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Total Number of Pages: 03

Course: B.Tech/IDD  
Sub\_Code: 23BS1003

1<sup>st</sup> Semester Regular/Back Examination: 2025-26

SUBJECT: Chemistry

BRANCH(S): ECE, EE, AE, AEIE, AERO, AG, AIML, AUTO, BIOMED, BIOTECH, CHEM, CIVIL, CS, CSE, CSE(CS), CSEAI, CSEAIML, CSEDS, CSEIOT, CSIT, CST, CST, ECE, EEE, ELECTRICAL, ELECTRICAL & C.E, ELECTRONICS & C.E, ETC, IT, MECH, METTA, MINERAL, MINING, MME

Time: 3 Hours

Max Marks: 100

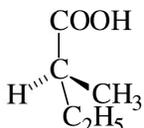
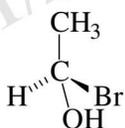
Q.Code: U582

Answer Q1 (Part-I) which is compulsory, any eight from Part-II, and any two from Part-III.  
The figures in the right-hand margin indicate marks.

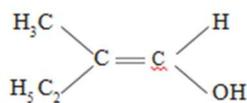
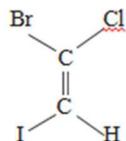
Part-I

Q1 Answer the following questions: (2 x 10)

- An element 'X' has a very high ionization energy and a highly negative electron affinity. Predict its most common oxidation state and its character (metallic/non-metallic) without naming the element.
- Compare the polarizability of the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions. Using this concept, predict, and justify the trend in the melting points of their silver salts ( $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ )
- A certain reaction is exothermic ( $\Delta H < 0$ ) but results in a decrease in the disorder of the system ( $\Delta S_{\text{sys}} < 0$ ). Under what temperature condition can this reaction still be spontaneous? Justify using a free energy argument.
- The entropy of a substance increases during the phase transition from ice to liquid water at  $0^\circ\text{C}$ . Identify the two primary physical reasons for this increase.
- Calculate the number of vibrations in carbon dioxide molecule. Explain why one of the vibrations in this molecule is infra-red inactive.
- Calculate the vibrational absorption frequency of the carbonyl ( $>\text{C}=\text{O}$ ) group, if the force constant for the double bond is  $1 \times 10^6$  dynes  $\text{cm}^{-1}$ .
- Differentiate between chromophore and auxochrome with examples.
- Give one similarity and one difference between meso compounds and racemic mixture with one example.
- Assign the R, S configurations of the following compounds:



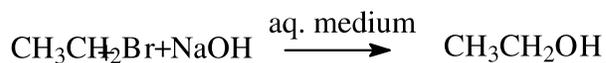
- Assign E and Z nomenclature to the following compounds



Part-II

Q2 Only Focused-Short Answer Type Questions- (Answer Any Eight out of Twelve) (6 x 8)

- a) I. Define "penetration effect" and "shielding effect." With the help of an energy level diagram, explain why, for  $n = 4$ , the orbital energy order is  $4s < 4p < 4d < 4f$ , but the filling order for the first few elements is  $4s \rightarrow 3d \rightarrow 4p$ .
- II. Write the electronic configurations of the following species and justify the anomalies in their ground state:
- Chromium (Cr,  $Z = 24$ )
  - Copper (Cu,  $Z = 29$ )
- III. How do these anomalous configurations directly influence the common oxidation states exhibited by chromium and copper in their compounds?
- b) State Fajans' Rules. Define polarizing power and polarizability. List the factors affecting each. Apply these concepts to compare and explain the following observed trends:
- The thermal stability order:  $\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}$ .
  - The solubility order in water:  $\text{AgF}$  (highly soluble)  $> \text{AgCl} > \text{AgBr} > \text{AgI}$  (highly insoluble).
  - The melting point order:  $\text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$ .
- c) I. Show that a thermodynamically irreversible process is always accompanied by an increase in entropy of the system and surroundings taken together.
- II. Calculate the entropy change when 1 mole of an ideal gas is heated from  $20^\circ\text{C}$  to  $40^\circ\text{C}$  at a constant pressure. The molar heat at constant pressure of the gas over this temperature range is  $6.189 \text{ cal deg}^{-1}$ .
- d) I. Show that
- $$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$
- II. For the following reaction,  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ , the value of enthalpy change and free energy change are  $-68.32$  and  $-56.69 \text{ kcal}$  respectively at  $25^\circ\text{C}$ . Calculate the value of free energy change at  $30^\circ\text{C}$ .
- e) Define vibrational frequency. Explain in detail the various factors affecting the vibrational frequency of the molecules.
- f) Explain in detail the various transitions taking place in UV-visible spectroscopy. Explain the effect of polarity of the solvent on each of these transitions.
- g) The pure rotational spectrum of gaseous  $^1\text{H}^{35.5}\text{Cl}$  shows a series of equally spaced spectral lines separated by  $20.80 \text{ cm}^{-1}$ . Calculate the bond length of the HCl.
- h) Discuss the formation, structure, and stability of carbocations.
- i) Compare and contrast  $S_N1$  and  $S_N2$  reactions with suitable example.
- j) Define enantiomers and diastereomers. Explain with the help of 2-bromo-3-chlorobutane.
- k) Define conformational isomerism. Draw the potential energy diagram for the various conformations of  $n$ -butane.
- l) Give mechanism and stereochemistry of the following reaction:



### Part-III

#### Only Long Answer Type Questions (Answer Any Two out of Four)

- Q3** a) Explain how effective nuclear charge ( $Z_{\text{eff}}$ ) arises from the combined effects of actual nuclear charge and electron shielding. How do the concepts of orbital penetration and the relative energies of s, p, d, and f orbitals for a given principal quantum number (n) logically follow from this understanding? Use this to justify why, for example, the 4s orbital is filled before the 3d orbital in the first-row transition metals. (5)
- b) Derive the following relations (6)
- $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
- $$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$
- c) Calculate the entropy of mixing of 1 mole of  $\text{N}_2$  and 2 moles of  $\text{O}_2$ , assuming the gases to be ideal. Express the result in S.I. units. (5)
- Q4** a) Write Beer-Lambert's Law. Derive the expression for the absorbance of a homogeneous absorbing solution based on the application of this law. (6)
- b) Calculate the molar absorptivity of a  $0.5 \times 10^{-3}$  M solution, which has an absorbance of 0.17, when the path length is 1.3 cm. (2)
- c) Discuss the theory of electronic spectroscopy. Give the various types of transitions involved in this technique with one example in each case. (8)
- Q5** a) Give a note on the conformations of cyclohexane and their stability. (6)
- b) Considering the example of tartaric acid and explain the following terms (i) enantiomer, (ii) diastereomers, (iii) mesomers, (iv) Racemic Mixture (6)
- c) List the basic requirements for a molecule to show (i) Geometrical isomerism, and (ii) Optical isomerism. (4)
- Q6** Discuss the following reaction and detailed mechanism with one suitable organic reaction example each that involves: (4 x 4)
- Nucleophilic substitution via carbocation intermediate.
  - Addition reaction involving a free radical intermediate.
  - Elimination reaction generating a carbanion intermediate.
  - Electrophilic Substitution reaction