2023

M.Sc.

4th Semester Examination

CHEMISTRY (SPECIAL)

PAPER : CEM-403

Full Marks : 40

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.

Illustrate the answers wherever necessary.

Answer from *any* **one** Section.

SECTION—I
(Physical Chemistry)

Answer from **all** the Groups as directed.

GROUP—A

Answer *any* **four** questions from the following : $2 \times 4 = 8$

1. Define polarizable interface and non-polarizable interface.

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

3. What is the role of flippase protein in a cell membrane?

4. For macromolecules we always determine average molecular weight – Justify.

5. The rate of a reaction at 25 °C is doubled when the pressure is increased from 1 atm to 2000 atm. Calculate $\Delta^{\ddagger}V$, volume of activation, assuming it to be independent of pressure.

6. Why is 'Number Average Molecular Weight' determined by osmometry method, a colligative property?

GROUP—B

Answer *any* **four** questions from the following : 4×4=16

7. The following reactions are essentially diffusion controlled :

   (a) The combination of iodine atoms in water

   (b) The combination of methyl radicals in toluene

If the viscosities of water and toluene at 20 °C are $1{\cdot}002\times10^{-2}$ kg $m^{-1}s^{-1}$ and $5{\cdot}90\times10^{-4}$ kg $m^{-1}s^{-1}$ respectively, estimate the ratio of the rate constants of the two reactions at that temperature. 4

8. A solution of a protein was investigated in an ultracentrifugation velocity measurement at 20 °C, the rotor speed being 50000 r.p.m. The boundary receded as follows :

t(s)	0	300	600	900	1200	1500	1800
r(cm)	6·127	6·153	6·179	6·206	6·232	6·258	6·284

Calculate the sedimentation coefficient and molar mass of the protein. Further data are as follows :

$\bar{v}$ = 0·728 cm^3g^{-1}, ρ = 0·9981 g cm^{-3},
$D = 7{\cdot}62\times10^{-11}$ m^2s^{-1} 4

9. The rate of a full diffusion controlled reaction ***does not*** depend on the sizes of the reactants – Justify the statement. 4

10. Write down the Staudinger equation and explain how the viscosity average molecular weight ($\bar{M}_v$) is determined by using this equation. 1+3=4

11. Briefly describe the mechanism of action of green fluorescent protein. 4

12. Briefly describe the strategies for the analysis of amino acid sequence in a peptide. 4

GROUP—C

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

13. Define weight average molecular weight ($\overline{M}_w$) of a macromolecule and hence derive the expression for determining $\overline{M}_w$ by sedimentation equilibrium method. 1+7=8

14. Trace out the course of the reaction between hydrogen atom and hydrogen molecule using appropriate diagrams of Potential Energy Surfaces (PES). 8

15. Using appropriate expressions for partition functions derive an expression for the rate constant of a reaction, based on the Transition State Theory (TST). 8

16. For a polarizable interface, prove that

$$d\gamma = -q_M dV - (q_M / Z_i F)d\mu_i - \Sigma\Gamma_i d\mu_i$$

where $d\gamma$ is the infinitesimal change in surface tension and the other terms bear useful significance. 8

SECTION—II

(Organic Chemistry)

Answer from **all** the Groups as directed.

GROUP—A

1. Answer *any* **four** questions from the following : $2 \times 4 = 8$

(a) How will you distinguish between cis-decalin and trans-decalin by ^{1}H-NMR spectroscopy?

(b) What are quasi-enantiomers? Give an example.

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

(d) Draw the structure of the most unstable stereoisomer of perhydrophenanthrene and comment on its stereochemical features.

(e) What do you mean by 'molar ellipticity'? Mention its unit.

(f) Why is very high level of diastereoselectivity found for Lewis Acid mediated reactions of enol silanes with aldehydes?

GROUP—B

2. Answer *any* **four** questions from the following : $4 \times 4 = 16$

(a) What are the symmetry elements present in cis decalin and cis-9-methyl decalin? Compare the stabilities of cis- and trans-9-methyl decalins. Draw the conformers of cis-1-thiadecalins and comment on their relative stability. 4

(b) Explain the dibenzoate chirality rule. What is meant by Davydov splitting? $2+2=4$

(c) Compare the stabilities of cis and trans $\Delta^{1,2}$- and $\Delta^{2,3}$-octalins. 4

(d) What is cotton effect? How will you study the conformational changes in (–)-menthone with change in polarity of the solvents using CD curves with Cotton effect? 4

(e) What are plane ORD curves? How do plane curves help to prove that ortho, meta and para isomers of iodophenyl ethers of lactic acids have the same configuration? 4

(f) Explain the Felkin Anh model with a proper example. What is meant by Bürgi-Dunitz trajectory? 4

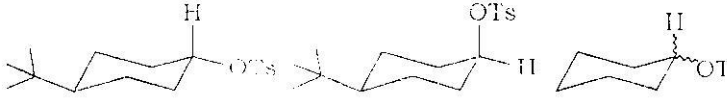
GROUP–C

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

(a) *(i)* Draw all the stereoisomers of cis-1-decalone and cis-1-decalol and comment on their relative stabilities. 5

(ii) State and explain Lowe's rule. 3

(b) Deduce the Winstein – Holness and Eliel – Ro equations. Why has it become obsolete? Calculate the value of equilibrium constant (k) for the system.

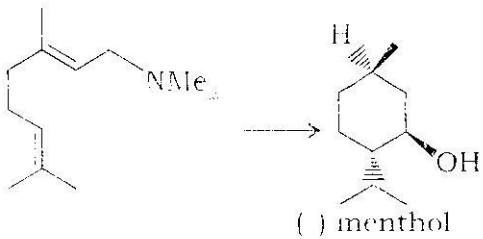


Given, the specific rate constants $k_e = 0$, $k_a = 7{\cdot}1\times10^{-3}\ dm^3\,mol^{-1}\,sec^{-1}$ and the overall empirical rate constant $k = 2{\cdot}4\times10^{-3}\ (dm^3\,mol^{-1}\,sec^{-1}$ at 298·15K. 5+1+2=8

(c) How many stereoisomers are possible for perhydroanthracenes? Write all the possible stereoisomers of perhydroanthracenes and discuss their stereochemical features. 2+6=8

(d) (i) Explain Ciepiak model with a suitable example. What are the drawbacks of this model? 4+2=6

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



( ) menthol

SECTION—III

(Inorganic Chemistry)

Answer from **all** the Groups as directed.

GROUP—A

1. Answer *any* **four** questions from the following : 2×4=8

(a) What are the requirements of acid catalyzed hydrolysis reaction?

(b) Write a short note on 'Edward nucleophilicity scale'.

(c) What are the required conditions for base catalyzed hydrolysis reaction?

(d) State 'Marcus theory' for outer sphere cross reaction.

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

(f) What do you mean by 'residual current'?

GROUP—B

2. Answer *any* **four** questions from the following : 4×4=16

(a) $[M(bpy)_3]^{2+}$ shows acid catalyzed aquation while $[M(phen)_3]^{2+}$ complex does not. Explain with suitable mechanism. [M = Fe, Ni]

(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 large or very small, then what will be the effect on rate law.

(c) Give the mechanism of outer sphere electron transfer reaction with suitable example.

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

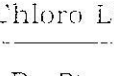
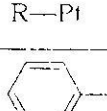
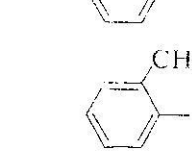
(e) What do you mean by half wave potential? Derive its expression.

(f) What are the advantages and disadvantages of droping Mercury electrode?

GROUP—C

Answer *any* **two** questions from the following : $8 \times 2 = 16$

3. *(a)* Rate constants for Replacement of the Chloro Ligand by Pyridine in $Pt(PEt_3)_2$ (R)Cl

R—Pt	$K(M^{-1} s^{-1})$ Trans (25 °C)	cis (0 °C)
	$1{\cdot}2 \times 10^{-4}$	8×10^{-2}
	$1{\cdot}7 \times 10^{-5}$	2×10^{-1}
	$3{\cdot}4 \times 10^{-6}$	1×10^{-6} (25 °C)

Rationalize the rate of the observed reaction.

(Continued)

(b) Rate of anation of $[Ti(H_2O)_6]^{3+}$ by Y^{n-} at 13 °C is given below :

Y^{n-} (n = 0)	$k(M^{-1}s^{-1})$	Y^{n-} (n = 1)	$k(M^{-1}s^{-1})$
$ClCH_2CO_2H$	$6{\cdot}7\times10^{-2}$	NCS^-	$8{\cdot}0\times10^{3}$
CH_3CO_2H	$9{\cdot}7\times10^{-2}$	$ClCH_2CO_2^-$	$2{\cdot}1\times10^{5}$
H_2O	$8{\cdot}6\times10^{3}$	$CH_3CO_2^-$	$1{\cdot}8\times10^{6}$

Comment on the variation of rate constant in the above reactions. Propose the suitable mechanism for the anation reaction.

4+4=8

4. *(a)* Effect of non leaving ligand on acid hydrolysis rates of some Co(III) complexes are given below :

Complex	$k(s^{-1})$
cis-$[Co(en)_2(OH)Cl]^+$	0·012
trans-$[Co(en)_2(OH)Cl]^+$	$1{\cdot}60\times10^{-3}$
cis-$[Co(en)_2Cl_2]^+$	$2{\cdot}4\times10^{-4}$
trans-$[Co(en)_2Cl_2]^+$	$3{\cdot}5\times10^{-5}$
cis-$[Co(en)_2(NH_3)Cl]^{2+}$	5×10^{-3}
trans-$[Co(en)_2(NH_3)Cl]^{2+}$	$3{\cdot}4\times10^{-3}$
cis-$[Co(en)_2(H_2O)Cl]^{2+}$	$1{\cdot}6\times10^{-5}$
trans-$[Co(en)_2(H_2O)Cl]^{2+}$	$2{\cdot}5\times10^{-6}$
cis-$[Co(en)_2(CN)Cl]^+$	$6{\cdot}2\times10^{-7}$
trans-$[Co(en)_2(CN)Cl]^+$	$8{\cdot}2\times10^{-5}$

Explain these observed trends of the reaction rates.

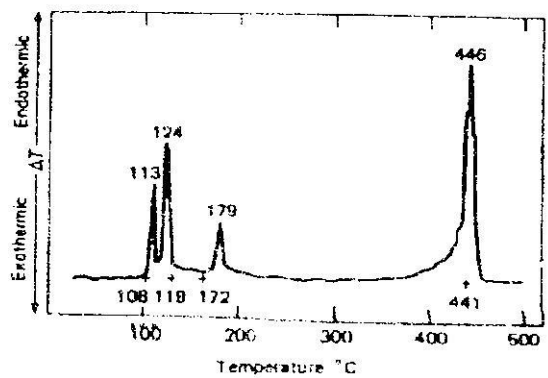
(b) The rate constant for anation by Y^n for $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ are given below at 25 °C :

Y^{n-}	$k(M^{-1}s^{-1})$ for $[Fe(H_2O)_6]^{3+}$	$k(M^{-1}s^{-1})$ for $[Fe(H_2O)_5(OH)]^{2+}$
SO_4^{2-}	$1{\cdot}1 \times 10^{-3}$	$2{\cdot}3 \times 10^{-3}$
Cl^-	$5{\cdot}5 \times 10^{-3}$	$4{\cdot}8$
Br^-	$2{\cdot}6 \times 10^{-3}$	$1{\cdot}6$
NCS^-	$5{\cdot}1 \times 10^{-3}$	90
$ClCH_2COO^-$	$4{\cdot}1 \times 10^{-4}$	$1{\cdot}5 \times 10^{-2}$

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

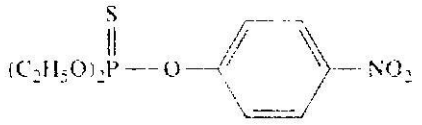
4+4=8

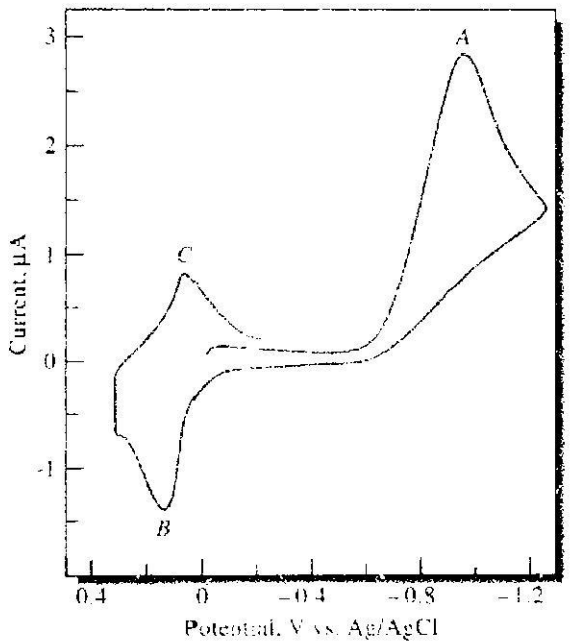
5. Differential thermogram for sulphur is given below :



Explain each peak of the thermogram with proper explanation. 8

6. The cyclic voltammogram for the agricultural insecticide parathion is given below in 0·5 M pH 5 sodium acetate buffer in 50% ethanol.





Using the observed cyclic voltammogram confirm the product produced at *A*, *B* and *C* position. 8

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