

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 most certain condition for a reaction to be spontaneous is
(a) both ΔH and ΔS are positive (b) both ΔH and ΔS are negative
(c) ΔH is negative, ΔS is positive (d) ΔH is positive, ΔS is negative.
- (ii) The screening effect of d-electrons is
(a) equal to the p-electrons (b) much more than p-electrons
(c) same as f-electrons (d) less than p-electrons.
- (iii) A cathode and an anode are the most common components of a galvanic cell. Which of the following claims about the cathode is correct?
(a) Oxidation occurs at the cathode
(b) Electrons move into the cathode
(c) Usually denoted by a negative sign
(d) Is usually made up of insulating material.
- (iv) 'A silver wire dipped in AgNO_3 solution forms the electrode'. Which one of following is applicable for the above statement?
(a) Metal-sparingly soluble salt electrode (b) Metal-metal ion electrode
(c) Redox electrode (d) None of (a), (b) & (c).
- (v) The hybridization pattern of ClF_3 molecule is
(a) sp^3 (b) sp^3d (c) sp^2 (d) sp^3d^2 .
- (vi) The number of molecules of the reactants involved in an elementary reaction indicates
(a) the order of the reaction (b) the molecularity of the reaction
(c) the rapid step of the reaction mechanism (d) the reaction half-life.
- (vii) Identify the correct answer:
The boiling point of cis-1,2-dichloroethene is more than trans-1,2-dichloroethene due to the presence of
(a) H-bond (b) Ion-dipole interaction
(c) London dispersion force (d) Dipole-dipole interaction.

- (viii) Which statement is wrong for S_N2 reaction?
 (a) It is a bimolecular nucleophilic substitution reaction
 (b) It proceeds with retention in configuration
 (c) It proceeds with inversion in configuration
 (d) Reaction rate depends on both the concentration of substrate and nucleophile.
- (ix) 1-fold alternating axis of symmetry is equivalent to
 (a) plane of symmetry (b) centre of symmetry
 (c) both the plane and centre of symmetry (d) none of (a), (b) & (c).
- (x) Which of the following is not a nucleophile?
 (a) CN^- (b) BF_3 (c) H_2O (d) Carbanion.

Group- B

2. (a) Under what conditions heat can be completely converted into work? State any one statement of the 2nd law of thermodynamics. [[CO2](LOCQ)]
 (b) Derive the expression for the isothermal change of entropy of nth mole of an ideal gas from an initial volume of V_1 to a final volume of V_2 . [[CO4](IOCQ)]
 (c) A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity? (mass of electron = 9.11×10^{-31} kg; $h = 6.625 \times 10^{-34}$ J s). [CO4/IOCQ]
 (d) Calculate (i) wave number and (ii) frequency of a yellow radiation having wavelength 580 nm. [[CO4](IOCQ)]
 (e) CO_2 does not have a permanent dipole moment but it is IR active. Explain. [CO5/IOCQ]
2 + 2 + 3 + 3 + 2 = 12
3. (a) Calculate the entropy of mixing 1 mole of N_2 and 2 moles of CO_2 gas, assuming that no chemical reaction occurs and the gas mixture behave ideally. [CO5/HOCQ]
 (b) Derive the energy expression for particle in one dimensional box. [CO4/LOCQ]
 (c) Gibbs free energy is given by $G = H - TS$. Starting from this equation, explain what is meant by G, and using the condition that $\Delta G = 0$ at Liquid \rightleftharpoons Vapour equilibrium, derive the Clapeyron-Clausius equation. [[CO4](IOCQ)]
 (d) On passing monochromatic light through a 0.04 (M) solution in a cell of 2 cm thickness, the intensity of the transmitted light was reduced to 20%. Calculate the molar extinction coefficient. [CO5/HOCQ]
2 + 3 + (2 + 3) + 2 = 12

Group - C

4. (a) The bond angle $\angle HPH$ (93.3°) in PH_3 is less than $\angle FPF$ (97.8°) in PF_3 though both have the similar molecular structure. Explain with the help of VSEPR theory. [[CO2](IOCQ)]
 (b) Define solubility product (K_{sp}) for a sparingly soluble salt. If s is the solubility of calcium phosphate then express the K_{sp} of this salt in terms of s. [CO2/IOCQ]

- (c) Atomic radius of Zr(Z=40) is 159pm, which is less than the atomic radius of Hf(Z=72) 156pm, though the reverse is expected. Justify your answer. [CO2/IOCQ]
- (d) Explain the working mechanism of a basic buffer solution. [(CO2)(LOCQ)]
- (e) Draw the molecular orbital energy level diagram of HF molecule and explain its dipolar character using MOT. [CO2 / IOCQ]
- 2 + 3 + 2 + 2 + 3 = 12**
5. (a) Compare the electro-negativity values of Ga and Al. [CO2/LOCQ]
- (b) Evaluate the Slater's Z^* for 4s electrons of K (Z=19) and Cu (Z=29). Predict which of the 4s electrons has higher ionisation energy? [CO2/HOCQ]
- (c) Calculate the pH of pure water at 100°C, given K_w of pure water at 100°C is 56×10^{-14} . [CO2/HOCQ]
- (d) Why does conductance of a semiconductor increase with increase in temperature? [(CO2)(IOCQ)]
- (e) What is degree of hydrolysis of salt? Derive an expression for the 'degree of hydrolysis' and 'hydrolysis constant' of a salt of strong acid and weak base. [(CO2)(IOCQ)]
- 2 + 3 + 2 + 2 + 3 = 12**

Group - D

6. (a) Consider a 1st order reaction which gets 20% completed in 10 minutes. What will be the time taken by the reaction be 80% completed. [CO1/HOCQ]
- (b) Justify the following:
 (i) Mobility of Cs^+ > Mobility of Li^+ in aqueous electrolyte.
 (ii) 'Electrophoretic' effect retards the speed of ions in solution. [CO1/IOCQ]
- (c) Consider the two electrode reactions occurring at 25°C:
 Anode (oxidation): $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + e$ ($E^0_{\text{Fe}^{2+} / \text{Fe}^{3+}} = -0.77 \text{ V}$) and Cathode (reduction): $\text{Ag}^+(\text{aq}) + e \rightarrow \text{Ag}(\text{s})$ ($E^0_{\text{Ag}^+ / \text{Ag}} = 0.80 \text{ V}$). Write down the overall reaction, full cell Nernst equation and calculate the equilibrium constant of the overall reaction. [CO1/HOCQ]
- (d) Explain the role of probability factor (P) in Collision theory. [CO1/IOCQ]
- 3 + (1½ + 1½) + (1 + 1 + 2) + 2 = 12**
7. (a) Given that at 18°C, equivalent conductance of AgNO_3 is 115.8 mho cm^2 and transport number of Ag^+ ion is 0.466. Calculate ionic conductance and mobility of Ag^+ and NO_3^- ions. [CO1/HOCQ]
- (b) Give a schematic representation of $\text{H}_2\text{-O}_2$ fuel cell using polymer electrolyte membrane (PEM) in acid medium. [CO1/HOCQ]
- (c) Give account of the electrodes and electrolyte of lead-acid storage cell and the charging-discharging reaction occurring during the cell operation. [CO1/IOCQ]
- (d) For thermal decomposition of Nitrous oxide at 1125 K and 1085 K, the rate constants values are 5.16×10^4 and 3.76×10^3 respectively. Calculate the activation energy for the reaction in cal/mol (Given $R = 1.988 \text{ Cal/mol/K}$). [(CO3)(HOCQ)]
- 4 + 3 + 3 + 2 = 12**

Group - E

8. (a) Arrange and comment on the order of dipole moment in the molecules: CH₃F, CH₃Cl, CH₃Br and CH₃I. [[CO6](IOCQ)]
 (b) Define simple axis of symmetry. Identify the rotational axis of proper fold and the total number of σ planes present in chloroform molecule. [[CO6](IOCQ)]
 (c) Depict the synthetic route, uses and side effects of Ibuprofen. [[CO6](IOCQ)]
 (d) Predict the aromaticity of cyclobutadiene and cyclooctatetraene. [CO6/LOCQ]
2 + (2 + 2) + (2 + 1 + 1) + 2 = 12
9. (a) Identify the final product obtained when ethylene is treated with cold dilute alkaline KMnO₄. Explain mechanistically indicating the intermediate compound. [[CO6](HOCQ)]
 (b) S_N1 mechanism proceeds through racemisation whereas S_N2 mechanism proceeds through inversion in configuration of the product — Explain. Predict the major product obtained from the following reaction:
[CO6/HOCQ]
 (c) Draw all the possible stereoisomers for butane-2, 3-diol. Analyze their optical properties on the basis of symmetry elements. [CO6/IOCQ]
 (d) Assign R, S notation of the chiral centres (*) following compounds. [[CO6](IOCQ)]

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

Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	11.45	56.25	32.29

Course Outcome (CO):

After the completion of the course students will be able to learn about the topic and apply in their respective fields: The subject code CHEM1001 corresponds to chemistry theory classes for the first year B. Tech students, which is offered as Engineering Chemistry and is common for all branches of engineering subjects. The course provides basic knowledge of theory based subjects like quantum mechanics, thermodynamics, reaction dynamics, electrochemistry, structure and reactivity of molecules with the following outcome:

1. Knowledge of understanding the operating principles and reaction involved in batteries and fuel cells and their application in automobiles as well as other sectors to reduce environmental pollution.
2. An ability to analyse microscopic chemistry in terms of atomic and molecular orbitals and intermolecular forces for engineering applications.
3. Have knowledge of synthesizing nano materials and their applications in industry, carbon nano tube technology is used in every industry now-a-days.
4. Understanding of bulk properties and processes using thermodynamic considerations.
5. Elementary knowledge of IR, UV, NMR and X-ray spectroscopy is usable in structure elucidation and characterisation of various molecules.
6. Knowledge of electronic effect and stereochemistry for understanding mechanism of the major chemical reactions involved in synthesis of various drug molecules.

*LOCQ: Lower Order Cognitive Question; IOCQ: Intermediate Order Cognitive Question; HOCQ: Higher Order Cognitive Question.