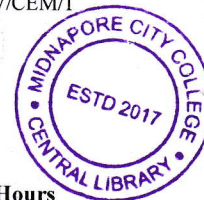


PG
M.Sc. Semester-IV Examination, 2022
CHEMISTRY
PAPER: CEM 403 (SPL PAPER)
(ADVANCED INORGANIC CHEMISTRY-II)



Full Marks: 40

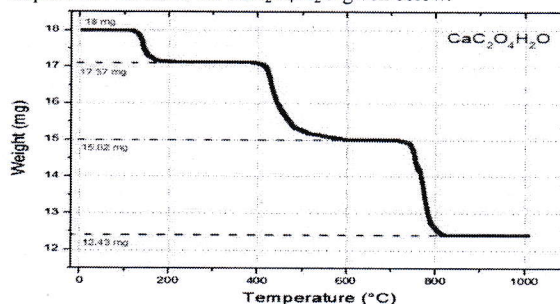
Time: 2 Hours

GROUP - A

1. Answer any four questions from the following questions: 2×4 = 8
- What are the complementary and non-complementary redox reactions? Give an example of each.
 - What are the differences between I_a and I_d mechanism?
 - What is meant by inert and labile complexes?
 - Write down the characteristics of the solvents used for cyclic voltammetry experiment.
 - Write down the application of cyclic voltammetry.
 - State the Marcus equation for outer sphere complexes.

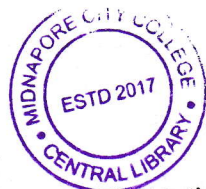
GROUP - B

1. Answer any four questions from the following questions: 4×4 = 16
- How dropping mercury electrode is constructed? What are the advantages and disadvantages of it? 2+2
 - Deduce the relationship between half wave potential and standard redox potential of a system. What is the significance of half-wave potential in cyclic voltammetry? 2+2
 - Explain the TG curve for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ given below.



- Derive the rate law for dissociative mechanism for octahedral ligand substitution.
- Why Polarographic Maxima is observed? Explain with Example.
- Write the characteristics of 'supporting electrolyte' for the CV experiment.

(P.T.O.)



(2)

GROUP - C

2. Answer any **two** questions from the following questions: **8×2 = 16**

- a) (i) "Acid catalyzed aquation reaction of chromium-ethylenediamine complex is slower than that of chromium-biguanide complex"-Explain with mechanism.
 (ii) The rate constant and activation parameters of the aquation of some Cr and Co complexes are given below

Rate constants and activation parameters for aquation of L of $[M(NH_3)_5L]^{3+}$.

L	$10^5 k_{aq} (s^{-1})$	$\Delta S^\ddagger (J K^{-1} mol^{-1})$	$\Delta V^\ddagger (cm^3 mol^{-1})$	
M = Cr	H ₂ O*	5.2	0	-5.8
	OSMe ₂	1.95	-15.1	-3.2
	OCHNH ₂	5.1	-12.2	-4.8
	OC(NH ₂) ₂	2.0	-22.3	-8.2

Rate constants and activation parameters for aquation of L of $[M(NH_3)_5L]^{3+}$.

L	$10^5 k_{aq} (s^{-1})$	$\Delta S^\ddagger (J K^{-1} mol^{-1})$	$\Delta V^\ddagger (cm^3 mol^{-1})$	
M = Co	H ₂ O*	0.59	+28.1	+1.2
	OSMe ₂	1.8	+10.1	+2.0
	OCHNH ₂	0.58	+12.2	+1.1
	OC(NH ₂) ₂	5.5	-10.1	+1.3

Propose the possible mechanism and give explanation in favour of your answer. 3+5

- b) (i) The rate constant for the aquation of some $[Ti(OH_2)_6]^{3+}$ complexes are given below

Rate constants for aquation of $[Ti(OH_2)_6]^{3+}$ (at 13°C).

Y^{n-}	$k (dm^3 mol^{-1} s^{-1})$
NCS ⁻	8×10^5 (at ca. 9°C)
CH ₃ CO ₂ ⁻	1.8×10^6
ClCH ₂ CO ₂ ⁻	2.1×10^5

Rationalize the trends observed.

- (ii) The $[Ni(bpy)_3]^{2+}$ complex follows acid catalyzed aquation reaction but $[Ni(phen)_3]^{2+}$ does not. Discuss the observation with proper mechanism.
 (iii) Give mechanistic pathway for a DCB substitution reaction. 2+3+3
- c) (i) Derive the Ilkovic equation.
 (ii) Write down the mechanistic pathway for outer sphere mechanism with a suitable example.
 (iii) What is CFAE? State its significance. 3+3+2
- d) (i) Why oxygen should be expelled from the polarographic cell before the experiment?
 (ii) Discuss the advantages and disadvantages of dropping Mercury electrode.
 (iii) Sketch an instrumental layout of a modern TGA instruments. 3+3+2
