M.Sc. 4th Semester Examination, 2024

CHEMISTRY

PAPER – CEM-403

Full Marks : 50

Time : 2 hours

The figures in the right hand margin indicate marks

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

(*Organic Special*)

GROUP – A

Answer any **four** questions : 2×4

1. What are the symmetry element(s) present in cis and trans-9-methyl decalin ?

2. What do you mean by "circular birefringence" ?

3. What do you mean by $A^{1,3}$-strain ? Give an example.

4. What is meant by Davydov splitting ?

5. What is meant by "Bürgi-Dunitz trajectory" ?

6. How will you distinguish between cis and trans-decalins by ^{1}H-NMR spectroscopy ?

GROUP – B

Answer any **four** questions : 4×4

7. Compare the stabilities of cis and trans-$\Delta^{1,2}$ - and $\Delta^{2,3}$ -octalins. $2 + 2$

8. Explain Brewster's Rule. Why R-lactic acid is weakly levorotatory whereas R-mandelic acid is strongly leavorotatory in water ? $2 + 2$

(*Continued*)

9. Draw the most stable and unstable conformers of perhydroanthracene and discuss their stereochemical features. 2 + 2

10. What do you mean by circular dichroism and molar ellipticipty ? Write down the unit of molar ellipticity. 3 + 1

11. What do you mean by Cotton effect ? How CD and ORD curves with Cotton effect can be used to determine the structure of proteins and polypeptides ? 2 + 2

12. What do you mean by a plane ORD curve ? Write down the Drude equation. How ORD curves help us to prove that ortho, meta and para isomers of iodophenyl ethers of lactic acids have the same configuration althrough $[\alpha]_{589}$ of the meta and para isomers show dextrorotation whereas the ortho isomer has leavo rotation ? 1 + 1 + 2

GROUP – C

Answer any **two** questions : 8×2

13. State and derive the Curtin-Hammett principle. In this context also cite an example where the less stable conformer leads to the major product.

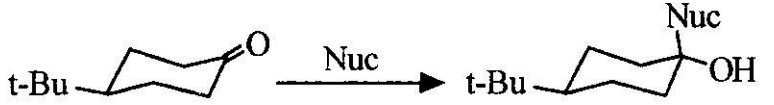
14. How many stereoisomers are possible for perhydrophenanthrenes ? Write all the possible stereoisomers of perhydrophenanthrenes and discuss their stereochemical features.

15. (*i*) Draw all the possible stereoisomers of cis- and trans-1-decalol and discuss their conformational analysis. 5

(*ii*) How will you study the conformational changes in (-)-menthone with solvent polarity using CD or ORD curves ? 3

16. (*i*) State the axial haloketone rule. How will you determine the absolute configuration of (-)-trans-1-decalone using axial haloketone rule ? 3

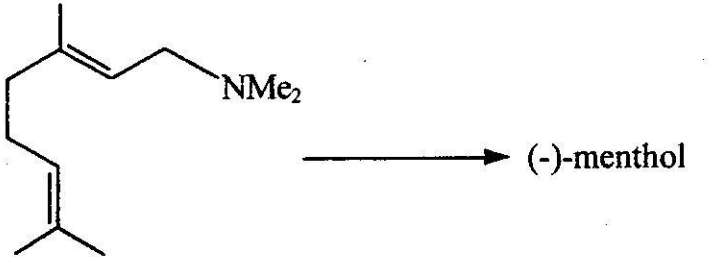
(*ii*) Using Cieplak model account for the following product distribution with variation in the electrophilicity of nucleophile. 3



$Nuc = NaCH_2NO_2$ > 90%

$Nuc = MgBrCH(CH_3)_2$ 18%

(*iii*) How will you carry out the following conversion ? 2



[Internal Assessment — 10 Marks]

(*Inorganic Special*)

GROUP – A

Answer any **four** questions : 2×4

1. Write down the expression for the effect of ionic strength on the rate constant.

2. Explain Edward nucleophilicity scale.

3. What factors affect the nucleophilicity of a ligand ?

4. What are the main criteria of ligand to show acid catalyzed hydrolysis ?

5. What is meant by polarographic maxima ? Write down the related expression.

6. What is residual current in polarography ?

GROUP – B

Answer any **four** questions : 4×4

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

8. Acid catalyzed aquation of chromium complex of ethylenediamine is almost inert but the biguanide complex is very fast. Explain.

9. Derive the expression for the intimate mechanism for L_5MX complex considering Y as an attacking nucleophile.

10. $[Fe(Phen)_3]^{+2}$ does not get hydrolyzed in presence of acid but $[Fe(bpy)_3]^{+2}$ can be readily hydrolyzed. Explain.

11. Derive the expression for half wave potential.

12. Discuss about the advantages and disadvantages of droping Mercury electrode.

GROUP – C

Answer any **two** questions : 8×2

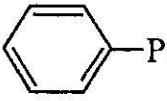
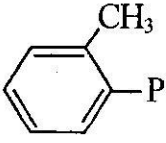
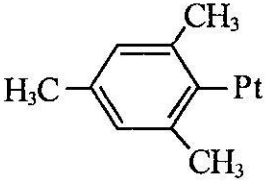
13. (*a*) The value of $\Delta V^{\#}$ are given for the aquation of $[M(NH_3)_5X]^{2+}$ in the following table.

	$[Co(NH_3)_5X]^{2+}$			$[Cr(NH_3)_5X]^{2+}$		
X^- :	Cl^-	Br^-	NCS^-	Cl^-	Br^-	NCS^-
$\Delta V^{\#}$:	−10.6	−9.2	−4.0	−10.8	−10.2	−8.6

$(cm^3\,mol^{-1})$

Explain why all the values of $\Delta V^{\#}$ is negative.

(*b*) Rate Constants for the replacement of the chloro ligand by pyridine in $Pt(PEt_3)_2(R)Cl$ complex is given below.

R – Pt	k ($M^{-1}s^{-1}$) trans (25°C)	cis (25°C)
	1.2×10^{-4}	8×10^{-2}
	1.7×10^{-5}	2×10^{-4}
	3.4×10^{-6}	1×10^{-6}

Discuss the observed results. Why the decrease in rate constant value is more in the cis-isomer ? Explain. 4 + 4

14. (*a*) Water exchange rate constants (k_{ex}) (at 25°C) for $[M(OH_2)6]^{n+}$ and their activation parameters are given in the following table.

	Bivalent metal ions						
Metal ion	: V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
d^n	: $3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
(~)log k_{ex}	: 2.0	>8.5	7.4	6.6	6.4	4.5	9.9
$\Delta H^{\neq}$(kJ mol^{-1})	: 62	–	33	41	47	57	23
$\Delta S^{\neq}$(J K^{-1} mol^{-1})	: 0	–	6.0	21.0	37.0	32.0	25.0
$\Delta V^{\neq}$(cm^3 mol^{-1})	: –4.1	–	–5.4	+3.8	+6.1	+7.2	–

Comment on the nature of the water exchange reaction.

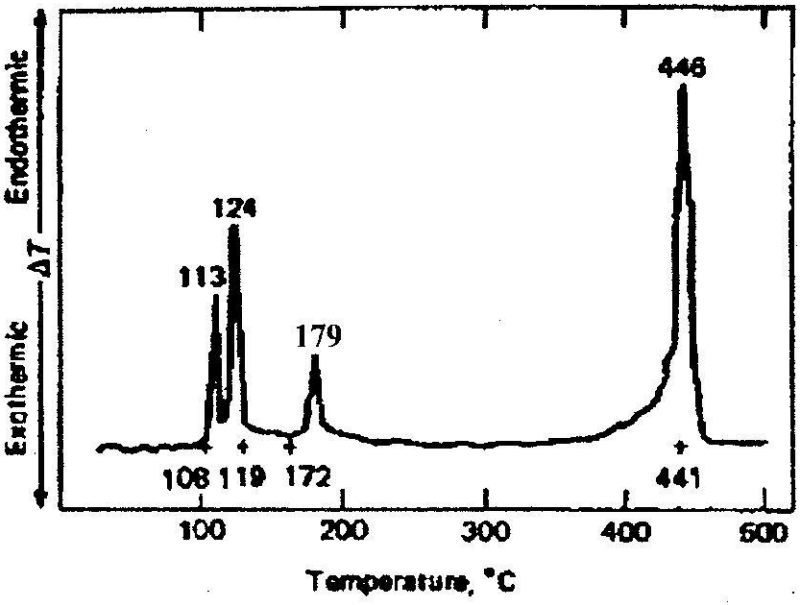
(*b*) The rate constant and activation parameters for aquation of $[M(NH_3)_5X]$ complexes

(where M = Cr and Co) are given below

M	X	$Kx10^{-5}(S^{-1})$	$\Delta H^{\#}$(kJ/mol)	$\Delta S^{\#}$(J/molK)	$\Delta V^{\neq}(cm^3/mol)$
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

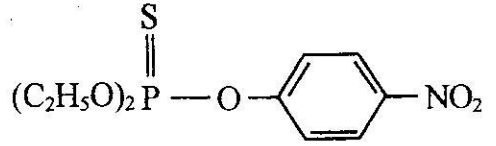
Discuss the meachism of the related reaction in the light of the above observation. 4 + 4

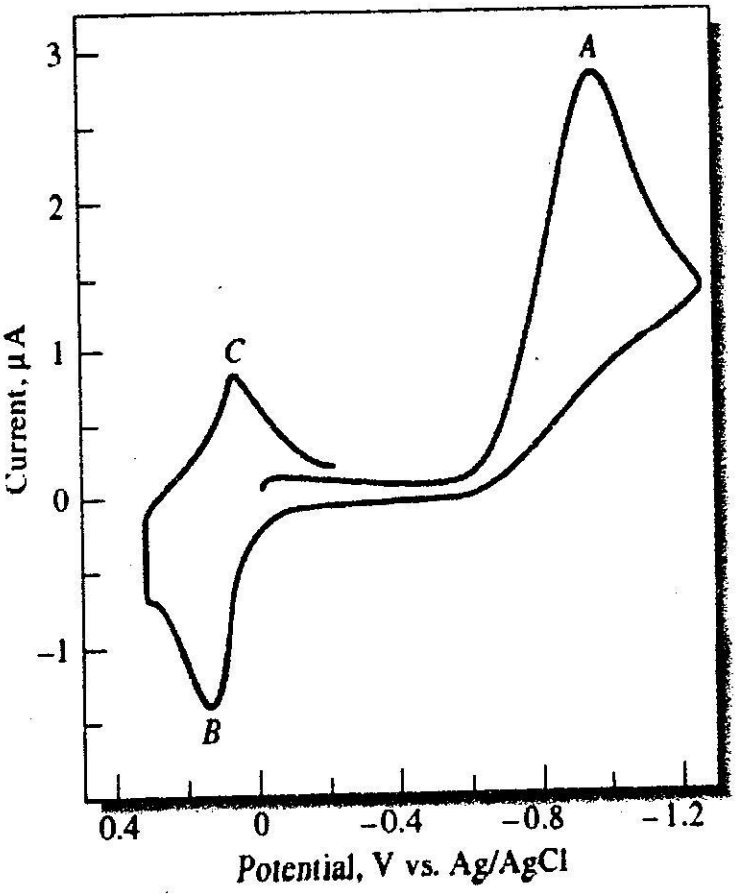
15. Differential thermogram for sulphur is given below



Explain the observed peaks at 113°, 124°, 179° at 446°C and discuss the related conformations with proper explanation. 8

16. The cyclic voltammogram for the agricultural insecticide 'parathion' is given below in 0.5M at pH = 5 in 50% ethanol-sodium acetate buffer solution.


S
(C2H5O)2P
O
NO2


A
B
C
3
2
1
0
−1
Current, μA
0.4
0
−0.4
−0.8
−1.2
Potential, V vs. Ag/AgCl

Identify the products formed at the positions A, B and C with proper explanation. 8

[Internal Assessment – 10 Marks]

(*Physical Chemistry Special*)

GROUP – A

Answer any **four** questions : 2×4

1. How is root mean square distance related with diffusion co-efficient ? What is its significance ? $1 + 1$

2. Define surface excess of solute.

3. State and explain a relation showing dependency of hydrostatic pressure on reaction rate.

4. Distinguish between polarizable and non-polarizable interface.

5. What are the advantages of SDS-PAGE over conventional PAGE ?

(*Continued*)

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

GROUP – B

Answer any **four** questions : 4×4

7. Define inherent viscosity and intrinsic viscosity. How is intrinsic viscosity determined experimentally ? 2 + 2

8. (*i*) What is the utility of Potential Energy Surface (PES) in reaction kinetics ?

   (*ii*) Define saddle point.

   (*iii*) How will you justify that saddle point is the suitable position of residing activated complex ? 1 + 1 + 2

9. At 25°C, the density of glucose is 1.55 gcm^{-3}; its diffusion co-efficient is 6.81×10^{-6} cm^2s^{-1} and the co-efficient of viscosity of water is 8.937×10^{-3} Poise. Assuming

that glucose molecule is spherical, estimate its molar mass.

10. State and explain Stokes-Einstein equation for the evaluation of diffusion co-efficient of a macromolecule. How is this equation utilized for determining the radius of the polymer molecule and the molar mass of the polymer ? 2 + 2

11. Write short note on ninhydrin reaction in identifying amino acids.

12. Why do you need to block the thiol side moiety in proteins while analysing it ? Explain it with suitable example.

GROUP – C

Answer any **two** questions : 8 × 2

13. Derive the expression for the rate constant for partial diffusion controlled reaction. Write down the condition at which it becomes full diffusion controlled reaction. 7 + 1

14. Derive the expression of viscosity co-efficient according to transition state theory.

15. Derive Zimm equation for determination of weight average molecular weight of a polymer sample.

16. Write note on solid phase peptide synthesis.

[Internal Assessment – 10 Marks]
