[This question paper contains 4 printed pages]

Roll No.	

ASME-24BC-CHEM-I
CHEMISTRY (PAPER-I)

Time Allowed : 3 Hours [Maximum Marks : 100

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions.

1. Question paper contains **EIGHT** questions printed in English.
2. Attempt **any FIVE** questions in all.
3. Question **No.1** is **compulsory. FOUR** questions are to be attempted out of the remaining **SEVEN** questions.
4. All questions carry equal marks. The number of marks carried by a question/ part are indicated against it.
5. Unless otherwise mentioned, symbols and notations carry their usual standard meanings.
6. Write answer in legible handwriting.
7. Each part of the question must be answered in sequence and in the same continuation. Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partially. Any page or portion of the page left blank in answer book must be clearly struck off.
8. Re-evaluation / Re-checking of answer book of the candidate is not allowed.

1. (a) Discuss the bonding between two Re atoms in octachlorodirhenate ion supported by bond energy consideration. 5

(b) The overall quantum yield for the photochemical decomposition of Cinnamic acid is 0.8 at 300 nm irradiation. How long time will it take (in minutes) to photo-decompose 1 mole of the compound under total absorption condition using a 100 W light source? 5

(c) Consider the reaction between 2-methylpropene and HBr. Draw the complete mechanism for this reaction, indicating all intermediates and transition states. Explain why the reaction follow Markonikov's rule. 5

(d) Draw a packing diagram of the perovskite A-type cell ($CaTiO_3/ABO_3$), determine the number of ABO_3 formula units, and describe the coordination geometry around each type of atom. 5

2. (a) Predict the geometry of the following lanthanide complexes: 7

(i) $[Er(NCS)_6]^{3-}$, (ii) $[Nd(H_2O)_9]^{3+}$, (iii) $[Ce(NO_3)_4(Ph_3PO)_2]$

(b) Define Joule-Thomson coefficient and show that it has a positive value for a real gas. 7

(c) How and why does the cohesive force in metals vary in a group and period in the periodic table? What physical properties are influenced by these changes in cohesive force? 6

3. (a) During nuclear explosion, one of the products is Sr-90 with half-life of 28 years. If 2 μg of Sr-90 was absorbed in the bones of a newly born baby instead of calcium, how much of Sr-90 will remain after 15 years and 75 years if it is not lost metabolically. 7

(b) Define Inversion temperature and critical temperature. Show that for a van der Waals gas, the inversion temperature is given by $T_i=2a/Rb$. 7

(c) The complexes $[Mn(H_2O)_6]^{2+}$, $[MnCl_4]^{2-}$, $[Fe(H_2O)_6]^{3+}$, and $[FeCl_4]^-$ have nearly similar magnetic moments. What does this indicate about the geometry and electronic structures of these complexes? Why is the spin-only formula so precise in these complexes? 6

4. (a) The wave function of a particle in a 1-D box with infinite wells is $\Psi=0.1\varphi_1 + 0.2\varphi_2 + 0.3\varphi_3$, where φ_1, φ_2, and φ_3 are the ground state and the first two excited states, respectively. What is the probability to observe the particle in the ground state? 7

(b) Compare the affinity of oxygen with haemoglobin and myoglobin by drawing oxygen binding curve for the both. Explain why haemoglobin has a lower affinity for oxygen than myoglobin. 7

(c) Write the relationships and differentiate between Freundlich and Langmuir adsorption isotherms. 6

5. (a) When $[Pt(NH_3)_4]^{2+}$ is allowed to stand in 0.1M HCl for many days at 30°C, no reaction is observed. Only under forcing conditions is the cation converted to trans-$[Pt(NH_3)_2Cl_2]$. However, when $[PtCl_4]^{2-}$ is treated with NH_3 it gives cis-$[Pt(NH_3)_2Cl_2]$ rapidly. Account for the difference in the rates of these two reactions. 7

(b) Give appropriate reactions when i) $NaNO_2$, ii) $Al(CH_3)_3$, iii) $NH_2C(O)NH_2$ is dissolved in ammonia. Will the solution be acidic or basic concerning the pure solvent and the solute act as a weak or a strong acid or base? 7

(c) The hydrolysis of an ester follows first-order kinetics in presence of an acid, and second-order kinetics in the presence of dilute alkali. Explain in detail. 6

6. (a) Account for the following: 7

(i) H_2O has an abnormally high boiling point compared to H_2S.

(ii) PCl_5 exist but NCl_5 does not.

(b) State and explain the term quantum yield. Account for the kinetics of the following photochemical reaction: 7

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

(c) Calculate the magnetic moments of Dy^{3+} and Yb^{3+}. (Atomic No. of Dy 66 and Yb is 70) 6

7. (a) Compare the electronic spectra of lanthanide and transition metal ions. Discuss how the filling of the 4f orbitals in lanthanides affects the periodic properties. 7

(b) Blue $CuSO_4 \cdot 5H_2O$ crystal releases its water of hydration when heated. How many phases and components are present in an otherwise empty heated container? 7

(c) Explain why there is depression in the freezing point when a non-volatile solute is dissolved in a solvent? Derive the relationship between depression in the freezing point and the molecular mass of the solute. 6

8. (a) Discuss thermodynamic and kinetic stability of complexes by citing suitable example of each type. What is the trend in the variation of thermodynamic stability constant? Explain giving examples. 7

(b) How can you determine magnetic susceptibility of a given compound following the Gouy's Method? Discuss with mathematical relationship. 7

(c) A galvanic cell operates on the following redox reaction: 6

$$2MnO_4^-(aq) + 10Br^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Br_2(l) + 8H_2O(l)$$

Calculate the cell potential at 25°C. Given that the concentrations of the aqueous components are: $[MnO_4^-]$= 0.025 M, $[Br^-]$ = 0.050 M, $[Mn^{2+}]$ = 0.40 M, and $[H^+]$ = 0.65 M.