

**CHEMISTRY I
(CHEM 1001)**

Time Allotted : 3 hrs

Full Marks : 70

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 5 (five) from Group B to E, taking at least one from each group.

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

**Group – A
(Multiple Choice Type Questions)**

1. Choose the correct alternative for the following: **10 × 1 = 10**
- (i) The de-Broglie hypothesis is associated with
 (a) wave nature of electrons only (b) wave nature of alpha-particles only
 (c) wave nature of radiations (d) wave nature of all material particles.
- (ii) In a reaction $A \rightarrow \text{Products}$, the half life period is found to be independent of initial concentration of reactant. What will be the order of the reaction?
 (a) Zero (b) One (c) Two (d) Three.
- (iii) The ground state energy of a particle in a one dimensional box is
 (a) zero (b) $h^2/8mL^2$ (c) $-h^2/8mL^2$ (d) none of the above.
- (iv) Bathochromic effect is
 (a) shift of absorption band to shorter wavelength
 (b) shift of absorption band to longer wavelength
 (c) absorption band remains as it is
 (d) none of the above.
- (v) The hybridization of the central atom in AsF_5 molecule is
 (a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2 .
- (vi) Which of the following aqueous solutions of same concentration will have highest pH value?
 (a) NaCl (b) KNO_3 (c) ZnCl_2 (d) Na_2CO_3 .
- (vii) Which ion has greatest ionic mobility?
 (a) Na^+ (b) Li^+ (c) H_3O^+ (d) K^+ .
- (viii) The initial concentration of the reactant and the rate constant for a zero-order reaction are A_0 and K respectively; the time required for 100 percent completion of this zero order reaction is
 (a) $A_0/2K$ (b) A_0/K (c) $0.693/K$ (d) $2A_0/K$.

- (ix) Which one of the following carbocations is most stable?
 (a) H_3C^+ (b) CH_3CH_2^+ (c) $(\text{CH}_3)_2\text{CH}^+$ (d) $(\text{CH}_3)_3\text{C}^+$.
- (x) Which of the following is capable of existing as a pair of enantiomers?
 (a) 2-methylpropane (b) 2-methylpentane
 (c) 3-methylpentane (d) 3-methylhexane.

Group – B

2. (a) Derive Clapeyron-Clausius equation and mention its applications.
 (b) Define work function and free energy. How can you comment on the spontaneity of a process with the help of free energy?
 (c) On passing monochromatic light through a 0.01 (M) solution in a cell of 1 cm thickness, the intensity of the transmitted light was reduced to 10%. Calculate the molar extinction coefficient.

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

- 3.(a) Derive the expression for entropy change of an ideal gas.
 (b) An ideal monoatomic gas (one mole) is heated from 27°C to 227°C and volume expands from 10 L to 100 L. What is the change in molar entropy (Given $C_v=3/2R$).
 (c) Explain what is chemical potential? What is Clausius inequality and explain the usefulness of it.
 (d) Write the wave function and the total energy of a particle in a one-dimensional box for $n=3$ state.

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

Group – C

- 4.(a) Calculate the effective nuclear charge experienced by a 3d-electron of Zn(30) using Slater rule.
 (b) The dipole moment of LiH is 1.964×10^{-29} Cm and the interatomic distance between Li and H is 1.596 Å. Compute the % ionic character.
 (c) Calculate the pH at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH. (Given K_a for acetic acid is 1.9×10^{-5}).
 (d) Carbon monoxide is a sigma donor and pi-acceptor ligand – explain with MO theory.
 (e) Why are the axial bonds longer than equatorial bonds in a trigonal bipyramidal geometry?

2 + 2 + 3 + 3 + 2 = 12

- 5.(a) Explain why addition of barium chloride solution to sodium sulphate solution precipitates only barium sulphate and not sodium chloride.
- (b) Why is B₂ paramagnetic?
- (c) What causes Ga and Ge to have higher electro-negativity than Al and Si respectively?
- (d) Arrange the hydrides of group-16 (O, S, Se, Te) in decreasing order of their boiling points and justify your answer.
- (e) Why is the 1st ionisation potential value of Cu higher than that of K although both K and Cu have their valence electron in 4s orbital?
- (f) Draw two molecular orbitals formed by the linear combination of two p_y orbitals (consider x-axis as the internuclear axis).

$$2 + 2 + 2 + 2 + 2 + 2 = 12$$

Group - D

- 6.(a) Derive the 2nd order rate equation considering : 2A → Products.
- (b) The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant?
- (c) Write the half cell reactions and the total cell reaction for the following cell
Zn|Zn²⁺||Cu²⁺|Cu.
- (d) Show the nature of titration curve for the estimation of the Cl⁻ ions concentration by conductometry.
- (e) Calculate the λ₀ for acetic acid, given λ₀(CH₃COONa), λ₀(NaCl) and λ₀(HCl) are 91 Scm⁻¹mol⁻¹, 126 Scm⁻¹mol⁻¹ and 426 Scm⁻¹mol⁻¹ respectively.
- (f) Calculate the ΔG° for the following cell:
Fe(s)|Fe²⁺(aq)(1M)||Cu²⁺(aq)(1M)|Cu(s)
Given E°(Cu²⁺/Cu) = 0.34V and E°(Fe²⁺/Fe) = -0.44V. Also find the equilibrium constant for the cell reaction.

$$3 + 1 + 2 + 2 + 2 + 2 = 12$$

- 7.(a) Illustrate the variation of equivalent conductance of strong and weak electrolytes with concentration.
- (b) The equivalent conductance of LiCl at infinite dilution is 0.0115 Sm²/mol and the transference number of the cation is 0.336. Compute the ionic mobility of the anion.
- (c) Illustrate the relaxation effect of the ion atmosphere in Debye-Onsager equation.
- (d) Transport number of Ag⁺ is 0.466 and that of NO₃⁻ is 0.534 at 20°C. The molar conductance of very dilute solution of AgNO₃ is 115.8 mho.cm² at the same temperature. Calculate the ionic conductance of Ag⁺ and NO₃⁻ ions.
- (e) Describe the calomel electrode and write down the half-cell reaction when taken as cathode.
- (f) For a given cell reaction (redox reaction),
Fe²⁺(aq) + Ag⁺(aq) = Fe³⁺(aq) + Ag(s)
Write down the cell configuration, half-cell reactions and also the Nernst equation for this constructed cell.

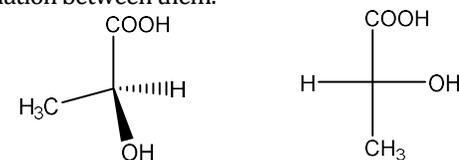
$$2 + 2 + 2 + 2 + 2 + 2 = 12$$

Group - E

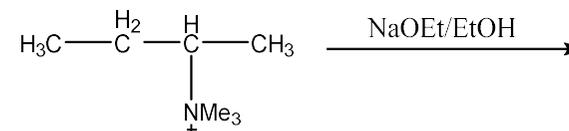
- 8.(a) Write down the Fischer projection structure and the absolute configuration of the each stereocentre of the following compound:
- (b) What is rotational axis of symmetry? Show all the rotational axes present in CH₄ molecule.
- (c) Why is p-nitro phenol more acidic than m-nitro phenol?
- (d) Write the molecular structure and the use of paracetamol.
- (e) Predict A and B for the following reaction:

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

- 9.(a) Find out the absolute configuration of stereocentres of each molecule and identify the relation between them.



- (b) Identify the elimination products. Which product should be major and why?



- (c) Illustrate the mechanism of S_N2 reaction.
- (d) Explain alternating axis of symmetry with suitable example.

$$(2 + 1) + (2 + 1 + 1) + 2 + (2 + 1) = 12$$