2022

M.Sc.

4th Semester Examination (CCAE)

CHEMISTRY

PAPER—CEM-403

ORGANIC, INORGANIC AND PHYSICAL SPECIAL

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

(Organic Special)

Group—A

1. Draw the 3d structures for the following conformers and show in them different steric interactions. (any *four*) 4×2

(a) *cis*-*transoid*-*cis*perhydroanthracene

(b) *trans-cisoid-cis*perhydrophenanthrene

(c) 9,10-dimethyl *cis*decalin

(d) *trans-transoid-trans*perhydrophenanthrene

(e) *cis-cisoid-cis* perhydroanthracene

(f) 1,2,3,4,5,6,7,8,9,10-decamethyl *trans* decalin

Group—B

2. Write in brief with one example in each case : (any *four*) 4×4

(a) Allylic 1,2-strain

(b) Cieplaak model

(c) Enantioselective reaction

(d) Allylic 1,3-strain

(e) *Syn* pentane interaction

(f) Hammett equation

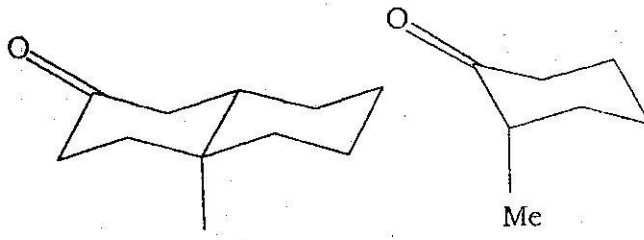
Group—C

3. Answer any *two* questions : 2×8

(a) State and derive Curtin-Hammett Principle with examples.

(b) cis-2-decalone enolises towards C-I whereas trans-2-decalone enolises at C-3. Explain.

(c) Applying the Octant Rule to predict the CE of the following compounds.



(d) (i) Explain 'M' and 'P' type chirality as per helicity rule with one example in each case.

(ii) If two enantiomers are present in 75% and 25% respectively, what is the e,e?

(Inorganic Special)

Group—A

1. Answer any *four* questions : 4×2

(a) What are the requirements of base hydrolysis reaction?

(b) Write short notes on Edward nucleophilicity scale.

(c) What do you mean by labile and inert metal centers? What factors affect this property?

(d) On what factors nucleophilicity of a ligand depend?

(e) Why is oxygen to be expelled from the polarografic cell before the experiment?

(f) What do you mean by residual current?

Group—B

2. Answer any *four* questions : 4×4

(a) The red isomer of $[CoCl(NH_3)(tren)]^{2+}$ hydrolyses faster than the purple isomer in presence of a base. Explain.

(b) Derive rate law for the dissociative mechanism for L_5MX complex where five coordinated intermediate have appreciable life time considering Y as an attacking ligand. If $K_2[Y]$ is very alrge or very small then what will be the effect on rate law.

(c) Rate constant for some redox reaction at 25°C are given below.

Oxidant	Reluctant	$k(M^{-1}s^{-1})$
$[CO(NH_3)_5H_20]^{3+}$	Cr^{2+}	<0.4
$[CO(NH_3)_5(OH)]^{2+}$	Cr^{2+}	1.5xl06
$[Co(NH_3)_5H_20]^{3+}$	$[Ru(NH_3)_6]^{2+}$	3.0
$[CO(NH_3)_5(OH)]^{2+}$	$[RU(NH_3)_6]^{2+}$	0.04

What type of reaction mechanism could be proposed in these reactions? Give reason for you answer.

(d) What do you mean by acid catalyzed Pseudo substitution? Explain the mechanism with suitable Examples.

(e) Derive the expression for half wave potential.

(f) Discuss about the advantages and disadvantages of droping Mercury electrode.

Group—C

Answer any *two* questions. 2×8

3. (a) Rate constant for acid catalyzed aquation of some $[Co(NH_3)_5X]^{n+}$ are given below

Complex	$k(s^{-1})$
$[Co(NH_3)_5(OP(OMe)_3)]^{3+}$	2.5×10^{-4}
$[CO(NH_3)_5(NO_3)]^{2+}$	2.4×10^{-5}
$[CO(NH_3)_5I]^{2+}$	8.3×10^{-6}
$[CO(NH_3)_5H_2O]^{3+}$	5.8×10^{-6}
$[CO(NH_3)_5(SO_4)]^{+}$	8.9×10^{-7}
$[CO(NH_3)_5F]^{2+}$	8.6×10^{-8}
$[CO(NH_3)_5N_3]^{2+}$	2.1×10^{-9}
$[CO(NH_3)_5(NCS)]^{2+}$	3.7×10^{-10}

Rationalize the rate of the observed reaction.

(b) Rate constant for anation by Y^- of $[CO(NH_3)_5H_2O]^{3+}$ are given below

Y^{n-}	$k(s^{-1})$
H_2O	100×10^{-6}
N_3^-	100×10^{-6}

SO_4^{2-}	24×10^{-6}
Cl^-	21×10^{-6}
NCS^-	16×10^{-6}
$H_2PO_4^-$	77×10^{-6}

Comment on the rate constant variation of these anation. By which mechanism reaction will proceed? 4+4

4. (a) Some volume of activation for base hydrolysis of Co complex is given below. Rationalize the trends observed.

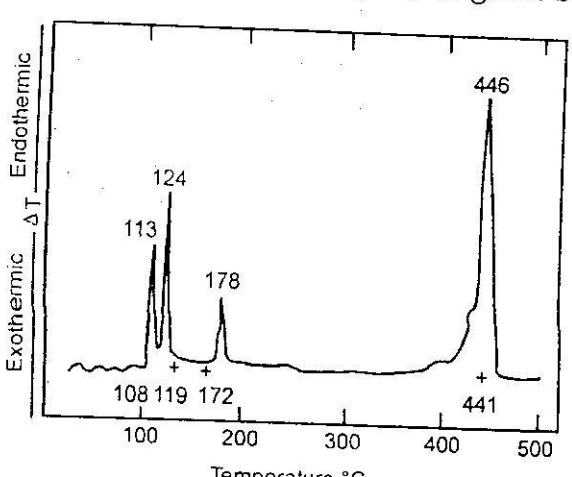
Complex	$\Delta V^{\neq}$ (cm^3/mol)
$[Co(NH_3)_5(0{=}C(NMe_2)H]^{3+}$	+43.2
$[Co(NH_2Me)_5Cl]^{2+}$	+32.7
$[Co(NH_2Et)_5Cl]^{2+}$	+31.1
trans – $[Co(en_2)Cl_2]^+$	+24.8
cis – $[Co(en_2)Cl_2]^+$	+27.9

(b) The rate constant and activation parameters for aquation of some $[M(NH_3)_5X]$ (where M= Cr and Co) are given bellow :

M	X	$k \times 10^{-5}(s^{-1})$	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)	$\Delta V^{\#}$ (cm^3/mol)
Cr	H_2O	5.2	97.0	0.0	-5.8
	$OSMe_2$	1.95	95.3	-15	-3.2
	$OCHNH_2$	5.1	94.0	-12	-4.8
	$OC(NH)_2$	2.0	93.5	-22	-8.2
	$OP(OMe)_3$	6.0	89.7	-23	-8.7
Co	H_2O	0.59	111	+28	+1.2
	$OSMe_2$	1.8	103	+10	+2.0
	$OCHNH_2$	0.58	107	+12	+1.1
	$OC(NH)_2$	5.5	94	+10	+1.3
	$OP(OMe)_3$	6.5	98	+5	+2.2

Explain the mechanism of these reactions on the basis of the above observation. 4+4

5. Differential thermogram for sulphur is given bellow :



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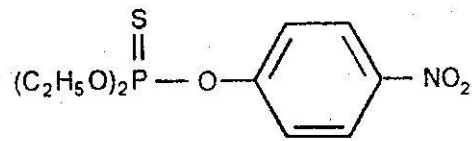
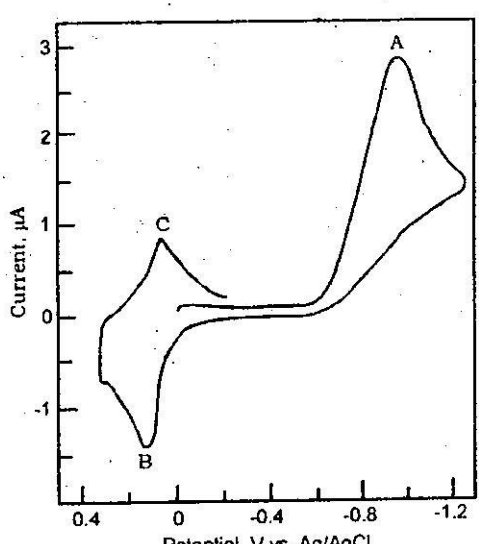
Explain the thermogram with proper explanation. 8

6. The cyclic voltammogram for the agricultural insecticide parathion is given bellow in 0.5 (M) sodium acetate buffer in 50% ethanol.





Explain the observed cyclic voltammogram confirming the product produced at A, B and C position. 8

(Physical Special)

Group—A

Answer any *four* questions. 4×2

1. What is saddle point?

2. What is macroscopic diffusion controlled reaction?

3. What is activation energy of chemical reaction?

4. The Osmometry method is suitable for determination of the number average molecular weight – Explain.

5. Define intrinsic viscosity. How is it determined? 1+1

6. Why acid hydrolysis is preferred over alkaline hydrolysis in case of proteins?

Group—B

Answer any *four* questions. 4×4

7. Using double sphere activated complex model for ionic reaction show that the value of pre-exponantial factor will increase by a factor 10^2 for each unit of Z_AZ_B. (Charge of reactants A & B).

8. Give the mechanism of bimolecular surface reaction (Langmuir-Hinshelwood Mechanism).

9. Show that the molecular Partition function is equal to the product of translational, rotational and vibrationl and electronic partition function.

10. Using Debye-Huckle theory, derive an expression to explain the effect of ionic strength on reaction rate.

11. Show that for an equimolecular mixture of two substances having molar mass Ml &M2

Ml = Mn + (Mn Mm – Mn2)1/2 and

M2 = Mn - (Mn Mm – Mn2)1/2

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

Group—C

Answer any *two* questions. 2×8

13. Using thermodynamic formulation, show that the expression of rate constant of a bimmoleculer reaction is

$$k = \frac{K_B}{h} Tee^{\Delta S^0_*/R} e^{-E_a/RT}$$

where the symbols used for their usual meaning.

14. Give *quantitative treatment* of Transition State theory using Partition Function.

15. Prove that the size of the molecules A and B does not have a strong effect on K_D for fully microscopic diffusion controlled reaction.

16. Define weight average molecular weight and derive an expression for the determination of the weight average molecular weight of a macromole by sedimentation equilibrium method. 1+7

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