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.

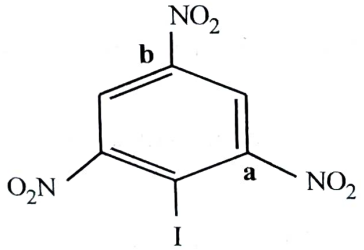
(f) "The reversible work of compression is minimum"— Justify or criticize (graphically).

(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 $A \rightarrow$ Product, for which the half-life is doubled as the initial concentration of A is doubled.

(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 :

(i) Statement with mathematical expression

(ii) Significance (*any one*)

(iii) Velocity of an electron in the first Bohr orbit of H – atom is v ms^{-1}. If the uncertainty in the position of electron is 5×10^{-12} m, what is the uncertainty in velocity? (Given, mass of electron is 9.109×10^{-31} kg). (1+1)+1+2

Or

(b) Write short note on 'electronegativity' using the following points :

(i) Definition

(ii) Difference with electron affinity

(iii) Trends of variation in group 15. 2+1+2

3. (a) Write short note on 'Resonance' using the following points :

(i) The criteria for drawing resonating structures of an organic molecule.

(ii) Resonating structures of phenol and phenoxide ion. Indicate which one is more stable.

(iii) Definition of 'Resonance Energy'. 2+2+1

Or

(b) Write short note on 'asymmetric' and 'disymmetric' molecules using the following points :

(i) Criteria for a molecule to be asymmetric with an example.

(ii) 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 :

(i) Criteria

(ii) Correlation of exact and inexact differentials with thermodynamic path function and state function.

(iii) "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 :

(i) Derivation of $t_{\frac{1}{2}}$ of an *n*-th order reaction.

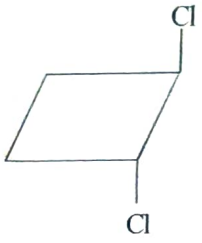
(ii) Ratio of $t_{\frac{1}{2}}$ and $t_{\frac{3}{4}}$ for an n-th order reaction.

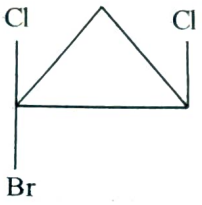
(iii) Significance of the above ratio. 3+1+1

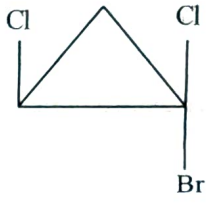
5. (a) What is 'inert pair effect'? Using this principle, explain the strong oxidizing property of sodium bismuthate ($NaBiO_3$).

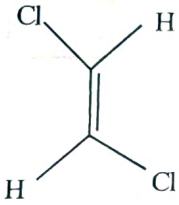
(b) Label the following molecules as enantiomers or diastereomers with explanation.

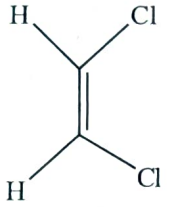
(i) 

and


(ii) 

and


(iii) 

and


(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.

$$\overset{*}{H_3C} - \overset{*}{CH} = \overset{*}{C} = \overset{*}{O}$$

Please Turn Over

(b) Consider the following first order consecutive reaction :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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.

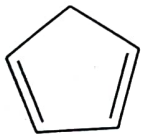
(b) State Hund's rules of maximum spin multiplicity. Calculate the exchange energy for d^6 system.

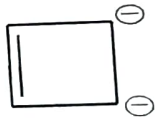
(c) Distinguish between *ortho*-, *meta*- and *para*-dichlorobenzenes based on their dipole moments with proper justification. 4+3+3

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.

(i) 

(ii) 

(iii) 

(c) A reaction ($2A \rightarrow$ Product) follows second order kinetics with $k = 3.5 \times 10^{-4}$ dm^3 mol^{-1} 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

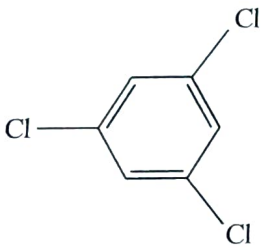
10. (a) Find the value of $\left(\frac{\partial U}{\partial V}\right)_T$ for one mole of (i) an ideal gas (ii) van der Waal's gas. Explain the results qualitatively.

(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 :

(i)



(ii) (*E*)-1, 2-dichloroethane. (1+1+2)+3+3
