M.Sc. 3rd Semester Examination, 2012

CHEMISTRY

PAPER—CEM-302

The figures in the right-hand margin indicate marks

(*Organic Special*)

[*Marks* : 40]

Time : 2 hours

Answer any *five* questions taking atleast *two* from each Group

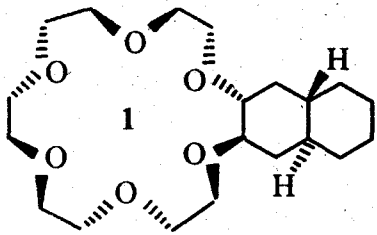
GROUP – A

1. (*a*) Define template effect. 2

(*b*) How does macrocyclization work even though it is an entropically disfavorable process ? 2

(*c*) How does 18-crown-6 bind a monovalent cation ? 2

(*d*) Name the compound **1** and propose a synthetic route. 2



2. (*a*) Write the applications of crown ethers. 2

(*b*) How can one use 'U'-tube transport experiment for the separation of ions/molecules ? 2

(*c*) Design a suitable receptor for monopotassium salts of a dicarboxylic acid, synthesize it and show the mode of its complexation. 4

3. (*a*) What is aromatic-aromatic (π-π) interaction ? 2

(*b*) Show schematically the potential energy diagram for two interacting π-atoms as a function of their orientation. 2

(*c*) Charge transfer transitions observed for EDA complexes are a consequence not a cause of the more general π-π interaction. 2

(*d*) Give an example of Host-Guest complexation utilizing aromatic-aromatic interaction. 2

4. (*a*) What are the different types of natural penicillin obtained from microbial sources ? Write their names. State the different path ways by which the pathogenic microbes are inhibited by antibiotics. 4

(*b*) Synthesise *d*-penicillamine starting from *d*, *l*-valine. 4

5. Outline the different steps for the synthesis of benzyl penicillin from phthalimide as carried out by sheehan et.al. 8

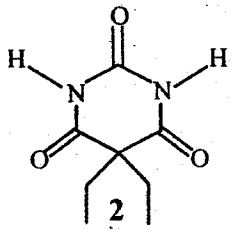
GROUP – B

6. (*a*) Write the significance of multiple recognition sites in the selection of substrates during host-guest complexation. 2

(*b*) Design a suitable **chiral** host for complexing **L-Trp** and show the mode of its complexation. 2

(*c*) Design a receptor for the complexation of barbital **2**. 2

(*d*) Design, and explain the mode of action of a protease enzyme mimic. 2



2

7. (*a*) What are cyclodextrins ? 2

(*b*) *p*-chlorination of anisole is preferred in water in the presence of β-CD with rate acceleration. How do you explain this observation ? 2

(*c*) Describe the use of a cyclodextrin derivative as a Ribonuclease enzyme mimic. 4

8. (*a*) Define hydrophobic effect. 2

(*b*) How can water act as a better solvent than common organic solvents for a simple Diels -Alder reaction ? Illustrate with examples. 3

(*c*) What are 'salting in' and 'salting out' agents ? 3

9. (*a*) Define : Synthon and Synthetic Equivalent. What are the synthetic equivalents for the following synthons: 5

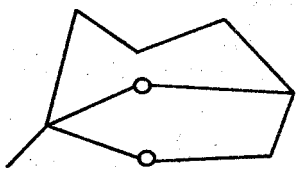
(*i*) $PhC\overset{\oplus}{H}_2$

(*ii*) $PhC\overset{\ominus}{H}_2$

(*iii*) Ph^-

(*b*) What are the criteria for good disconnection ? 3

10. Explain the term (*i*) Functional group interconversion and (*ii*) controll. Illustrate their uses in the retrosynthetic analysis of the following compound : 8



(*Inorganic Special*)

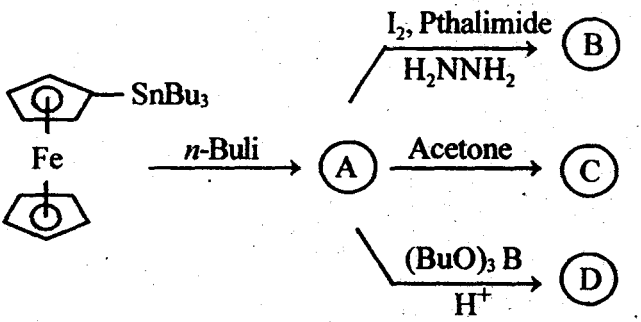
[*Marks* : 40]

Time : 2 hours

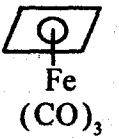
Answer any *four* questions

1. (*a*) $NiCp_2$ readily reacts with a weak acid HF to yield $[NiCp(\eta^4 - C_5H_6)]^{\oplus}$. On the other hand, ferrocene reacts with a strong acid and the protonation occurs at Fe to produce $[Fe(Cp)_2H]^+$. Why does the protonation occur at different sites in these complexes ? Which reaction is facile ? Give a plausible mechanism. 3

(*b*) Predict the products - (*A* - *D*) 4



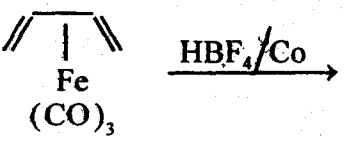
(*c*) Write down the synthesis of $(\eta^6\text{-arene})_2Cr$ by Fischer-Hafner method. What are the limitations for this method ? 2 + 1

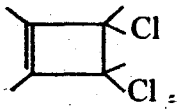
2. (*a*) Explain diamagnetism in  complex. 3

(*b*) Synthesize

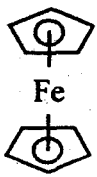
$(C_5H_5)_2\,Mo(H)_2$; starting from $MoCl_5$. 2

(*c*) Complete the following reaction : 5

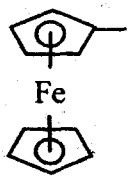
(*i*) 

(*ii*) 

$+ \ Ni(CO)_4 \longrightarrow$

(*iii*) 

$\xrightarrow[H_3PO_4]{Ac_2O}$ *i*) $POCl_3$./DMF, *ii*) NaOAc, *iii*) NaOH/dioxane

(*iv*) 

$\xrightarrow{Cu(OAc)_2}$

3. (*a*) Classify hydrogenation catalystic. 2

(*b*) Briefly discuss the catalytic cycle of alkene hydrogenation reaction by Wilkinson's Catalyst. 4

(*c*) Mention the name and structure of two hydrogenation catalysts other than Wilkinson catalyst. 2

(*d*) What is insertion reaction ? 2

4. (*a*) Write down the reactions involved in the 'Wacker Process'. 2

(*b*) Draw the catalytic cycle of wacker Oxidation. 4

(*c*) What is 'Hydroformylation Reaction' ? Which catalyst is generally used for this process ? 2

(*d*) Write down the drawbacks related to the 'Monsanto Process'. 2

5. (*a*) Explain why X-rays are suitable probe for exploring structure of crystalline solid materials. 1

(*b*) Show that the condition for bright diffraction spots in X-ray diffraction pattern from a solid crystalline material is $\Delta \mathbf{K} = \mathbf{G}$. Here $\Delta \mathbf{K}$ is the change in the wave vector and $\mathbf{G}$ is the reciprocal wave vector. 3

(*c*) From the above expression derive the Bragg's law of diffraction. 3

(*d*) Derive Laue diffraction conditions in case of diffraction from crystalline solids. Interpret these equations. 3

6. (*a*) What is reciprocal lattice and give its importance. 2

(*b*) Show that the reciprocal lattice of FCC lattice is BCC lattice. 4

(*c*) Derive an expression for the crystal structure factor and from it give the systematic absence conditions for a FCC lattice. 4

7. (*a*) How can you stabilize +VI oxidation state of Fe. Give example. 2

(*b*) How Ni(III) complex can be prepared ? Discuss with a suitable example. 1 + 2

(*c*) Write down the synthesis of $K_4[Ru_2OCl_{10}]$. Explain the diamagnesim of the complex. 2 + 3

(*Physical Special*)

[*Marks* : 40]

Time : 2 hours

Answer any *four* questions taking *two* from each Group

GROUP – A

1. Use, without derivation, the expression connecting entropy and molecular partition function and hence obtain Sackur-Tetrode equation for the molar entropy of an ideal monatomic gas. 10

2. Define the probability that a canonical system 'A' under the condition of statistical equilibrium is in a state with energy 'E_a' and derive the Gibbs canonical distribution. 10

3. What is meant by Bose-Einstein condensation? Obtain the expression for the temperature at which the condensation phenomenon may occur. 2 + 8

4. (*a*) Discuss different steps involved in the determination of heat of ion-solvent interaction by Eley-Evan's model. 4

(*b*) Why limiting Debye-Hückel equation of mean-ionic activity co-efficient needs modification? Convert the extended form to the limiting form of Debye-Hückel equation under proper condition. 2 + 4

GROUP – B

5. (*a*) What do you understand by the term microscopic diffusion controlled reaction ? Derive the expression of rate constant for full microscopic diffusion controlled reaction ? 2 + 6

(*b*) The rate of a reaction in solution at 30 °C is increased by 4 times when the pressure difference was made to 1000 atm. Calculate the volume of activation of the reaction. 2

6. Derive the appropriate expression which show the application of absolute reaction rate theory in viscosity problem. 10

7. (*a*) The following reaction occurs in aqueous solution

$$Cr(H_2O)_6^{3+} + CNS^- \longrightarrow Cr(H_2O)_5CNS^{2+} + H_2O$$

Deduce qualitatively the following :

(*i*) The effect on the rate of decreasing dielectric constant,

(*ii*) The effect on the rate of increasing ionic strength,

(*iii*) The effect on the rate of increasing the hydrostatic pressure,

(*iv*) The sign of the entropy of activation. 6

(*b*) For the reaction between two nonionic species *A* and *B* in water at 25 °C, radius of *A* and *B* are 0·3 nm and 0·4 nm respectively. Calculate the rate constant in $dm^3m^{-1}sec^{-1}$. Viscosity coefficient of water is 0·9 cp at this temperature. 4

8. (*a*) What is an electro-capillary curve ? What information can you obtain from such curve ? 1 + 2

(*b*) Starting from equation

$$d\gamma = -q_M dV - \frac{q_M}{Z_j F} d\mu_j - \sum \Gamma_i d\mu_j$$

Derive

$$\left(\frac{d\gamma}{2RTd\ln a_{\pm}}\right)_{\text{const. } V_{-/+}} = -\Gamma_{+/-}$$

for 1 : 1 type of electrolyte, where γ = surface tension and Γ_i = surface excess for *i*-th type of species at the interface, and all other terms bean usual significance. 7
