

**M.Sc. 4th Semester Examination, 2025**

**CHEMISTRY**

**PAPER—CEM-403**

*Full Marks : 50*

*Time : 2 hours*

**Answer all questions**

*The figures in the right hand margin indicate marks*

*Candidates are required to give their answers in their own words as far as practicable*

**CEM-403**

*(Physical Chemistry Special)*

**GROUP — A**

**Answer any four questions :**                      2 × 4

1. What types of reactions are studied by molecular beam technique and shock tube method ?

*( Turn Over )*

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2. Define saddle point.
3. The volume of activation of a reaction is  $-4 \times 10^6 \text{ m}^3 \text{ mol}^{-1}$  at 298 K. Calculate the pressure required to double the rate constant at  $10^5 \text{ Pa}$ .
4. Light scattering method is more acceptable than viscosity method for determination of average molecular weight of a polymer—Justify.
5. Define Fuel cell with an example.
6. Why acid hydrolysis is preferred over alkaline hydrolysis in case of proteins ?

GROUP – B

Answer any **four** questions : 4 × 4

7. Starting from the equation

$$d\gamma = -q_M dV - (q_M / Z_j F) d\mu_j - \sum \Gamma_i d\mu_i$$

Prove that

$$1/2 RT (d\gamma/d\ln a_{\pm})_{v\pm} = -\Gamma$$

Where the symbols have their usual meanings.

8. Derive the expression to determine the number average molecular weight of a polymer sample.
9. The size of the molecule does not have strong effect on the rate constant of diffusion controlled reaction—Explain.
10. What are the limitations of conventional Transition State Theory ?
11. At 20°C, the diffusion co-efficient, the molar mass and specific volume of haemoglobin are  $6.9 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ ,  $64500 \text{ gmol}^{-1}$  and  $0.75 \text{ cm}^3\text{g}^{-1}$  respectively. Calculate its frictional ratio and comment on your result. The co-efficient of viscosity of water at the given temperature is 1.005 cP.

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12. Explain, with the appropriate graphical representation, the pH metric titration of glutamic acid.

*Or*

Write and explain Hinshelwood theory for unimolecular reaction.

**GROUP – C**

Answer any two questions : 8 × 2

13. Using appropriate partition function derive the expression for the rate constant of absolute reaction rate theory.
14. Derive Flory-Huggins equation of vapour pressure for polymer solution.
15. Derive the expression for determination of weight average molecular weight by sedimentation equilibrium method.
16. Write note on solid phase peptide synthesis.

[ Internal Assessment – 10 Marks ]

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**CEM-403**

*(Inorganic Special)*

**GROUP – A**

Answer any **four** questions : 2×4

1. V(III) is more labile than V(II)— Why ?
2. What are the effects on the rate constant of positive and negative value of CFAE ?
3. What factors favor the associative mechanism ?
4. What are the requirements for to be labile and inert system ?
5. State the role of supporting electrolysis in polarographic measurement.
6. State the limitations of dropping Mercury electrode.

GROUP – B

Answer any **four** questions :

4 × 4

7. Derive the expression for dissociative mechanism for octahedral complex. What happen when the concentration of nucleophile is very high ?
8. Amino acid exchange reaction at the square planar complexes of Cu(II) shows the rate sequence glycine > sarcosine (i.e. N-methyl glycine) > glycine while octahedral complexes of Co(II) rate sequence, i.e. dimethyl Glycine > sarcosine (i.e. N-methyl glycine) > glycine. Discuss.
9. The observed rate of the aquation of  $\text{Cl}^-$  ligand in the chlorido-ammine complexes of Co(III) and Cr(III)-complexes are given bellow :

Complex:  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$   $[\text{CoCl}_2(\text{NH}_3)_4]^+$   $[\text{CoCl}(\text{en})_2(\text{NH}_3)]^{2+}$   
 $k_{\text{ex}}(\text{s}^{-1}, 25^\circ\text{C})$   $\sim 10^{-6}$   $\sim 10^{-2}$  to  $10^{-3}$   $\sim 10^{-7}$

$[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$   
 $\sim 10^{-5}$

Complex:  $[\text{CrCl}(\text{NH}_3)_5]^{2+}$   $[\text{CrCl}_2(\text{NH}_3)_4]^+$   $[\text{CrCl}_2(\text{en})]^{2+}$   
 $k_{\text{ex}}(\text{s}^{-1}, 25^\circ\text{C})$ :  $9.7 \times 10^{-6}$   $4 \times 10^{-5}$   $\sim 10^{-4} - 10^{-5}$

Why these type of differences are found in rate constant though they have same ligand ?

10. The water exchange rates for the following  $[\text{M}(\text{OH}_2)_6]^{3+}$  follow the sequence :

$[\text{Sc}(\text{OH}_2)_6]^{3+} > [\text{Ti}(\text{OH}_2)_6]^{3+} > [\text{V}(\text{OH}_2)_6]^{3+} > [\text{Fe}(\text{OH}_2)_6]^{3+}$

Explain with justification.

11. What is a polarographic maximum ? How do you eliminate this problem ?

12. Deduce the relationship between half wave potential and standard redox potential of a system.

## GROUP – C

Answer any two questions :

8 × 2

13. (a) Aquation rates of  $[\text{Co}(\text{NH}_3)_5(\text{L})]^{n+}$  complexes (at 25°C)

$L$	$k_{aq}(s^{-1})$	$L$	$k_{aq}(s^{-1})$
$\text{NO}_3^-$	$2.4 \times 10^{-5}$	$\text{SO}_4^{2-}$	$8.9 \times 10^{-7}$
$\text{I}^-$	$8.3 \times 10^{-6}$	$\text{F}^-$	$8.6 \times 10^{-8}$
$\text{Cl}^-$	$1.7 \times 10^{-6}$	$\text{N}_3^-$	$2.1 \times 10^{-9}$
$\text{Br}^-$	$6.3 \times 10^{-6}$	$\text{NCS}^-$	$3.7 \times 10^{-10}$
		$\text{H}_2\text{PO}_4^-$	$2.6 \times 10^{-7}$

Comment on the rate constant variation. By which mechanism the reactions will proceed ?

(b) Rate constants for aquation of  $[\text{Ti}(\text{OH})_6]^{3+}$  (at 13°C).

$Y^{n-}$	$k (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
$\text{NCS}^-$	$8 \times 10^3$ (at ca. 9°C)
$\text{CH}_3\text{CO}_2^-$	$1.8 \times 10^6$
$\text{ClCH}_2\text{CO}_2^-$	$2.1 \times 10^5$

What do these data suggest about the mechanism of these reactions ? 4 + 4

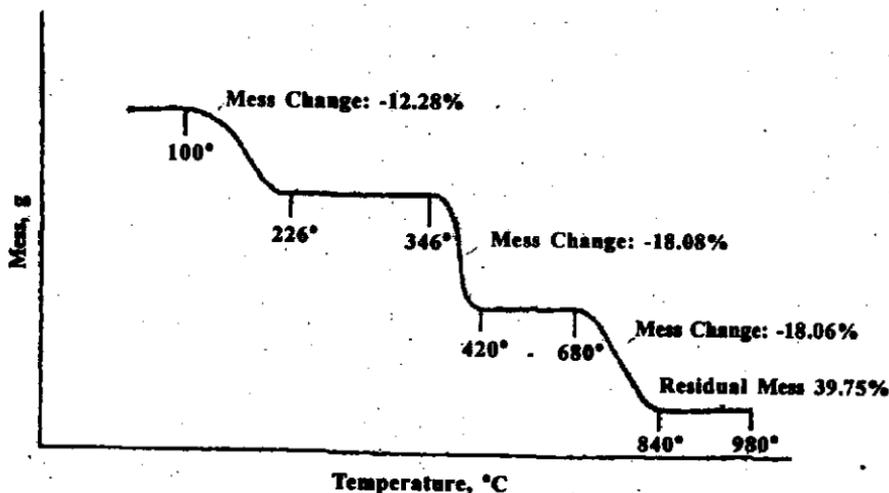
14. (a) The second order rate constant for reduction of  $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}]^{\text{n}+}$  by  $[\text{Cr}(\text{OH}_2)_6]^{2+}$

x =	NH <sub>3</sub>	OH <sub>2</sub>	-OH	Cl <sup>-</sup>	N <sub>3</sub> <sup>-</sup>	NCS <sup>-</sup>	SCN <sup>-</sup>
k(dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )= 25°C	9 × 10 <sup>-5</sup>	0.5	1.5 × 10 <sup>6</sup>	6 × 10 <sup>5</sup>	3 × 10 <sup>5</sup>	20	1.8 × 10 <sup>5</sup>

Explain why these variation observed in the rate constant ?

(b) Write down the mechanism for the base hydrolysis of  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ . 4 + 4

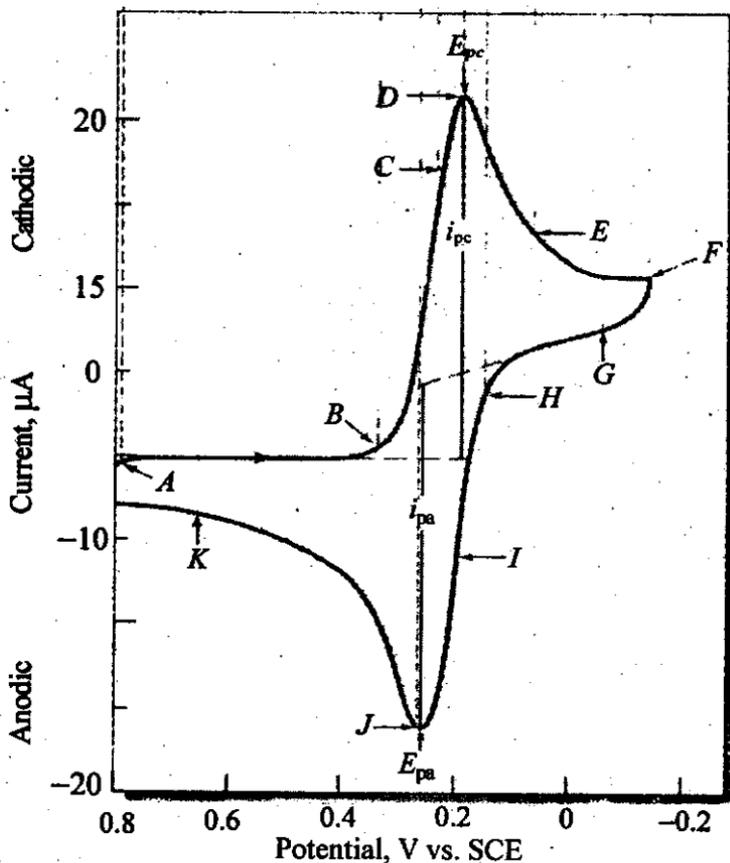
15. A Thermogram for decomposition of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  is shown below



Correlate the thermogram with mass of the product with proper explanation. 4 + 4

16. Cyclic voltammogram for a solution is 6.0 mM in  $K_3Fe(CN)_6$  and 1.0 M in  $KNO_3$  is given bellow

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Identify the products at the position B, D, F, H, J and K on observed cyclic voltammogram. 8

[ Internal Assessment – 10 Marks ]

**CEM-403**

*(Organic Special)*

**GROUP – A**

Answer any **four** questions :  $2 \times 4$

1. What is point group of  $\Delta^{1,9}$ -Octalin ? Where is its chiral centre ?
2. What are quasi-enantiomers ? Give an example.
3. What do you mean by  $A^{1,2}$ -strain ? Give an example.
4. Write down the Drude equation and explain the terms involved in it. Why Cotton effect curves do not obey simple Drude equation ?
5. What do you mean by "Mean Residue Ellipticity (MRE)" ?

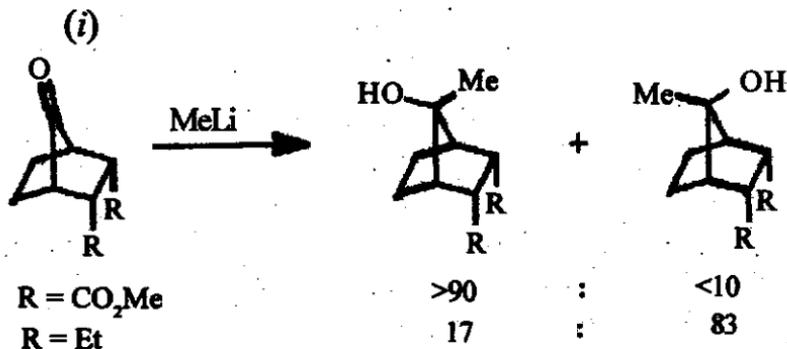
6. Draw the most stable stereoisomer of perhydrophenanthrene and discuss its salient features.

GROUP – B

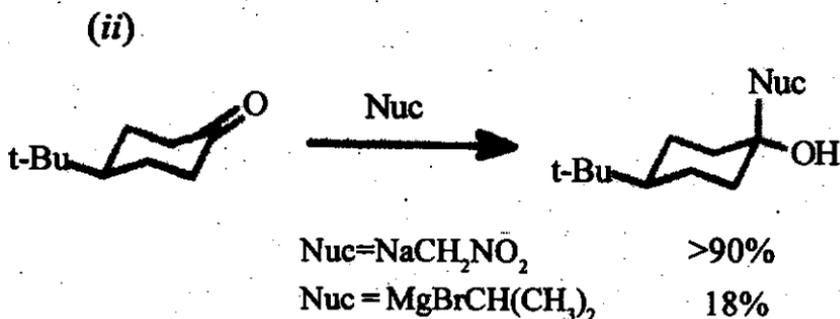
Answer any four questions :  $4 \times 4$

7. State and explain the axial haloketone rule. How will you determine the absolute configuration of (-)-trans-1-decalone using axial haloketone rule ?  $2 + 2$
8. What do you mean by atomic asymmetry ? Why *R*-lactic acid is weakly levorotatory whereas *R*-mandelic acid is strongly leavorotatory in water ?  $2 + 2$
9. How will you rationalize the tendency of trans-2-decalones to enolise to give a 2, 3-double bond instead of 1,2-bond whereas cis-2-decalones tend to enolise towards C-1 instead of C-3 ?  $4$

10. How will you account for the product distribution in the following reactions with the help of Cieplak model ?



Nucleophilic Attack of Substituted Norbornones.

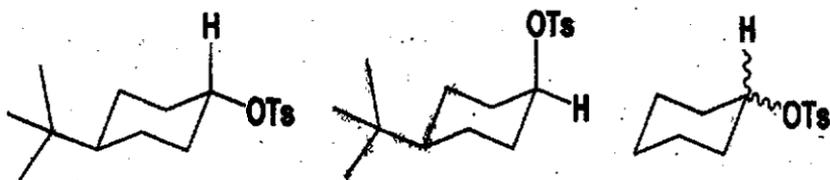


11. What are bisignate CD curves ? How will you study the conformational changes in (-)-menthone with solvent polarity using CD or ORD curves ? 1 + 3
12. Discuss the effect of ring size on the sign of the Cotton effect. How CD and ORD with Cotton effect curves help to determine the structure of proteins and nucleotides ? 2 + 2

GROUP – C

Answer any two questions : 8 × 2

13. State and derive the Curtin-Hammatt principle. In this context also cite an example where the less stable conformer leads to the major product.
14. Deduce the Winstein-Holness and Eliel-Ro equations. Why has it become obsolete ? Calculate the value of equilibrium constant (K) for the system.



Given, the specific rate constants,  $k_e = 0$ ,  
 $k_a = 7.1 \times 10^{-3}$  and the overall empirical rate  
 constant,  $k = 2.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  at  
 298.15 K. 5 + 1 + 2

15. Write all the possible stereoisomers of perhydroanthracenes and discuss their stereochemical features.
16. What are the symmetry elements present in cis- and trans-decalins? What are symmetry elements present in cis-9-methyl decalin and trans-9-methyl decalin? Draw all the stereo-

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isomers of trans-1-decalol and comment on their stability. Draw the conformers of cis-1-thiadecalins and comment on their stabilities.

2 + 2 + 2 + 2

[ Internal Assessment — 10 Marks ]

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