

M.Sc. 4th Semester Examination, 2013

CHEMISTRY

PAPER—CEM - 402

Full Marks : 40

Time : 2 hours

*The figures in the right-hand margin indicate marks
Candidates are required to give their answers in their
own words as far as practicable
Illustrate the answers wherever necessary*

(Organic Special)

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

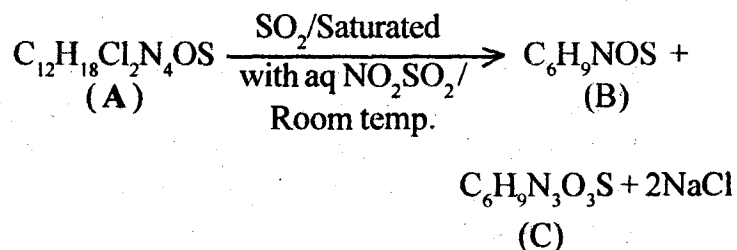
GROUP – A

1. (a) How plant based chemicals are defined as 'renewable' chemicals ?
(b) What is the significance of 'renewable chemicals' in society ?

(Turn Over)

- (c) Write the principles of green chemistry.
- (d) Give examples of (i) a green synthesis of gold nanoparticles and (ii) a green organic synthesis. $2 + 2 + 2 + 2$
2. (a) Define self-assembly.
- (b) What is self-replication ?
- (c) Propose a self-replicating scheme based on a model compound and explain how it self replicates. $2 + 2 + 2 + 2$
3. (a) How is a 'supramolecular gel' formed ?
- (b) What is the difference between a supramolecular gel and a polymeric gel ?
- (c) Give some examples of Low Molecular Mass Organogelators.
- (d) What are the techniques used in studying gel morphologies. $2 + 2 + 2 + 2$

4. The following compound (A) undergoes the degradation reaction as follows : 4 × 2



Identify (B) and (C) and establish their point of attachment and hence deduce the structure of (A).

5. (a) Write the structure of the following co-enzymes and state their mode of reactivity :

- (i) FAD
- (ii) NAD.

- (b) Show how the different Vitamins restore their original state of reactivity after participating reaction with the end product of glucose metabolism. 4 + 4

GROUP – B

6. Why proline is called helix breaker ? Elaborate

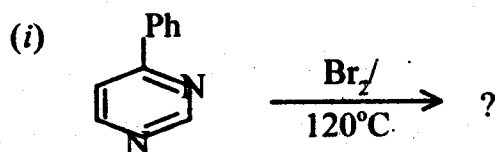
on the following secondary structural elements of proteins : α -helix, β -pleated sheet, β -turn. 4 + 4

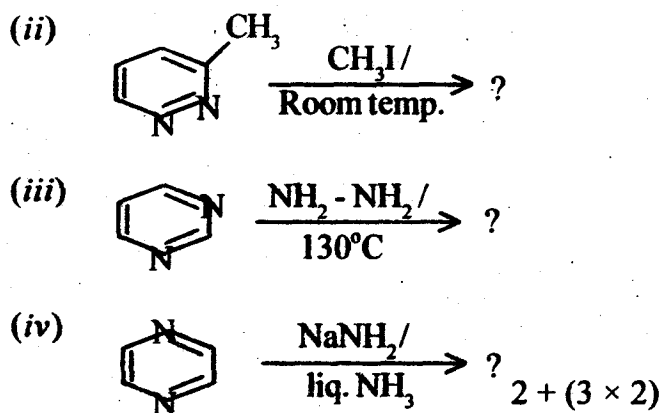
7. How are the dihedral angles defined in a peptide chain ? Define Ramachandran plot and locate the following secondary structural element in proteins : α -helix, parallel β -pleated sheet, antiparallel β -pleated sheet, 3.10 helix. 3 + 2 + 3

8. Draw all the steps involved during the glucose metabolism where the end product is pyruvic acid and show how the cocarboxylase degrades it to acetaldehyde. 4 + 4

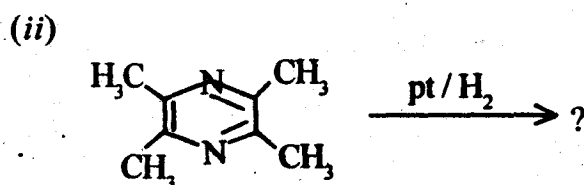
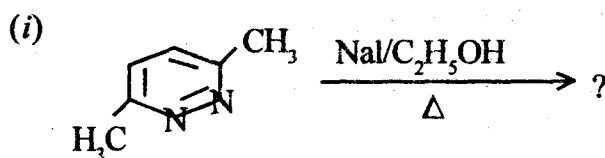
9. (a) Why diazines are less basic than pyridin ? Arrange the diazine systems in order of increasing basicity.

(b) Predict the product/s of the following reactions with plausible mechanism(attempt any three) :





10. (a) What would be the fate of the following molecule when reduction carried out as follows. Explain with the reason stating product if at all in each case.



(b) Outline the synthesis of the following (attempt any three) :

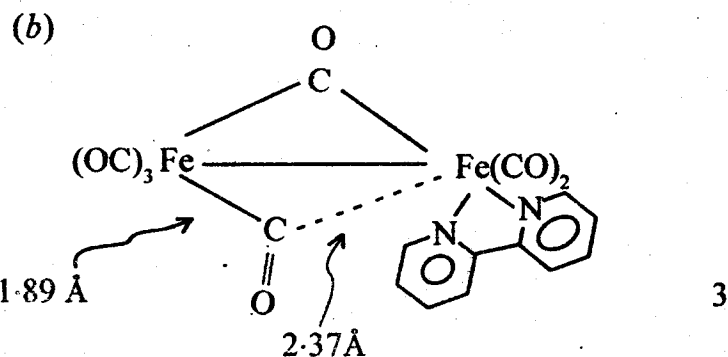
- (i) 2, 4, 6 - trichloropyrimidine
- (ii) 6-methyl-3-chloro pyridazine
- (iii) 4-methoxy pyrimidine
- (iv) 3-Hydroxy methyl pyridazine. 2 + (3 × 2)

(Inorganic Special)

Answer any *four* questions

1. (a) Give one example of transition metal carbonyl complex for each of the following :

- (i) CO as $4e'$ donor
- (ii) CO as $6e'$ donor. 3



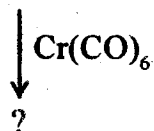
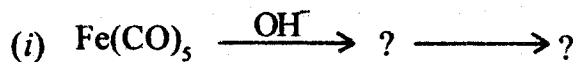
Explain the Fe—C bond distance for the above complex.

(c) Synthesize the following : 4

(i) $\text{V}(\text{CO})_6$ starting from VCl_3

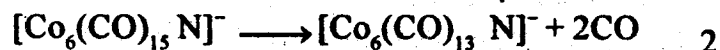
(ii) $\text{Cr}(\text{CO})_6$ Starting from CrCl_3 .

2. (a) Complete the following reaction : 5



(b) $\text{Os}_5(\text{CO})_{18}$ has a 'raft structure'. Is this consistent with the number of valence electrons available? 3

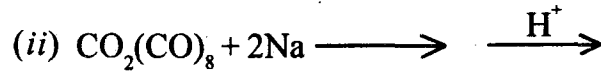
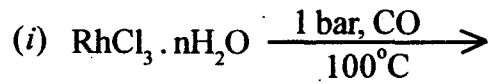
(c) Suggest what change in cluster structure might accompany the reaction



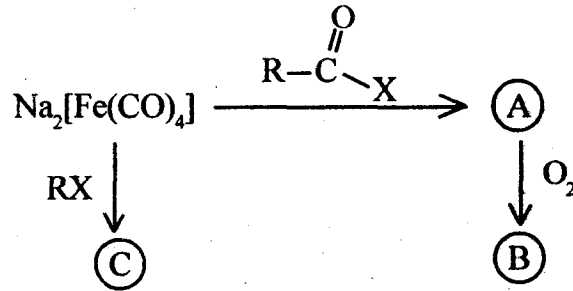
3. (a) Predict the ESR spectrum of *p*-benzosemiquinone radical anion showing all possible transition. 3
- (b) "Spin angular momentum" of electron act just opposite in direction with "spin magnetic moment". Explain. 3
- (c) "What type of solvents are used for ESR measurements? – Explain. 2
- (d) Some commercial ESR spectrometer use 8 mm microwave radiation. What magnetic field is needed to satisfy the resonance condition? 2
4. (a) Write down the structural features of Cytochrome P₄₅₀. 3
- (b) Draw the active site structure of SOD. Comment on its catalytic activity on replacement of Cu(II) by suitable metal ion. 2 + 1
- (c) Write down the cycle of enzymatic activity of SOD in disproportionation of O₂⁻. 4

5. (a) What is ascorbic acid oxidase ? Give the cycle of mechanism of catalytic oxidation of ascorbic acid oxidase. 1 + 3
- (b) Write down the functions of catalase and peroxidase. 2
- (c) What is xanthine Oxidase ? Give some of its clinical significance. 1 + 3
6. (a) Explain the appearance of three lines in the ESR spectrum of naphthalene radical. 4
- (b) Predict the intensity distribution in the hyperfine lines of the ESR spectrum of the radical CD_3 . 3
- (c) The benzene radical anion $C_6H_6^-$ has a I -value of 2.003. At what field would you search for resonance in a spectrometer operating at 8.832 GHz. 3
7. (a) Is the triangular core of $[Co_3(CO)_{10}]^-$ consistent with the electron count ? 2
- (b) Write down the synthesis procedure for $[Co_3(CO)_{10}]^-$ and $Ir_4(CO)_{12}$. Draw the structure of $[Co_3(CO)_{10}]^-$. 3

(c) Complete the following reaction : 2



(d)



3

(Physical Special)

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

GROUP – A

Answer any *one* of the followings

1. (a) Explain, what is meant by phenomenological co-efficient. How these co-efficients are related to the forces and the fluxes. Explain the significance of these linear equations of motion. 5

(b) Derive the equation for entropy production in the case of flow of matter. 5

2. Consider a system provided with a membrane separating two sides of a solution, across which an electric field is applied causing a pressure difference ΔP . Obtain the expression for the rate of entropy production and hence define the term streaming current and electroosmotic pressure in terms of the appropriate phenomenological co-efficients. 10

GROUP – B

Answer any *one* of the following

3. Describe the torsion angles of polypeptide chain. What is Ramachandran Plot? Indicate the allowed torsion angles of different secondary structure of a protein in this plot. 3 + 3 + 4

Or

What do you mean by nucleoside and

nucleotide? Draw the structures of dAMP (deoxy adenosine - monophosphate) and CTP (cytosine-triphosphate). Describe Watson Crick model of DNA in short. 3 + 3 + 4

4. (a) The molar mass M_m of haemoglobin is $64,450 \text{ g mol}^{-1}$. 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.
- (b) Calculate the molar mass of haemoglobin from the fact that in an equilibrium ultracentrifuge experiment at 20°C $C_2/C_1 = 9.40$, $r_1 = 5.5 \text{ cm}$ and $r_2 = 6.5 \text{ cm}$. The ultracentrifuge rotor is operated at 120 rps. $\bar{v} = 0.749 \text{ cm}^3 \text{ g}^{-1}$ and $\rho = 0.9982 \text{ g/cc}$.
- (c) Calculate the time required for glucose molecule to diffuse through a distance of $10,000 \text{ \AA}$. The diffusion co-efficient of glucose is $0.462 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

- (d) At 20°C, the diffusion co-efficient, the molar mass and specific volume of haemoglobin are $6.9 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, 64,500 g mol⁻¹ and 0.75 cm³ g⁻¹, respectively. Calculate its frictional ratio and comment on your result. The co-efficient of viscosity of water at the given temperature is 1.005 CP.

3 + 2 + 2 + 3

GROUP – C

Answer any *one* of the following

5. What is weight average molecular weight of a macromolecule? Describe a suitable method for determination of weight average molecular weight. 2 + 8
6. (a) What is intrinsic viscosity and how does it determined?
- (b) What is root mean square distance and why it is more appropriate than average distance for a polymer sample.
- (c) Write down the name of a suitable method for determination of number average

molecular weight (\bar{M}_n) and state the reason of its huge applicability for determination of \bar{M}_n .

- (d) What is sedimentation co-efficient and is its unit? $\left\{ (1+2) + \left(1\frac{1}{2} + 1\frac{1}{2} \right) + (1+1) + (1+1) \right\}$

GROUP – D

Answer any *one* of the following

7. (a) What is nanomaterials? What do you understand by the step-up and step-down approach for the synthesis of metal nanoparticles? Give one example for each. $1 + 2 + 4$
- (b) What is Surface Plasmon Resonance (SPR)? How do you explain the origin of colour (golden yellow) for silver hydrosol? $1\frac{1}{2} \times 2$
8. (a) What is density of states (DOS) for metal clusters? Schematically describe the variation of DOS with cluster sizes. What is kubo gap, δ ? $2 + 2 + 1$

- (b) "Melting temperature of nanomaterial is lower than its bulk counterpart". – Explain. How do you explain the negative heat capacity for isolated S_8 clusters. 3 + 2
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