M.Sc 4th Semester Examination, 2011

CHEMISTRY

PAPER — CH - 2202

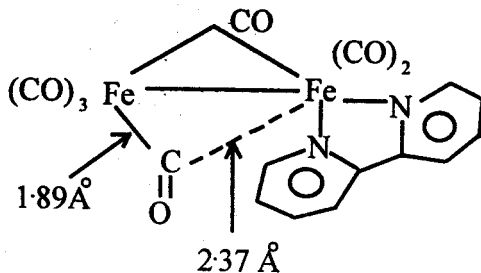*The figures in the right-hand margin indicate marks*

(*Inorganic Special*)

Full Marks : 40

Time : 2 hours

Answer any **four** questions

1. (*a*) Write down all the possible binding modes of carbonyl ligand with example.   2

(*b*)

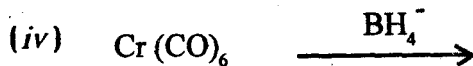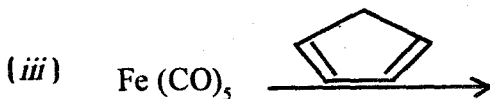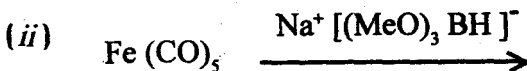Explain the Fe—C bond distance (given) in the above complex.   2

(c) How Fe $(CO)_5$ is synthesized conventionally ? Is it possible to synthesize Fe$(CO)_5$ at room temp. ? 2

(d) Complete the following reaction : 4

(i) Mo $(CO)_6$ $\xrightarrow[\substack{n\text{-octane} \\ 160\ °C}]{}$

(ii) Fe $(CO)_5$ $\xrightarrow{Na^+ [(MeO)_3 BH]^-}$

(iii) Fe $(CO)_5$ $\xrightarrow{}$

(iv) Cr $(CO)_6$ $\xrightarrow{BH_4^-}$
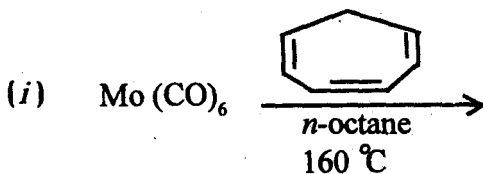
2. (a) How will you synthesize H_2 Fe $(CO)_4$ starting from Fe$(CO)_5$? 2

(Continued)

(b) Synthesize $Na_3[V(CO)_5]$ from $Na[V(CO)_6]$. 1

(c) How will you synthesize $K[Co_3(CO)_{10}]$ starting from $Co_2(CO)_8$. Write down the structure of $K[Co_3(CO)_{10}]$. 2

(d) Confirm the mono-capped octahedron structure of $Os_7(CO)_{21}$ is consistent with the number of valence electrons available. 3

(e) Discuss "edge-sharing bioctahedra" geometry in $M—M$ bonded system. 2

3. (a) Explain why the energy of α-spin $\left(m_s = +\frac{1}{2}\right)$ of electron increases linearly whereas that of β-spin $\left(m_s = -\frac{1}{2}\right)$ decreases with increasing external magnetic field. 3

(b) What do you mean by "X-band frequency" and "Q-band frequency" in ESR spectroscopy? What are the advantages and limitations in using "Q-band frequency"? 1 + 2

(c) Showing all possible transitions discuss the ESR spectra of methyl radical ($\dot{C}H_3$). 4
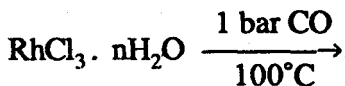
4. (a) A radical containing two non-equivalent protons with splitting constants 2.0 mT and 2.6 mT gives a spectrum centred on 332.5 mT. At what fields do the hyperfine lines lie, and what are their relative intensities ?   3

(b) Explain the ESR spectra of napthalene diradical.   4

(c) For $\dot{N}H_2$ radical, $a_N = 20$ gauss and $a_H = 10$ gauss. How many ESR spectral line may be expected from this data and what will be their intensity ratio ?
($a =$ hyperfine coupling constant).   3

5. (a) Give the active site structure of super oxide dismutase. Discuss the enzymatic activity of SOD. What is the role of Zinc (II) ion in this enzyme ? $2 + 3 + 2$

(b) Write a short note on urease enzyme.   3

6. (a) Draw the active site structure of cytochrom-C.   2

(b) What is the function of the enzyme carboxypeptidase ? Write down the active site structure and mechanism of action of carboxypeptidase A. $1 + 2 + 4$

(c) What is the role of the enzyme sulphite oxidase ?   1

(Continued)

7. (a) Discuss briefly the principle of Mössbauer spectroscopy. 3

(b) Predict $A - D$. 4

$$Na_2 Fe(CO)_4 \xrightarrow{R\overset{\overset{\displaystyle O}{\|}}{C}X} [A] \xrightarrow{O_2} [B]$$

$$[A] \xrightarrow{X_2} [C] \xrightarrow{R'R''NH} [D]$$
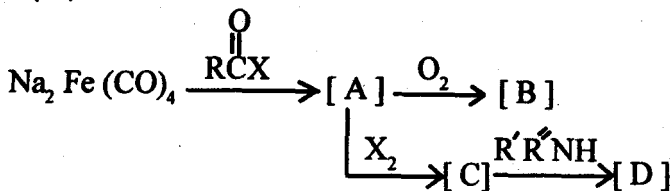
(c) Complete the following reaction : 1

$$RhCl_3 \cdot nH_2O \xrightarrow[100°C]{1 \text{ bar } CO}$$

(d) Predict the structure of $HRn_6(CO)_{17}B$ and $Co_3(CO)_9 Ni(\eta^5 - C_p)$ by applying total valence electron count method. 2

(*Organic Special*)

Full Marks : 40

Time : 2 hours

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

GROUP—A

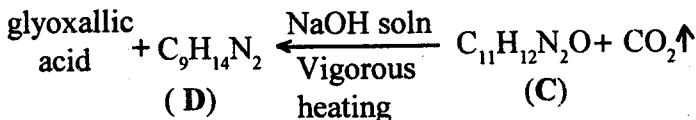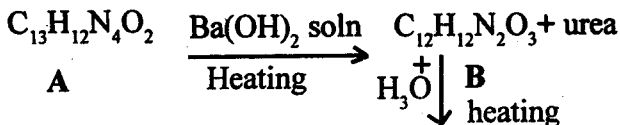1. (*a*) Define Green chemistry. 2

   (*b*) Write the principles of Green chemistry. 3

   (*c*) Give two examples of green synthesis with
   plausible mechanism. 3

2. (*a*) Define self-replication. 2

   (*b*) What is the significance of such studies ? 1

   (*c*) Propose a self-replication scheme based on the
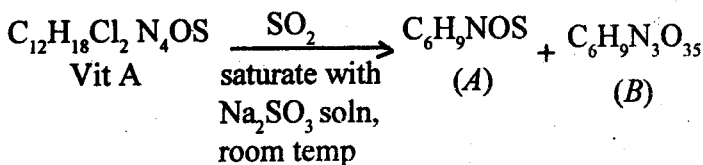   Troegers Base analogue 1. 3
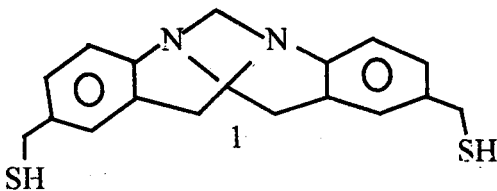
   (*d*) Propose a synthesis of compound 1. 2

(*Continued*)

3. A compound (Vit B_2) with molecular formula $C_{17}H_{20}N_4O_6$ yields $C_{13}H_{12}N_4O_2$ (A) on exposure to sunlight in dil NaOH solution, compound A on following transformation yields as follows :

$$C_{13}H_{12}N_4O_2 \xrightarrow[\text{Heating}]{\text{Ba(OH)}_2 \text{ soln}} C_{12}H_{12}N_2O_3 + \text{urea}$$
$$\quad\;\; A \qquad\qquad\qquad\qquad\quad H_3\overset{+}{O} \downarrow \text{ B}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{ heating}$$

$$\underset{\text{acid}}{\text{glyoxallic}} + C_9H_{14}N_2 \xleftarrow[\text{Vigorous}]{\text{NaOH soln}} C_{11}H_{12}N_2O + CO_2 \uparrow$$
$$\qquad\qquad (D) \qquad\;\; \text{heating} \qquad\qquad (C)$$

Identify compound D and deduce the structure (A). 8

4. Vitamin B_1 is cleaved through following treatment ;

$$\underset{\text{Vit A}}{C_{12}H_{18}Cl_2N_4OS} \xrightarrow[\substack{\text{saturate with} \\ \text{Na}_2\text{SO}_3 \text{ soln,} \\ \text{room temp}}]{SO_2} \underset{(A)}{C_6H_9NOS} + \underset{(B)}{C_6H_9N_3O_{35}}$$

Identify the fragment (A) only and (B) was identified as 4-amino-5-amino-methyl-2-methyl pyrimidin and hence indicate the point of attachment of (A) and (B) in Vitamin $\underline{B}_1$ and write the structure. 8

5. (a) Define template effect. How does template effect favours Diels-Alder reaction ?   1 + 2
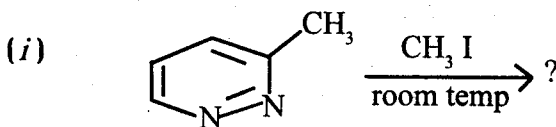
   (b) What are the essential criteria present in the chemo-sensor molecule ? Write a possible synthesis for following chemo-sensor molecule (*I*).   2 + 3
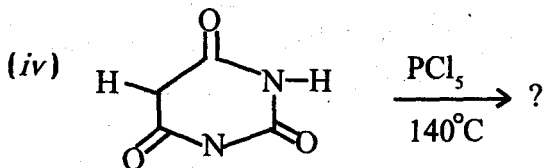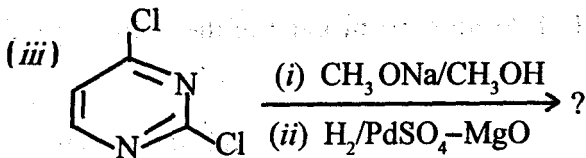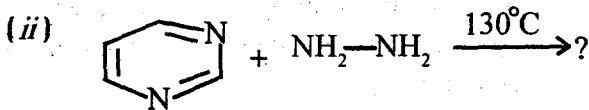

I
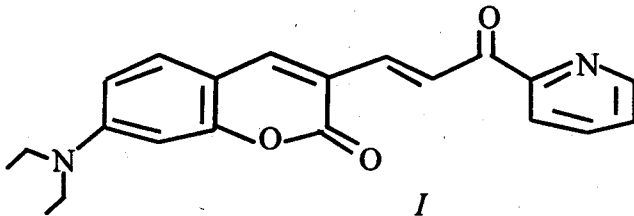
GROUP—B

6. (a) 'Pyridazine shows high boiling point in comparison to other diazines.' Explain.   2

   (b) Predict the product of the following reaction indicating mechanism (attempt any *three*) : 2 x 3

   (*i*)

(*Continued*)

(ii)

$+ NH_2-NH_2 \xrightarrow{130°C} ?$

(iii)

$\xrightarrow[\text{(ii) } H_2/PdSO_4-MgO]{\text{(i) } CH_3ONa/CH_3OH} ?$

(iv)

$\xrightarrow[140°C]{PCl_5} ?$

7. Synthesize the following compounds (attempt any *four*) :   2×4

(a) 6 – methyl – 3 – chloro pyridazine
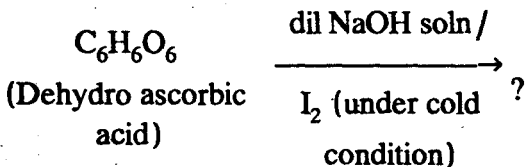
(b) 3 – phenyl – 5 – methyl pyridazine

(c) 6 – Amino – 2 – methyl pyrimidine.

(d) 6 – methyl pyrimidine.

(e) 5 – phenyl–pyrimidine.

8. (a) What is Cocarboxylase ? Indicate in which step it takes part in carbohydrate metabolism and write the chemical reaction involved therein.   4

(b) What is 'FAD' molecule ? Indicate the reacting system present in it and taking part in biological reaction. 2

(c) Predict the product of the following reaction : 2

$$C_6H_6O_6 \xrightarrow[\substack{I_2 \text{ (under cold} \\ \text{condition)}}]{\text{dil NaOH soln}/} ?$$
(Dehydro ascorbic acid)

9. (a) Define gels. 2

(b) Classify different types of gels. 2

(c) What are the differences between polymeric gel and supramolecular gel ? 1

(d) Give some examples of low molecular weight organo gelators. 2

(e) How are the gel morphologies studied ? 1

10. (a) Why preline is called helix breaker ? 2

(b) What are α-helix, β-pleated sheet, β-turn ? 4

(c) What is Ramachandran plot ? 2

(*Continued*)

(*Physical Special*)

Full Marks : 40

Time : 2 hours

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

GROUP—A

Answer any *one* of the following

1. What is number average molecular weight of a polymer solution ? Describe a suitable method which is used to determine the number average molecular weight. $2 + 8$

2. (*a*) Between sedimentation velocity method and sedimentation equilibrium method which one is better and why ?   3

   (*b*) Which type of average molecular weight is determined by sedimentation equilibrium method and how ?   7

GROUP—B

Answer any *one* of the following

3. (*a*) Without any derivation show how the weight average molecular weight is determined by 'Zimm' analysis'.   5

(b) Calculate the vapour pressure lowering, the boiling point elevation and the osmotic pressure of a 1·0 mass percent solution of polystyrene ($\bar{M}_n = 50.0 \, \text{kgmol}^{-1}$) in toluene ($M_m = 92.15 \, \text{g mol}^{-1}$) at 25°C and comment on your result. At 25°C, for toluene $K_b = 3.33 \, \text{Km}^{-1}$ and the vapour pressure of pure toluene is 3760 Pa. 5

4. (a) The molar mass M_m of haemoglobin is 64,450 g mol^{-1}. If it contains 0·35 mass percent of Fe, what is its minimum molar mass ? Also, calculate the number of Fe atoms present in haemoglobin. 3

(b) A solution of a protein was investigated in an ultracentrifugation velocity measurement at 20°C, the rotor speed being 50,000 rpm. The boundary receded as follows :

t (s)	0	300	600	900	1200	1500	1800
r (cm)	6·127	6·153	6·179	6·206	6·232	6·258	6·284

Calculate the sedimentation coefficient and the molar mass of the protein. Further data are as follows : $\bar{v} = 0.728 \ \text{cm}^3\text{g}^{-1}$; $D = 7.62 \times 10^{-11} \ \text{m}^2\text{s}^{-1}$; $\varrho = 09981 \ \text{gcm}^{-3}$. 7

Answer any *one* of the following

5. (a) Explain what is meant by phenomenological coefficients and discuss the significance of the cross co-efficients L_{ij}.

4

(b) What do you mean by entropy production for a system which is composed of two parts, both enclosed in the same adiabatic enclosure at temperatures T_1 and T_2 respectively ($T_2 > T_1$). How would you identify the force and the flux ?

6

6. (a) Explain Prigogine's principle of minimum entropy production.

5

(b) Obtain the expression for the entropy production due to flow of matter.

5

GROUP—D

Answer any *one* of the following

7. Consider a system consisting of two parts I and II, joined by a capillary. The temperature and concentration of the solutions are uniform and

the two portions differ with respect to pressure and electrical potential. Obtain the expression for the rate of entropy, production and define the electrokinetic effects in terms of the ratio of the phenomenological co-efficients. 10

8. Discuss the basic principle of the Mössbauer spectroscopy and explain the nuclear Zeeman splitting. 10

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