2018

M.Sc. 4th Semester Examination

CHEMISTRY

PAPER—CEM-402

Subject Code—24

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

Answer any *four* questions.   2×4

Group—A (1)

Draw the 3d structures for the following conformers and show in them different steric interactions including their optical properties :

1. *cis-transoid-cis* perhydroanthracene

2. *trans-cisoid-cis* perhydrophenanthrene

3. *trans-transoid-cis* perhydroanthracene

4. *trans-transoid-trans* diphenic acid

Group—A (2)

Give the products of the following reactions. Where more than one product is likely to be formed in significant yield, indicate which will be the major product and also predict the mechanism of the reaction involved.

5. OH^- →

6. CH_2I_2 / Zn-Cu →

7. NaOEt →

8. 1) CH_3Li, Et_2O 2) H_2O →

(Continued)
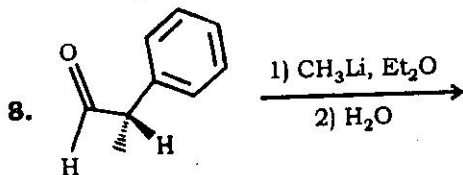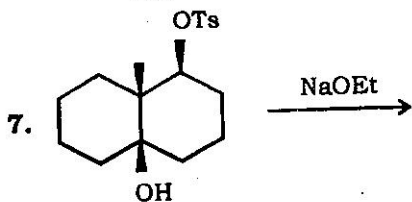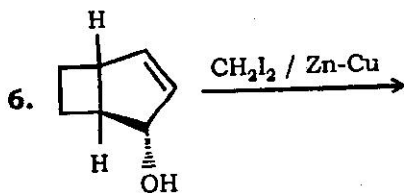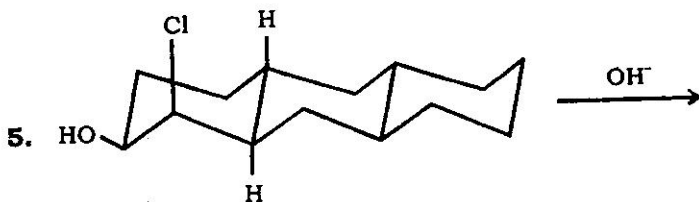
Group—B

4×4

Group—B (1)

Write in brief with *one* example in each case :

9. Allylic 1, 2-strain

10. Allylic 1, 3-strain

11. 2-alkylketone effect

12. 3-alkylketone effect

Group—B (2)

Write in brief about the following terms :

13. ORD

14. CD

15. Cotton Effect (CE)

16. Octant Rule

Group—C

Answer any *two* questions.   8×2

17. Write all the possible streoisomers of perhydrophenanthrenes and correlate them with perhydrodiphenic acids by epimerization protocols.

18. Predict the product with appropriate mechanism and product's sterochemistry :   4×2

(a)

LiAlH₄, Et₂O, 35°C →

(b)

OsO₄ / H₂O →

I₂ + AgOAc / H₂O ↓
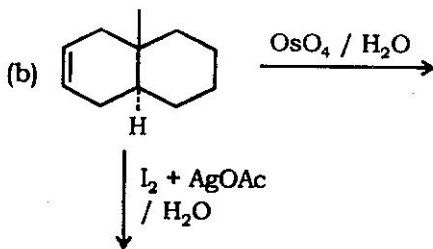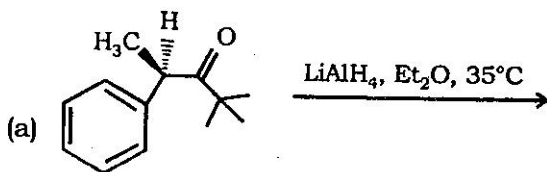
19. State and derive Curtin Hammett Principle with examples of all the cases.

20. Write all the methods known for determining (e, e) (enautiomeric excess) with appropriate examples.

———

(*Inorganic Special*)

Group—A

1. (a) Answer any *two* questions : 2×4

   (i) What is intimate mechanism (I) ?

   (ii) What is the difference between I_a and I_d mechanism ?

   (iii) What are substitutionally inert and labile systems ?

   (iv) What is η_{pt} Scale ? Write down the equation.

   (b) Answer any *two* questions : 2×4

   (i) Derive Ilkovic equation.

   (ii) Discuss the effect of pH on polarograms.

   (iii) Write the characteristics of used solvent for cyclic voltammetry experiment.

   (iv) Write the characteristics of supporting electrolytes for the cyclic voltammetry experiment.

Group—B

2. (a) Answer any *two* questions : 2×4

   (i) Derive the rate law of associative mechanism for L_5MX complex where seven coordinated intermediate possess appreciable life time. Considering Y as attacking molecule.

(ii) The rate of equation of $[Co(NH_3)_5X]^{2+}$ and $[Co(CN)_6X]^{3-}$ $(X = F^-, Cl^-, Br^-, I^-)$ follows the order $I^- > Br^- > Cl^- > F^-$ and $F^- > Cl^- > Br^- > I^-$, respectively. Explain.

(iii) Discuss conjugate base mechanism (CB) with a suitable example.

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

(b) Answer any *two* questions :   2×4

(i) Represent cyclic voltametric profile using US convension and IUPAC convension. Indicate the (i) current of forward peak, (ii) current return peak, (iii) potential of the forward peak and (iv) potential of the return peak.

(ii) Write short notes on saturated calomel electrode (SCF).

(iii) State the merits of polarographic analysis.

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

Group—C

3. Answer any *two* questions.   8×2

(i) (a) Deduce the relaltionship between half wave potential and standard redox potential of a system.   5

(b) What condition should be maintained in polarographic analysis ?   3

(ii) (a) Show how the energy of electrons inside the electrode change with electrode potential.   4

(b) Explain the TG curve for $CaC_2O_4.H_2O$.   4

(iii) (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	$ClCH_2CO_2^-$	2.1×10^5
H_2O	8.6×10^3	$CH_3CO_2^-$	1.8×10^6

Comment on the variations of the rate constants of the above reactions.

Propose the possible mechanism of the above reactions.   4

(b) The kinetic parameters of the anation reaction of $[Cr(NH_3)(H_2O)]$ at 50°C are given below :

Entering ligand	$10^4k\ (s^{-1})$	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/mol K)
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

Propose the possible mechanism for the reactions.

4

(iv) (a) Volume of activation of base hydrolysis reactions are given below. Rationalize the trends observed.   3

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-$[Co(en)_2Cl_2]^+$	+ 24.8
Cis-$[Co(en)_2Cl_2]^+$	+ 27.9

(Continued)

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

Oxidant	Reluctant	k ($M^{-1}s^{-1}$)
$[Co(NH_3)_5H_2O]^{3+}$	Cr^{2+}	≤0.4
$[Co(NH_3)_5(OH)]^{2+}$	Cr^{2+}	1.5×10^6
$[Co(NH_3)_5H_2O]^{3+}$	$[Ru(NH_3)_6]^{2+}$	3.0
$[Co(NH_3)_5(OH)]^{2+}$	$[Ru(NH_3)_6]^{2+}$	0.04

Predict the possible mechanism (inner/outer) for the above reactions.   3

(c) In acidic medium the rate of ligand exchange reaction of Ni(11)-bipyridine is increased, however, for Ni(11)-1, 10-phenanthroline no change in reaction rate is found. Explain.   2

―――

(*Physical Special*)

Group—A

Answer any *four* questions.   2×4

1. Write down the postulate of local equilibrium in non-equilibrium thermodynamics.

2. How does diffusion method is helpful to determine the average molecular weight of a macromolecule.

3. What is sedimentation co-efficient ? What is it's unit ?

4. Define root mean square distance.

5. Define quasicrystal.

6. What is 'geometrical structure factor' of a lattice ?

7. Define 'R_2' center and 'M' center in a crystal.

8. Crystal A diffracts from (111) and (200) planes but not from (110) plane, while crystal B diffracts from (110) and (200) planes but not from the (111) plane. Predict the nature of crystal lattice of A and B.

Group—B

Answer any *four* questions. 4×4

9. Obtain the expression for the entropy production due to flow of heat and hence establish the relation of Newton's law of cooling.

10. Obtain the mathematical formulation of Prigogine's principle of minimum entropy production.

11. Derive the expression for thermoelectric power of a thermocouple.

12. At 25°C, the density of glucose is 1.55 gm cm^{-3} ; its diffusion co-efficient is 6.81×10^{-6} cm^{2}s^{-1} and the co-efficient of viscosity of water is 8.937×10^{-3} Poise. Assuming that the glucose molecule is spherical, estimate its molar mass.

13. Write short note on excition.

14. Discuss BCS theory of superconductivity.

15. Justify the phenomena

(i) A decrease in quantum yield of the reaction $2F \to F'$ in the beginning of the irradiation with F light is observed at temperatures below 140 K.

(ii) A decrease in quantum yield of the reaction $2F \to F'$ decreases as the time of irradiation increases.

2+2

16. Without derivation describe how molecular weight of high polymers is determined using Zimm plot.

(Turn Over)

Group—C

Answer any *two* questions.   8×2

17. The expression for the rate of entropy production for a process having an electrochemical affinity A is given by

$$\frac{diS}{dt} = J\frac{\Delta p}{T} + I\frac{\Delta\phi}{T}.$$

The terms having usual significance. Write the equations for the forces I and J and define
(i) Streaming potential, (ii) Streaming current, (iii) Electroosmotic pressure, (iv) Electroosmosis
and hence write down the relations extremly useful in membrane science.

18. What is the advantage of sedimentation equilibrium method over sedimentation velocity method ? Discuss the sedimentation equilibrium method for the determination of molar mass of a polymeric molecule.

19. Describe the thermodynamics involved in Flory-Huggins model for a polymeric molecule.

20. (a) Discuss the mechanism of formation of 'F' center in a crystal.

    (b) The density of Li metal is 0.53 g/cc and the separation of the (100) planes of the metal is 350 pm. Determine whether the lattice is fcc or bcc ?   6+2

————