# 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**).

2×10

**1.** Answer ***any ten*** questions :

(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 4*d* 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 $t_{½}$ of a zero order reaction is related to initial concentration of the reactant?

(j) What information are conveyed by magnetic quantum number?

(k) A compound has molecular formula $C_7H_6O_2$. Calculate its DBE. If the compound produces effervesence 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.

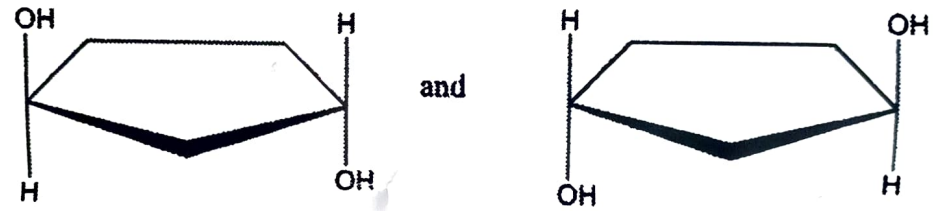
(ii) Find the minimum value of azimuthal quantum number ($l$) that allows 'g' subshell to exist. Identify the subshell. 3+2

***Or,***

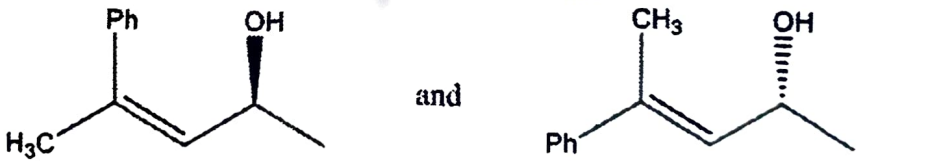
(b) Write down the mathematical expressions of Pauling, Mulliken and Allred-Rochow electronegativity scales mentioning the significance of each term. Which among the three scales is most acceptable and why? 3+2

3. (a) Define : Enantiomers and diastereomers with an example of each. Label the following pair of structures as enantiomers/diastereomers :

(i)




(ii)



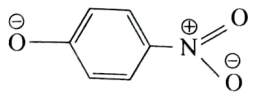

3+2

***Or,***

(b) (i) Three isomeric pentanes have b.p. 9.5°C, 28°C, 36°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

(A)



(B)

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 $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, 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) $\psi_2$ for allyl cation; (ii) $\psi_4$ 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 = $9.1 \times 10^{-31}$ 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 :

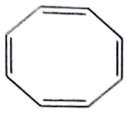
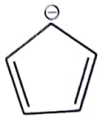
$4f$, $5d$, $6s$, $6p$.

(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 *meso*isomer. 4+3+3

**Please Turn Over**

**8.** (a) 'Every wave function obtained from the soultions of Schrödinger equation cannot represent an orbital.' Justify the statement mentioning the acceptibility conditions of the wave functions.

(b) Comment on aromatic, antiaromatic or nonaromatic nature of the following compounds with proper reason :

(i)  ; (ii) 

(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 $H-C(CN)_3$.

(iii) Give example of a non-aromatic molecule.

(iv) Give example of a dissymmetric molecule.

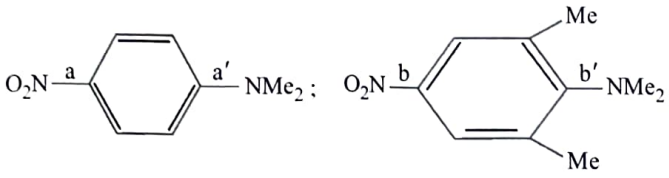
(b) Show that for an ideal gas, its internal energy is not a function of its volume, i.e. $\left(\frac{\partial u}{\partial v}\right)_T = 0$.

(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