B. Sc. CHEMISTRY EXAMINATION, 2025

(5th Semester)

CHEMISTRY (CORE)

PAPER : CORE 14

Time : *Two Hours* *Full Marks* : 40

(*20 marks for each Unit*)

Use a separate answer script for each Unit.

The figures in the margin indicate full marks.

UNIT—5141-I

Answer ***all*** questions.

1. *(a)* For a mechanistic scheme of a reaction

$A + B \rightleftharpoons C$ (Equilibrium Constant K)

$C \rightarrow$ Products (Rate Constant k)

Here, with the initial condition $[B]_0 \gg [A]_0$, how could you kinetically estimate K and k? 4

(b) What is/are the intrinsic difference(s) between D and I_d mechanism for a transition metal octahedral substitution reaction? Discuss. 3

(c) KCN is insoluble in benzene but in the presence of 18-Crown-6, a nucleophilic substitution takes place using CN^- as nucleophile. Justify the reaction with appropriate mechanism. 3

2. *(a)* The ν(NO) stretching frequency depends on the M—N—O angle in the nitrosyl complexes. Comment. 2

(b) What happen to υ(CO) when CO gets coordinated to BH_3 and $Ni(CO)_3$, respectively? 2

(c) Determine the number of metal-metal bonds in $(\eta^5\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)_2Fe(CO)(\eta^5\text{-}C_5H_5)$. 1

(d) Interpret the C—C and Pt—C bond distances in $Pt(C_2H_4)Cl_3$ ($d_{C—C}$, 1.37 Å, $d_{Pt—C}$, 2.55 Å) and $Pt(C_2H_4)(PPh_3)_2$ ($d_{C—C}$, 1.43 Å, $d_{Pt—C}$, 2.11 Å) and $Pt(C_2(CN)_4)(PPh_3)_2$ ($d_{C—C}$, 1.49 Å, $d_{Pt—C}$, 2.09 Å). 2½

(e) Match the υ(CO) frequency with the relevant complex with justification and comment on the nature of bonding on the nature of bonding of CO (ν_{CO} of free CO : 2143 cm^{-1}). 2½

Complex	ν(CO), cm^{-1}
$[V(CO)_6]^-$	1858
$[Cr(CO)_6]$	2000
$[Mn(CO)_6]^+$	2095

(OR)

Presence of a dielectric in a parallel plate capacitor decreases its electric field — explain.

(d) Molar polarization of a certain vapor obeys the relation $P_m(cm^3\ mol^{-1}) = 60 + \frac{20.5}{T}(K)$. Assuming ideal behavior, calculate its molar polarization, dipole moment and dielectric constant at STP.

(OR)

Outline in brief the Gouy balance method to determine the magnetic susceptibility of a substance.

1½+1½+1½+2½

★ ★ ★

UNIT—5142-P

3. *(a)* How many spectral lines are expected for 1-D SHO in the IR region? Justify your answer.

(b) Evaluate the expectation value of potential energy of the harmonic oscillator in the ground state. The ground state normalized wave-function of the harmonic oscillator is $\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{\alpha x^2}{2}\right)$, here α is a constant. 1½+2½

4. Answer *any* **three** : 3×3

(a) Verify whether the following function is an eigenfunction of 1-D SHO, $\Psi = x\exp\left(\frac{-\beta x^2}{2}\right)$, where $\beta = \frac{2\pi(mk)^{\frac{1}{2}}}{h}$, k = force constant, m = mass and h = Planck's constant.

(b) Find the probability of getting the electron for H atom in its ground state beyond the Bohr radius (a_0). Given normalized radial part of the ground state wave function, $R_{1s} = \frac{2}{a_0^{3/2}}\exp\left(-\frac{r}{a_0}\right)$.

(c) What are spherical harmonics? Verify that $\Phi_m(\phi) = \frac{1}{(2\pi)^{\frac{1}{2}}}\exp(im\phi)$ constitutes an orthonormal set for particle in a ring.

(d) Write down the Hamiltonian operator for H_2 molecule. The Ψ_{2s} atomic orbital of hydrogen atom is given as, $\Psi_{2s} = \frac{1}{(32\pi a_0^3)^{\frac{1}{2}}}\left(2-\frac{r}{a_0}\right)\exp\left(\frac{r}{2a_0}\right)$. Calculate the radius of nodal surface of H atom in SI unit.

5. *(a)* What are the various ways by which a molecule can get polarized in the presence of an electrostatic field? How are these related?

(b) Molecules with small HOMO-LUMO gaps can be polarized easily — explain.

(c) Calculate the magnitude of dipole moment of H_2O molecule (in addition to the permanent dipole moment) induced by an applied field strength of $1.0\times10^5\ V\ m^{-1}$ (given $\alpha'(H_2O) = 1.48\times10^{-30}\ m^3$ and $\varepsilon_0 = 8.854\times10^{-12}\ J^{-1}\ C^2\ m^{-1}$).