

2025

CHEMISTRY — HONOURS

Paper : DSCC-1

(Fundamentals of Chemistry - I)

Full Marks : 75

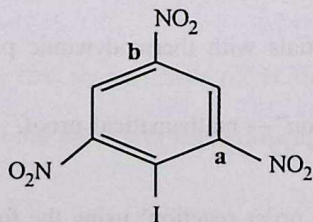
*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*

Answer *question nos. 1, 2, 3, 4* (compulsory) and
any four questions from the rest (*question nos. 5 to 10*).

1. Answer *any ten* questions :

2×10

- (a) Write down l and m_l values of p_z and d_{z^2} orbitals.
- (b) Arrange isomeric pentanes with increasing order of boiling points and explain.
- (c) Show that for an ideal gas $P - V$ curve for adiabatic reversible process is steeper than the same for isothermal reversible one.
- (d) State the hypothesis of de Broglie and explain the terms.
- (e) Draw the orbital picture HOMO of 1, 3-butadiene molecule in the first excited state showing nodes.
- (f) "The reversible work of compression is minimum"—Justify or criticize (graphically).
- (g) Write the significance of :
 - (i) Principal quantum number
 - (ii) Azimuthal quantum number.
- (h) Which C – N bond (**a** or **b**) has a higher bond length and why?



- (i) Find the order of a reaction $A \rightarrow \text{Product}$, for which the half-life is doubled as the initial concentration of A is doubled.

Please Turn Over

(5629)

- (j) Draw the shapes of (i) $d_{x^2-y^2}$ and (ii) d_{xy} orbitals.
- (k) Distinguish the terms with suitable examples : Chiral centre and Stereogenic centre.
- (l) "A Zero-order reaction cannot be a single-step reaction"— Explain.
2. (a) Write short note on 'Heisenberg's Uncertainty Principle' using the following points :
- Statement with mathematical expression
 - Significance (*any one*)
 - Velocity of an electron in the first Bohr orbit of H – atom is $v \text{ ms}^{-1}$. If the uncertainty in the position of electron is $5 \times 10^{-12} \text{ m}$, what is the uncertainty in velocity? (Given, mass of electron is $9.109 \times 10^{-31} \text{ kg}$). (1+1)+1+2

Or

- (b) Write short note on 'electronegativity' using the following points :
- Definition
 - Difference with electron affinity
 - Trends of variation in group 15. 2+1+2
3. (a) Write short note on 'Resonance' using the following points :
- The criteria for drawing resonating structures of an organic molecule.
 - Resonating structures of phenol and phenoxide ion. Indicate which one is more stable.
 - Definition of 'Resonance Energy'. 2+2+1

Or

- (b) Write short note on 'asymmetric' and 'disymmetric' molecules using the following points :
- Criteria for a molecule to be asymmetric with an example.
 - Criteria for a molecule to be disymmetric with an example. 2½+2½
4. (a) Write short note on exact and inexact differentials using the following points :
- Criteria
 - Correlation of exact and inexact differentials with thermodynamic path function and state function.
 - "Pressure of an ideal gas is a state function"— mathematical proof. (1+1)+1+2

Or

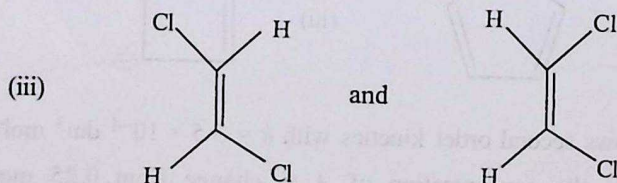
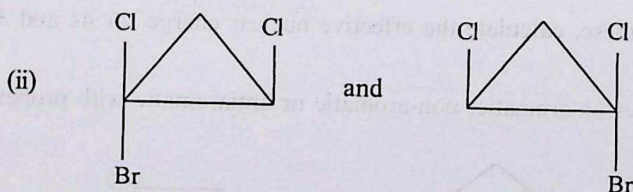
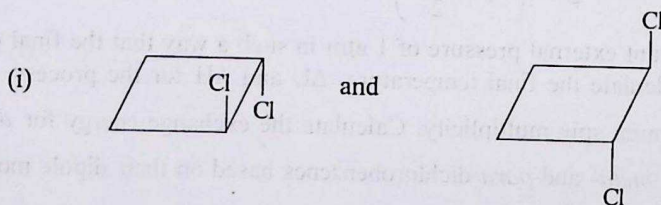
- (b) Write short note on 'Half-life period of an n -th order reaction' using the following points :
- Derivation of $t_{\frac{1}{2}}$ of an n -th order reaction.

(ii) Ratio of $t_{\frac{1}{2}}$ and $t_{\frac{3}{4}}$ for an n -th order reaction.

(iii) Significance of the above ratio.

3+1+1

5. (a) What is 'inert pair effect'? Using this principle, explain the strong oxidizing property of sodium bismuthate (NaBiO_3).
- (b) Label the following molecules as enantiomers or diastereomers with explanation.



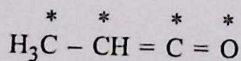
(c) Prove that :

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

Hence, show that for one mole of an ideal gas, $C_P - C_V = R$.

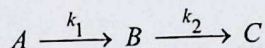
4+3+3

6. (a) Draw the orbital picture of the following compound and indicate the hybridization state of marked (*) atoms.



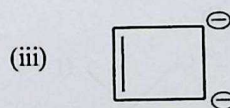
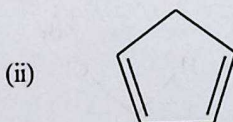
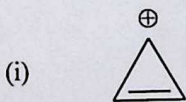
Please Turn Over

- (b) Consider the following first order consecutive reaction :



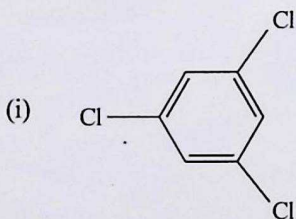
Determine the concentration of B at time ' t '. Given, at $t = 0$, $[A] = [A]_0$ and $[B] = [C] = 0$.

- (c) Compare the penetrating ability of 4s and 3d orbitals by drawing qualitatively the radial probability distribution curves of the orbitals. 4+3+3
7. (a) One mole of a monatomic ideal gas $\left(\overline{C_V} = \frac{3}{2}R\right)$ at 80°C and 5 atm pressure is expanded adiabatically against a constant external pressure of 1 atm in such a way that the final pressure of the gas becomes 1 atm. Calculate the final temperature, ΔU and ΔH for the process.
- (b) State Hund's rules of maximum spin multiplicity. Calculate the exchange energy for d^6 system.
- (c) Distinguish between *ortho*-, *meta*- and *para*-dichlorobenzenes based on their dipole moments with proper justification. 4+3+3
8. (a) State Slater's rules and using these, calculate the effective nuclear charge for 4s and 3d electron in Zn-atom ($Z = 30$).
- (b) Classify the following molecules as aromatic, non-aromatic or antiaromatic with proper reasons.



- (c) A reaction ($2A \rightarrow \text{Product}$) follows second order kinetics with $k = 3.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Calculate the time required for the concentration of A to change from 0.25 mol dm^{-3} to 0.01 mol dm^{-3} . 4+3+3
9. (a) Draw all the π -MOs (orbital picture) of benzene. Identify the HOMO and LUMO in the diagram.
- (b) Justify or criticize the following statements :
- (i) A system must be isolated if neither heat nor matter can enter or leave the system.
- (ii) $\Delta H = q$ for a process in which P is not constant throughout, but for which the final and initial pressures are equal.
- (c) Comment on relative radii of O^{2-} , F^- , Na^+ and Mg^{2+} . 4+(1+2)+3

10. (a) Find the value of $\left(\frac{\partial U}{\partial V}\right)_T$ for one mole of (i) an ideal gas (ii) van der Waal's gas. Explain the results qualitatively.
- (b) Calculate Pauling's electronegativity of hydrogen (H) atom from the following data —
Bond energies (kJ mol^{-1}) : H_2 (458), F_2 (155), HF (565) and Pauli's electronegativity of F = 4.0.
- (c) Indicate symmetry elements present in the following molecules :



- (ii) (*E*)-1, 2-dichloroethane.

(1+1+2)+3+3
