M.Sc. 3rd Semester Examination, 2010

CHEMISTRY

(*Physical Special/Inorganic/Organic Special*)

PAPER—CH-2102

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Physical Special*)

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

GROUP—A

Answer any *two* of the following

1. (*a*) Obtain the Sackur-Tetrode equation for the molar entropy of a monoatomic gas.

   (*b*) Calculate the characteristic rotational temperature for H_2 gas at 2727 °C, given that the moment of Inertia of hydrogen gas molecule is $4{\cdot}60\times10^{-48}$ kgm^2, $h = 6{\cdot}62\times10^{-34}$ Js and $k = 1{\cdot}38\times10^{-23}$ JK^{-1}. 7 + 3

2. Define grand partition function for bosons and show that the Bose-Einstein distribution leads to an ideal gas equation. 10

3. Considering an appropriate composite system of two non-interacting systems in thermal contact, derive the Gibbs canonical distribution. 10

4. (*a*) State the postulate of equal a priori probabilities and define the ensemble average and time average of a quantity. What is Ergodic hypothesis ?

   (*b*) Define the Lagrangian multiplier β and obtain its expression in term of temperature. Can β be negative ? Explain your answer.

(2 + 2 + 1) + (2 + 3)

GROUP – B

Answer any *two* of the following

5. (*a*) Describe a suitable method by which the kinetic reactions which do not obey Maxwellian distribution, are studied.

(*b*) What is the utility of potential energy surface (PES) in a kinetic reaction ?

(*c*) Justify the statements –

(*i*) In a reaction between two ions entropy of activation always decreases after formation of activated complex due to electrostriction.

(*ii*) The plot of log K_r(K_r = rate constants) against $\sqrt{\mu}$ (μ = ionic strength) for the reaction of base catalysed hydrolysis of ethyl acetate is parallel to X-axis.

3 + 1 + (3 + 3)

6. (*a*) Is the absolute reaction rate theory applicable to calculate viscosity co-efficient (η) of a liquid ?

(*b*) Prove that

$$\eta = \left(\frac{N}{V}\right)^{2/3} \frac{\mathrm{CRT}}{\Delta E_{vap}} (2\pi mkT)^{1/2} e^{\epsilon_0/KT}$$

where the symbols have their usual meanings.

1 + 9

7. (*a*) A reaction between two ionic species of same charge is carried out two different solvents (*i*) acetone and (*ii*) hexane. The reaction rate in acetone was found higher than that of hexane. Justify.

(*b*) What do you understand by microscopic diffusion controlled reactions? Derive the expression for the rate constant of full microscopic diffusion controlled reaction.

4 + (1 + 5)

8. (*a*) Starting from equation

$$d\gamma = -q_\mu d_v - \frac{q_\mu}{Z_j F} d\mu_j - \sum \Gamma_i \, d\mu_i$$

derive

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

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 bear usual significance.

(*b*) The standard electrode potentials E°(298 K) for Cu^{2+}/Cu and Cu^{+}/Cu are 0·337 and 0·530 V, respectively. In general, is it easier to oxidize Cu to the +2 or +1 state ? Can you suggest any reason for your answer based on the electronic structures of the ions and related factors ? What is the equilibrium constant for the reaction

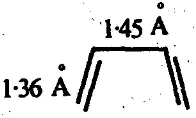
$$2Cu^{+} \rightarrow Cu^{2+} + Cu \text{ at } 298K$$

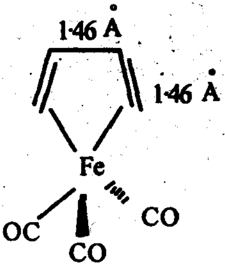
Describe what happens when a piece of Cu_2O is dissolved in dilute H_2SO_4. 6 + (1 + 1 + 1 + 1)

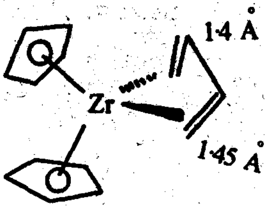
(*Inorganic*)

Answer any **four** questions

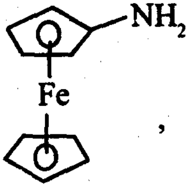
1. (*a*) Consider the bonding of 1, 3-butadiene to Fe and Zr and explain the bond length data 3







(*b*) Synthesize the following compounds starting from ferrocene : 6



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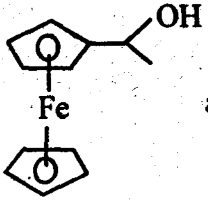

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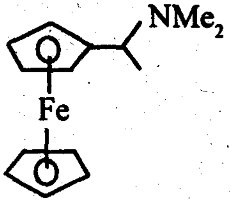


(*c*) How will you synthesize $(C_p)_2Ti$ starting from $TiCl_4$. 1

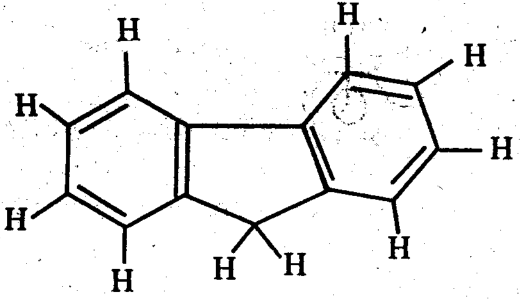
2. (*a*) Compound 'A' forms an ionic organometallic compound with a CpFe fragment and obeys 18e rule. It has molecular formula

$$[C_5H_5Fe\,(C_{13}H_{10})]^+\,[PF_6]^-$$

(B)

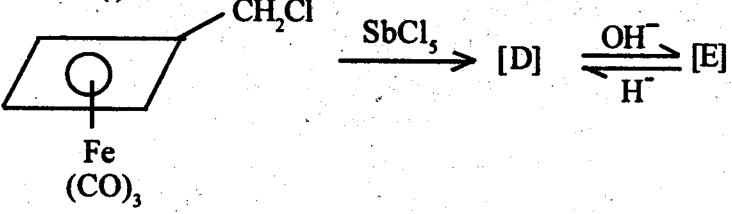
Treatment of 'B' with a base results in another 18e organometallic complex 'C' with the formula $[(C_5H_5)Fe\,(C_{13}H_9)]$. Draw reasonable structures of complexes 'B' and 'C'. 4

A =

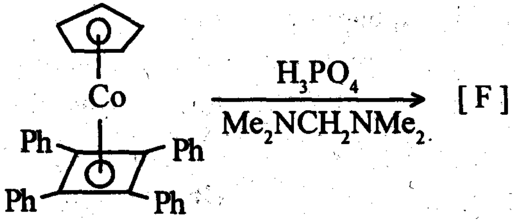


(*b*) Identify [D] to [G] 4

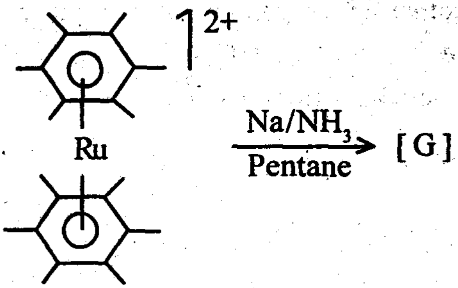
(*i*)



(*ii*)



(*iii*)



(*c*) How ferrocene is prepared industrially? 2

3. (*a*) What do you mean by 'Turnover number (TON)' and 'Turnover Frequency (TOF)'? 3

(*b*) Discuss the catalytic cycle for hydrogenation using Wilkinsons catalyst. 3

(*c*) Write down the name of two catalysts (other than Wilkinson's catalyst) with their structures which catalyzes homogeneous hydrogenation reaction. 2

(*d*) What is 'Suzuki-Miyaura coupling'? 2

4. (*a*) What is inorganic dendrimers? 2

(*b*) Construct [$OsRu_9$] taking 2, 3-dpp; 2,5-dpp; Me-bpy, bpy as ligands wherever necessary you can use any number of ligands
(2, 3-dpp = 2, 3-Dipyridyl pyrazine;
2, 5-dpp = 2, 5-Dipyridylpyrazine
Me-bpy = 4-Methyl-2, 2′-bipyridyl;
bpy = 2, 2′-Bipyridyl). 5

(*c*) What do you mean by divergent and convergent mode of dendrimer formation? 3

5. (*a*) What are the empirical rules governing the chemotheraputic potential of platinum ammine complexes? 2

(*b*) What is the rate-determining step of the platinum-DNA complex formation? 2

(*c*) How would you prepare [Os(bpy) $(Cl_4Cat)_2$] [bpy = 2, 2′-Bipyridyl; Cl_4Cat = 3, 4, 5, 6-Tetrachlorocatechol]. 4

(*d*) Cite an example of each of Platinum (III) and Palladium (III) complex with structure. 2

6. (*a*) Distinguish between single crystal, polycrystal and amorphous materials. 1

(*b*) Distinguish between primitive and non -primitive lattice. 1

(*c*) Briefly describe the powder method in X-ray crystallography with a schematic description of the experimental set up and the utility of this method. 4

(*d*) What is reciprocal lattice and why is it relevant? Show that the reciprocal lattice of F.C.C. lattice is a B.C.C. lattice. 1 + 3

7. (*a*) Why X-ray is appropriate probe for exploring internal structure of crystalline material? 1

(*b*) Derive Laue conditions for X-ray diffraction from crystalline materials. 3

(*c*) Derive the expression for crystal structure factor. 3

(*d*) What are systematic absences? Derive the systematic absence condition of a B.C.C. lattice. 1 + 2

(*Organic Special*)

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

GROUP – A

1. (*a*) Define template effect. How does macrocyclization works even though it is an entropically disfavorable process? 2 + 2

(*b*) Design, synthesize and illustrate the mode of complexation of a receptor for mono-potassium salt of maleic acid. 4

2. (*a*) Write the significance of multiple recognition sites in the selection of substrates during host-guest complexation. 3

(*b*) Design a suitable chiral host for complexing L-Trp. 2

(*c*) Design, synthesize and explain the mode of action of a protease enzyme mimic. 3

3. Account for any *two* of the following observed results : 4 x 2

(*a*) Treatment of $Cr(CO)_3$ complex of toluene with *n*-butyl lithium in tetrahydrofuran is devoid of any regiocontrol but the same compound is regioselectively deprotonated in the benzylic position when treated with potassium tertiary butoxide in dimethyl sulfoxide.

(*b*) Chromiumtricarbonyl complex of 1-methoxycarbonyl indane exists as a mixture of two diastereomers. However a single product results when both of these diastereomers are treated successively with a base and an alkylating agent.

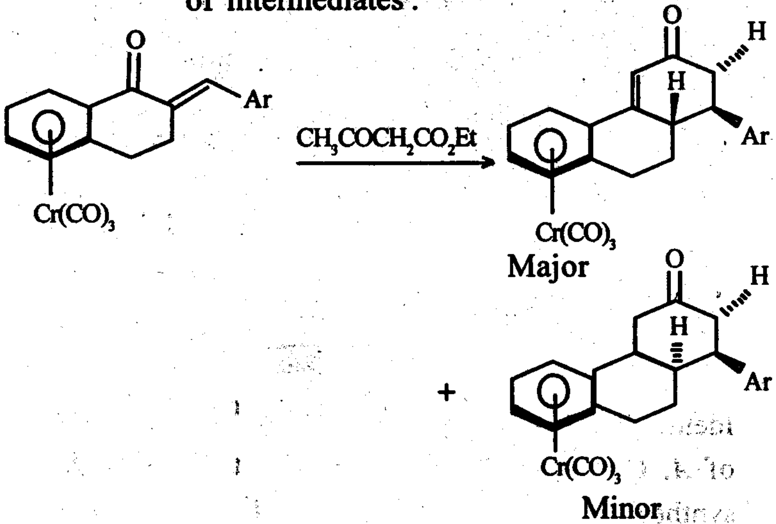
(*c*) Acidities of both the ring and the benzylic protons of chromiumtricarbonyl complexes of aromatic compounds in comparison to the uncomplexed species.

4\. (*a*) Define the term, (*i*) synthon (*ii*) Disconnection. 2

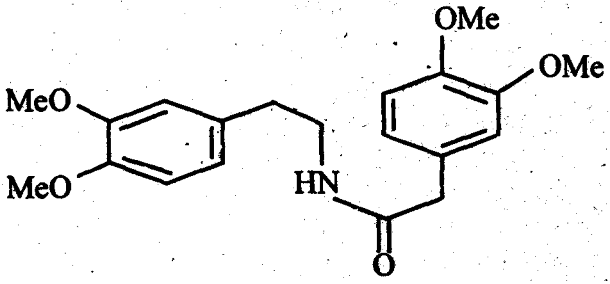
(*b*) Answer any *one* of the following questions : 6

(*i*) Account for the difference in regioselectivity observed in the formation of products when chromiumtricarbonyl complexes of anisole and phenyl triisopropyl silyl ether are treated with *n*-butyl lithium followed by an electrophile.

(*ii*) Explain the following conversion with mechanistic interpretation of the formation of intermediates :



5. What is meant by functional group interconversion ? Illustrate the use of functional group interconversion in the retro synthetic analysis of the following compound : 2 + 6



GROUP—B

6. Complete the following transformation :

$$\begin{tikzcd}
\underset{[A]}{C_{17}H_{20}N_4O_6} \arrow[r, "\text{Sunlight}", "\text{NaOH soln}"'] & {[B]} \arrow[r, "Ba(OH)_2", "\text{soln}"'] & {[C] + \text{urea}} \arrow[d, "\text{dil } H_2SO_4"] \\
 & {\text{CHO} - \text{CHO} + [E]} & {[D] + CO_2} \arrow[l, "\text{Vigorous}", "\text{hydrolysis in NaOH soln}"']
\end{tikzcd}$$

Identify *B*, *C*, *D* and hence deduce the structure of *A*. Confirm the structure of '*A*' through its synthesis. 6 + 2

7. What is coenzyme ? How NAD and FAD take part in Biological reactions ? Indicate all steps through which vitamins participate in carbohydrate metabolism and maintain their original state of reactivity. 4 + 4

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

   (*b*) Design, synthesize and explain the mode of action of a Ribonuclease mimic based on cyclodextrins. 3

   (*c*) How the rates of common Diels-Alder reactions are effected when carried out in water ? 3

9. (*a*) Design, synthesize and explain the complexation of a receptor for adipic acid. 3

   (*b*) How banzoin condensation is effected when carried out in water than in ethanol ? How benzoin condensation in water will be effected when carried out in the presence of 5·0 M LiCl and 5·0 M $LiClO_4$? 3

(*c*) How can cryptands be used as a light conversion and energy transfer device ? 2

10. Discuss the catalytic cycle of Sonogashira reaction. What are the merits and demerits of using a copper cocatalyst in this reaction ? What is a "Copper free" Sonogashira reaction ? 3 + 3 + 2