

2025

## CHEMISTRY — HONOURS

Paper : DSCC-1

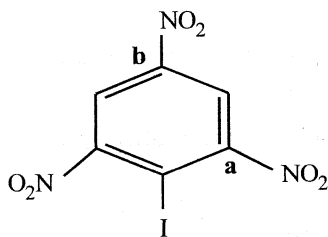
(Fundamentals of Chemistry - I)

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

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



- 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.  $2\frac{1}{2}+2\frac{1}{2}$
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.

(3)

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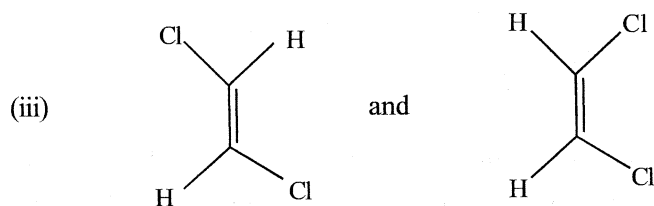
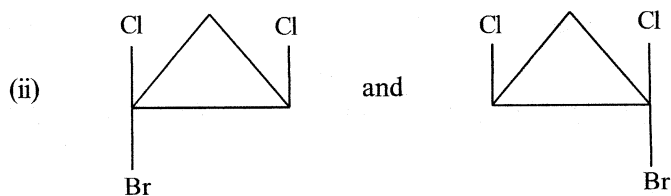
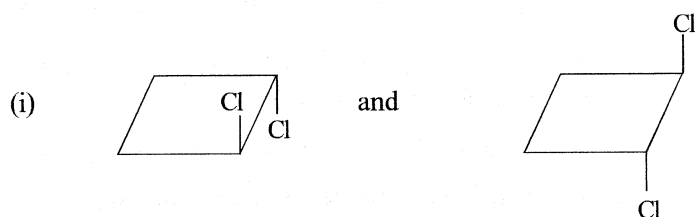
(ii) Ratio of  $t_{\frac{1}{2}}$  and  $t_{\frac{3}{4}}$  for an  $n$ -th order reaction.

(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 ( $\text{NaBiO}_3$ ).

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



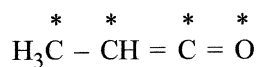
(c) Prove that :

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

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

4+3+3

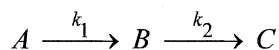
6. (a) Draw the orbital picture of the following compound and indicate the hybridization state of marked (\*) atoms.



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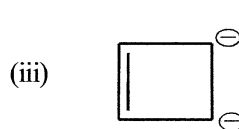
- (b) Consider the following first order consecutive reaction :



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

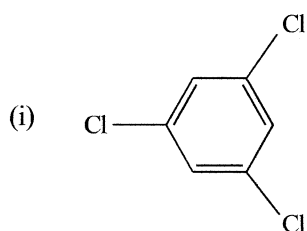
- (c) Compare the penetrating ability of 4s and 3d orbitals by drawing qualitatively the radial probability distribution curves of the orbitals. 4+3+3

7. (a) One mole of a monatomic ideal gas  $\left(\overline{C_V} = \frac{3}{2}R\right)$  at  $80^\circ\text{C}$  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,  $\Delta U$  and  $\Delta H$  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  $0.25 \text{ mol dm}^{-3}$  to  $0.01 \text{ mol dm}^{-3}$ . 4+3+3
9. (a) Draw all the  $\pi$  - 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  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . 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 ( $\text{kJ mol}^{-1}$ ) :  $\text{H}_2$  (458),  $\text{F}_2$  (155),  $\text{HF}$  (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

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