M.Sc. 4th Semester Examination, 2015

CHEMISTRY

PAPER – CEM- 402

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(*Inorganic Special*)

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

GROUP –A

1. (*a*) Calculate the bond valence in the following transition metal cluster compounds : 2 × 2

(*i*) $[Nb_6(\mu_2-Cl)_{12}Cl_6]^{4-}$

(*ii*) $Co_2(\mu_2-CH_2)(\mu_2-Co)(C_p^*)_2$

(*b*) $[Rh_{11}(CO)_{23}]^{3-}$ displays a structure with three face sharing octahedra ($g = 148$, $b = 25$). Draw the metal core structure for this cluster. 2

(*c*) '$[Os_2Cl_8]^{2-}$ displays staggered structure'— Explain. 2

2. (*a*) Show the orbital overlap in 'tetragonal prismatic structure' in a metal-metal bonded species. 3

(*b*) What do you mean by 'Aurophilicity' ? Explain with example. 3

(*c*) Give a brief account on 'quintuple bond'. 2

3. (*a*) What is the active site structure of the enzyme 'Xanthine Oxidase' ? 2

(*b*) Give the mechanism involved in the oxidation of Xanthines to uric acids. 2

(*c*) Draw the active site structure of SOD. Explain the mechanism of oxidation of ascorbic acid to dehydro-ascorbic acid. 2 + 2

4. (*a*) What is 'nitrate reductase'. Write down the active site structure and discuss the mechanistic pathway of nitrate reduction. 1 + 2 + 2

(*b*) Show the structure of 'Cobalamine' and explain its activity. 3

GROUP –B

5. (*a*) Justify the structure of the following Cluster compounds with respect to the number of valence electrons : 2 × 2

	Cluster	Structure
(*i*)	$Os_5(CO)_{19}$	'Bow-tie'
(*ii*)	$Os_5(CO)_{18}$	'Raft'

(*b*) How will you synthesize $Rh_4(CO)_{12}$ starting from $Rh_2(\mu\text{–}Cl)_2(CO)_4$? Draw the structure of $Rh_4(CO)_{12}$. 3

(*c*) Predict the structure of $Fe_4C(CO)_{13}$. 1

6. (*a*) Draw the active site structure of cytochrome *p* - 450 and write down the mechanistic pathway of hydroxylation activity. 2 + 2

(*b*) Write short notes on : 2 + 2

(*i*) Chlorophyll

(*ii*) PS-I and PS -II in Photosynthesis.

7. (*a*) Discuss the 'semibridging binding mode' of CO in $Fe_2(CO)_7$ (4, 4' – bipy). 3

(*b*) Cite one complex where CO acts as 6e'-donor. Show the binding mode of CO in the complex. 2

(*c*) 'Removal of all CO ligands in a transition metal carbonyl complex is rarely possible'– Justify. 2

(*d*) How will you synthesize $Na_2[Fe(CO)_4]$? 1

8. (*a*) Write down the basic principle involved in Mössbauer spectroscopy. 2

(*b*) Define self-assembly. 2

(*c*) What do you mean by ion-ion interaction and ion-dipole interaction. 2

(*d*) What is van der Waals interaction in supramolecular chemistry ? 2

(*Organic Special*)

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

GROUP – A

1. (*a*) Define self-assembly ? 2

(*b*) What type of interaction are involved in the self-assembly process ? 2

(*c*) Write the different types of supramolecular structures that can form by self-assembly. 2

(*d*) Write the applications of self-assembled structures (at least four). 2

2. (*a*) What is a 'supramolecular gel' and how is it formed ? 2

(*b*) What are the major differences between a 'supramolecular' and a 'polymeric' gel ? 2

(*c*) Give some examples of Low Molecular Mass Organogelators. 2

(*d*) How can one study the morphology of a supramolecular gel ? 2

3. (*a*) What is self-replication ? 2

(*b*) Write briefly the significance of such studies. 2

(*c*) Propose a self-replicating scheme based on a model compound and explain how a simple template molecule can amplify. 4

4. The following compound, Vit. B_1 on treating gives the products as follows :

$$C_{12}H_{18}Cl_2N_4OS \xrightarrow[\text{Saturated with } Na_2SO_3,\ \text{room temp.}]{SO_2} \underset{\textbf{(A)}}{C_6H_9NOS} + \underset{\textbf{(B)}}{C_6H_9N_3O_3S}$$

Identify the compound (**A**) and (**B**) and establish the structure of Vit. B_1. 8

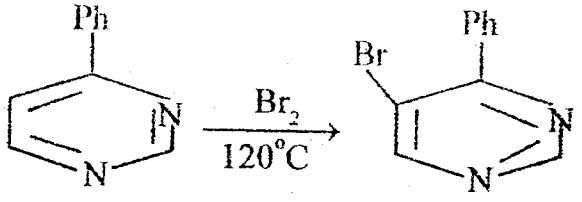
5. (*a*) Write down the structures of (*i*) NAD and (*ii*) FAD and show their chemical mode of action in biological systems. 4

(*b*) Show how coenzyme of Vit. B_1 takes part in decarboxylation of pyruvic acid, the end product of carbohydrate metabolism and depict the chemical reactions involved therein. 4

GROUP – B

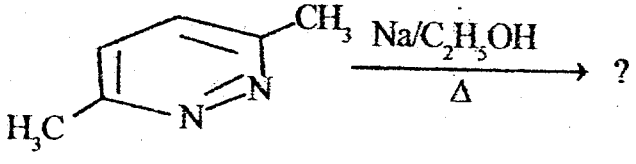
6. (*a*) Write the principles of green chemistry. 3

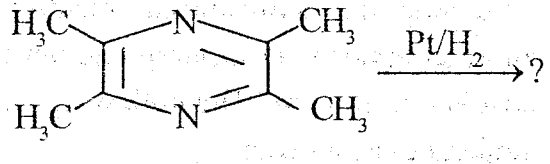
(*b*) "Nucleophilic substitution reactions are more common than electrophilic substitution in diazine system. The following reaction undergoes as shown :

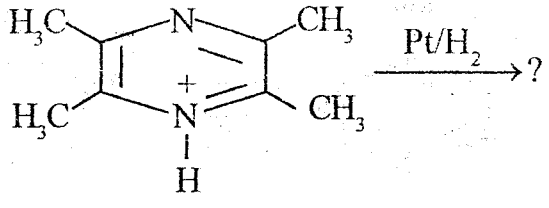


Depict the mechanism of the reaction and state what kind of reaction path is followed during the transfunction. 3

(*c*) What would be the product/s when treated as follows and indicate the reason with explanation : $1\frac{1}{2} \times 2$

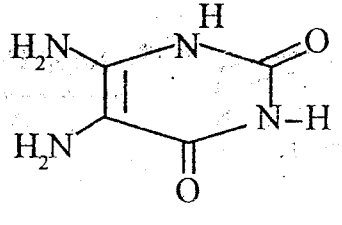






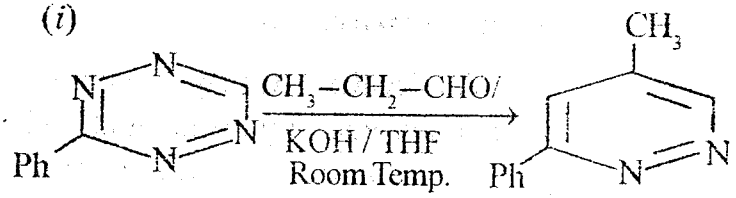
10. (*a*) Synthesise the sedative drug, pentothal starting from Ethyl isopentyl diethyl malonate and thiourea. 2

(*b*) Synthesis sulphapyrazine, an antibacterial drug from glyoxal and 2

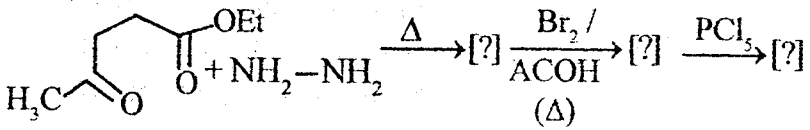


(*c*) Carry out the following transformation and indicate the product/s in each case with mechanism (any *two*) : 2 × 2

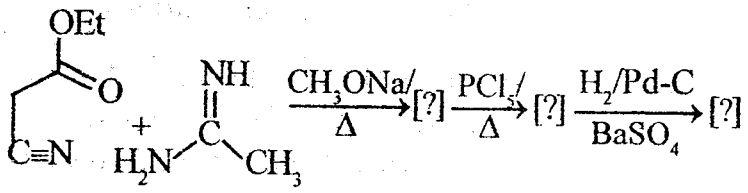
(*i*)



(*ii*)



(*iii*)



(Physical Special)

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

GROUP –A

Answer any **two** questions

1. (*a*) What type of molecular weight is determined by sedimentation equilibrium method and how ? Why is it more advantageous than sedimentation velocity method ? 1 + 5 + 1

(*b*) Calculate the molar mass of haemoglobin from the fact that in an equilibrium ultracentrifuge experiment at 20°C, $c_2/c_1 = 9{\cdot}40$, $r_1 = 5{\cdot}5$ cm and $r_2 = 6{\cdot}5$ cm. The ultracentrifuge rotor is operated at 120 rps. $\bar{v} = 0{\cdot}749\ cm^3\ g^{-1}$ and $\rho = 0{\cdot}9982\ g\ cm^{-3}$. 3

2. (*a*) Derive Flory-Huggins equation for the vapour pressure of a polymer solution. 8

(*b*) 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 ? 2

3. Write down the basic principle of chromatographic separation of the proteins. What is the basic difference in between the ion-exchange chromatography and affinity chromatography ? What is HPLC (high pressure liquid chromatography) and why do this method give high resolution of protein components ? 3 + 4 + 3

4. What is meant by entropy production is an irreversible process ? Illustrate your answer with respect to heat flow. Establish Prigogene's principle of minimum entropy production. 2 + 3 + 5

GROUP –B

Answer any **two** questions

5. Derive the expression for the rate of entropy production for any electrokinetic process where an electric potential difference causes a pressure difference. Define any one such phenomenon in term of the phenomenological coefficients. 8 + 2

6. (*a*) Why in normal cases the frequency of γ emission of a excited radio nucleus is not equal to that of frequency of reabsorption of that nucleus ? 3

(*b*) What do you mean by 'Doppler effect' ? The half-life of ^{67}Zn nucleus is 9400 ns. Calculate the line-width of γ-ray emission. 1 + 2

(*c*) Give an estimate of the valence state of an unknown tin compound using Mössbauer isotope ^{119}Sn. 2

(*d*) Explain why Mössbauer spectra of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NO]^{2-}$ are different although in both the cases the central atom is in same oxidation state ? 2

7. State and prove Hellmann-Feynman theorem. Use this theorem to deduce the following expression of electrical polarizability (α_{zz}).

$$\alpha_{zz} = 2 \sum_{n \neq 0} \frac{(\mu_z)_{on}}{E_n^{(0)} - E_0^{(0)}}$$

where symbols have their usual meaning. 4 + 6

8. Write the name (three letter code) and molecular structure of acidic, basic, polar but uncharged and non-polar amino acid residues (one from each group) found in the protein structure. What is the isoelectric point of a protein ? Describe the acid-base titration curve of any acidic amino acid residue and show the different associated ionic forms of the residue. 4 + 2 + 4
