[This question paper contains 4 printed pages]

Roll No.	

ASME-23B-CHEM-I

CHEMISTRY (Paper-I)

Time Allowed : Three Hours	Maximum Marks: 100

QUESTIONS 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.**
4. **FOUR** questions are to be attempted out of the remaining **SEVEN** questions.
5. Each question has **FOUR parts** (**a, b, c, d**). Attempt all **FOUR parts** of a question.
6. Each question carried **20 marks**. Each part of a question carries equal marks (**05 marks**).
7. Unless otherwise mentioned, symbols and notations carry their usual standard meanings.
8. Write answer in legible handwriting.
9. Each part of the question must be answered in sequence and in the same continuation.
10. Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partially.
11. Any page or portion of the page left blank in answer book must be clearly struck off.
12. Re-evaluation / Re-checking of answer book of the candidate is not allowed.

1. **(a)** A particle of mass 1×10^{-30} kg is confined to a one dimensional box of length 1nm. Calculate the minimum uncertainty in its linear momentum in the ground state?

(b) What are spin forbidden and symmetry forbidden transitions in photochemistry?

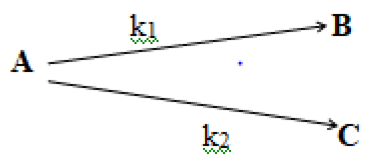
(c) Assuming Hückel's approximation of separating π orbitals from σ orbitals, give a M.O. description of BeH_2 molecule.

(d) For HCl^{35} molecule, the separation between successive rotational lines in Raman spectra is $41.64 cm^{-1}$. Calculate the internuclear distance, assuming the molecule to be a rigid rotor.

2. **(a)** Interpret: ***(i)*** Bragg's law for crystal diffraction, ***(ii)*** Bohr's quantization of angular momentum in the hydrogen atom in terms of wave particle dualism.

(b) A solid compound with a vapour pressure of 4.15mm at 340 K melts at 350 K under a triple point pressure of 7.63mm. The liquid has a vapour pressure of 11.17mm at 360 K. Estimate the molar latent heat of fusion of the solid.

(c) Discuss the kinetics of the parallel reactions as given below, assuming each reaction to be the first order.



(d) Write the electrode reactions and the overall cell reactions in the $H_2 - O_2$ fuel cell in acidic and alkaline media.

3. **(a)** Write the merits of Tanabe–Sugano diagram over the Orgel diagram for a d^2 configuration.

(b) For a given reaction:

$$2C\,(s) + 2H_2\,(g) \rightleftharpoons C_2H_4\,(g)$$

Calculate the Gibbs free energy for the formation of C_2H_4 (g) and comment on the spontaneity or otherwise of the reaction at 298 K. $\Delta H_{298\ K}$ and the standard entropy values at 25 ^oC in cal deg^{-1} mol^{-1} are given as:

$\Delta H_{298\ K} = +8.0$ kcal

C(s) $S^o = 1.4$ cal deg^{-1}

H_2(g) $S^o = 31.2$ cal deg^{-1}

C_2H_4(g) $S^o = 52.2$ cal deg^{-1}

(c) Explain why Ce^{4+} is oxidizing and Eu^{2+} is reducing in their reactions?

(d) "Dielectric constants, dipole moments, and autoionization play a significant role in understanding the solubilities of substances in various solvents." Justify the given statement.

4. (a) Explain the complete mechanism of olefin hydrogenation using Wilkinson's catalyst.

(b) Explain why the EPR spectra of many metal ions in complexes show hyperfine splitting patterns? Justify answer citing suitable examples.

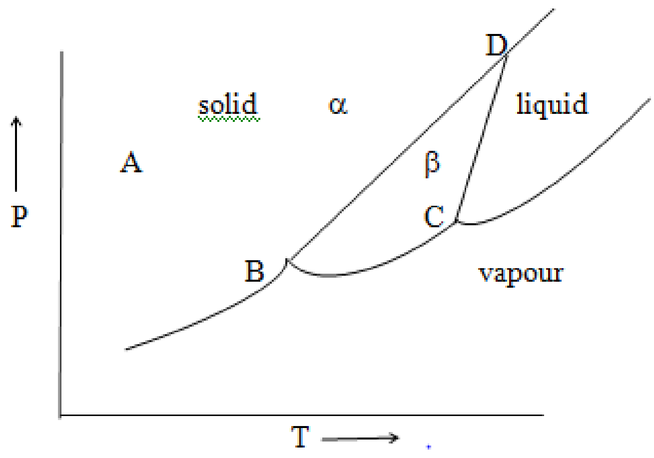
(c) In a photohalogenation reaction, radiation of λ=340 nm is absorbed at the rate of 1.5x10^{-3} Js^{-1} for 30 minutes. Calculate the quantum yield if 80 % of the absorbed energy is effective for photohalogenation and if 45x10^{16} molecules are consumed.

(d) "The mechanism of substituted reactions of square planar complexes appears to be associative S_N^2 instead of dissociative S_N^1." Justify the above statement with some suitable examples.

5. (a) Explain how are the slopes of isothermal and adiabatic curves related in the pressure-volume diagram?

(b) What are the degenerate levels for a particle in a three dimensional box with energy (E) = 3 n^2/(4 m l^2) ?

(c) The phase diagram of a one component system having solid phase (α, β) are shown below. Starting from the point A, indicate the phases observed if the system is heated at constant pressure. Evaluate the degrees of freedom at A and B



(d) When 30.0 g of a non-volatile solute having the empirical formula CH_2O is dissolved in 800 g of water, the solution freezes at -1.16 °C. Determine the molecular formula of the solute (K_f=1.86 °C/m).

6. **(a)** What are the weakness of collision theory? Why was the steric factor introduced into the equation of collision theory?

(b) Explain the deactivation process responsible for fluorescence and phosphorescence.

(c) For the enzyme catalysed reaction schematically shown below:

$$\mathbf{E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P}$$

Assuming that the concentration of the complex reaches a steady state after an initial transient stage, prove that:

$$\mathbf{[ES] = \frac{k_1\,[E]_o\,[S]}{k_{-1} + k_2 + k_1[S]}}$$

where $[E]_o$ is the initial enzyme concentration.

(d) Explain through a cyclic sketch the four steps involved in oxidation of water to release O_2 in photosystem II.

7. **(a)** Using equipartition theorem, calculate the ratio of specific heats for He an H_2 gases assuming ideal classical behaviour.

(b) Explain law of Rotational Indices citing appropriate examples.

(c) What is meant by the term "fluxional molecules"? How they can be identified by NMR technique?

(d) What type of isomerism is shown by the complex $[Pt(NH_3)_4(OH)_2](SO_4)$? Write the IUPAC names of its isomers.

8. **(a)** Account for the fact that the magnetic moments for Eu^{2+} and Sm^{2+} complexes are higher than those calculated by the spin only values and also by the total angular momentum J values of the ground state.

(b) Complete the following reactions:

(i) $Co_2(CO)_8 + NO \longrightarrow$

(ii) $K_2[PtCl_4] + H_2C{=}CH_2 \xrightarrow[\text{Catalyst}]{SnCl_2}$

(iii) $Fe_2(CO)_9 \xrightarrow[Et_4NI]{KOH/MeOH}$

(iv) $2CH_3COOAg + SOCl_2 \xrightarrow{\text{Liq. } SO_2}$

(v) $Zn(NH_2)_2 + 2NH_4Cl \xrightarrow{\text{Liq. } NH_3}$

(c) Describe the role of metal ions in ion-transport across the membrane (molecular mechanism) in biological system.

(d) What is meant by polar and non-polar molecules? Arrange in the order of decreasing polarity of the bonds: SbH_3, AsH_3, PH_3, NH_3

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