (a) : Nitrobenzene is strongly deactivated, hence will not undergo Friedel-Crafts reaction.

33. (c) : $\text{CH}_3 - \text{C}(\text{CH}_3) = \text{CH}_2 + \text{HBr}$

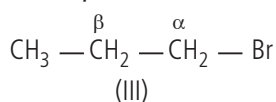


34. (d) : $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}} - \text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{Br}$

is the order of rate of β -elimination with alcoholic KOH.



(has 2 β -substituents) (has no β -substituent)

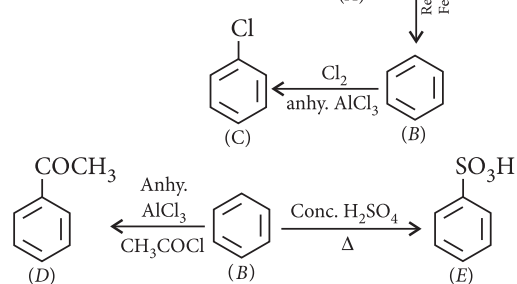


(has 1 β -substituent)

More the number of β -substituents (alkyl groups), more stable alkene it will form on β -elimination and more will be the reactivity. Thus, the decreasing order of the rate of β -elimination reaction with alcoholic KOH is: I > III > II.

35. (c) : The most common reactions shown by benzene are electrophilic substitution reactions.

36. (b) : $\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$ (A)



37. (c)

38. (c)

39. (b)

40. (d)

41. (b)

42. (c)

43. (c) :

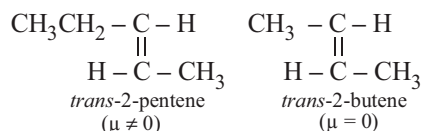
44. (b) :

45. (a) :

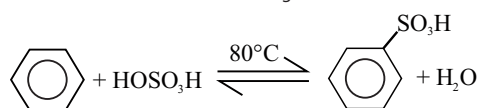
46. (a) : Greater is the molecular mass, greater is the magnitude of van der Waal's forces of attraction and hence higher the boiling point.

47. (b) : The acidic nature in acetylene is described on the basis of higher electronegativity of sp hybridized carbon atom which pulls the $\text{C} - \text{H}$ bond pair more effectively to lose H^+ .

48. (b) : The vector sum of all polar bonds in *trans*-pent-2-ene is not zero but the vector sum is zero in *trans*-but-2-ene.



49. (a) : Sulphonation of benzene is an electrophilic substitution reaction in which SO_3 acts as the electrophile.



50. (d) : Sodium acetate on Kolbe's electrolysis gives ethane. It is formed at anode.

51. (a) : $\text{HC}\equiv\text{C}^-$ has 50% s -character and $\text{H}_2\text{C}=\text{CH}^-$ has 33% s -character. Stability of carbanions increases with an increase in the s -character at the carbanion. So, $\text{HC}\equiv\text{C}^-$ is more stable than $\text{H}_2\text{C}=\text{CH}^-$.

52. (c) : The two H-atom on first carbon and the two H-atoms on the third carbon atom are attached to sp^2 hybridised carbon atoms. The central carbon atom is sp -hybridized.

53. (a) : Wurtz reaction involves the formation of alkanes by heating alkyl halide with sodium in ether.

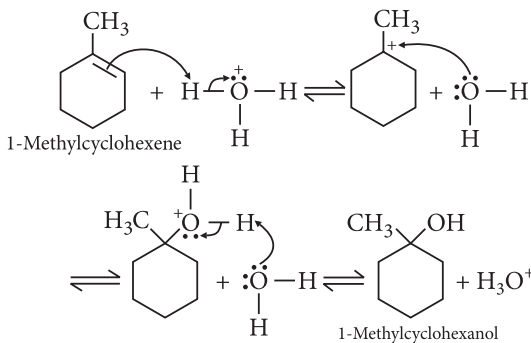
In this reaction two alkyl radicals join together to form an alkane. The net result in this reaction is the formation of symmetrical alkane ($R-R$) having an even number of carbon atoms.

54. (c) : Less reactivity of saturated hydrocarbons is due to the presence of single bonds between carbon atoms. Paraffins (alkanes) may have straight chain or branched chain isomers which have different parent names.

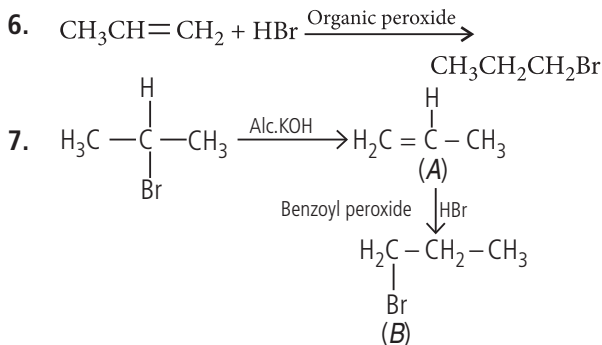
55. (b) : The Friedel Crafts reaction does not take place with nitrobenzene because the ring has been too greatly deactivated. Moreover, any coordination of $AlCl_3$ with unshared electrons of oxygen of NO_2 group would further deactivate the ring making $-NO_2$ electrophilic.

SUBJECTIVE TYPE QUESTIONS

- The product will be colourless.
- 1-Methylcyclohexanol will be formed because a 3° carbocation will be formed as an intermediate.

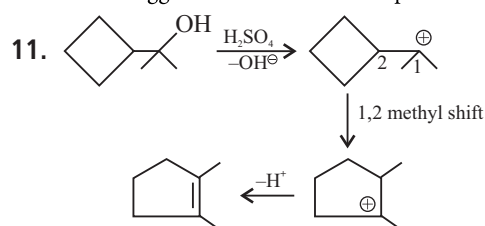
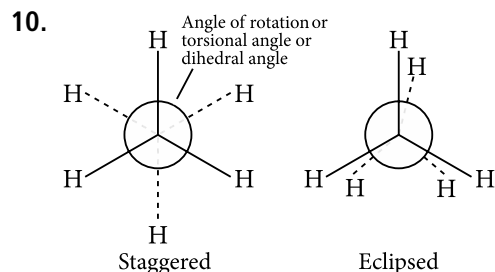


- Boiling point decreases with increase in branching due to decrease in surface area of the molecule.
- Wurtz reaction occurs between two alkyl halides to yield alkane. Methane has only one carbon atom, hence cannot be prepared by using Wurtz reaction.
- Due to sp -hybridisation of C-atom in acetylene, proton is strongly attracted by nucleus and cannot be abstracted easily therefore, it does not react with NaOH or KOH.

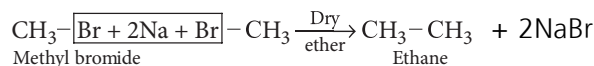


8. 2-Methylbutane, $(CH_3)_2CH - CH_2 - CH_3$.

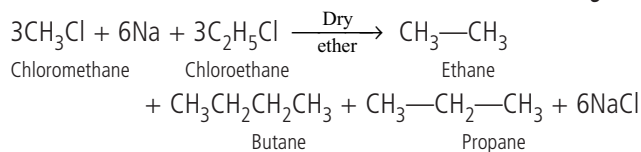
9. In Wurtz reaction, pure sodium is used which is highly violent towards water therefore, dry ether is used.



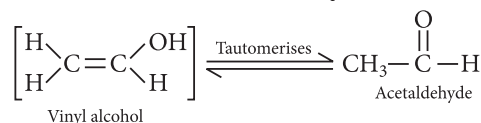
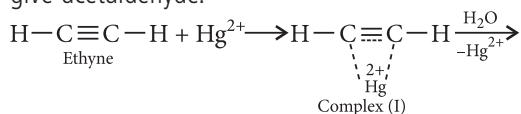
12. Two moles of methyl bromide react with sodium metal in presence of dry ether as solvent to give ethane. This reaction is known as Wurtz reaction.



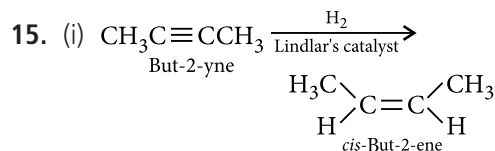
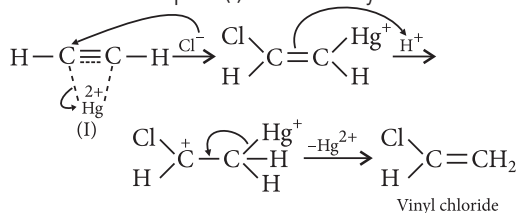
13. It is because mixture of alkanes will be formed e.g.,

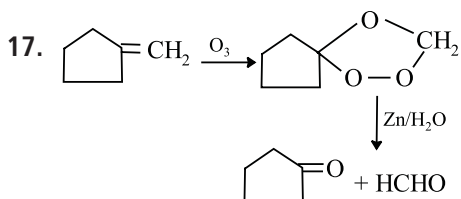
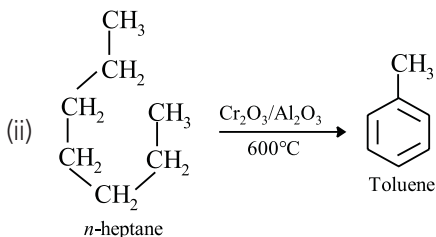
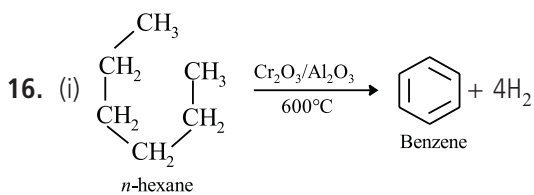
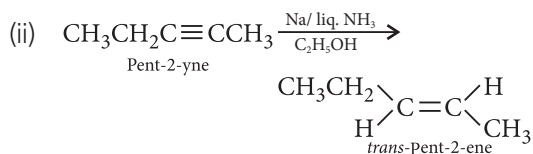


14. Mercuric ion forms a complex (I) with acetylene. Since, H_2O is more nucleophilic than SO_4^{2-} ion, it attacks the complex (I) to form first vinyl alcohol which further tautomerises to give acetaldehyde.

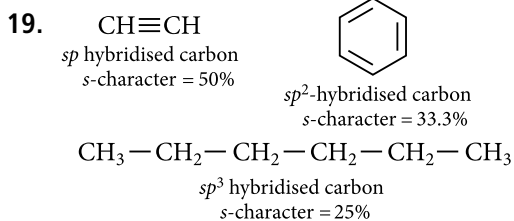


In case of dil. HCl, Cl^- ion is more nucleophilic than H_2O , it reacts with complex (I) to form vinyl chloride.



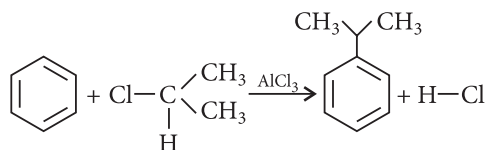


18. On heating with *alc.* KOH in inert solvent, the triple bond of 1-alkyne is shifted towards the centre to form an isomeric 2-alkyne. On heating with sodamide (NaNH₂ in liq. NH₃) the triple bond shifts towards end.



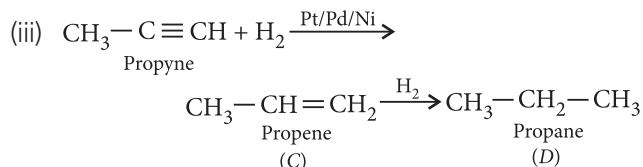
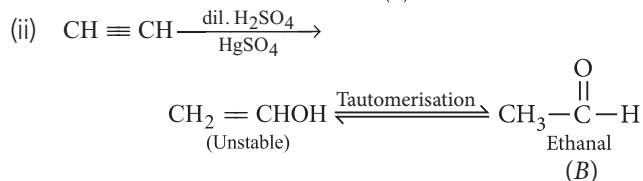
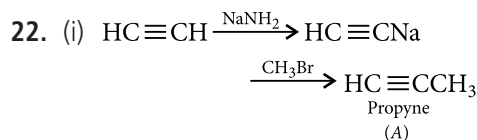
Since s -orbitals are closer to the nucleus, hence due to more s -character in ethyne (sp hybridised), the hybridised orbital is nearest to this carbon atom in comparison to sp^3 or sp^2 hybridised carbon. This leads to the movement of C — H bond pair more towards sp hybridised carbon, leading to the development of partial positive charge on the hydrogen attached to sp hybridised carbon. Thus, such a hydrogen behaves as acidic hydrogen. Hence, order of acidic nature is, ethyne > benzene > *n*-hexane.

20. Friedel–Crafts alkylation is a Lewis acid-catalyzed electrophilic aromatic substitution reaction that allows the synthesis of alkylated products via the reaction of arenes with alkyl halides. With anhydrous aluminium chloride as a catalyst, the stable alkyl carbocation is generated which attacks the benzene ring. An example of this type of reaction is shown below :

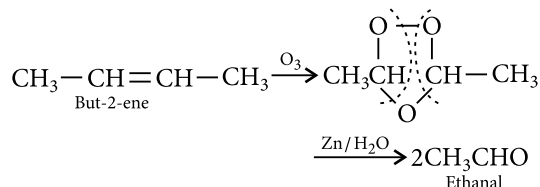


21. Alkyne X is C₅H₈. Since it does not react with sodamide or ammoniacal cuprous chloride, the triple bond cannot be terminal.

∴ X is CH₃CH₂C ≡ CCH₃ (Pent-2-yne)

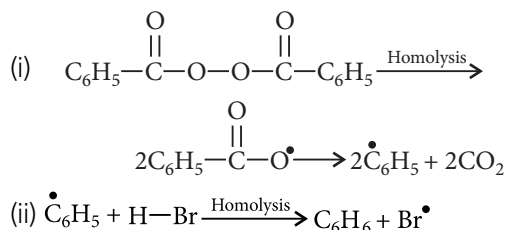


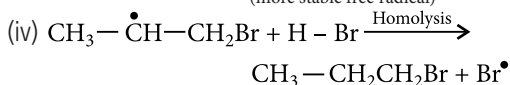
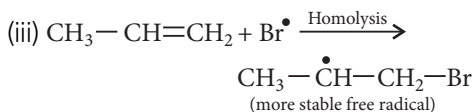
23. Alkene A contains 3C — C, 8C — H and one C=C bonds. An aldehyde containing one —CHO group and having molar mass of 44 amu has to be CH₃CHO and since two moles of CH₃CHO are obtained by ozonolysis of alkene A, the alkene has to be joined by two CH₃CH— groups by a double bond. It has to be CH₃ — CH = CH — CH₃, *i.e.*, but-2-ene. But-2-ene contains 3C—C σ bonds, 8C — H σ bonds and one C=C bond.



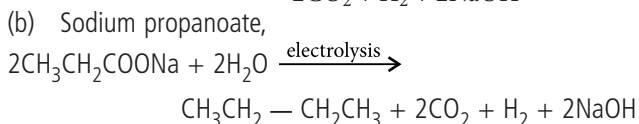
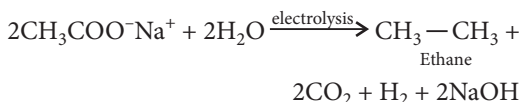
24. (a) Stability of carbocations decreases as 3° > 2° > 1°. Alkyl groups have +I effect. When an alkyl group is attached to positively charged carbon atom of a carbocation, it tends to release electrons towards that carbon and reduces the positive charge on the carbon. Thus, positive charge gets dispersed. This dispersal of the positive charge stabilises the carbocation.

(b) Mechanism : Peroxide effect proceeds via free radical mechanism as given below :





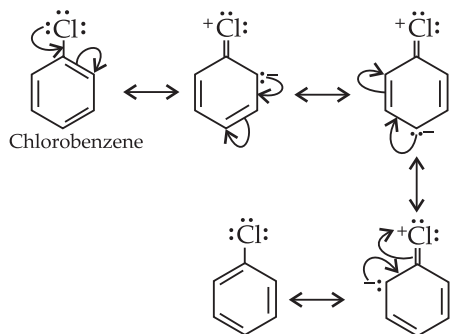
25. (a) Kolbe's reaction : In this reaction, an aqueous solution of sodium or potassium salt of carboxylic acid on electrolysis gives alkane having even number of carbon atoms at anode.



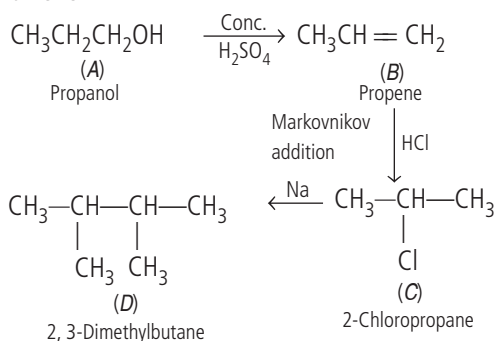
26. Due to higher dipole moment, the boiling point of *cis*-isomer is higher than the corresponding *trans*-isomer.

27. In case of aryl halides, halogens are little deactivating because of their strong $-I$ -effect. Therefore, overall electron density on the benzene ring decreases. In other words, halogens are deactivating due to $-I$ -effect. However, because of the $+R$ -effect, *i.e.*, participation of lone pairs of electrons on the halogen atom with the π -electrons of the benzene ring, the electron density increases more at *o*- and *p*-positions than at *m*-positions.

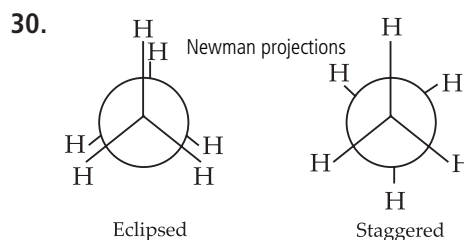
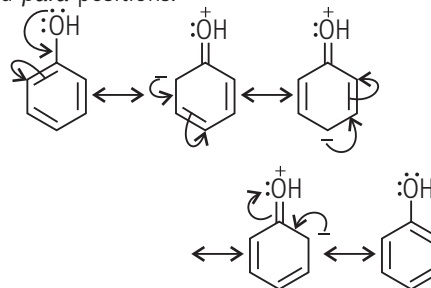
As a result, halogens are *o*, *p*-directing. The combined result of $+R$ -effect and $-I$ -effect of halogens is that, halogens are deactivating but *o*, *p*-directing.



28. Compound A is an alcohol which on reaction with H_2SO_4 gives alkene B.

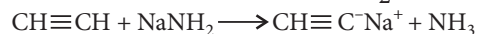
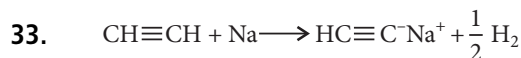
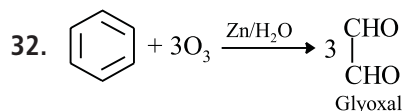
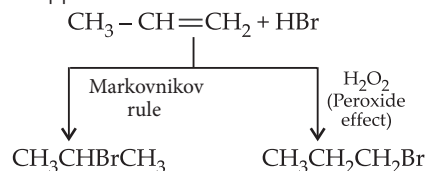


29. $-\text{OH}$ group attached to benzene ring release electrons and activate the benzene ring, direct the incoming groups to *ortho* and *para* positions.



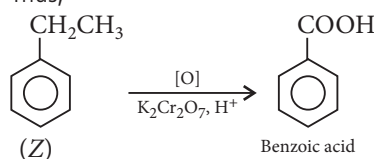
In staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon-hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. Thus, the molecule has more energy and therefore, has lesser stability.

31. Peroxide effect : Addition of HBr in presence of peroxide gives products opposite to Markovnikov rule.



34. There will be no reaction between 2-butyne and Cu_2Cl_2 because it has no acidic hydrogen. In 1-butyne the terminal hydrogen is acidic ($\text{CH}_3\text{CH}_2-\text{C}\equiv\text{CH}$) so it will give a red ppt. with ammoniacal Cu_2Cl_2 .

35. Since, it does not decolourise bromine water, it is arene. Thus,



PRACTICE PAPER

1*

Time allowed : 2 hours

Maximum marks : 35

General Instructions : Read the following instructions carefully.

- There are 16 questions in this question paper. All questions are compulsory.
- Section A : Q. No. 1 to 8 are objective type questions. Q. No. 1 is passage based question carrying 4 marks while Q. No. 2 to 8 carry 1 mark each.
- Section B : Q. No. 9 to 12 are short answer questions and carry 2 marks each.
- Section C : Q. No. 13 and 14 are short answer questions and carry 3 marks each.
- Section D : Q. No. 15 and 16 are long answer questions carrying 5 marks each.
- There is no overall choice. However, internal choices have been provided.
- Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions :

Le-Chatelier's principle allows us to predict the effects of changes in temperature, pressure and concentration on a system at equilibrium. It states that if a system at equilibrium experiences a change, the system will shift its equilibrium to try to compensate for the change.

Increasing the volume has the same effect as decreasing the pressure and vice-versa. When we increase the pressure, the system will shift so the least number of gas molecules are formed because the more gas molecules there are, the more collisions there are. These collisions and the presence of gas molecules are what cause the pressure to increase. Likewise, when we decrease the pressure, the system will shift so the higher number of gas molecules are produced.

A reaction is endothermic if it takes heat from its surroundings. On the other hand, a reaction is exothermic if it gives heat to the surroundings. If we increase the temperature, then the endothermic reaction will be favoured because that will take in some of the excess heat. If we decrease the temperature, the exothermic reaction will be favoured because it will produce the heat that was lost. A catalyst increases the speed in which a reaction takes place, however it never has any effect on the equilibrium.

The following questions are multiple choice questions. Choose the most appropriate answer :

- The equilibrium constant of a reaction is 300. If the volume of a reaction flask is tripled, the equilibrium constant will be
(a) 300 (b) 100 (c) 600 (d) 150
- In $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ reversible reaction, increase in pressure will favour
(a) reversible reaction (b) forward direction
(c) irreversible reaction (d) backward direction.
- Which of the following information can be obtained on the basis of Le-Chatelier's principle?
(a) Equilibrium constant of a chemical reaction (b) Dissociation constant of a weak acid
(c) Entropy change in a reaction (d) All of these

(iv) Of the following which change will shift the reaction towards the product?



- (a) Increase in concentration of I (b) Decrease in concentration of I₂
 (c) Increase in temperature (d) Increase in total pressure

OR

The role of a catalyst in a reversible reaction is

- (a) to increase the rate of forward reaction (b) to alter the equilibrium constant of the reaction
 (c) to decrease the rate of backward reaction (d) to allow the equilibrium to be achieved quickly.

Following questions (Q. No. 2-6) are multiple choice questions carrying 1 mark each :

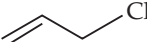
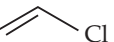
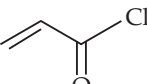
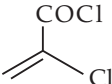
2. Two vessels of volumes 16.4 L and 5 L contain two ideal gases of molecular existence at the respective temperature of 27°C and 227°C and exert 1.5 and 4.1 atmospheres respectively. The ratio of the number of molecules of the former to that of the latter is
 (a) 2 (b) 1 (c) $\frac{1}{2}$ (d) $\frac{1}{3}$
3. For the properties mentioned, the correct trend for the different species is in
 (a) strength as Lewis acid – $\text{BCl}_3 > \text{AlCl}_3 > \text{GaCl}_3$ (b) inert pair effect – $\text{Al} > \text{Ga} > \text{In}$
 (c) oxidising property – $\text{Al}^{3+} > \text{In}^{3+} > \text{Tl}^{3+}$ (d) first ionization enthalpy – $\text{B} > \text{Al} > \text{Tl}$

OR

The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence

- (a) $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$ (b) $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
 (c) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$ (d) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$.

4. Which of the following compounds will not undergo Friedel-Crafts reaction with benzene?

- (a)  (b)  (c)  (d) 

5. What should be the correct order of lattice energy values of the following alkali halides?

LiCl, KI, KCl and NaCl

- (a) $\text{KI} > \text{KCl} > \text{NaCl} < \text{LiCl}$ (b) $\text{NaCl} > \text{KCl} > \text{LiCl} > \text{KI}$
 (c) $\text{LiCl} > \text{KCl} > \text{KI} > \text{NaCl}$ (d) $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{KI}$

OR

The correct order of first ionisation enthalpies of the following elements is

- (a) $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ra} > \text{Ba}$ (b) $\text{Ra} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{Be}$
 (c) $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Ra}$ (d) $\text{Ra} > \text{Sr} > \text{Ba} > \text{Mg} > \text{Ca} > \text{Be}$

6. 2-Hexyne gives *trans*-2-hexene on treatment with which of the following reagents?

- (i) Li/NH_3 (ii) Pd/BaSO_4 (iii) LiAlH_4 (iv) Pt/H_2
 (a) Only (ii) (b) Both (ii) and (iii)
 (c) Both (i) and (iii) (d) All of these

In the following questions (Q. No. 7 and 8), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

7. **Assertion** : Boron differs from aluminium and other members of group 13 in a number of properties.
Reason : Boron shows anomalous behaviour.

OR

Assertion : The relative strength of the various boron trihalides increase in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$.

Reason : The trihalides of boron are planar molecules in which the central B atom is sp^3 hybridized.

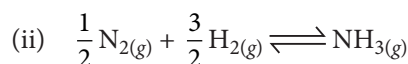
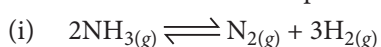
8. **Assertion :** Propene reacts with HBr to give isopropyl bromide.

Reason : Addition of hydrogen halide to alkenes follows Markownikoff's rule.

SECTION - B

The following questions Q. No. 9-12 are short answer type and carry 2 marks each.

9. For the reaction $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$, at 400 K, $K_p = 41$. Find the value of K_p for each of the following reactions at the same temperature



10. Discuss the trend of ionisation energy of the elements of group 14.

11. What happens when

(i) sodium metal is dropped in water?

(ii) sodium metal is heated in free supply of air?

OR

On combustion Li forms Li_2O ; sodium gives the peroxide, Na_2O_2 ; and potassium, rubidium and caesium give superoxides, MO_2 . Why Li does not form a peroxide?

12. $\text{F}_3\text{C}-\text{CH}=\text{CH}_2$ gives anti-Markownikoff product. Why?

OR

An alkene 'A' contains three C—C, eight C—H σ bonds and one C—C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.

SECTION - C

Q. No. 13 and 14 are short answer type II carrying 3 marks each :

13. (a) 22 g of dry ice is placed in an evacuated bottle of 1 litre capacity and tightly stoppered. What would be the pressure inside the bottle, when it is heated to 37°C ?

(b) 3.12 g of sulphur is vapourised at 427°C and 760 mm pressure, when the vapours occupy a volume of 700 mL. Find the molecular formula of sulphur. (atomic mass of sulphur = 32).

OR

An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molar mass of the gas.

14. (a) Which hydrocarbon can't be prepared by Kolbe's electrolytic method?



(b) What happens when sodium acetate is heated with sodalime?

(c) An alkene (C_5H_{10}) on ozonolysis yielded two products. Both of them gave iodoform test, but only one responds to Tollen's test. Identify the hydrocarbon.

SECTION - D

Q. No. 15 and 16 are long answer type carrying 5 marks each.

15. (a) A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water at 290 K. Calculate final temperature of water. Specific heat of water = $4.184 \text{ J g}^{-1} \text{ K}^{-1}$

(b) Given the following standard enthalpies of reactions:

- (i) Enthalpy of formation of water = $-285.8 \text{ kJ mol}^{-1}$
- (ii) Enthalpy of combustion of acetylene = $-1299.6 \text{ kJ mol}^{-1}$
- (iii) Enthalpy of combustion of ethylene = $-1410.8 \text{ kJ mol}^{-1}$

Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume (25°C).

OR

(a) For a reaction, $M_2O_{(s)} \longrightarrow 2M_{(s)} + \frac{1}{2}O_{2(g)}$, $\Delta H = 30 \text{ kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm. Calculate upto which temperature the reaction would not be spontaneous.

(b) Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298 K.

Given :

- (i) Lattice energy of NaCl = 778 kJ mol^{-1}
- (ii) Hydration energy of NaCl = $-774.3 \text{ kJ mol}^{-1}$
- (iii) Entropy change at 298 K = 43 J mol^{-1}

16. (a) (i) What are the products formed when alkali metal oxide (M_2O), peroxide (M_2O_2) and superoxide (MO_2) hydrolysed by water?

(ii) List two properties showing similarity between lithium and magnesium.

(b) (i) Mg form Mg^{2+} , but Na^{2+} does not exist. Explain.

(ii) Write balanced equations for the reactions between :

(I) Na_2O_2 and H_2O

(II) KO_2 and H_2O .

OR

(a) Halides of Be dissolve in organic solvents while those of Ba do not. Why is it so?

(b) Why are compounds of beryllium much more covalent than other group 2 elements?

(c) What is milk of magnesia? Give its one use.

(d) Solubility of $MgCl_2$ is greater than that of MgF_2 . Why?

(e) Why is $BeCO_3$ stored in carbon dioxide atmosphere?

ANSWERS

1. (i)(a) : Equilibrium constant will remain unaffected.

(ii) (b) : According to Le-Chatelier Principle increase in pressure will favour the direction where there are lesser no. of species.

(iii) (a) : According to Le-Chatelier's principle, if a system at equilibrium is subjected to change of concentrations, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect. So the equilibrium constant of reaction can be calculated.

(iv) (c) : The given reaction is endothermic, so on increasing the temperature, it will shift in forward direction.

OR

(d)

$$2. (a) : \frac{P_1V_1}{P_2V_2} = \frac{n_1T_1}{n_2T_2} \Rightarrow \frac{n_1}{n_2} = \frac{P_1V_1T_2}{P_2V_2T_1}$$

$$\frac{n_1}{n_2} = \frac{1.5 \times 16.4 \times 500}{4.1 \times 5 \times 300} = \frac{2}{1}$$

3. (a) : Lewis acid strength decreases down the group.

OR

(d) : Due to the inert pair effect (the reluctance of ns^2 electrons of outermost shell to participate in bonding) the stability of M^{2+} ions (of group IV elements) increases as we go down the group.

4. (b) : Formation of more stable carbocation is the condition for Friedel-Crafts reaction which is not possible in case of $CH_2 = CHCl$.

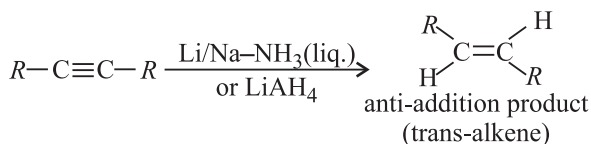
5. (d) : Order of lattice energy :

$LiCl > NaCl > KCl > KI$

OR

(a) : On moving down the group, ionisation enthalpy decreases because of the increase in atomic size due to addition of new shells and screening effect of the electrons in the inner shells which outweigh the effect of increased nuclear charge.

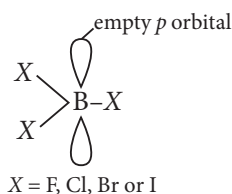
6. (c) : For *trans* products we should take Na or Li metal in NH_3 or EtNH_2 at low temperature or LiAlH_4 as reducing agent (anti-addition).



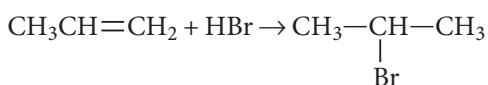
7. (b) : This is due to small atomic size, high electronegativity, high ionization energy and absence of *d*-orbital in B.

OR

(c) : The central boron atom in boron trihalides is sp^2 hybridized. It has an unhybridized *p* orbital which is empty and is perpendicular to the plane of the three σ B-X bonds. Since B atom has only 6 electrons in its outer shell, so all boron trihalides are electron deficient compounds. The structure of boron trihalides is represented below.



8. (a) : Addition of unsymmetrical addendum on unsymmetrical alkene takes place according to Markownikoff's rule, *i.e.*, negative part of addendum goes on less hydrogenated carbon atom.

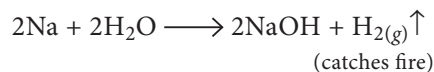


9. (i) $K'_p = \frac{1}{K_p} = \frac{1}{41}$

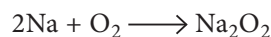
(ii) $K'_p = \sqrt{K_p} = \sqrt{41}$

10. Ionization energy of carbon is quite high due to small size of the carbon atom. It then decreases to silicon due to the increase in size of silicon atom. Then there is a decrease in ionization energy from Si to Sn. This is because the '*d*' electrons which are present in the inner configuration of Ge, and Sn shield the nuclear charge less effectively than is done by *s*- and *p*-electrons. The outer electrons are held strongly by the nucleus and there is only a small decrease in ionization energy as we move from Si to Sn. In the case of Pb, there is only a marginal increase of atomic radius as we move from Sn to Pb and also there are *f*-electrons in the inner configuration which shield the nuclear charge less effectively than the *d*-electrons. So, the ionization energy instead of decreasing, shows a marginal increase.

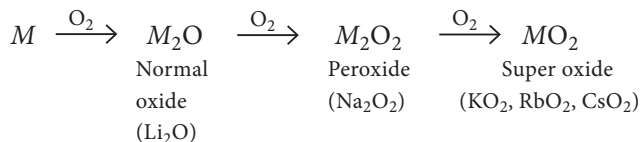
11. (i) Sodium metal catches fire and hydrogen gas is evolved.



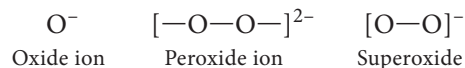
(ii) Sodium peroxide is formed.



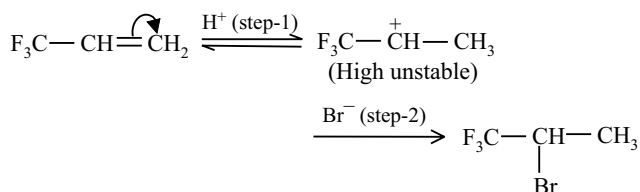
OR



The normal oxides contain O^{2-} ion, the peroxides contain O_2^{2-} ion and superoxides contain O_2^- ion. The peroxides and superoxides become more stable with increase in atomic number of the alkali metal. The formation and stability of these oxides can be explained on the basis of lattice energy effects. Li^+ ion being a small ion has a strong positive field around it and can stabilise only a small anion, O^{2-} whereas Na^+ being a large cation can stabilise a large ion and so on.



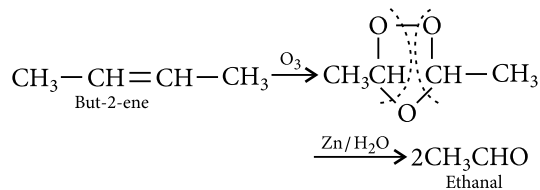
12. If the given compound follows Markownikoff's rule,



The carbocation produced in step-1 is highly unstable due to strong electron withdrawing group, hence it does not follow Markownikoff's rule.

OR

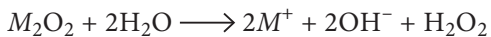
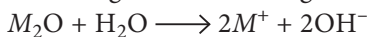
Alkene A contains 3C-C, 8C-H and one C=C bonds. An aldehyde containing one -CHO group and having molar mass of 44 amu has to be CH_3CHO and since two moles of CH_3CHO are obtained by ozonolysis of alkene A, the alkene has to be joined by two $\text{CH}_3\text{CH}-$ groups by a double bond. It has to be $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$, *i.e.*, but-2-ene. But-2-ene contains 3C-C σ bonds, 8C-H σ bonds and one C=C bond.



$$\begin{aligned}\therefore \Delta G_{\text{dissolution}} &= \Delta H - T\Delta S \\ &= 3700 - 298 \times 43 = -9114 \text{ J}\end{aligned}$$

$$\text{or } \Delta G_{\text{dissolution}} = -9.114 \text{ kJ.}$$

16. (a) (i) Alkali metal oxide, peroxide and superoxide are easily hydrolysed by water to form the hydroxides according to the following reactions:

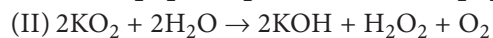
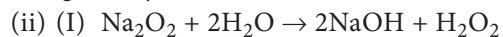


(ii) Both lithium and magnesium are harder and lighter than other elements in respective groups.

The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(b) (i) Mg atom after losing one electron does not attain noble gas configuration whereas Na metal after the loss of one electron attains a noble gas configuration of neon. Therefore, the removal of second electron is

energetically not favorable. Hence, Na^{2+} does not exist.



OR

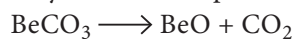
(a) This is because halides of Be are covalent while those of Ba are ionic.

(b) The extremely small size and high charge of Be^{2+} makes it strongly polarizing so that Be (II) compounds are almost covalent in nature.

(c) A suspension of magnesium hydroxide in water is called milk of magnesia. It is used as an antacid to neutralize excess of acid in the stomach.

(d) Because the fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(e) Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2 .



PRACTICE PAPER **2***

Time allowed : 2 hours

Maximum marks : 35

General Instructions : Read the following instructions carefully.

- There are 16 questions in this question paper. All questions are compulsory.
- Section A : Q. No. 1 to 8 are objective type questions. Q. No. 1 is passage based question carrying 4 marks while Q. No. 2 to 8 carry 1 mark each.
- Section B : Q. No. 9 to 12 are short answer questions and carry 2 marks each.
- Section C : Q. No. 13 and 14 are short answer questions and carry 3 marks each.
- Section D : Q. No. 15 and 16 are long answer questions carrying 5 marks each.
- There is no overall choice. However, internal choices have been provided.
- Use of calculators and log tables is not permitted.

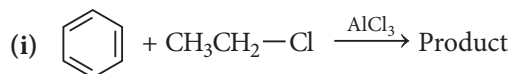
SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions :

In the presence of Lewis acid catalysts such as aluminium chloride or ferric chloride (FeCl_3), alkyl halides were found to alkylate benzene to give alkyl benzenes. The reaction is called Friedel-Crafts alkylation. It involves

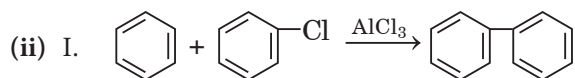
- formation of carbocation.
 - attack of electrophile (carbocation) over ring to form arenium ion.
 - abstraction of hydrogen.
- When $R - X$ is a primary halide, a simple carbocation probably doesn't form. Instead, the aluminium chloride forms a complex with the alkyl halide, and this complex acts as electrophile.
 - FC alkylation is not restricted to the use of alkyl halides and aluminium chloride. Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well.
 - Polyalkylation and rearrangement of carbocation are necessary evils of FC alkylation.
 - Highly activating and highly deactivating groups, usually don't give good yield.

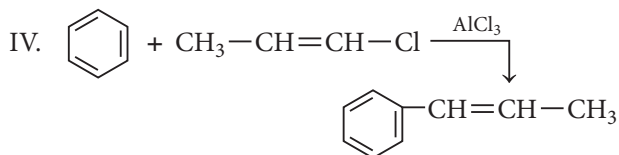
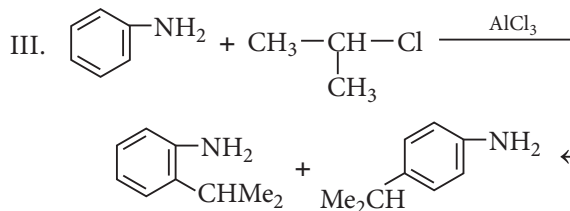
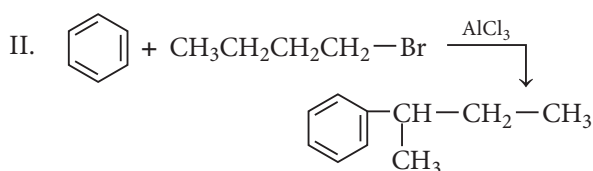
The following questions are multiple choice questions. Choose the most appropriate answer.



Which of the following is actual electrophile involved in the reaction ?

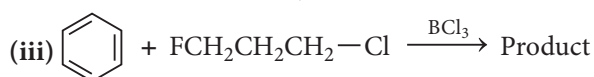
- | | |
|---|---|
| (a) $\text{CH}_3\text{CH}_2^\oplus$ | (b) $\text{CH}_3-\text{CH}_2-\overset{\delta+}{\text{Cl}}\cdots\overset{\delta-}{\text{AlCl}_3}$ |
| (c) $\text{CH}_3-\overset{\delta+}{\text{CH}_2}\cdots\overset{\delta+}{\text{Cl}}\cdots\text{AlCl}_3$ | (d) $\text{CH}_3-\overset{\delta+}{\text{CH}_2}\cdots\overset{\delta-}{\text{Cl}}\cdots\text{AlCl}_3$ |





Which of the above mentioned Friedel-Crafts reactions is/are not feasible?

- (a) II and IV only (b) II and III only
(c) I, II and IV only (d) I, III and IV only



The main product is

- (a)  (b) 
(c)  (d) 



Friedel-Crafts reaction proceeds most efficiently when G is

- (a) $-\text{NHR}$ (b) $-\text{CH}_3$ (c) $-\text{CHO}$ (d) $-\text{NO}_2$

OR

Among the following statements on the nitration of aromatic compounds, the false one is

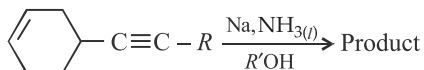
- (a) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene
(b) the rate of nitration of toluene is greater than that of benzene
(c) the rate of nitration of benzene is greater than that of hexadeuterobenzene
(d) nitration is an electrophilic substitution reaction.

Following questions (Q. No. 2-6) are multiple choice questions carrying 1 mark each :

2. When Friedel-Crafts alkylation of benzene is carried out with *n*-propyl bromide, the major product is
(a) *n*-propyl benzene (b) isopropyl benzene
(c) 2-ethyl benzene (d) none of the above.

OR

The main product of the reaction is



- (a)  (b) 
(c)  (d) 

3. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is
 (a) London force (b) hydrogen bond
 (c) ion - ion interaction (d) ion-dipole interaction.
4. Both lithium and magnesium display several similar properties due to the diagonal relationship, however, the one which is incorrect, is
 (a) both form nitrides
 (b) nitrates of both Li and Mg yield NO_2 and O_2 on heating
 (c) both form basic carbonates
 (d) both form soluble bicarbonates.

OR

Among LiCl, RbCl, BeCl_2 , MgCl_2 the compounds with greatest and least ionic character respectively are

- (a) LiCl and RbCl (b) RbCl and BeCl_2
 (c) RbCl and MgCl_2 (d) MgCl_2 and BeCl_2
5. An organic compound with molecular formula C_6H_{12} upon ozonolysis gave only acetone as the product. The compound is
 (a) 2,3-dimethyl-1-butene (b) 3-hexene
 (c) 2-hexene (d) 2,3-dimethyl-2-butene
6. A reaction is spontaneous at high temperatures if
 (a) ΔH and ΔS both are negative (b) ΔH and ΔS both are positive
 (c) ΔH is positive and ΔS is negative (d) none of these.

In the following questions (Q. No. 7 and 8), a statement of assertion followed by a statement of reason is given.

Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.
7. **Assertion** : K_p can be less than, greater than or equal to K_c .
Reason : Relation between K_p and K_c depends on the change in number of moles of gaseous reactants and products (Δn).
8. **Assertion** : Although aluminium is above hydrogen in electrochemical series, it is stable in air and water.
Reason : The thin protective layer of oxide (Al_2O_3) on aluminium is stable in air and water.

OR

Assertion : Carbon atom is tetravalent though it has two unpaired electrons.

Reason : Carbon has unique ability to form $p\pi - p\pi$ multiple bonds like $\text{C} = \text{C}$, $\text{C} \equiv \text{C}$.

SECTION - B

The following questions, Q. No. 9 - 12 are short answer type and carry 2 marks each.

9. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 litre to 5 litre. Calculate q , W and ΔU for this process. ($R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, atomic weight of Argon = 40)

OR

The molar heat of formation of $\text{NH}_4\text{NO}_3(s)$ is -367.54 kJ and those of $\text{N}_2\text{O}(g)$ and $\text{H}_2\text{O}(l)$ are $+81.46 \text{ kJ}$ and -285.78 kJ respectively at 25°C and 1.0 atmospheric pressure. Calculate ΔH and ΔU for the reaction,



10. BCl_3 exists as monomer whereas AlCl_3 is dimerised through chlorine bridging. Give reason. Also explain the structure of the dimer of AlCl_3 .

OR

Discuss the Lewis acid nature of boron halides.

11. An iron cylinder contains helium at a pressure of 250 kPa at 300 K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not (melting point of the cylinder = 1800 K).
12. (i) Name the chief factors responsible for the anomalous behaviour of lithium.
 (ii) Complete the following reactions :
 (a) $4\text{LiNO}_3 \xrightarrow{\Delta}$ (b) $2\text{NaNO}_3 \xrightarrow{\Delta}$

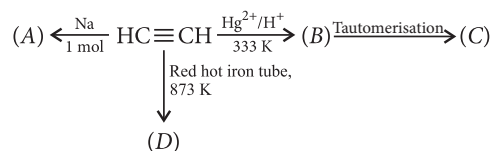
SECTION - C

Q. No. 13 and 14 are short answer type II carrying 3 marks each.

13. At 300 K, the standard enthalpies of formation of $\text{C}_6\text{H}_5\text{COOH}_{(s)}$, $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(l)}$ are -408 , -393 and -286 kJ mol^{-1} , respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
14. (a) Benzene is highly unsaturated compound but behaves like a saturated compound. Why?
 (b) Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?

OR

- (a) Identify 'A', 'B', 'C' and 'D' in the following sequence of reactions :



- (b) Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

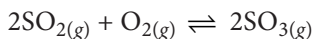
SECTION - D

Q. No. 15 and 16 are long answer type carrying 5 marks each.

15. (a) Classify the following as acid or base and also mention the concept on the basis of which these are so.
 (i) $\text{HCl}_{(aq)}$ (ii) $\text{Na}_2\text{CO}_{3(aq)}$ (iii) H_2O (iv) NH_4^+
 (b) Predict whether a precipitate will be formed or not on mixing equal volumes of 2×10^{-4} M BaCl_2 solution and 2×10^{-5} M Na_2SO_4 solution if solubility product of BaSO_4 is 1×10^{-10} .

OR

- (a) For the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas phase :



$$K_p = 40.5 \text{ atm}^{-1} \text{ at } 900 \text{ K and } \Delta_r H = -198 \text{ kJ mol}^{-1}$$

- (i) Write the expression for the equilibrium constant for the reaction.
 (ii) At room temperature (≈ 300 K) will K_p be greater than, less than or equal to K_p at 900 K?
 (iii) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant. What happens?
 (iv) What is the effect of adding 1 mole of $\text{He}_{(g)}$ to a flask containing SO_2 , O_2 and SO_3 at equilibrium at constant volume?
 (b) A vessel at 1000 K contains carbon dioxide at a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K , if the total pressure at equilibrium is 0.8 atm.




16. (a) Explain the difference in properties of diamond and graphite on the basis of their structures.
 (b) Rationalise the given statements and give chemical reactions :
 (i) Lead (II) chloride reacts with Cl_2 to give PbCl_4 .
 (ii) Lead (IV) chloride is highly unstable towards heat.
 (iii) Lead is known not to form an iodide, PbI_4 .

OR

- (a) How can the fullerenes be prepared?
 (b) Account for the following : PbCl_4 is a powerful oxidising agent.
 (c) Account for the following :
 (i) PbCl_2 is more stable than PbCl_4 .
 (ii) $[\text{SiF}_6]^{2-}$ is known whereas $[\text{SiCl}_6]^{2-}$ not.
 (d) Why carbon shows anomalous behaviour?

ANSWERS

1. (i) (d) : Complex electrophile

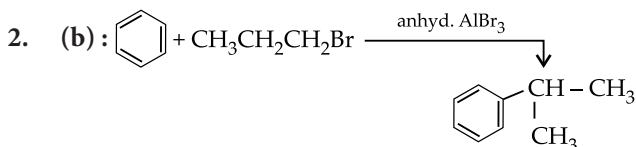
(ii) (d) :  and $\text{CH}_3 - \text{CH} = \text{CH}^+$ are not possible.,  coordinates with AlCl_3 , first giving, , ring becomes deactivated, thus alkylation is not possible.

(iii) (a) : $R - \text{F}$ is more reactive than $R - \text{Cl}$.

(iv) (b) : Highly activating and deactivating groups are not favourable for Friedel-Craft reaction.

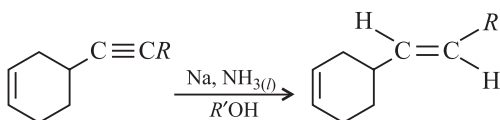
OR

(a) : Hexadeuterobenzene, C_6D_6 is less reactive than benzene C_6H_6 due to isotopic effect.



OR

(d) : An isolated olefinic bond is not affected by the Birch reagent except in an end methylene ($=\text{CH}_2$) or in strained system like cyclobutenes or cyclopropenes. Acetylenes readily give olefinic compounds with alkali metal in liq. NH_3 and gives *trans* product.



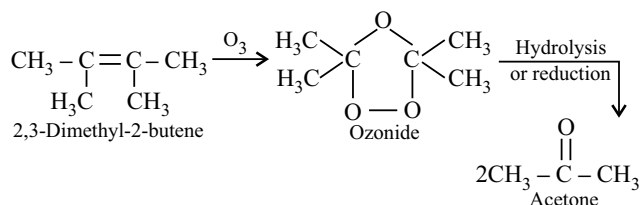
3. (b) : Dipole-dipole interaction (hydrogen bonding) is proportional to $1/r^3$, where r is the distance between the polar molecules.

4. (c) : Due to diagonal relationship, both Li and Mg display some similar properties, but in the case of carbonates, Mg can form basic carbonates such as $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. In contrast, Li only form typical carbonate Li_2CO_3 as other alkali metals. It does not form any basic carbonate having both carbonate and hydroxide ions.

OR

(b) : The larger the size of cation, the greater is the ease with which the valence electrons can be removed from it and hence more will be the ionic character.

5. (d) : The reaction sequence is as follows :



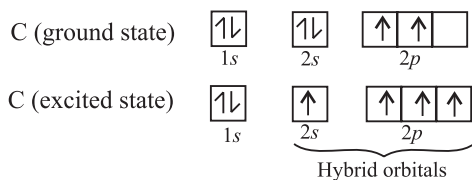
6. (b) : A reaction is spontaneous at high temperature, if ΔH and ΔS are positive and it is an entropy driven process.

7. (a) : $K_p = K_c (RT)^{\Delta n}$

8. (a) : Due to Al_2O_3 layer, the metal is protected from further attack of air and water.

OR

(b) : Carbon is tetravalent due to empty p -orbitals which hybridise in excited state to give sp^3 hybridisation with one electron each in $2s$ and $2p$ -orbitals showing tetravalency.



$$9. \quad W_{\text{iso, rev}} = -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{5}{10}$$

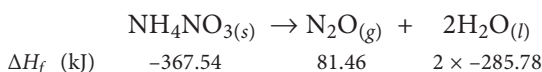
$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log \frac{5}{10} = 103.9 \text{ cal}$$

For isothermal process $\Delta U = 0$

From 1st law of thermodynamics, $\Delta U = q + W$

$$\therefore q = -W = -103.9 \text{ cal}$$

OR



$$\Delta H = \Delta H_f(\text{Products}) - \Delta H_f(\text{Reactants})$$

$$= [2 \times (-285.78) + 81.46] - (-367.54)$$

$$= -122.56 \text{ kJ} = -122.56 \times 10^3 \text{ J}$$

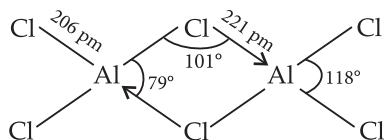
$$\Delta n_g = n_p - n_r = 1 - 0 = 1$$

$$\Delta H = \Delta U + \Delta n_g RT \Rightarrow \Delta U = \Delta H - \Delta n_g RT$$

$$\Delta U = -122.56 \times 10^3 - 1 \times 8.314 \times 298 = -125.04 \times 10^3 \text{ J}$$

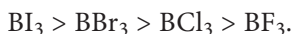
$$= -125.04 \text{ kJ}$$

10. Due to absence of *d*-orbitals in boron, BCl_3 exists as an electron deficient monomer and achieves stability through accepting electrons from a base like NH_3 . BCl_3 cannot exist as dimer due to small size of B which cannot accommodate four bigger size Cl-atoms around it. AlCl_3 achieves stability by forming a dimer as shown :

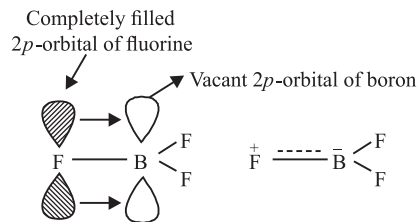


OR

The Lewis acid character of boron trihalides follows the order :



The above order is just the reverse of the expected order on the basis of relative electronegativities of the halogens. This can be explained on the basis of the tendency of the halogen atom to back-donate its electrons to the boron atoms resulting in the formation of an additional $p\pi-p\pi$ bond. This type of bond formation is known as dative or back bonding.



Formation of back bonding between boron and fluorine in BF_3 molecule.

As a result of back donation of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and therefore, the Lewis acid character of BF_3 decreases.

The tendency to form $p\pi-p\pi$ bond is maximum in the case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3 .

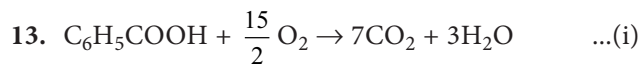
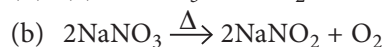
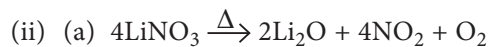
11. According to Gay-Lussac's law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{250}{300} = \frac{P_2}{1800} \Rightarrow P_2 = 1500 \text{ kPa}$$

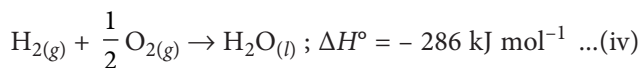
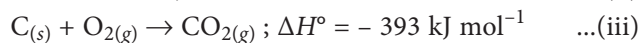
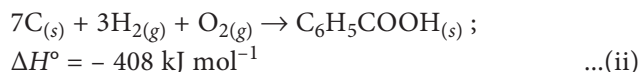
As the cylinder can withstand a pressure of $10^6 \text{ Pa} = 10^3 \text{ kPa} = 1000 \text{ kPa}$, hence, it will blow up.

12. (i) Chief factors responsible for the anomalous behaviour of lithium are :

- its very small size
- high electronegativity
- high ionization enthalpy and
- absence of vacant *d*-atomic orbital in the valence shell.



Given,



In order to obtain eqn (i) operate $7 \times (\text{iii}) + 3 \times (\text{iv}) - (\text{ii})$

$$\Delta H^\circ = [-393 \times 7 - 286 \times 3 + 408]$$

$$\therefore \Delta H^\circ = -3201 \text{ kJ mol}^{-1}$$

$$\text{Also } \Delta H_p = \Delta H_v + \Delta nRT$$

$$\therefore -3201 = \Delta H_v + (-1/2) \times 8.314 \times 10^{-3} \times 300$$

$$(\because \Delta n = -1/2 \text{ and } R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$$

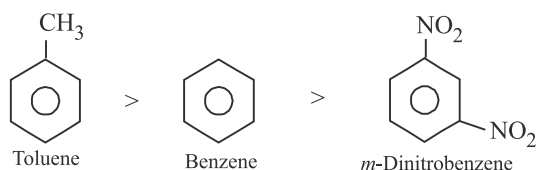
$$\therefore \Delta H_v = -3201 + 1.2471 = -3199.7529 \text{ kJ mol}^{-1}$$

14. (a) The benzene molecule is unsaturated but the double bonds present inside the benzene ring are delocalized due to bond resonance (π -structure). This

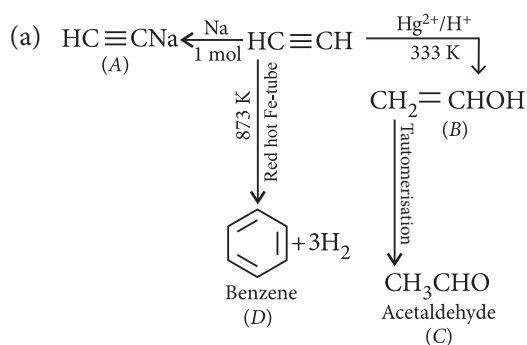
makes the double bonds of benzene much less reactive than more discrete double bonds. This makes it behave more like a saturated compound.

(b) During nitration, the electrophile NO_2^+ attacks the benzene ring. Nitration will be easier if the benzene ring shows increased electron density. This happens when electron releasing groups such as $-R$, $-\text{NH}_2$, $-\text{NHCOCH}_3$, $-\text{OH}$, $-\text{OMe}$ etc. are attached to the ring whereas, the attachment of electron withdrawing groups such as $-\text{NO}_2$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$ reduces the electron availability for NO_2^+ and nitration becomes difficult.

Therefore, relative ease of nitration of given molecules may be arranged as :

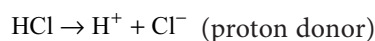


OR

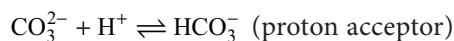
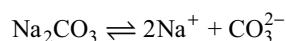


(b) Due to the presence of an electron cloud containing 6 π -electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophiles (electron-deficient reagents) towards it and repels nucleophiles (electron-rich reagents). As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty.

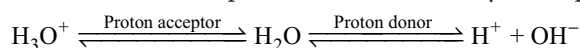
15. (a) (i) $\text{HCl}_{(aq)}$: Acid, according to Arrhenius concept and Bronsted-Lowry concept,



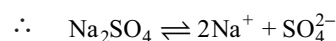
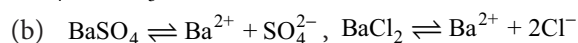
(ii) $\text{Na}_2\text{CO}_{3(aq)}$: Base, according to Bronsted-Lowry concept,



(iii) H_2O : Both acid and base *i.e.*, amphoteric according to Arrhenius concept and Bronsted-Lowry concept



(iv) NH_4^+ : Acid, according to Arrhenius, Bronsted-Lowry concept.



Since equal volumes of BaCl_2 and Na_2SO_4 are mixed, concentration of Ba^{2+} and SO_4^{2-} after mixing would be

$$[\text{Ba}^{2+}] = \frac{[\text{BaCl}_2]}{2} = \frac{2 \times 10^{-4}}{2} = 10^{-4} \text{ M}$$

$$[\text{SO}_4^{2-}] = \frac{[\text{Na}_2\text{SO}_4]}{2} = \frac{2 \times 10^{-5}}{2} = 10^{-5} \text{ M}$$

Ionic product of BaSO_4

$$= [\text{Ba}^{2+}][\text{SO}_4^{2-}] = [10^{-4}][10^{-5}] = 10^{-9} \text{ M}$$

Ionic product (10^{-9} M) > K_{sp} (1×10^{-10})

Hence, precipitation will take place.

OR

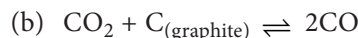
(a) (i) The equilibrium constant for this reaction is written in terms of the partial pressure of the reactants and products. So,

$$K_p = \frac{p_{\text{SO}_3(\text{g})}^2}{p_{\text{SO}_2(\text{g})}^2 \times p_{\text{O}_2(\text{g})}$$

(ii) This reaction is exothermic. So, its equilibrium constant should increase with the lowering of temperature ($d \ln K/dT = \Delta_r H^\circ/RT^2$). Therefore, the value of K_p at 300 K will be greater than the value at 900 K.

(iii) When the volume of the vessel is reduced, the volume of the reaction mixture will decrease. As a result, pressure of the gaseous mixture will increase. According to the Le Chatelier's principle, the system will move in a direction to undo the effect of the pressure increase. The system therefore will move in a direction so as to decrease the number of moles of the gaseous substances in the system. The number of moles decrease in going from reactants to the product side. Therefore, a decrease in the volume of the reacting system will shift the equilibrium to the right. That is, more $\text{SO}_3(\text{g})$ will be formed from the reactants.

(iv) Addition of helium to the reaction mixture at equilibrium under constant volume has no effect on the equilibrium.



Let the decrease in pressure of CO_2 after reaction = p atm

Then, increase in pressure due to CO after reaction = $2p$ atm

Final total pressure = $(0.5 - p) + 2p = 0.8 \text{ atm}$

$\Rightarrow p = 0.3 \text{ atm}$

Thus after reaction, $p_{\text{CO}_2} = 0.5 - 0.3 = 0.2 \text{ atm}$

$p_{\text{CO}} = 2p = 2 \times 0.3 = 0.6 \text{ atm}$

$\Rightarrow K = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$

16. (a)

Criterion	Diamond	Graphite
Hybridisation	sp^3	sp^2
Structure of C	Tetrahedral carbon which gives rise to a 3-dimensional structure.	Planar trigonal which gives rise to a 2-dimensional sheet like structure of carbon.
C — C	154 pm	141.5 pm
Hardness	Due to 3-D structure, diamond is the hardest natural element on the earth.	It is made up of 2-D sheets of carbon which slip over each other. This gives graphite a slippery surface.
Electrical Conductivity	Diamond is an insulator.	Graphite is a good conductor of electricity due to presence of delocalised π -electrons.

(b) (i) $\text{PbCl}_2 + \text{Cl}_2 \nrightarrow \text{PbCl}_4$

Lead is more stable in +2 oxidation state than in +4 state due to inert pair effect. Thus, the reaction is not feasible.

(ii) $\text{PbCl}_4 \xrightarrow{\Delta} \text{PbCl}_2 + \text{Cl}_2$

Pb is more stable in its +2 oxidation state due to inert pair effect. As a result, when subjected to heat, Pb (IV) goes to Pb (II) state.

(iii) $\text{Pb} + 2\text{I}_2 \nrightarrow \text{PbI}_4$

I^- is a good reducing agent and therefore, reduces Pb (IV) to Pb (II) easily. That is why, PbI_4 does not exist.

OR

(a) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.

(b) In PbCl_4 , the oxidation state of Pb is +4. Due to inert pair effect, Pb^{2+} is more stable than Pb^{4+} . Hence, Pb^{4+} is easily reduced to Pb^{2+} , thereby acting as a good oxidising agent.

(c) (i) +2 oxidation state of Pb is more stable due to inert pair effect. Thus, lead (IV) chloride readily decomposes to lead(II) chloride.

$\text{PbCl}_4 \xrightarrow{\Delta} \text{PbCl}_2 + \text{Cl}_2$

(ii) Due to small size of F, six fluorine atoms can be accommodated around silicon but six chlorine atoms cannot due to large size of Cl-atoms.

(d) Due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d -orbitals.



PRACTICE PAPER

3*

Time allowed : 2 hours

Maximum marks : 35

General Instructions : Read the following instructions carefully.

- (a) There are 16 questions in this question paper. All questions are compulsory.
- (b) Section A : Q. No. 1 to 8 are objective type questions. Q. No. 1 is passage based question carrying 4 marks while Q. No. 2 to 8 carry 1 mark each.
- (c) Section B : Q. No. 9 to 12 are short answer questions and carry 2 marks each.
- (d) Section C : Q. No. 13 and 14 are short answer questions and carry 3 marks each.
- (e) Section D : Q. No. 15 and 16 are long answer questions carrying 5 marks each.
- (f) There is no overall choice. However, internal choices have been provided.
- (g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions.

The salts of alkali metals are ionic and soluble in water. The solubility of an ionic compound depends on two factors : (i) Lattice energy and (ii) Hydration energy. These two factors oppose each other. If hydration energy is high, the ions will have greater tendency to be hydrated and therefore the solubility will be high. The smaller the cation, the greater is the degree of its hydration. Hydration of ions is an exothermic process. Higher is the energy released if greater is the degree of hydration. Reducing power of alkali metals in solutions is also dependent on the hydration energy beside other factors.

- (i) The radius of which ion (hydrated) is lowest?
(a) $[\text{Li}_{(aq)}]^+$ (b) $[\text{Na}_{(aq)}]^+$ (c) $[\text{K}_{(aq)}]^+$ (d) $[\text{Cs}_{(aq)}]^+$
- (ii) The ion which has maximum value of hydration energy is
(a) Li^+ (b) Na^+ (c) Cs^+ (d) K^+

OR

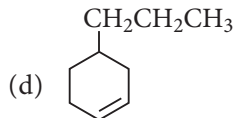
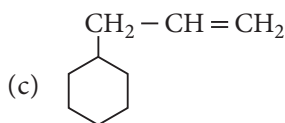
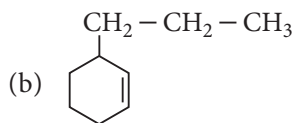
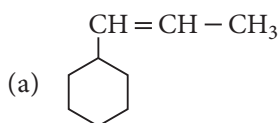
Ionic mobility of Li^+ is less than Na^+ and K^+ ions in solutions because

- (a) ionisation potential of lithium is small (b) charge density of Li^+ is high
 - (c) high hydration tendency of Li^+ (d) Li^+ keeps two electrons.
- (iii) Strongest reducing agent amongst alkali metals in solutions is
(a) Li (b) Na (c) K (d) Cs
 - (iv) Which has least solubility?
(a) CsF (b) LiF (c) NaF (d) KF

Following questions (Q. No. 2 - 6) are multiple choice questions carrying 1 mark each:

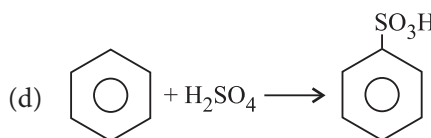
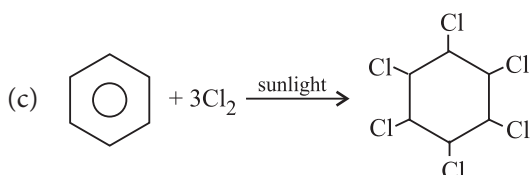
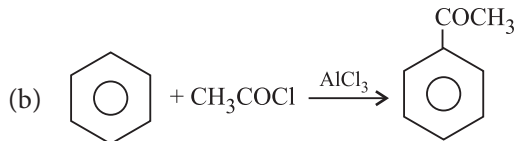
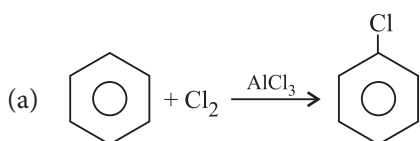
- 2. Which of the following statements is incorrect?
 - (a) $\text{B}(\text{OH})_3$ partially reacts with water to form H_3O^+ and $[\text{B}(\text{OH})_4]^-$, and behaves like a weak acid.
 - (b) $\text{B}(\text{OH})_3$ behaves like a strong monobasic acid in the presence of sugars, and this acid can be titrated against an NaOH solution using phenolphthalein as an indicator.
 - (c) $\text{B}(\text{OH})_3$ does not donate a proton and hence does not form any salt with NaOH.
 - (d) $\text{B}(\text{OH})_3$ reacts with NaOH, forming $\text{Na}[\text{B}(\text{OH})_4]$.

3. An alkene on ozonolysis gives methanal as one of the product. Its structure is

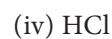
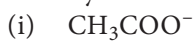


OR

Which of the following reactions is not an example of electrophilic substitution in benzene ring?



4. Classify the following as acid or base according to Bronsted - Lowry concept.



(i)

(ii)

(iii)

(iv)

(a) Bronsted base

Bronsted base

Bronsted base

Bronsted acid

(b) Bronsted acid

Bronsted acid

Bronsted acid

Bronsted base

(c) Bronsted base

Bronsted acid

Bronsted base

Bronsted acid

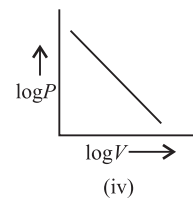
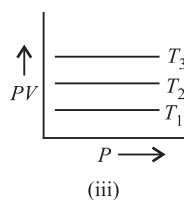
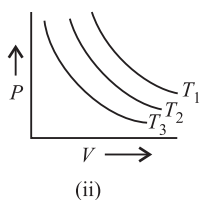
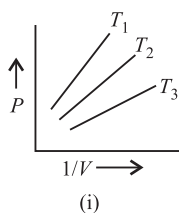
(d) Bronsted acid

Bronsted acid

Bronsted base

Bronsted base

5. Graphs between pressure and volume are plotted at different temperatures. Which of the following isotherms represents Boyle's law as $PV = \text{constant}$?



(a) Only (ii) is correct representation of Boyle's law.

(b) Only (iv) is correct representation of Boyle's law.

(c) All are correct representations of Boyle's law.

(d) None of these representations is correct for Boyle's law.

OR

Molecular mass of a gas is 78. Its density at 98°C and 1 atm will be

(a) 200 g L^{-1}

(b) 2.56 g L^{-1}

(c) 256 g L^{-1}

(d) 78 g L^{-1}

6. The concentration of Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20°C is $1.5 \times 10^{-4} \text{ mol L}^{-1}$. The solubility product of Ag_2CrO_4 at 20°C is

(a) 1.687×10^{-12}

(b) 1.75×10^{-10}

(c) 3.0×10^{-8}

(d) 4.5×10^{-10}

In the following questions (Q. No. 7 and 8) a statement of assertion following by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is the correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not the correct explanation of assertion.
- (c) Assertion is correct statements but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

7. **Assertion** : Lithium resembles magnesium diagonally placed in next group.

Reason : The size of Li^+ and Mg^{2+} are different and their electronegative character is same.

OR

Assertion : Alkali metals are obtained by electrolysis of molten salt and not aqueous solution.

Reason : The discharge potential of H^+ ions is lower than alkali metal cation hence hydrogen is discharged at cathode instead of metal.

8. **Assertion**: Wurtz reaction is not preferred for the preparation of alkanes containing odd number of carbon atoms.

Reason : It is not possible to prepare alkanes with odd number of carbon atoms through Wurtz reaction.

SECTION - B

The following questions, Q. No. 9-12 are short answer type and carry 2 marks each.

9. (a) Diamond is very hard while graphite is soft. Why?
(b) CO_2 is a gas while SiO_2 is a solid. Why?

OR

- (a) Why aluminium chloride forms a dimer?
- (b) Lead pollution is caused by car exhaust. Explain.

10. Account for the formation of both 3-bromo-2,2-dimethylbutane and 2-bromo-2,3-dimethylbutane from the reaction of HBr with 3,3-dimethyl-1-butene.
11. At 3000 K, the equilibrium pressures of CO_2 , CO and O_2 are 0.6, 0.4 and 0.2 atm respectively.
(a) Calculate K_p for the reaction : $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$.
(b) Show how K_p is related to K_c .
(c) Calculate K_c ($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$).
12. If 1 kcal of heat is added to 1.2 L of oxygen in a cylinder at constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE for the process.

OR

Calculate the minimum work which must be done to compress 1/2 mole of oxygen at 300 K from a pressure of 2 atm to a pressure of 200 atm.

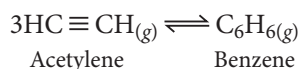
SECTION - C

Q. No. 13 and 14 are short answer type II carrying 3 marks each.

13. An aqueous solution of a gas (X) shows the following reactions:

- (a) It turns red litmus blue
- (b) When added in excess to copper sulphate solution, a deep blue colour is obtained.
- (c) On addition of FeCl_3 solution a brown precipitate, soluble in dilute HNO_3 is obtained. Identify (X) and give reactions.

14. (a) Using the data given below, calculate the value of equilibrium constant for the reaction at 298 K



assuming ideal gas behaviour.

$$\Delta G_f^\circ (\text{HC} \equiv \text{CH}_{(g)}) = 2.09 \times 10^5 \text{ J mol}^{-1}$$

$$\Delta G_f^\circ (\text{C}_6\text{H}_6_{(g)}) = 1.24 \times 10^5 \text{ J mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

- (b) Based on your calculated value, comment whether this process can be recommended as a practical method for making benzene.

OR

For the reaction, $2A_{(g)} + B_{(g)} \longrightarrow 2C_{(g)}$, calculate ΔG° and predict whether the reaction may occur spontaneously, $\Delta E^\circ = -2.50 \text{ kcal}$ and $\Delta S^\circ = -10.5 \text{ cal K}^{-1}$.

SECTION - D

Q. No. 15 and 16 are long answer type carrying 5 marks each.

15. (a) Write IUPAC names of the products obtained by the ozonolysis of the following compounds:
- 3,4-dimethylhept-3-ene
 - 2-ethylbut-1-ene
 - 1-phenylbut-1-ene
- (b) An alkene A on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of A.

OR

- (a) Explain the following:
- Benzene is highly unsaturated but undergoes substitution reactions easily rather than addition.
 - All *m*-directors are deactivating.
 - Halogens, as exceptions, are *o*- and *p*-directors but are deactivating.
 - Most *o*- and *p*-directors are activating.
- (b) Draw Newman and Sawhorse projections of ethane molecule (eclipsed form).
16. (a) When 2 g of a gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atm. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behavior, calculate the ratio of molar masses M_A and M_B .
- (b) A spherical balloon of 21 cm diameter is to be filled up with hydrogen at STP from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.82 lit. of water. Calculate the number of balloons that can be filled up.

OR

- (a) What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1 L vessel at 27°C?
- (b) A 20 g chunk of dry ice is placed in an empty 0.75 litre wine bottle tightly closed. What would be the final pressure in the bottle after all CO_2 has been evaporated and temperature reaches to 25°C?

ANSWERS

1. (i) (d) : Larger the cation, smaller is the degree of its hydration.

(ii) (a) : Smaller the cation, greater is the degree of its hydration.

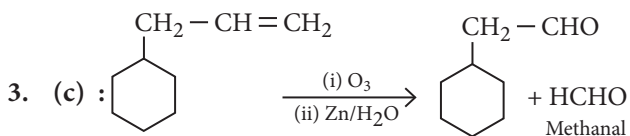
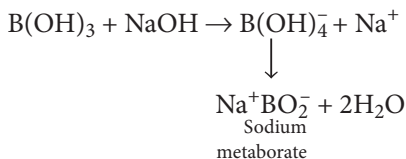
OR

(c)

(iii) (a) : Due to smallest size hydration of Li^+ is maximum hence large amount of energy is released.

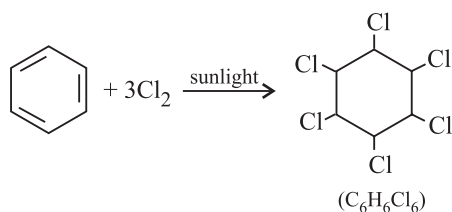
(iv) (b) : LiF has high lattice energy due to small size of Li^+ and F^- .

2. (c) : Boric acid being acidic in nature forms salt with NaOH known as metaborate.



OR

(c) : Cl_2 is added to benzene ring in presence of sunlight to give benzene hexachloride.



4. (c) : Any species which can accept a proton is Bronsted base while which can give a proton is Bronsted acid.

5. (c)

OR

(b) : $P = 1 \text{ atm}$, $T = 273 + 98^\circ\text{C} = 371 \text{ K}$,

$M = 78 \text{ g mol}^{-1}$

$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$PM = dRT \quad \text{or} \quad d = \frac{PM}{RT} = \frac{1 \times 78}{0.0821 \times 371} = 2.56 \text{ g L}^{-1}$$

6. (a) : $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$
 $\text{Ag}^+ = 1.5 \times 10^{-4} \text{ M}$

$$\text{CrO}_4^{2-} = 0.75 \times 10^{-4} \text{ M} \left(\frac{1}{2} \text{ of } \text{Ag}^+ \right)$$

$$K_{sp} = (1.5 \times 10^{-4})^2 \times (0.75 \times 10^{-4}) = 1.687 \times 10^{-12}$$

7. (c) : The size of Li^+ and Mg^{2+} are nearly the same.

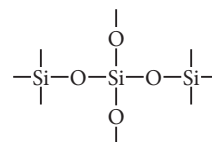
OR

(a) : The solution of alkali metal salts contains H^+ ions, metal cations and OH^- anions. Since discharge potential of H^+ ions is lower than M^+ cations. H^+ is discharged at cathode and not the metal cation.

8. (c) : Wurtz reaction is not preferred for odd number hydrocarbons since many side products are formed *i.e.*, a mixture of alkanes are formed because both alkyl halides react with each other and also with themselves. *e.g.* $A - X + 2\text{Na} + X - B \rightarrow A - A + B - B + A - B + B - A$

9. (a) Diamond has giant three dimensional polymeric structure in which each carbon is sp^3 hybridized and linked to four carbon atoms. This structure makes diamond hardest. On account of small radii of carbon atoms, the various atoms are closely packed in the crystal lattice. Graphite possesses layer structure in which each carbon atom is sp^2 hybridized. There is wide separation between various layers. One layer can slide easily on the other. This makes graphite soft in nature.

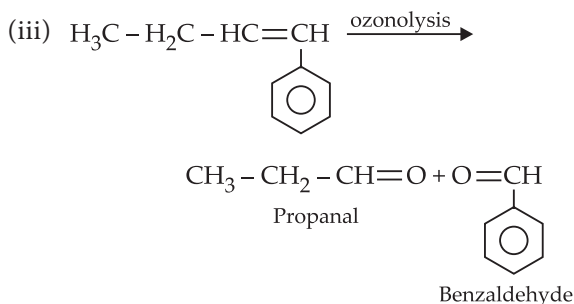
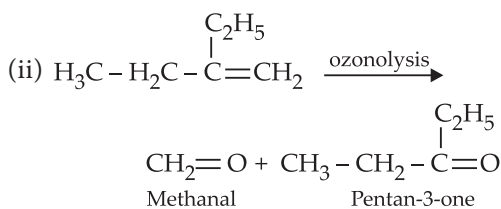
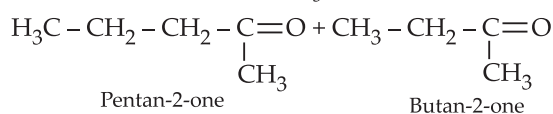
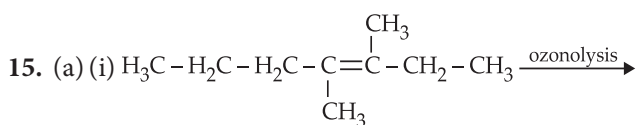
(b) In carbon dioxide discrete molecules are present. In each molecule carbon is linked with two oxygen atoms by double bonds (OCO), while silica possesses a giant three dimensional structure in which each silicon is linked with four oxygen atoms tetrahedrally and each oxygen is linked with two silicon atoms.



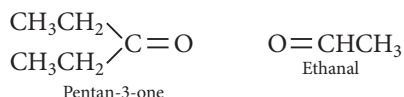
This structure is extremely stable and considerable energy is required to break SiO bond. Thus, CO_2 is a gas and silica is a solid.

OR

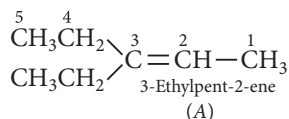
(a) Aluminium atom in aluminium chloride contains 6 electrons in its outermost orbit. So it requires 2 more



(b) **Step 1** : Write the structure of the products side by side with their oxygen atoms pointing towards each other.



Step 2 : Remove the oxygen atoms and join the two ends by a double bond, then structure of the alkene 'A' is obtained



OR

(a) (i) Benzene molecule is stabilised by resonance (delocalisation of π -electrons) and as substitution does not disturb this stabilisation, it occurs easily. Addition reactions, on the other hand disturb the resonance stabilisation or aromatic character, thus they are resisted.

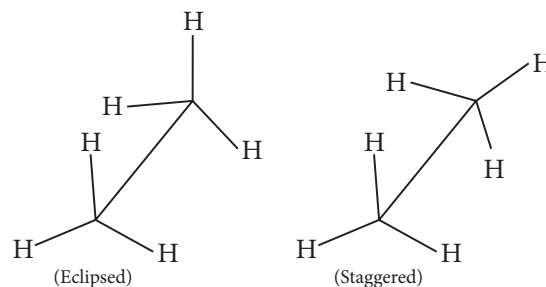
(ii) The *meta* directing substituents withdraw electrons from the benzene ring and thus, deactivate it for further substitution.

(iii) If a halogen substituent is present, two opposing effects operate simultaneously. Halogen atom releases

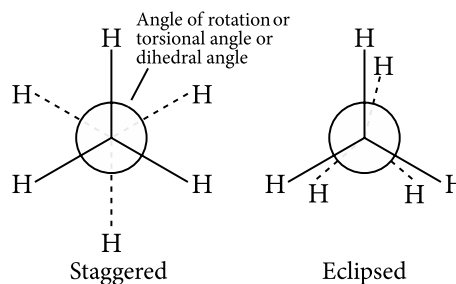
electrons due to resonance but withdraws electrons due to its high electronegativity ($-I$ effect). The $-I$ effect is greater than resonance effect, therefore the benzene ring is deactivated.

(iv) The *o*- and *p*-directing substituents release electrons to the benzene ring thereby activating it for further substitution.

(b) Conformations of ethane using sawhorse projection:



Conformation of ethane according to Newman:



16. (a) $PV = \frac{m}{M} RT$ or $M = \frac{mRT}{PV}$

Hence, $M_A = \frac{(2g)RT}{(1\text{atm})V}$ and $M_B = \frac{(3g)RT}{(0.5\text{atm})V}$

$\Rightarrow \frac{M_A}{M_B} = \left(\frac{2}{1}\right)\left(\frac{0.5}{3}\right) = \frac{1}{3}$

(b) Volume of one balloon = $\frac{4}{3} \pi r^3$

$= \left(\frac{4}{3}\right) \times \left(\frac{22}{7}\right) \times \left(\frac{21\text{cm}}{2}\right)^3 = 4851\text{cm}^3$

Total volume of the gas available at STP conditions is

$V_0 = \frac{P_1 V_1 T_0}{T_1 P_0} = \frac{(20)(2.82)(273)}{(300)(1\text{atm})} = 51.324\text{L} = 51324\text{cm}^3$

When the balloons are being filled, the pressure in the cylinder will decrease. We can continue filling the cylinder till the pressure within the cylinder is also 1 atm. At this stage the volume of 2820 cm^3 of the gas will remain within the cylinder.

Volume of hydrogen available for balloons

$$51324 \text{ cm}^3 - 2820 \text{ cm}^3 = 48504 \text{ cm}^3$$

$$\begin{aligned} \text{Number of balloons that can be filled} &= \frac{48504 \text{ cm}^3}{4851 \text{ cm}^3/\text{balloon}} \\ &= 10 \text{ balloons} \end{aligned}$$

OR

(a) Partial pressure of hydrogen gas

$$V_1 = 0.5 \text{ L} \quad V_2 = 1.0 \text{ L}$$

$$P_1 = 0.8 \text{ bar} \quad P_2 = ?$$

Applying Boyle's law (constant T and n)

$$P_1 V_1 = P_2 V_2 \quad \text{or} \quad P_2 = \frac{P_1 V_1}{V_2}$$

$$\therefore P_2 = \frac{(0.8 \text{ bar}) \times (0.5 \text{ L})}{(1.0 \text{ L})} = 0.40 \text{ bar}$$

Partial pressure of oxygen gas,

$$V_1 = 2.0 \text{ L}, \quad V_2 = 1.0 \text{ L}$$

$$P_1 = 0.7 \text{ bar} \quad P_2 = ?$$

$$\text{or } P_2 = \frac{P_1 V_1}{V_2} = \frac{(0.7 \text{ bar}) \times (2.0 \text{ L})}{(1.0 \text{ L})} = 1.40 \text{ bar}$$

Pressure of the gas mixture,

$$\begin{aligned} P_{\text{mix}} &= P_{\text{H}_2} + P_{\text{O}_2} = 0.40 + 1.40 \\ &= 1.80 \text{ bar} \end{aligned}$$

(b) $W = 20 \text{ g CO}_2$ will evaporate to give pressure P

$$m = 44, V = 0.75 \text{ litre}, T = 298 \text{ K}$$

$$PV = \frac{W}{m} RT$$

Substituting values

$$P \times 0.75 = \frac{20}{44} \times 0.0821 \times 298$$

$$P = 14.828 \text{ atm.}$$

Final pressure in bottle = P + atmospheric pressure

$$= 14.828 + 1 = 15.828 \text{ atm.}$$

