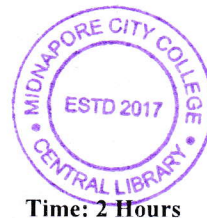


PG (CBCS)
M.Sc. Semester-IV Examination, 2026
CHEMISTRY
PAPER: CEM 403
(ADVANCED INORGANIC CHEMISTRY-IV)



Full Marks: 40

Time: 2 Hours

The figures in the right-hand margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

GROUP – A1. Answer any **FOUR** of the following questions:

2×4 = 8

- The rate of base catalysed hydrolysis reaction is very fast in *trans*-isomer than *cis*-isomer.-Explain.
- What is polarisable and non-polarizable electrode? Give an example of each.
- Draw the energy profile diagram for dissociative and associative mechanism of reaction?
- What is 'Electroprotic reaction'? Give an example.
- Write the advantages of polarography experiment.
- Write the characteristics of solvent used in cyclic voltammetry experiment.

GROUP – B2. Answer any **FOUR** of the following questions:

4×4 = 16

- What is the basic principle of coulometry? Write few application of coulometry. (4)
- Derive the rate law for the associative mechanism of an octahedral complex. (4)
- Explain inner sphere electron transfer reaction mechanism with suitable example. (4)
-



In the above reaction shows following observations

- With excess PR₃ & DMSO a first order reaction is followed in both PR₃ and Ru
- K₀ vs PR₃ gives saturation kinetics
- Added excess DMSO slow down the reaction

Comment on this observation with proper explanation.

(4)

- What are the merits and demerits of dropping mercury electrode (DME)

(4)

P.T.O

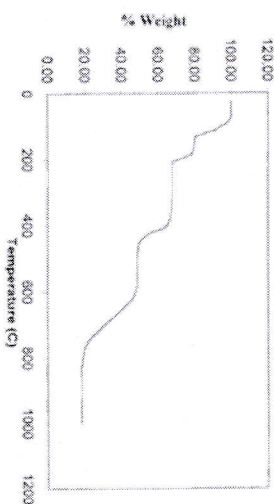
- f) Why polarographic maxima are observed? How do you eliminate this problem? (4)

GROUP - C

3. Answer any TWO of the following questions:

8×2 = 16

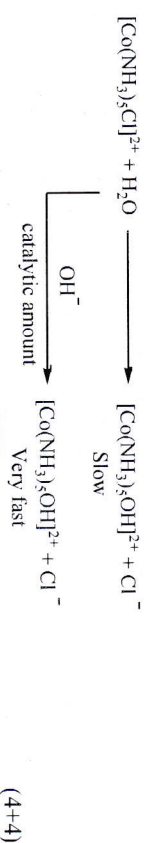
- a) (i) Deduce the relationship between half wave potential and standard redox potential of a system.
 (ii) What condition should be maintained in polarographic analysis? (5+3)
- b) (i) What factors affect thermogravimetric (TGA) curve?
 (ii) Find out the decomposition products of calcium oxalate monohydrate (CaC₂O₄·H₂O) from the TG curve below. (3+5)



- c) (i) Rate constants and activation parameters for the aquation of ammonia and methylamine complexes of Co(III) and Cr(III) at 25°C is given below:

Complex	10 ⁶ k (s ⁻¹)	ΔH [‡] (kJ/mol)	ΔS [‡] (J/mol)	ΔV [‡] (cm ³ mol ⁻¹)
[Co(NH ₃) ₅ Cl] ²⁺	1.72	93	-44	-9.9
[Co(NH ₂ CH ₃) ₅ Cl] ²⁺	39.6	95	-10	-2.3
[Cr(NH ₃) ₅ Cl] ²⁺	8.70	93	-29	-10.6
[Cr(NH ₂ CH ₃) ₅ Cl] ²⁺	0.26	110	-2	+0.5

Comment on the rate constant and activation parameters of these aquation reactions.
 (ii) Explain following observation with suitable mechanism.



(4+4)

P.T.O



- d) (i) The rate constant for anation by Yⁿ⁻ for [Fe(H₂O)₆]³⁺ and [Fe(H₂O)₅(OH)]²⁺ complex at 25°C are given below:

Y ⁿ⁻	k (M ⁻¹ s ⁻¹) for [Fe(H ₂ O) ₆] ³⁺	k (M ⁻¹ s ⁻¹) for [Fe(H ₂ O) ₅ (OH)] ²⁺
SO ₄ ²⁻	1.1 × 10 ⁵	2.3 × 10 ³
Cl ⁻	5.5 × 10 ³	4.8
Br ⁻	2.6 × 10 ³	1.6
NCS ⁻	5.1 × 10 ³	90
ClCH ₂ CO ₂ ⁻	4.1 × 10 ³	1.5 × 10 ²

Explain the observations with proper explanation.

- (ii) The rates of anation of [Ti(H₂O)₆]³⁺ by Yⁿ⁻ at 13°C is given below:

Y ⁿ⁻ (n=0)	k (mol ⁻¹ sec ⁻¹)	Y ⁿ⁻ (n=1)	k (mol ⁻¹ sec ⁻¹)
ClCH ₂ CO ₂ H	6.7 × 10 ²	ClCH ₂ CO ₂ ⁻	2.1 × 10 ⁵
CH ₃ COOH	9.7 × 10 ²	CH ₃ COO ⁻	1.8 × 10 ⁶
H ₂ O	8.6 × 10 ⁶	NCS ⁻	8 × 10 ³

What type of mechanism can suggest from these data?

(4+4)



(3)