

CHEMISTRY-I
(CHM1001)

Time Allotted : 2½ hrs

Full Marks : 60

Figures out of the right margin indicate full marks.

*Candidates are required to answer Group A and
any 4 (four) from Group B to E, taking one from each group.*

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

Group – A

1. Answer any twelve:

12 × 1 = 12

Choose the correct alternative for the following

- (i) Joule Thomson expansion of an ideal gas is
 - (a) Isochoric process
 - (b) Isobaric process
 - (c) Isoenthalpic process
 - (d) Isothermal process
- (ii) Which of the following behaves as rechargeable battery?
 - (a) Zn (s) / ZnSO₄ (aq.) // CuSO₄ (aq.) / Cu (s)
 - (b) Pb(s) / H₂SO₄ (aq.) (saturated with PbSO₄) / PbO₂(s)
 - (c) PbO₂(s) / H₂SO₄ (aq.) (saturated with PbSO₄) / Pb (s)
 - (d) Zn (s) / H₂SO₄ (aq.) / Cu (s)
- (iii) Choose correct pair of hard acid and hard base from the following sets
 - (a) Li⁺ and F⁻
 - (b) Al³⁺ and I⁻
 - (c) BH₃ and H⁻
 - (d) Ag⁺ and O²⁻
- (iv) The hybridization pattern of PCl₅ molecule
 - (a) sp³
 - (b) sp³d
 - (c) sp²
 - (d) sp³d²
- (v) Which among the followings is not an acceptable solution of Schrodinger's wave equation?
 - (a) ψ must be continuous
 - (b) ψ must be infinite
 - (c) ψ must be single valued
 - (d) $+\infty$ to $-\infty$, ψ^2 must be equal to 1
- (vi) The molecule having highest absorption maxima ($\lambda_{\max}$) among the following is
 - (a) Ethylene
 - (b) Napthalene
 - (c) Anthracene
 - (d) Benzene
- (vii) The most appropriate statement regarding fluorescence and phosphorescence is
 - (a) Singlet-singlet and triplet-singlet transition
 - (b) Singlet-singlet and triplet-triplet transition
 - (c) Triplet-singlet and singlet-singlet transition
 - (d) Singlet-triplet and triplet-singlet transition

- (viii) Which of the following isomerism is shown by only alkenes but not by alkanes?
 (a) Conformational (b) Geometrical
 (c) Optical (d) Chain
- (ix) Anti-Markonikoff's addition of HBr is not observed in
 (a) 1-butene (b) 2-butene
 (c) 1-pentene (d) Propene
- (x) (2R, 4S)-2, 4-dichloropentane and (2R, 4R)-2, 4-dichloropentane are
 (a) Enantiomers (b) Diastereomers
 (c) Identical (d) None of these

Fill in the blanks with the correct word

- (xi) In a mixture of several components, the partial molar free energy of any particular component at constant temperature and pressure is called the _____ of that constituent
- (xii) When Pt wire is dipped in an acidic solution of FeSO_4 (redox couple $\text{Fe}^{+2/+3}$), the electrode formed is classified as _____ electrode.
- (xiii) The first ionisation potential of Be is _____ than that of B.
- (xiv) The range of fingerprint region in infrared spectroscopy is _____ cm^{-1} .
- (xv) Isomerism among compounds due to migration of proton is known as _____.

Group - B

2. (a) Derive Gibbs-Duhem equation for a multi-component system. [[C01](Remember/LOCQ)]
- (b) 10 moles of an ideal gas initially at 1atm pressure and 0°C is expanded reversibly and isothermally to a final pressure of 0.1atm. Calculate the work done by the gas, internal energy change and heat absorbed by the system. (Given: $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$). [[C01](Apply/IOCQ)]
- (c) What is the underlying principle of the Hydrogen-Oxygen Fuel Cell? Illustrate with schematic diagram. What is the advantage of using such cell for electricity generation? [[C02](Remember/LOCQ)]
- (d) Consider the cell reaction $\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{+2} + 2\text{Ag}$. Represent the cell configuration and find out the E°_{cell} (given that, $E^\circ_{\text{Zn}/\text{Zn}^{+2}} = 0.76 \text{ V}$ & $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.80 \text{ V}$). [[C02](Apply/IOCQ)]
- 3 + 3 + 4 + 2 = 12**
3. (a) For the change of state (liquid $\rightleftharpoons$ vapour) arrive at the Clausius-Clapeyron equation. [[C01](Remember/LOCQ)]
- (b) Starting from the expression for efficiency of a Carnot Engine arrive at the definition of entropy function. [[C01](Remember/LOCQ)]
- (c) If the standard reduction potential of Ag^+/Ag is 0.80 volt and Ag is dipped in H_2SO_4 predict whether the cell represented by $\text{Ag}/\text{Ag}^+//\text{H}^+(\text{a}=1)/\text{H}_2(25^\circ\text{C}, 1\text{atm})$ will give positive EMF or not? [[C02](Apply/IOCQ)]

- (d) How does localized electrochemical cell formation aggravate rusting of iron? Illustrate with half-cell oxidation and reduction reactions. [[CO2](Apply/IOCQ)]

4 + 2 + 3 + 3 = 12

Group - C

4. (a) Calculate the bond orders for the species O_2 , O_2^+ , O_2^- (superoxide) and O_2^{2-} (peroxide); compare their relative stabilities and indicate their magnetic properties. [[CO3](Apply/IOCQ)]
- (b) What do you understand by doping? Why Germanium doped with phosphorus is called as n-type semiconductor? [[CO3](Remember/LOCQ)]
- (c) Using Slater's rule calculate screening constant and effective nuclear charge experienced by a valence electron of K ($Z=19$). [[CO4](Apply/IOCQ)]
- (d) What do you understand by polarizability of anion? How does Fajans' rule explain the relative covalent character for LiF and LiI molecules. [[CO4](Remember/LOCQ)]

4 + 3 + 2 + 3 = 12

5. (a) Draw the structure of XeF_2 molecule and mention the hybridization of the central atom. Write down the differences between the bonding and antibonding molecular orbitals. [[CO3](Remember/LOCQ)]
- (b) Using energy band diagram differentiate an intrinsic semiconductor and a metal. Give an example of intrinsic semiconductor. [[CO3](Remember/LOCQ)]
- (c) The first ionization energy of elements increases from left to right in a given period of the periodic table but Zn ($IE = 906 \text{ kJ mol}^{-1}$) has higher ionization energy than Ga ($IE = 578 \text{ kJ mol}^{-1}$) – Explain. [[CO4](Apply/IOCQ)]
- (d) Which one among $[AlF_6]^{3-}$ and $[AlI_6]^{3-}$ is more stable and why – Explain on the basis of SHAB principle. [[CO4](Remember/LOCQ)]

(2 + 2) + 3 + 3 + 2 = 12

Group - D

6. (a) What is the importance of de Broglie's relation? Consider a beam of electron with a speed of $5.31 \times 10^6 \text{ m/s}$, calculate the de Broglie wavelength (Mass of electron = $9.11 \times 10^{-31} \text{ kg}$; $h = 6.626 \times 10^{-34} \text{ Js}$). [[CO3](Apply/IOCQ)]
- (b) What is ψ ? What information is conveyed by ψ and ψ^2 ? [[CO3](Remember/LOCQ)]
- (c) Relate the λ_{max} values (i) 277 ($\epsilon \sim 100$) and 185nm ($\epsilon \sim 2000$) and (ii) 324 ($\epsilon \sim 24$) and 219nm ($\epsilon \sim 3660$) to the compounds $\text{CH}_3\text{COCH}_2\text{CH}_3$ and $\text{CH}_3\text{COCH}=\text{CH}_2$. Identify the electronic transitions in each case. [[CO5](Apply/IOCQ)]
- (d) Explain why ethylene fails to absorb at 1600 cm^{-1} . [[CO5](Remember/LOCQ)]

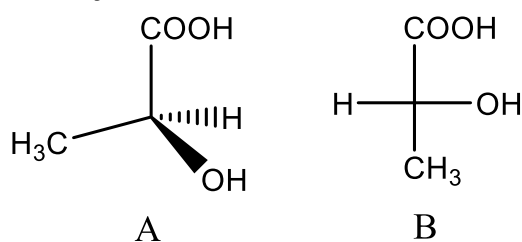
(1 + 2) + 3 + 4 + 2 = 12

7. (a) Write the wave function and the total energy of particle in a one-dimensional box for $n=2$ state. Indicate the number of nodes in the wave. [[CO3](Remember/LOCQ)]
- (b) The fundamental frequency of vibration of CO molecule is 2140 cm^{-1} . Calculate the force constant of the bond. (Given: atomic mass of C is $1.99 \times 10^{-6} \text{ kg}$ and of O is $2.66 \times 10^{-6} \text{ kg}$). [[CO5](Remember/LOCQ)]

- (c) Explain the terms internal conversion and inter system crossing by drawing a labelled Jablonski diagram. [[CO5](Remember/LOCQ)]
- (d) Write down the conditions for a well-behaved wavefunction. What is the name of orbital having $n=4, l=3$? [[CO3](Remember/LOCQ)]
- (2 + 2) + 2 + 3 + (2 + 1) = 12**

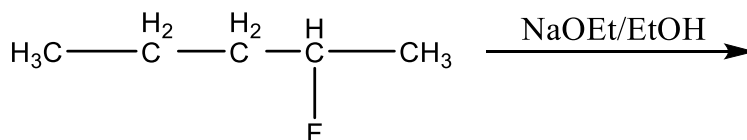
Group - E

8. (a) Find out the absolute configuration of each of the stereocentres of the following molecules A and B. Identify the relation between them.



[[CO6](Remember/LOCQ)]

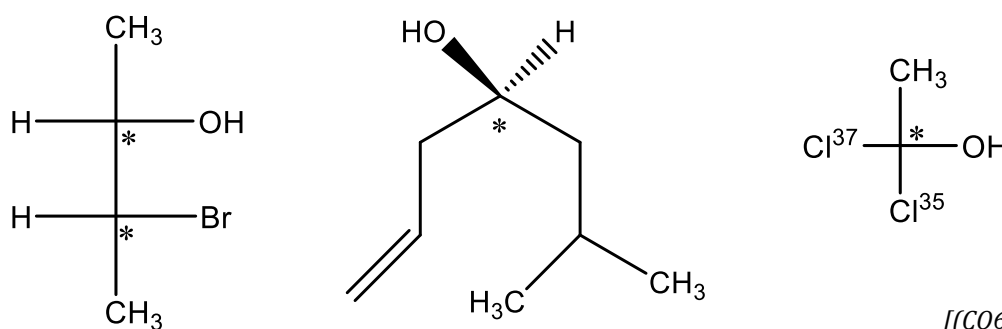
- (b) Draw the structure of fully eclipsed and anti-staggered conformation of active tartaric acid in Newman projection formula. [[CO6](Apply/IOCQ)]
- (c) Draw the energy profile diagram of the different conformations of n-butane. Identify the most stable and unstable conformation. [[CO6](Remember/LOCQ)]
- (d) Write the products obtained in the following reaction. Predict the major product. Justify your answer.



[[CO6](Apply/IOCQ)]

3 + 2 + (3 + 1) + 3 = 12

9. (a) Identify the absolute configuration of each marked stereo centre of the following structures.



[[CO6](Apply/IOCQ)]

- (b) Differentiate between asymmetric and dissymmetric molecule. [[CO6](Remember/LOCQ)]
- (c) Depict the synthetic route of Aspirine. Mention its uses and side effects. [[CO6](Remember/LOCQ)]
- (d) Arrange the following molecules in the order of increasing reactivity in $\text{S}_{\text{N}}2$ reaction.

CH_3Br , Me_3CBr and PhCH_2Br

[[CO6](Apply/IOCQ)]

4 + 2 + (2 + 1 + 1) + 2 = 12

Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	58	42	0