

2024

CHEMISTRY — HONOURS

Paper : DSCC-1

(Fundamentals of Chemistry - 1)

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) Electron affinity of fluorine is less than that of chlorine. Justify.
- (b) Depict the symmetry elements present in the following molecules in terms of plane of symmetry (σ) and simple axis of symmetry (C_n) :
 - (i) Chloroform
 - (ii) *trans*-1, 2-dichloroethene.
- (c) Classify the following properties as state or path functions :
 - (i) Heat, (ii) Enthalpy, (iii) Internal Energy, (iv) Work.
- (d) Calculate the number of radial nodes of $4d$ subshell of an atom.
- (e) 1, 3-Butadiene is a conjugated diene while 2, 3-ditertiarybutyl-1, 3-butadiene behaves as a non-conjugated diene. Explain.
- (f) Calculate the difference between C_P and C_V of one mole of an ideal gas using the following expression :

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

[where all the terms have their usual significance.]

- (g) Tl (III) is stronger oxidising species than Al (III). Justify.
- (h) Butan-2, 3-dione exhibits less dipole moment than 1, 2-cyclopentadione. Why?
- (i) How $t_{1/2}$ of a zero order reaction is related to initial concentration of the reactant?
- (j) What information are conveyed by magnetic quantum number?

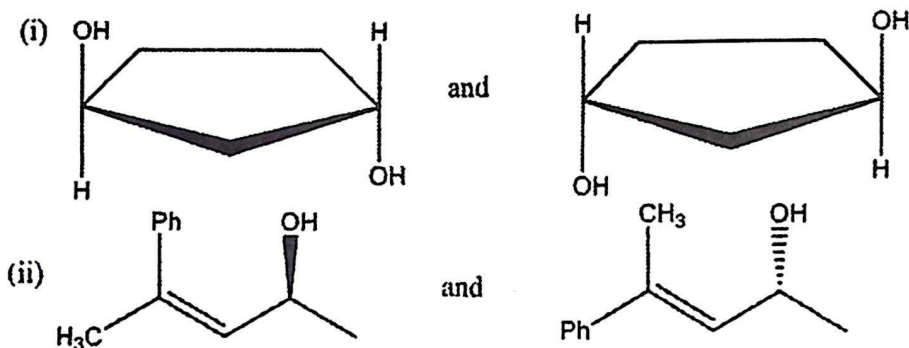
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(1181)

- (k) A compound has molecular formula $C_7H_6O_2$. Calculate its DBE. If the compound produces effervescence with saturated $NaHCO_3$ solution, then predict the structure of the compound.
- (l) Define pseudounimolecular reaction. Give an example.
2. (a) (i) State Pauli's Exclusion principle. Using the principle, show that the maximum capacity of accommodating electrons in 3d subshell is 10.
- (ii) Find the minimum value of azimuthal quantum number (l) that allows 'g' subshell to exist. Identify the subshell. 3+2

Or,

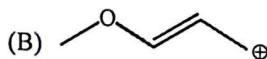
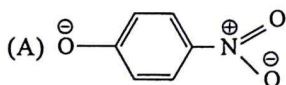
- (b) Write down the mathematical expressions of Pauling, Mulliken and Allred-Rochow electronegativity scales mentioning the significance of each term. Which among the three scales is most acceptable and why? 3+2
3. (a) Define : Enantiomers and diastereomers with an example of each. Label the following pair of structures as enantiomers/diastereomers :



3+2

Or,

- (b) (i) Three isomeric pentanes have b.p. $9.5^\circ C$, $28^\circ C$, $36^\circ C$. Match each b.p. with the correct one with reason.
- (ii) Draw all the possible canonical forms for the following species indicating the most important contributor of the resonance hybrid. Justify your answer. 3+2



4. (a) Derive the relation between pressure and temperature of one mole of an ideal gas undergoing reversible adiabatic expansion, indicating proper usage of all the assumptions. 5

Or,

- (b) (i) For a first order opposing reaction $A \xrightleftharpoons[k_2]{k_1} B$, find out the final expression of k_1 , in terms of equilibrium concentration of 'B' (x_{eq}).
- (ii) Draw the concentration vs time curves for the above reaction. 3+2

5. (a) Compare the ionisation energy and atomic radii of ferrous and ferric ions with proper reason.
- (b) Arrange the following compounds in order of their increasing dipole moments with proper explanation :
- (i) H_3C-CH_2-Cl ; (ii) $H-C \equiv C-Cl$; (iii) $H_2C=CH-Cl$.
- (c) One mole of Helium gas kept at 300 K and 10 atm expands to 1 atm. Assuming the gas to be ideal, calculate the work done if the process is carried out through—
- (i) Reversible isothermal way,
- (ii) Irreversible isothermal way against a constant external pressure of 1 atm.

Interpret the results obtained.

4+3+3

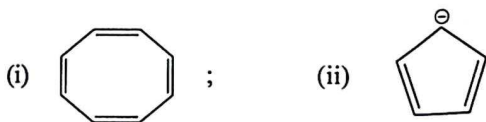
6. (a) Draw the π -MOs for (i) ψ_2 for allyl cation; (ii) ψ_4 for pentadienyl anion. Indicate the number of nodes and electronic arrangement in each case.
- (b) "Work done involving one mole of an ideal gas in any reversible isothermal expansion process is always greater than its irreversible analogue." Justify it mathematically.
- (c) Suppose an electron is confined within a nucleus of diameter 10^{-14} m. Find the uncertainty in determination of its velocity. Hence, show that the electron can never reside inside the nucleus. (Given the mass of electron = 9.1×10^{-31} kg). 4+3+3
7. (a) The first order rate constant (K) for the decomposition of a gaseous substance follows the equation :

$$\log K \left(\text{min}^{-1} \right) = 33.91 - \frac{1800}{T}$$

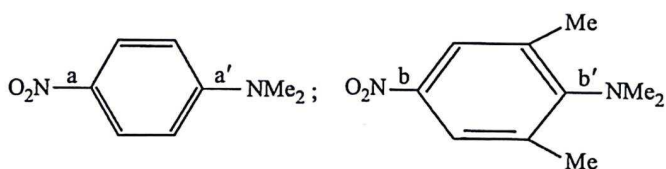
- (i) How long will it take for one mole to decompose 75% at 227°C?
- (ii) Calculate the energy of activation.
- (b) State the $(n + l)$ rule. Using this rule, arrange the following subshells in increasing order of energy :
- 4f, 5d, 6s, 6p.
- (c) Draw the Fischer projection formulae for all the possible stereoisomers of 2, 3, 4-trihydroxypentane. Comment on the stereogenicity of C-3 centre of any one active isomer and one mesoisomer. 4+3+3

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8. (a) 'Every wave function obtained from the solutions of Schrödinger equation cannot represent an orbital.' Justify the statement mentioning the acceptability conditions of the wave functions.
- (b) Comment on aromatic, antiaromatic or nonaromatic nature of the following compounds with proper reason :



- (c) A second-order reaction in which initial concentrations of both the reactants are same, gets 25% completed in 600 seconds. How long will it take to go to 70% completion? 4+3+3
9. (a) (i) Draw the structure of a compound possessing a stereocentre.
 (ii) Write the IUPAC name of $\text{H}-\text{C}(\text{CN})_3$.
 (iii) Give example of a non-aromatic molecule.
 (iv) Give example of a dissymmetric molecule.
- (b) Show that for an ideal gas, its internal energy is not a function of its volume, i.e. $\left(\frac{\partial u}{\partial v}\right)_T = 0$.
- (c) Electronegativity of germanium (Ge) is more than that of silicon (Si). — Explain. 4+3+3
10. (a) 1 mole of a monoatomic ideal gas is allowed to expand adiabatically and reversibly from 22.7 L at 1 bar and 0°C to a volume of 48.4 L. Calculate the final temperature and work done in this process.
- (b) Define ionisation energy. Between Li^\oplus and He, which one has greater ionisation energy? — Explain.
- (c) Compare the C–N bond lengths (a versus a') and (b versus b') in the following compounds with proper explanation :



4+3+3