M.Sc. 4th Semester Examination, 2010

CHEMISTRY

Paper—CH-2202

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)

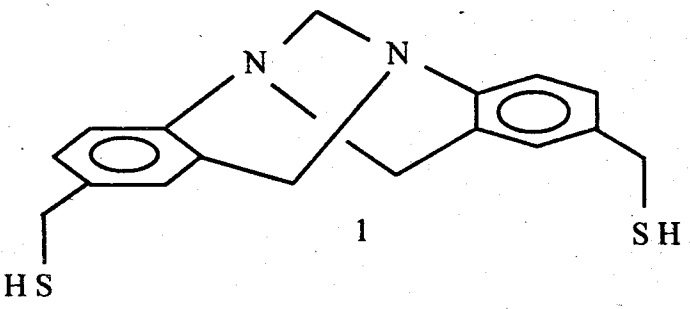
Answer any *five* questions, taking at least *two* from each Group

GROUP—A

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

(*b*) Write briefly the significance of such studies. 1

(*c*) Propose a self-replicating scheme based on the Troegers Base analogue 1. 2



1

(*d*) Write a possible synthesis of compound 1. 3

2. (*a*) Define gels. 2

(*b*) Classify different types of gels. 2

(*c*) Give some examples of low molecular mass organogelators. 2

(*d*) What are the techniques used for studying gel morphologies ? 1

(*e*) Write some applications of supramolecular organogelators. 1

3. A compound with molecular formula $C_6H_8O_6$ (A) shows positive test for unsaturation with dil $KMnO_4$ treatment, forms phenylhydrazone and precipitates silver on treating with Tollen's reagent. It gives violet colouration with $FeCl_3$. Further compound (A) on treating with I_2 gives $C_6H_6O_6$ (B) which is a neutral compound and behaves as the lactone of monobasic acid. Compound (B) on treatment with (I_2|NaOH) under cold condition yields oxalic acid and L-threonic acid ($C_4H_8O_5$). Identify (A) and explain the above observations. 8

4. Indicate the different reaction steps of glucose metabolism and show the end products there from. How the co-carboxylase reacts with the end product to produce acetaldehyde. 5+3

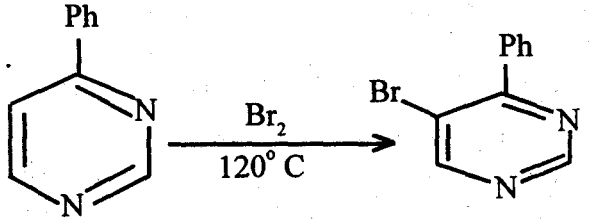
5. (*a*) What is 'NAD' and 'FAD' ? How they react in the Biological systems ? Show the reactions. $1\frac{1}{2} \times 2$

   (*b*) How vitamins react with the end product of glucose metabolite and restore their original state of reactivity after completion of the reaction. Show the reaction steps. 5

GROUP–B

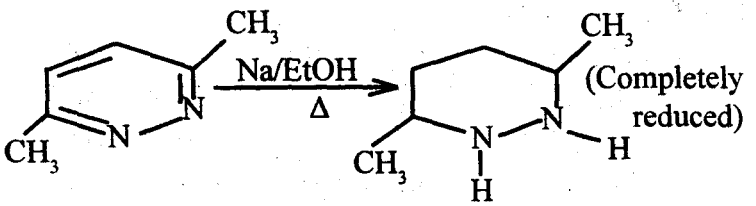
6. (*a*) 'Diazines are less basic than pyridine'– Explain. Why the boiling point of pyridazine is much higher than that of the other two diazine systems ? $1\frac{1}{2} \times 2$

(*b*) Carry out the following transformation with machanism ; 3

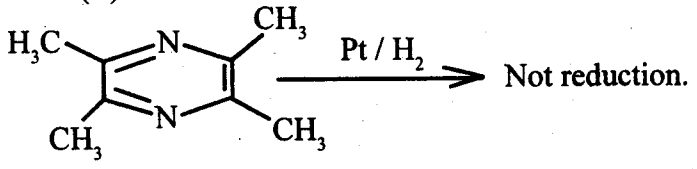


(*c*) Rationalize the following reactions : 2

(*i*)



(*ii*)

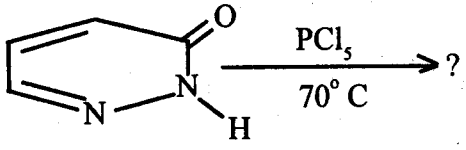


7. (*a*) "Electrophilic substitution is less common in diazines but Nucleophilic substitution occurs preferentially." Explain. 2

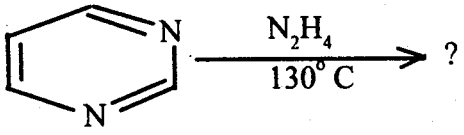
(*b*) Among 2-chloropyrimidine and 4-chloropyrimidine which one is more susceptible towards nucleophilic substitution when treating with (CH_3ONa/MeOH) at room temperature. Write the product/s in each case. 2

(*c*) Predict the product/s of the following reactions with mechanism (attempt any *two*) : 2×2

(*i*)



(*ii*)



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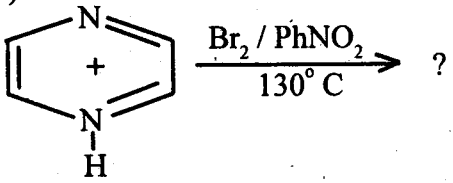
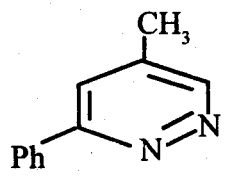
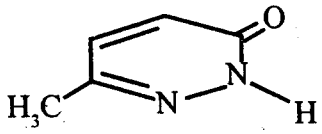


8. (*a*) Outline the synthesis of any *two* of the following : 2×2

(*i*)



(*ii*)



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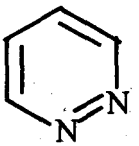
(*iii*)



(*b*) Outline the synthesis of Vitamin-C starting from L-Lyxose. 4

9. (*a*) How are the dihedrals in a peptide defined ? 3

(*b*) Define Ramachandran plot and locate the following structural element in proteins : α-helix, parallel β-pleated sheet, antiparallel β-pleated sheet, 3·10 helix. 5

(*Inorganic*)

Answer any *four* questions

1. (*a*) How will you synthesize $Cr(CO)_6$ by reductive carbonylation ? 2

(*b*) Synthesize

(*i*) $H_2Fe(CO)_4$ from $Fe(CO)_5$

(*ii*) RCHO from $Na_2[Fe(CO)_4]$. 3

(*c*) What happens when $Cr(CO)_6$ is treated with $NaBH_4$ (Cite all steps) ? 2

(*d*) How will you synthesize $[Fe_3(CO)_{11}]^{2-}$? Write down the structure of $[Fe_3(CO)_{11}]^{2-}$. 3

2. (*a*) What are the significance of chemical shift in Mössbauer Spectroscopy ? Explain. Illustrae any one of the significances with example. 4

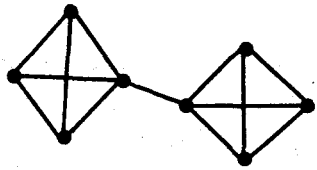
(*b*) Why Doppler shift is so important in Mössbauer Spectroscopy ? 2

(*c*) Relative line width is very much smaller in Mössbauer Spectroscopy – Why ? 1

(*d*) What is the difference between spectra of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NO]^{2-}$ under normal electric field ? 3

3. (*a*) $Os_5(CO)_{18}$ has a raft structure. Is this consistent with the number of valence electron available ? 3

(*b*) The metal core structure of $[Ir_8(CO)_{22}]^{2-}$ is what would be an appropriate electron counting scheme for this cluster ? 3



(*c*) $[Re_2Cl_8]^{2-}$ is staggered while $[Os_2Cl_8]^{2}$ is eclipsed. Explain. 2

(*d*) What is the metal framework geometry of $Co_3(\eta^5\text{-}C_p)_3(CO)_3$ cluster ? 2

4. (*a*) What are the probable transitions in case of quadrupole spectra arising from ^{129}I. (excited state I = 5/2 and ground state (I = 7/2). 5

(*b*) Predict the plausible structure of $Fe_3(CO)_{12}$ by Mössbauer spectroscopy. 3

(*c*) What is the principle of Mössbauer spectroscopy ? 2

5. (*a*) What are the functions of cytochrome P450 ? Give the catalytic cycle for the enzyme. Why is it so named ? 3 + 3 + 1

(*b*) Draw the active site structure of chlorophyll. 1

(*c*) Write a short note on peroxidase. 2

6. (*a*) A radical contains one ^{14}N nucleus (I=1) with hyperfine constant 1.61 mT and two equivalent protons ($I=\frac{1}{2}$) with hyperfine constant 0.35 mT. Predict the form of the EPR spectrum. 3

(*b*) Predict the number of lines in the e.s.r spectrum of the following radicals: 2 + 2

(*i*) $[CF_2D]^{\bullet}$

(*ii*) $[C^{35}ClH_2]^{\bullet}$

$[I_D=1, I_{19_F}=\frac{1}{2}, I_{35_{Cl}}=\frac{3}{2}]$.

(*c*) Explain why Mn (II) is EPR active but Cr(II) is EPR inactive . 3

(*Continued*)

7. (*a*) Draw the active site structure of cyanocobalamine. 4

(*b*) What is the function of SOD ? Which metal is present in its active site structure ? 2

(c) Write a short note on ascorbic acid oxidase and Amavadin. 2 + 2

(*Physical Special*)

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

GROUP–A

Answer any *two* of the following :

1. (*a*) For macromolecules we always determine average molecular weight. Justify. 2

(*b*) Write down the principle of ultracentrifugation. 2

(*c*) Describe the sedimentation velocity method for determination of number average molecular weight and hence define sedimentation co-efficient. 6

2. Derive the final expression to show how does the weight average molecular weight is determine by light scattering method. 10

3. (*a*) State and derive the Flory-Huggins theory of polymer solution. 8

(*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. $\overline{V} = 0{\cdot}749\ cm^3g^{-1}$ and $\rho = 0{\cdot}9982\ gcm^{-3}$. 2

4. (*a*) What is the principle of Mössbauer spectroscopy and write one application of Mössbauer spectroscopy. 3

(*b*) A photon of wavelength λ has an equivalent momentum of h/λ. Calculate the recoil velocity of a free Mössbauer nucleus of mass 1.67×10^{-25} kg (i.e.atomic weight 100) when emitting a γ-ray of 0.1 nm wavelength. What is the Doppler shift of the γ-ray frequency to an outside observer ? 4

(*c*) A particular Mössbauer nucleus has spins 5/2 and 3/2 in its excited and ground states respectively. Into how many lines will the γ-ray spectrum split if :

(*i*) the nucleus is under the influence of an internal electric field gradient, but no magnetic field is applied ;

(*ii*) there is no electric field gradient at the nucleus but an external magnetic field is appild ;

(*iii*) both an internal electric field gradient and an external magnetic field are present ? 3

GROUP–B

Answer any *two* of the following :

5. (*a*) What is intrinsic viscosity ? How does the molar mass of a macromolecule is determined by viscosity method. 1 + 4

(*b*) At 30°C the density of glucose is 1·55g cm^{-3} ; its diffusion coefficient is $6{\cdot}81 \times 10^{-6}$ cm^2 sec^{-1}

and the coefficient of viscosity of water is $8{\cdot}937 \times 10^{-3}$ Poise. Assuming that the glucose molecule is spherical,estimate its molar mass. 5

6. (*a*) What is meant by phenomenological coefficient ? Write the equation of motion for a two-flux two-force system and explain the significance of these equation. State the Onsager reciprocity relation. 6

(*b*) Obtain the mathematical formulation of Prigogene's principle of minimum entropy production. 4

7. What do you mean by entropy production ? Obtain an expression for the rate of entropy production in heat flow in a system consisting of two parts, both enclosed within the same adiabetic enclosure and hence establish the Newton law of cooling. 7+3

8. Obtain the expression for the rate of entropy production for the transfer of material when an applied electric field causes a pressure difference

at equilibrium and hence obtain an expression for electro-osmotic pressure in terms of appropriate phenomenological coefficients. 7+3
