2022

M.Sc.

4th Semester Examination

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)

1. Answer any *four* questions : 4×2

(a) What are the symmetry elements present in trans-decalin ?

(b) Draw the two enantiomeric forms of trans-1-decalone and indicate the absolute configurations of the chiral centres.

(c) What do you mean by $A^{1,2}$-strain ? Give an example.

(d) How will you determine the absolute configuration of (–)-trans-1-decalone using axial haloketone rule ?

(e) What do you mean by "circular birefringence" ?

(f) What is meant by "Bürgi-Dunitz trajectory" ?

2. Answer any *four* questions : 4×4

(a) Draw the structures of cis (c) cis and trans (c) trans perhydrophenanthrenes and discuss their stereochemical features.

(b) Explain Brewster's Rule. Why *R*-lactic acid is weakly levorotatory whereas *R*-mandelic acid is strongly leavorotatory in water ? 2+2

(c) What do you mean by specific ellipticity, molar ellipticity and mean residue ellipticity ? What is the unit of molar ellipticity ? 3+1

(d) What is the torsion angle at the junction for $\Delta^{1,2}$-octalin and $\Delta^{2,3}$-octalin in their trans configuration ? Why cis-decalones enolise towards C-1 instead of C-3 ? 2+2

(e) How CD and ORD curves with Cotton effects help us to determine the position of the functional group and study the conformational changes in a molecule ? Explain with suitable examples.

(f) Give a suitable example where a chiral ring system was used as a chiral adjuvant and later removed to get almost totally enantimerically pure products.

3. Answer any *two* questions : 2×8

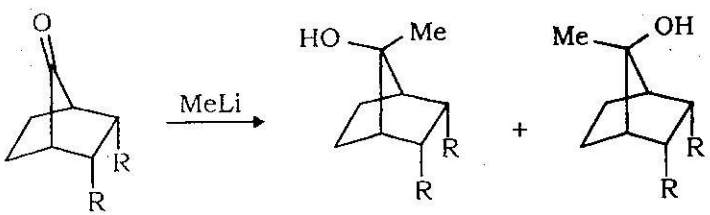
(a) State and derive the Curtin-Hammett principle. In this context also cite an example where the less stable conformer leads to the major product. 6+2

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

(c) (i) Discuss the change in stereochemical features when cis- and trans-1-decalones are reduced to their corresponding decalols. Draw all the possible stereoisomers of cis- and trans-1-decalol and discuss their conformational analysis.

(ii) Draw the possible conformers of cis-decahydroquinolines and compare their relative stabilities. 6+2

(d) State and explain Cieplak model. What are the drawbacks of this model ? Using this model how will you account for the following product distribution for nucleophilic attack by MeLi in substituted norbonones.



R = CO2Me	>90	:	<10
R = Et	17	:	83

Nucleophilic Attack of Substituted Norbornones.

3+2+3

(Inorganic Special)

Group—A

1. Answer any *four* questions : 4×2

(a) What are the requirements for labile and inert system ?

(b) What factors affects the nucleophilicity of a ligand ?

(c) What is two term rate law for square planar complex ?

(d) What are the requirements for labile and inert system ?

(e) What is the role of supporting electrolytes in polarographic measurement ?

(f) State the limitations of dropping Mercury electrode.

Group—B

2. Answer any *four* questions : 4×4

(a) Derive the expression for intimate mechanism for L_5MX complex. Considering Y as an attacking molecule.

(b) Explain the Conjugate base mechanism (CB) with a *suitable example.*

(c) The rate of aquation of $[Co(NH_3)_5X]^{2+}$ ($X = F^-$, Cl^-, Br^-, I^-) follows the order $I^- > Br^- > Cl^- > F^-$ but in case of $[Co(CN)_5X]^{3-}$ is $F^- > Cl^- > Br^- > I^-$. Explain the results.

(d) Acid catalyzed aquation of chromium complex of ethylenediamine is slower than that of the biguanide complex. Explain.

(e) What is a polarographic maximum ? How do you eliminate this problem ?

(f) Deduce the relationship between half wave potential and standard redox potential of a system.

Group—C

Answer any *two* questions. 2×8

3. (a) 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)	$k(M^{-1}s^{-1})$
$ClCH_2CO_2H$	6.7×10^2	NCS^-	8.0×10^3
CH_3CO_2H	9.7×10^2	$ClCH_2CO_2^-$	2.1×10^3
H_2O	8.6×10^3	$CH_3CO_2^-$	1.8×10^6

Comment on the rate constant variation. By which mechanism the reactions will proceed ?

(b) The table below presents rate constants and activation parameters for interchange of the entering and leaving groups in the coordination sphere of anation of $[Cr(NH_3)(H_2O)]$ at 50°C.

Entering ligand	10^4k (s^{-1})	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)
NCS^-	6.12	102	12
$HC_2O_4^-$	6.2	112	39
$C_2O_4^{2-}$	6.2	104	33
H_3PO_4	1.45	–	–
$H_2PO_4^-$	1.45	–	–
$[Co(CN)_6]^{3-}$	2.5	103	26
H_2O (exchange)	13.7	97	0

What do these data suggest about the mechanism of these reactions ? 4+4

4. (a) Activation parameters for the following Co(III) reductions by V^{2+} are as follows :

Complex	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)
$[CoF(NH_3)_5]^{2+}$	46.4	–77.4
$[CoCl(NH_3)_5]^{2+}$	31.4	–120
$[CoBr(NH_3)_5]^{2+}$	30.1	–115

Complex	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)
$[CoI(NH_3)_5]^{2+}$	30.5	–103
$[Co(N_3)(NH_3)_5]^{2+}$	48.9	–58.5
$[Co(SO_4)(NH_3)_5]^{2+}$	48.5	–54.8

Assign the mechanism for these reactions with suitable explanation.

(b) Rate constant for some redox reaction at 25°C are given below :

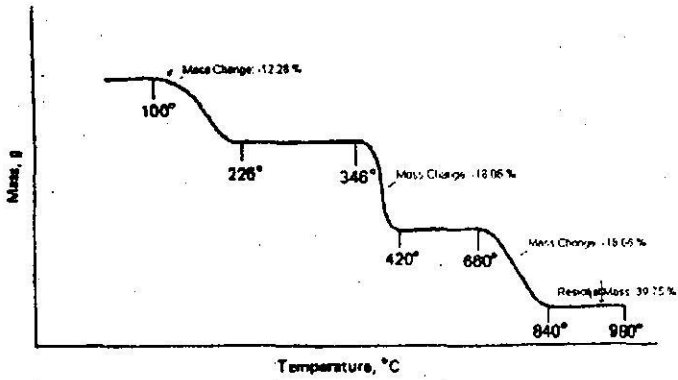
Reaction	Product	$k(M^{-1}s^{-1})$
$[CoNCS(NH_3)_5]^{2+} + Cr^{2+}$	$CrSCN^{2-}$	19
$[CoN_3(NH_3)_5]^{2+} + Cr^{2+}$	CrN_3^{2+}	3×10^5
$[CoSCN(NH_3)_5]^{2+} + Cr^{2+}$	71% $CrNCS^{2+}$ + 29% $CrSCN^{2+}$	1.9×10^5

Rationalize the observed trends of these reactions. 4+4

5. (a) Some volumes activation for base hydrolysis is given below. Rationalize the trends observed.

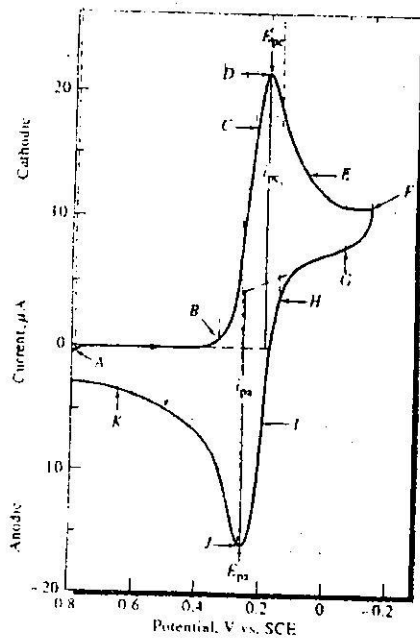
Complex	$\Delta V^{\#}$ (cm^3/mol)
$[Co(NH_3)_5(O = C(NMe_2)H]^{3+}$	+ 43.2
$[Co(NH_2Me)_5Cl]^{2+}$	+ 32.7
$[Co(NH_2Et)_5Cl]^{2+}$	+ 31.1
trans – $[Co(en_2)Cl_2]^+$	+ 24.8
cis – $[Co(en_2)Cl_2]^+$	+ 27.9

(b) A thermogram for decomposition of $CaC_2O_4 \cdot H_2O$ is shown below :



Explain the thermogram. 4+4

6. Cyclic voltammogram for a solution that is 6.0 mM in $K_3Fe(CN)_6$ and 1.0 M in KNO_3 is given below :



Explain the observed cyclic voltammogram. 8

(Physical Special)

Group—A

Answer any *four* questions. 4×2

1. How does the rate of a reaction depend on hydrostatic pressure ?

2. Why viscosity method for determination of average molecular weight of a polymer is not an accurate method ?

3. What do you mean by surface excess ?

4. What is Einstein Smoluchowski equation ?

5. Define particle scattering factor of a macromolecule.

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

Group—B

Answer any *four* questions. 4×4

7. Equal number of molecules with M_1 = 10,000, M_2 = 50,000 and M_3 = 1,00,000 are mixed. Calculate the polydispersity index (PDI) of the polymer solution. Interpret the result.

8. Predict (with brief explanation) the sign of the entropy of activation for the following reaction :

   (a) $ClCH_2COO^- + HO^- \longrightarrow HO\,CH_2COO^- + Cl^-$

   (b) $CH_3Br - 2H_2O \longrightarrow CH_3OH + H_3O^+ + Br^-$

   2+2

9. Estimate the diffusion controlled rate constant for the recombination of iodine atom in n- Hexane solution at 25°C, given η for Hexane is 0.325 cP.

10. Define fuel cell and its efficiency. Differentiate between low temperature fuel cell and high temperature fuel cell. (1+1)+2

11. Explain with the appropriate graphical representation, the pH metric titration of glutamic acid.

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

Group—C

Answer any *two* questions. 2×8

13. Describe the thermodynamics involved in Flory Huggins model for a polymer solution.

14. Derive the expression for the rate constants for full microscopic diffusion controlled reaction.

15. Derive the relation between the viscosity co-efficient of a liquid and entropy of activation of a reaction which occurs in the liquid phase.

16. Write short notes on ESIMS and TOFSIMS in identifying/determining the molecular weights of proteins.

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