

## Set I

IRC -1 (Chemistry)

Full Marks: 75

Time: 3 Hours

*Answer the questions as per instruction given.*

*The figures in the right-hand margin indicate marks.*

*Candidates are required to give answers in their own words as far as practicable.*

### Group A

#### (Short Answer Type Questions)

Answer all the following questions.

1. Answer the following questions in a few words or maximum in one sentence. (5x1=5)
  - a) Which series of lines of the hydrogen spectrum lies in the visible region ?
  - b) Which element has the highest ionisation energy?
  - c) What is the shape of  $\text{NH}_4^+$  ion?
  - d) Write down the SI value of universal molar gas constant.
  - e) What is the IUPAC name of diethyl ether?
2. What is molarity? Write down its unit. What is effect of increase in temperature on the molarity and molality of a solution? (5)
3. Write down the van der Waals equation for n moles of a real gas and give the significance of the terms involved in it. (5)

### Group B

#### (Long /Descriptive Answer Type Questions)

Answer any four of the following questions.

4.
  - a) Discuss Bohr's atomic theory?
  - b) Calculate the radius of third orbit of  $\text{He}^+$  ion.  
(radius of first orbit of H atom is  $0.53\text{\AA}$ ) (10+5)
5.
  - a) Define ionisation energy and illustrate with an example.
  - b) Discuss the variation of ionisation energy in the periodic table.
  - c) The ionisation energy of nitrogen is greater than that of oxygen, why? (5+5+5)
6.
  - a) What is valence shell electron pair repulsion theory? Illustrate briefly.
  - b) explain the shape of  $\text{XeF}_4$ ,  $\text{SF}_4$ ,  $\text{NH}_3$  and  $\text{ClF}_3$  molecules with the help of VSEPR theory. (7+8)
7. a) Write down the postulates of kinetic theory of gases.

b) Calculate the kinetic energy of 8 g methane gas at 27°C.

(10+5)

8. a) What is isomerism?  
b) Define structural isomerism.  
c) Write down structure and IUPAC name of all the structural isomers of C<sub>4</sub>H<sub>10</sub>O. (4+4+7)
9. a) What do you mean by homolytic and heterolytic fission of covalent bonds? Explain with the help of suitable examples.  
b) what is mesomeric effect?  
c) What are carbocations? What is shape of methyl carbocation?

(5+5+5)

**Answer:**

1. a) Balmer series  
b) Helium  
c) Tetrahedral  
d) 8.314 J mole<sup>-1</sup> K<sup>-1</sup>  
e) Ethoxyethane
2. The number of moles of solute present per litre of a solution is called its molarity.

$$\text{Molarity} = \frac{\text{No. of moles of solute(B)}}{\text{Volume of the solution (in L)}}$$

$$\text{Unit of molarity} = \frac{\text{mole}}{\text{L}} \\ = \text{mole L}^{-1} = \text{molar} = \text{M}$$

The molarity of the solution decreases slightly with increase in the temperature due to slight increase in the volume.

3. The van der Waals equation for n moles of a real gas is given below:

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

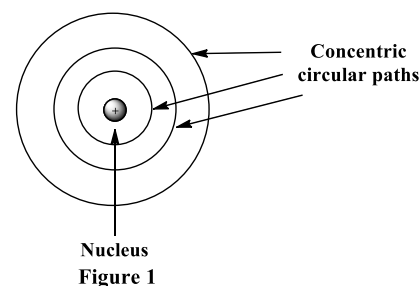
Here,

**a** = van der Waals constant. It is the measure of strength of intermolecular attractive force. The greater the value of a, the stronger will be the intermolecular attractive force. Its unit is atm L<sup>2</sup>mole<sup>-2</sup>.

**b** = van der Waals constant. It represents the effective volume of one mole molecules of a gas. Its unit is L mole<sup>-1</sup>.

4. a) The main points of Bohr's atomic theory are given below:

- i) A number of concentric circular paths are available to electrons to move around the nucleus as shown in the figure 1. However, the electrons move on only certain selected circular paths.



Nucleus  
Figure 1

- ii) The electrons move on only those circular paths in which their angular momentum is integral multiple of  $\frac{h}{2\pi}$ .

It means,

$$mvr = n \times \frac{h}{2\pi}$$

Where,

m = Mass of electron

v = Tangential velocity of electron

h = Planck's constant

$$= 6.626 \times 10^{-34} \text{ Js}$$

n = Circular path number

$$= 1, 2, 3, 4, \dots\dots\dots$$

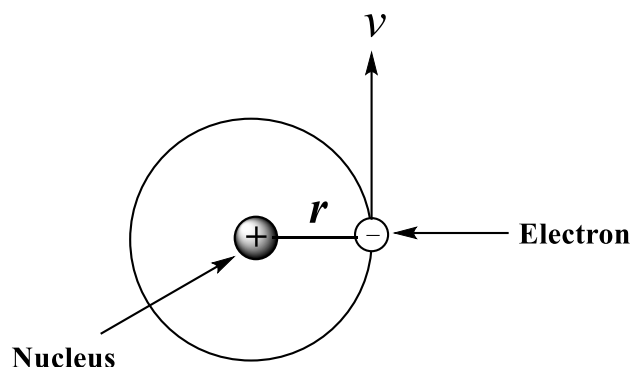


Figure 2

- iii) When the electrons move on such circular paths, they do not lose energy. Such circular paths are called stationary orbits, orbits, main energy levels, or shells.

n = 1, K Shell, First orbit

n = 2, L Shell, Second orbit

n = 3, M Shell, Third orbit

n = 4, N Shell, Fourth orbit

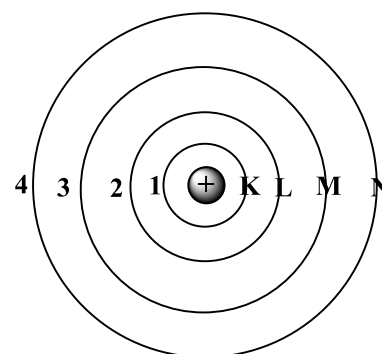


Figure 3

- iv) The energy of orbit or electron present in the orbit increases with increase in the distance from the nucleus.

$$E_1 < E_2 < E_3 < E_4$$

Where,

$E_1$  = Energy of first orbit

$E_2$  = Energy of second orbit

$E_3$  = Energy of third orbit

$E_4$  = Energy of fourth orbit

- v) When the electron moves in a certain orbit, it does not lose energy. But when an electron jumps from one orbit to another orbit, energy is either released or absorbed in the form of electromagnetic radiation.

The energy of electromagnetic radiation releases or absorbed is given by

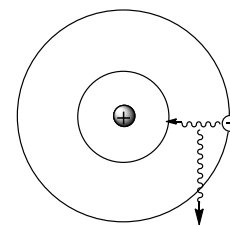


Figure 4

Energy of emr = Energy difference between the concerned orbits

$$h\nu = \Delta E$$

$$\text{or, } h \times \frac{c}{\lambda} = \Delta E$$

$$\text{or, } \lambda = \frac{hc}{\Delta E}$$

Where,  $\lambda$  is the wavelength of electromagnetic radiation released or absorbed.

- b) We know that

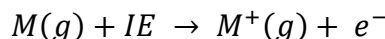
$$r_n = a_0 \times \frac{n^2}{Z} \text{ \AA}$$

Where,

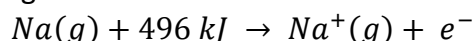
$$a_0 = \text{Radius of first orbit of H atom} \\ = 0.53 \text{ \AA}$$

$$\text{Therefore, radius of third orbit of He}^+, r_3(\text{He}^+) = 0.53 \times \frac{3^2}{2} \text{ \AA} \\ = 2.385 \text{ \AA}$$

5. a) The minimum amount of energy required to remove the most loosely bound electron *i.e.*, the *outermost electron* from an isolated gaseous atom in its ground state to produce gaseous cation is called its ionisation energy. It is abbreviated as IE and its unit is  $\text{kJ mole}^{-1}$ .



An illustrative example is given below:



It is obvious that the ionisation energy of sodium is  $496 \text{ kJ mole}^{-1}$ .

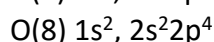
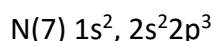
- b) On moving down a group in the periodic table, the  $Z_{\text{eff}}$  remains almost constant but atomic radius increases. As a result, the electrostatic attractive force acting on the outermost electron becomes increasingly weaker and hence the ionisation energy goes on decreasing as illustrated below:

Group 1	
Elements	IE (kJ/mole)
Li	520
Na	496
K	419
Rb	403
Cs	376

On moving from left to right in a period in the periodic table, the atomic radius decreases and the  $Z_{\text{eff}}$  increases. As a result, the electrostatic attractive force acting on the outermost electron becomes increasingly stronger and hence the ionisation energy goes on increasing as illustrated below:

Period	Elements	Li	Be	B	C	N	O	F	Ne
2	IE (kJ/mole)	520	<b>899</b>	801	1086	<b>1403</b>	1314	1681	2080

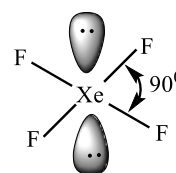
- c) The half-filled or full-filled subshell is relatively more stable and it is more difficult to remove electron from such subshell.



In the case of N atom, the electron is to be removed from extra stable half-filled  $2p^3$  subshell while the removal of one electron from O atom produces such subshell. This is why the ionisation energy of nitrogen is greater than that of oxygen.

6. a) The valence shell electron pair repulsion theory has been proposed to explain the shapes of covalent molecules and ions. The main points of this theory are given below:

- i) The electron pairs present in the valence shell of the central atom of a molecule /ion arrange themselves in the space in such a way that there is maximum distance among them and there is minimum repulsion among them so that the molecule may have minimum energy and maximum stability.



Shape: Square planar

Valence shell electron pairs = lone pairs + bond pairs

- ii) If the central atom of a molecule or ion is surrounded only by bond pairs and no lone pair, the molecule has regular geometry.
- iii) The bond pair is attracted by two nuclei while the lone pair is attracted by only one nucleus. Therefore, the lone pair occupies greater angular space than the bond pair around the central atom

Therefore, the lone pair causes greater repulsion than the bond pair. The order of repulsion between various electron pairs is in the order:



This is why the presence of lone pair in the valence shell of the central atom of a molecule produces distortion in the bond angle from the regular geometry.

- iv) All the bond pairs do not occupy the same angular space around the central atom. The bond pair attached to the less electronegative substituent occupies greater angular space around the central atom than the bond pair attached to the more electronegative substituent. Therefore, the bond angle decreases with increase in the electronegativity of substituents or decrease in the electronegativity of the central atom.
- v) Two electron pairs of a double bond cause greater repulsion than one electron pair of a single bond. Similarly, three electron pairs of a triple bond cause greater repulsion than two electron pairs of a double bond.

#### b) SF<sub>4</sub>:

Central atom = S

No. of electrons in the valence

shell of S atom in SF<sub>4</sub> molecule = 6(S) + 1x4(F) = 10

No. of electron pairs = 10/2 = 5

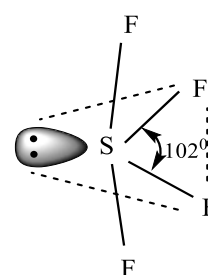
No. of bond pairs = 4

No. of lone pairs = 1

Sum of no bond pairs and lone pairs = 5

Geometry = Distorted trigonal bipyramidal with one equatorial corner occupied by lone pair.

Shape: See-saw



Shape: See-saw

#### XeF<sub>4</sub>

Central atom = Xe

No. of electrons in the valence

shell of Xe atom in XeF<sub>4</sub> molecule = 8(Xe) + 1x4(F) = 12

No. of electrons pairs =  $12/2 = 6$

No. of bond pairs = 4

No. of lone pairs = 2

Sum of no bond pairs and lone pairs = 6

Geometry = Octahedral with two axial corners occupied by lone pairs.

Shape: Square planar

### **NH<sub>3</sub>**

Central atom = N

No. of electrons in the valence

shell of N atom in NH<sub>3</sub> molecule =  $5(N) + 1 \times 3(H) = 8$

No. of electrons pairs =  $8/2 = 4$

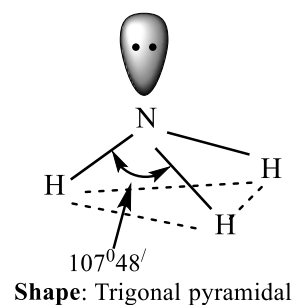
No. of bond pairs = 3

No. of lone pairs = 1

Sum of no bond pairs and lone pairs = 4

Geometry = Distorted tetrahedral with one corner occupied by lone pair.

Shape: Trigonal pyramidal



### **ClF<sub>3</sub>**

Central atom = Cl

No. of electrons in the valence

shell of Cl atom in ClF<sub>3</sub> molecule =  $7(Cl) + 1 \times 3(F) = 10$

No. of electrons pairs =  $10/2 = 5$

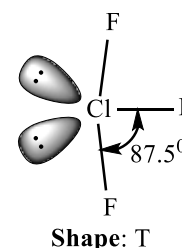
No. of bond pairs = 3

No. of lone pairs = 2

Sum of no bond pairs and lone pairs = 5

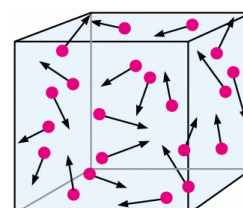
Geometry = Distorted trigonal bipyramidal with two equatorial corners occupied by lone pairs.

Shape: T-shaped



## **7. a)** The postulates of kinetic theory of gases are summarised below:

- i. Any gas is made up of extremely small fast-moving spherical particles which are called molecules.
- ii. All the molecules of a gas are identical in shape, size and mass (but not in energy).
- iii. The total volume of the gaseous molecules is negligible in comparison to the volume of the vessel.
- iv. There acts neither attractive nor repulsive force among the molecules of a gas.
- v. The gaseous molecules are not in rest. They execute random motion on zig-zag path. the direction of their movement changes after each collision. But the



- molecules travel on the straight line between two successive collisions.
- vi. The gaseous molecules collide among themselves and with the wall of the vessel during their motion.
  - vii. The molecular collisions are perfectly elastic in nature. It means there is neither loss nor gain of energy during molecular collisions. There is only exchange of energy between the colliding molecules.
  - viii. The pressure of a gas is due to the hits recorded by the gaseous molecules on the wall of the vessel.
  - ix. Different molecules of a gas may have different velocities and hence different kinetic energies. But the average kinetic energy per molecule of a gas is directly proportional to the absolute temperature of the gas.

$$\frac{1}{2}mv^2 \propto T$$

**b)** First of all, we have to calculate the number of moles present in 8 g of methane gas.

$$n = \frac{W}{M_m} = \frac{8 \text{ g}}{16 \text{ g mole}^{-1}} = 0.5 \text{ mole}$$

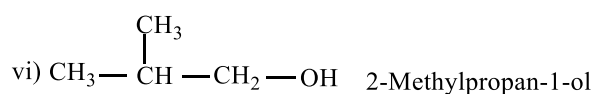
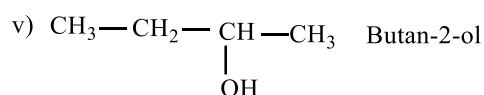
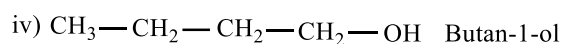
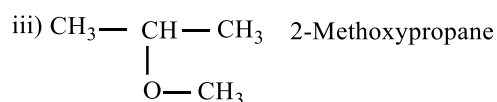
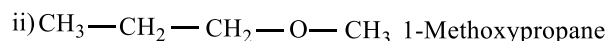
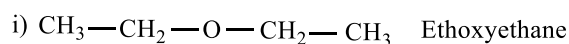
Thereafter, the kinetic energy of methane gas can be calculated using the following equation:

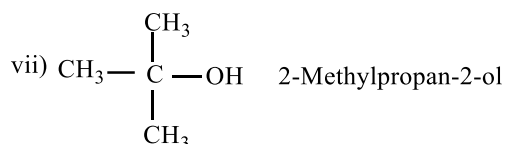
$$\begin{aligned} KE &= n \times \frac{3}{2} RT \\ &= 0.5 \text{ mole} \times 1.5 \times 8.314 \text{ J mole}^{-1} \text{ K}^{-1} \times 300 \text{ K} \\ &= 1870.65 \text{ J} \end{aligned}$$

**8. a)** The compounds having the same molecular formula but different physical and/or chemical properties due to different arrangement of atoms/groups of the molecule in the space are called isomers and this phenomenon is called isomerism.

**b)** The organic compounds having the same molecular formula but different structural formula or the different connectivities of atoms are called structural isomers and this phenomenon is called structural isomerism.

c) The structure and IUPAC name of all the structural isomers of  $C_4H_{10}O$  are given below:

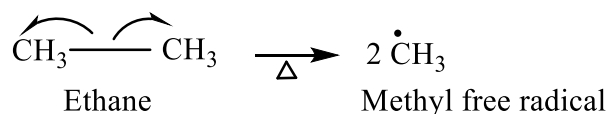




9. a)

**Homolytic fission:**

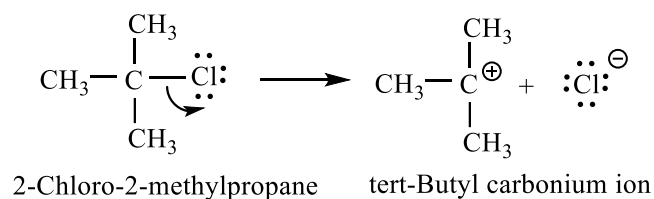
When the atoms linked together by a covalent bond withdraw their electron from the bond pair during the fission of covalent bond, it is called homolytic fission or cleavage or dissociation of bond. It is denoted by half curly arrow, which is also called fishing hook).



The homolytic fission of covalent bond leads to the formation of free radicals.

**Heterolytic fission:**

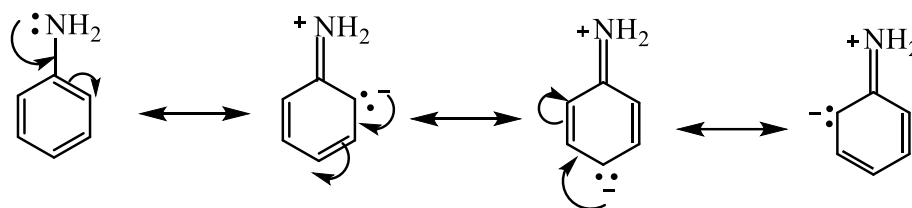
When both the electrons of the bond pair are transferred to a single atom during the fission of a covalent bond, it is called heterolytic fission. It is denoted by full curly arrow.



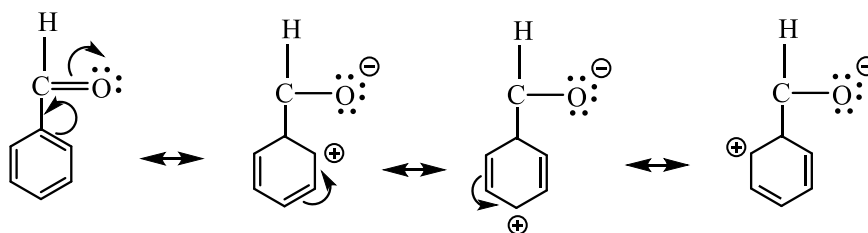
The heterolytic fission of covalent bond leads to the formation of cation and anion.

**b) Mesomeric effect:**

The polarity produced within the substrate molecule due to lone pair- $\pi$  electron pair ( $n, \pi$ ) or  $\pi, \pi$  – interaction is called mesomeric effect or resonance effect.



If an atom or group releases electron due to mesomeric effect, it is said to have + M effect or + R effect. Examples: -OH, -OR, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>, -Cl, -Br, -I, etc. have + M effect if attached directly to aromatic nucleus. It must be noted that all these atoms/groups have lone pair of electrons on the atom with free valency.

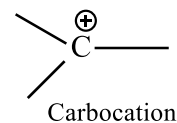




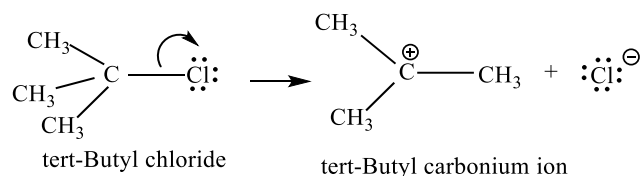
If a group withdraws electron towards itself due to mesomeric effect, it is said to have  $-M$  effect of  $-R$  effect. Example:  $-CHO$ ,  $>CO$ ,  $-NO_2$ ,  $-COOH$ ,  $-COOR$ ,  $-SO_3H$ ,  $-CN$ , etc. have  $-M$  effect if attached directly to the aromatic nucleus.

### c) Carbocation:

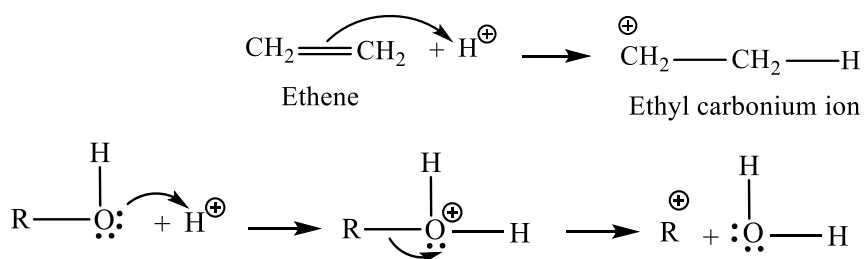
The organic reaction intermediate containing trivalent positively charged carbon atom is called carbocation.



**Formation:** The carbocation intermediate is formed by the heterolytic fission of  $C - X$  bond where  $X$  is more electronegative than  $C$  atom.

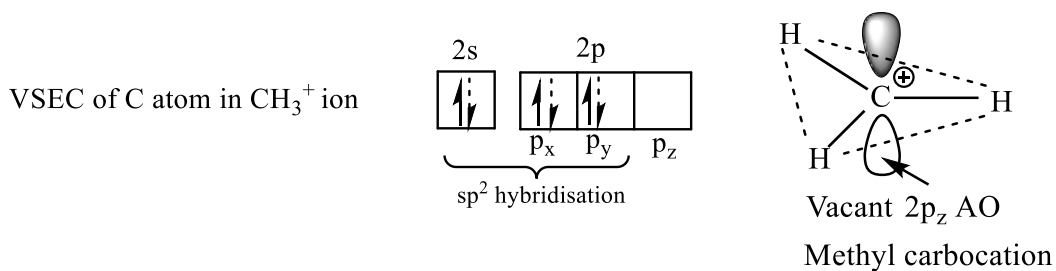


The protonation of alkenes and alcohols also leads to the formation of carbocation intermediates as shown below:



### Shape of methyl carbocation:

The carbocation intermediate has triangular planar geometry arising from  $sp^2$  hybridisation on positively charged carbon atom.



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