M.Sc. 3rd Semester Examination, 2011

CHEMISTRY

PAPER—CHE-302

Full Marks : 40

Time : 2 hours

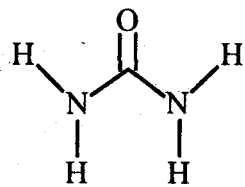
The figures in the right-hand margin indicate marks

(*Organic Special*)

Answer any **five** questions, taking at least **two** from each Group

GROUP – A

1. Define molecular recognition. What are the forces involved in molecular recognition ? Design a suitable receptor for urea, synthesize it and show the mode of its complexation. 2 + 2 + 4



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

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

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

(*d*) Give an example of Host-Guest complexation utilizing aromatic-aromatic interaction. 2 × 4

3. Account for the following observed results : 4 × 2

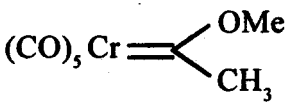
(*a*) Two different isomers are obtained when fluorene with one of the aromatic sings coordinated with $Cr(CO)_3$, after treatment with base is treated with methyliodide at – 40 °C and – 20 °C respectively.

(*b*) While carrying out nucleophilic displacement of chlorine of chlorobenzene chromium tricarbonyl complex with lithium isobutyronitrile, a mixture of products is obtained if the reaction is oxidatively quenched before completion.

4. Explain the following : 4 + 4

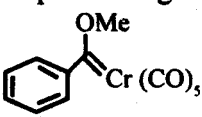
(*a*) Successive treatments of the dimethyl acetal of benzaldehyde chromiumtricarbonyl with R R-butane-2, 3-diol in the presence of catalytic amount of *para*-toluenesulfonic acid, Me_3Al in the presence of 1 equivalent of $TiCl_4$ and finally acetonitrile in the presence of sulfuric acid gives a homochiral products.

(*b*) Discuss the preparation of the following Fischer carbene from $Cr(CO)_6$:

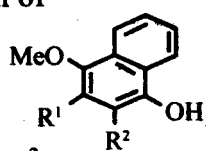


How would you convert it into α-methylene-γ-butyrolactone ? Explain the reason behind the facile aminolysis of this carbene.

5. (*a*) What are the essential differences between Fischer and Schrock Carbenes ? Discuss the steps leading to the conversion of



into a

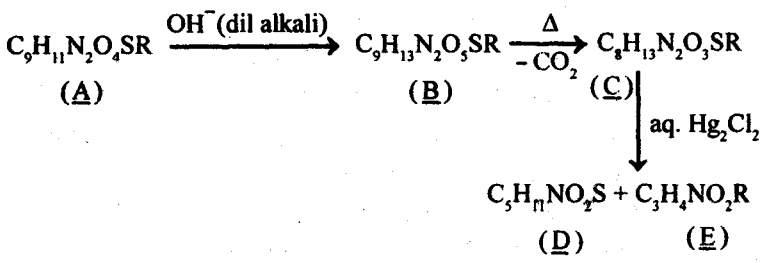


through reaction with $R^1-\equiv-R^2$.

(*b*) Account for the chirality of the chromium tricarbonyl complex of *ortho*-methexy benzaldehyde. How the racemic mixture obtained upon complexation of the aldehyde is resolved with the aid of *L*-valinol ? 4 × 2

GROUP – B

6. The following reaction sequence of Penicillin yields the products as :



Identify compounds (D) and (E) and hence deduce the possible structure of (A) showing the intermediate structures (B) and (C). 8

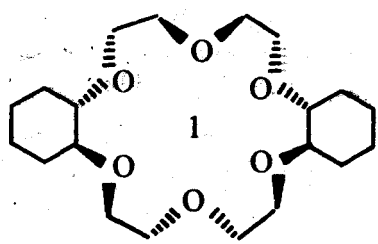
7. Confirm the structure of Penicillin through IR spectroscopic evidences. 8

8. (*a*) Define hydrophobic effect.

(*b*) Describe the effect of water as a medium on the rates of an organic reaction.

(*c*) *p*-chlorination of anisole is preferred in water in the presence of β-CD with rate acceleration. How do you explain this observation ? 2 + 3 + 3

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



(*b*) How can crown ethers be used for the transport of metal ions through liquid membrane ?

(*c*) Write the applications of crown ethers. 3 + 3 + 2

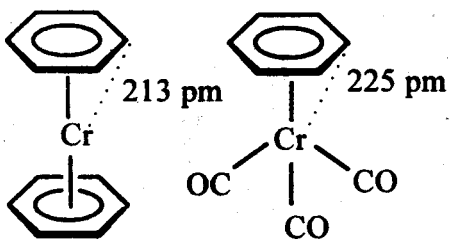
10. (*a*) Define cryptands. Give examples and elaborate on their complexation properties.

(*b*) How can cryptands be used for light conversion devices ? 4 + 4

(*Inorganic Special*)

Answer any **four** questions

1. (*a*) Based on the following data comment on the reactivity order of the following compounds towards electrophilic substitution reaction into the η^6-arene ring and justify your answer. 2

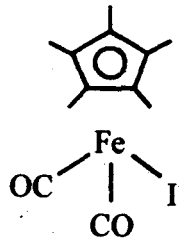


(*b*) Complete the following reactions : 6

(*i*)  $+ RuCl_3 . nH_2O \xrightarrow{EtOH}$

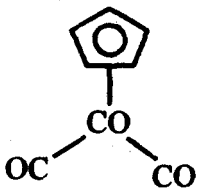
(*ii*) $Mn(CO)_5 Cl +$  $\xrightarrow{AlCl_3}$

(*iii*)



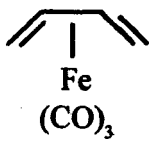
$\xrightarrow[(ii)\ C_5H_6]{(i)\ AgBF_4}$ $\xrightarrow{Et_3N}$

(*iv*)



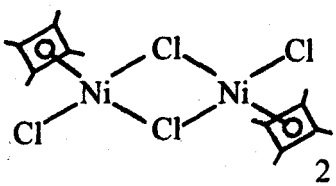
$\xrightarrow[\Delta]{RC \equiv CR}$ Xylene

(*v*)



$\xrightarrow{HCl}$

(*c*) How will you synthesize



and $(\eta^6\text{-arene})_2Cr$? 2

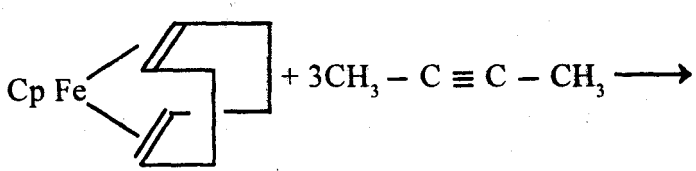
2. (*a*) When η^3-allyl-Ru $(NO)(PPh_3)_2$ reacts with CO, a new 18 e compound with the formula

allyl-Ru(NO) $(PPh_3)_2$ (CO) is produced. Draw two possible structures of the new compound showing the binding modes of the ligands. For each compound, indicate the *d*-electron count around the metal centre. 2

(*b*) Nickel carbonyl reacts with cyclopentadiene to produce a stable red, diamagnetic compound of formula $NiC_{10}H_{12}$. The ^{11}H NMR spectrum of this compound at RT shows four different types of hydrogen; integration gives relative areas of 5 : 4 : 2 : 1, with the most intense peak in the aromatic region. Suggest a structure for $NiC_{10}H_{12}$ that is consistent with this NMR spectrum. 3

(*c*) Discuss the diamagnetism of $(\eta^4\text{- } C_4H_4)\ Fe(CO)_3$. 3

(*d*) Complete the following reaction : 2



3. (*a*) What is oxidative addition reaction ? What are the main features for this reaction ? Write down the essential requirements for this type of reaction. 1 + 1 + 2

(*b*) Write down the catalytic cycle for Monsanto acetic acid process. What are the problems with the Monsanto acetic acid process ? 3 + 2

(*c*) What is the catalyst used for British Petroleum's cativa process for the production of acetic acid ? 1

4. (*a*) Discuss the catalytic cycle for hydroformylation reaction. 4

(*b*) Write down the structure of two hydrogenation catalysts other than Wilkinson's catalyst. 2

(*c*) What is catalytic converter ? 2

(*d*) What do you mean by insertion reaction and oxidative coupling ? 2

5. (*a*) Describe the three broad classes of DNA adducts that can be made by bifunctional Platinum complexes ? 3

(*b*) What are the biological consequence of Platinum -DNA binding ? 2

(*c*) What type of spectral transition is expected in inorganic transition metal-based dendrimers ? 3

(*d*) What do you mean by convergent and divergent approach of formation of dendrimers ? 2

6. (*a*) Explain why X-rays are suitable probe for exploring structure of crystalline solid materials ? 2

(*b*) Discuss the role of electron and neutron diffraction in the analysis of crystal's interior, mentioning the points where their application outstands from X-ray diffraction. 4

(*c*) Distinguish between Laue diffraction pattern and powder X-ray diffraction pattern. 4

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

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

(*c*) The Bragg angle for reflection from the (III) planes in aluminium (fcc) is $19{\cdot}2^{\circ}$ for an X-ray wavelength of $\lambda = 1{\cdot}54$ Å. Compute : (*i*) the cube edge of the unit cell. (*ii*) the interplanar distance for these planes. 2 + 2

(*Physical Special*)

GROUP – A

Answer any *one* of the following

1. (*a*) Explain the term partition function and derive the expression relating entropy and molecular partition function.

(*b*) Calculate the vibrational contribution to the molar entropy of F_2 at 300K. (Given : fundamental vibrational frequency $\gamma = 2{\cdot}676 \times 10^{13}\ s^{-1}$, $h = 6{\cdot}62 \times 10^{-34}$ Js and $K = 1{\cdot}38 \times 10^{-23}\ JK^{-1}$). 6 + 4

2. Define grand partition function for fermions and hence obtain the Fermi-Dirac quantum statistical distribution. 10

GROUP – B

Answer any *one* of the following

3. Explain the significance of the Lagrangian multipliers α and β with reference to particle and energy exchanges in statistical equilibrium, evaluate β and obtain the relation between α and β. 2 + 3 + 5

4. (*a*) What is the basic principle for studying a chemical reaction in Shock-tube method ?

(*b*) Using appropriate partition function, obtain the expression for the reaction rate constant according to the transition state theory ? 2 + 8

GROUP – C

Answer any *one* of the following

5. (*a*) What is COL or saddle point ?

(*b*) Find out the rate constant of a reaction between two charged species according to the double sphere activated. Complex model and hence discuss the effect of solvent dielectric constant on the rate of the reaction. 1 + 9

6. (*a*) What is the influence of hydrostatic pressure on the rate of a reaction ?

(*b*) The activation energy and frequency factor for the reaction

$$H(g) + Br(g) \rightarrow HBr(g) + Br(g)$$

are $15{\cdot}5\ kJmol^{-1}$ and $1{\cdot}09 \times 10^{11}\ dm^3mol^{-1}s^{-1}$ respectively. What are the values of $\Delta^{\neq} H^0$, $\Delta^{\neq}S^0$ and $\Delta^{\neq}G^0$ at 1000K based on a standard state of $1{\cdot}00\ moldm^{-3}$? Assume ideal gas behavior.

(*c*) The following reactions are found to be essentially fully diffusion controlled :

(*i*) The combination of iodine atoms in water.

(*ii*) The combination of methyl radicals in toluene.

If the viscosities of water and toluene at 20 °C are $1{\cdot}002 \times 10^{-3}\ kgm^{-1}s^{-1}$ and $5{\cdot}90 \times 10^{-4}\ kgm^{-1}s^{-1}$, respectively, estimate the ratio of the rate constants of the two reactions at that temperature. 2 + 4 + 4

GROUP – D

Answer any *one* of the following

7. (*a*) Show that the parallel plate condenser model can explain electro-capillary curve which is perfect parabola. 4

(*b*) Derive :

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

for an electrolyte, where γ = surface tension and Γ_i = surface excess for *i*-th type of species at the interface and all other terms bear usual significance. 6

8. (*a*) Give a schematic representation of the Stern double layer and explain briefly its salient features. How would you express the total capacity at an electrode solution interface at high and low concentrations separately following Stern model ? 5

(*b*) Derive an expression of enthalpy change of ionic solvation using Born model. 5
