

RANI RASHMONI GREEN UNIVERSITY

DEPARTMENT OF CHEMISTRY

Semester – I, Final Examination – 2025

M.Sc. Course in Chemistry

Course ID: CHEM-C13

Full Marks: 40

Time: 2 h

Answer **any one** question from **each unit** in your own words with proper scientific justification.

Unit-1: Atomic Structure

1. a) Explain the normal Zeeman effect and derive the expression for the Zeeman splitting in weak magnetic fields.
b) What is the anomalous Zeeman effect? How does it differ from the normal Zeeman effect?
c) Define spin-orbit interaction and explain its significance in atomic structure.
d) What is the fine structure in atomic spectra? [3+2+2+1=8]

2. a) Derive the expression for Lande g-factor and explain its significance in atomic transitions.
b) Discuss the effect of a high magnetic field on atomic energy levels.
c) Explain the concept of atomic terms and their notation.
d) What is meant by the term "fine structure constant"? [3+2+2+1=8]

Unit 2: Quantum Mechanics-1

3. (a) Which of the following functions are acceptable? Give explanation of your answer.

(i) $\psi = \tan x$ (ii) $\psi = e^{-x^2}$

- (b) Prove that the non-degenerate eigenfunctions of a Hermitian operator are orthogonal.

(c) Normalize the wave function $\Psi_\varphi = e^{im\varphi}$ (0,2 π) [3 + 3 + 2=8]

4. (a) Evaluate the commutators $[\hat{x}^2, \hat{p}_x]$ using $[\hat{x}, \hat{p}_x] = i\hbar$.

(b) "If ψ_1 and ψ_2 be the two degenerate solutions of the Schrödinger equation, then their linear combination $\Psi = (c_1\psi_1 + c_2\psi_2)$ is also the solution of the Schrödinger equation." — Justify

(c) Which of the following operators are linear? Give explanation of your answer.

$$(i) \hat{A}\psi = \psi^2 \quad (ii) \hat{B}\psi = \psi^* \quad [2 + 3 + 3=8]$$

Unit 3: Thermodynamics

5. a) The mean enthalpy of vaporization of water in the temperature range between 363 K and 373 K is 40824 J mol^{-1} . Calculate the vapour pressure of water at 363 K, if the given value at 373 K is 76 cm of Hg.

b) What are the Legendre transformations? If $dU=TdS-pdV$, show the following:

$$i) dH=Tds+Vdp$$

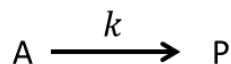
$$ii) dG=-SdT+Vdp \quad [4+4=8]$$

6. a) The vapour pressure of toluene is 0.0788 bar at 313 K and 0.398 bar at 353 K. Calculate the molar enthalpy of vaporization.

b) Show that the energy of a closed system is a state function. [4+4=8]

Unit-4: Kinetics-1

7. a) Consider an autocatalytic reaction

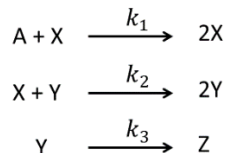


with initial concentration of A and P as $[A]_0$ and $[P]_0$. If concentrations of A and P are $[A]_0 - x$ and $[P]_0 + x$ at a time t , show that

$$\frac{x}{[P]_0} = \frac{e^{at} - 1}{1 + be^{at}}$$

where $a = ([A]_0 + [P]_0)k$ and $b = \frac{[P]_0}{[A]_0}$. Represent the result graphically.

b) The Lotke-Volterra mechanism of an oscillatory reaction is given as



Show that this mechanism leads to chemical oscillation. [4+4=8]

8. a) The current-over potential equation is given as

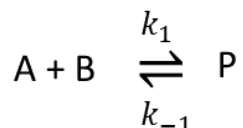
$$i = i_0 \left\{ \frac{[\text{Ox}](0,t)}{[\text{Ox}]^*} e^{-\alpha n f \eta} - \frac{[\text{Red}](0,t)}{[\text{Red}]^*} e^{-(1-\alpha) n f \eta} \right\}$$

where terms are of usual significance.

(i) Explain how this equation reduces to Butler-Volmer equation?

(ii) Under what condition it reduces to Tafel equation?

b) Consider the fast reaction



The initial concentration of A and B are a and b , respectively. Show that the expression of relaxation time $\tau = \frac{1}{k_1([A]_{eq} + [B]_{eq}) + k_{-1}}$ where $[A]_{eq}$ and $[B]_{eq}$ are the equilibrium concentrations of A and B, respectively. [(2+2)+ 4=8]

Unit-5: Absorption Spectroscopy

9. a) For a two-level transition, derive the following relation using Einstein model

$$\frac{A_{mn}}{B_{mn}} = \frac{8h\pi\nu^3}{c^3}$$

(Terms have the usual meaning)

b) For electric dipole transition, $g \rightarrow g$ or $u \rightarrow u$ is forbidden, but $g \rightarrow u$ or $u \rightarrow g$ is allowed. Explain using symmetry argument.

c) What are the possible causes of error in the optical density measurement in a single beam absorption spectrophotometer? [3+3+2=8]

10. a) For a double beam absorption spectrophotometer show that Optical Density (OD) = $A_S - A_R = \log(I_R/I_S)$, (Terms have usual meaning. S and R refer to sample and reference).

b) Write the instrumental components and their function in a double beam absorption spectrophotometer.

c) Explain: -i) Spin forbidden transition, ii) Charge Transfer transition.