PG/IVS/CEM-402/14

M.Sc. 4th Semester Examination, 2014

CHEMISTRY

PAPER – CEM-402

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(*Organic Special*)

Answer any **five** questions

1. (*a*) Write the principles of green chemistry.

(*b*) Give examples of (*i*) a green synthesis of gold nanoparticles and (*ii*) a green organic synthesis.

(*c*) How plant based chemicals are defined as 'renewable' chemicals ?

(*d*) What is the significance of 'renewable chemicals' in society ? 3 + 2 + 1 + 2

2. (*a*) What is self-assembly ?

(*b*) What are the driving forces for the self -assembly ?

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

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

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

(*b*) What is the difference between a supramolecular gel and a polymeric gel ?

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

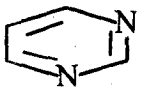
(*d*) Write the application of supramolecular gels (at least *four*). 2 + 2 + 2 + 2

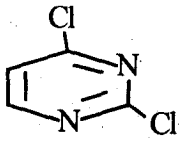
4. A compound (**A**), having molecular formula. $C_{13}H_{12}N_4O_2$ on boiling with $Ba(OH)_2$ solution yields (**B**), molecular formula $C_{12}H_{12}N_2O_3$ and one molecule of urea. The compound (**B**) on treating with dil. HCl eliminates CO_2 and gives the product (**C**) mol. formula $C_{11}H_{12}N_2O$. Compound (**C**) on vigorous heating with NaOH soln. yields compound (**D**), mol, formula $C_9H_{14}N_2$ and glyoxylic acid. Compound (**C**) exhibits the property of lactam and (**D**) shows the properties of ortho phenylene diamino compound. Identify the compound **A, B, C** and **D** and establish the structures.

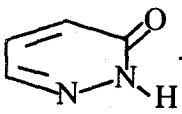
Establish the five-membered ring in Vitamin C and establish its structure by synthesis. 8

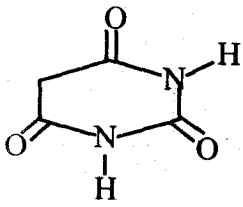
5. (*a*) Explain why pyridazine has higher boiling point than the other two diazines and they are less susceptible towards electrophilic substitution. 2

(*b*) Predict the product of the following reaction with plausible mechanism (any *three*) : 2 × 3

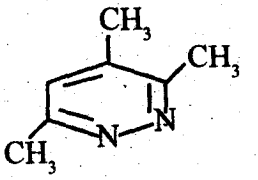
(*i*)  $\xrightarrow[130^{\circ}C]{NH_2 - NH_2}$?

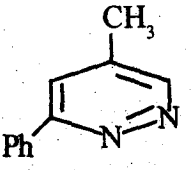
(*ii*)  $\xrightarrow[CH_3\,OH,\ room\ temp]{CH_3ONa}$?

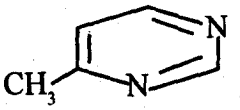
(*iii*)  $\xrightarrow[140^{\circ}C]{PCl_5}$?

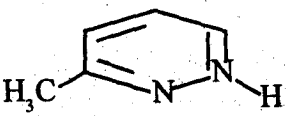
(*iv*)  $\xrightarrow[\Delta]{PCl_5}$?

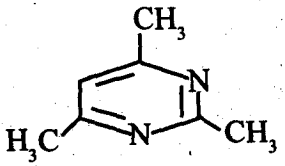
6. Synthesise the following compounds stating reagents and reaction conditions in each case (attempt any *four*) : 2 × 4

(*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

(*v*) 

7. (*a*) What is protein tertiary structure ?

(*b*) What types of bonds are involved in protein tertiary structure ?

(*c*) What is protein denaturation ?

(*d*) Protein 3D structure fall into two main groups. Elaborate with examples. 2 × 4

8. (*a*) Define Ramachandran plot.

(*b*) Locate the following secondary structural element of proteins in Ramachandran plot : α -helix, parallel β-pleated sheet, antiparallel β-pleated sheet, 3.10 helix.

(*c*) What is protein quarternary structure ? 2 + 3 + 3

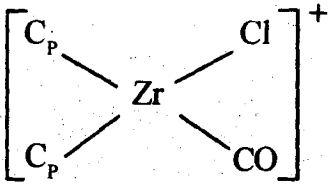
(*Inorganic Special*)

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

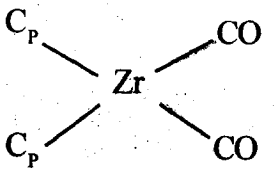
GROUP – A

1. (*a*) Among the given two complexes I and II, which will show a lower carbonyl stretching

frequency ? Explain. 2



I



II

(*b*) Complete the following reaction and draw the structure of the product. 2

$[CO_6(CO)_{15}]^{2-} + H^+ \longrightarrow$

(*c*) N_2 and CO are iso-electronic molecules but $M-N_2$ complexes are much weaker compared to M–CO complexes. Offer a reasonable explanation. 2

(*d*) Predict A and B in the following scheme of reaction– 2

$Fe(CO)_5 \xrightarrow{NaOH} (A) \xrightarrow{MnO_2} (B)$

2. (*a*) Predict the structure of $[Os_8(CO)_{22}]^{2-}$. 2

(*b*) $Os_6(CO)_{18}$ has 'three face sharing tetrahedral structure'. Show that this structure is consistent with the number of valence electrons available. 3

(*c*) Rationalise why $Os_3(CO)_{12}$ has triangular Os_3 core but in $Os_3(CO)_{12}\ I_2$, the Os atoms are in linear arrangement. 2

(*d*) $[Os_6(CO)_{18}\ P]^-$ adopts a trigonal prismatic structure– Rationalise. 1

3. (*a*) Discuss the structural features of Vitamin B_{12}. 2

(*b*) Draw the active site structure of the enzyme 'Catalase'. 2

(*c*) Discuss the mechanism of the dispropor -tionation of H_2O_2 by the Catalase enzyme. 3

(*d*) What is the function nitrate reductase enzyme? 1

4. (*a*) Write down the catalytic activity of cytochrome P_{450} in various reaction. 2

(*b*) Draw the active site structure of chlorophyll–A. 2

(*c*) Write down the active site structure of ascorbate oxidase enzyme and explain the oxidation mechanism of ascorbic acid. 2 + 2

GROUP – B

5. (*a*) How will you synthesize $K[CO_3(CO)_{10}]$, starting from $CO_2(CO)_8$? Explain the structure of $K[CO_3(CO)_{10}]$. 3

(*b*) Write down the structure of $[Fe_4(CO)_{13}]^{2-}$ and cite the different types of CO-binding in the structure. 2

(*c*) Discuss 'Super reduced species'. 2

(*d*) Predict the structure of $'CO_3(CO)_9 Ni(\eta^5 - C_p)$ using valence electron count method. 1

6. (*a*) Discuss the mechanism of peroxidase enzyme in the reduction of H_2O_2 to H_2O by various organic reductants. 3

(*b*) What do you mean by Gamma-ray spectroscopy ? 2

(*c*) Explain the Mössbauer spectra of $[Fe(CN)_5NO]^{2-}$. 3

7. (*a*) ESR spectrum of trimesitylborate in THF shows four peaks. What information can you predict from this result ? 2

(*b*) The ESR spectrum of

$$[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5]^{5+}$$

shows fifteen lines. Derive the structural information of this complex ion from this data. 3

(*c*) Showing all possible transitions discuss the ESR spectrum of *p*-benzosemiquinone radical anion. 3

8. (*a*) 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

(*b*) Comment about the ESR activity of the metal ions in the octahedral complexes of the following ions : Cr (III), Mn(II), Ni (II). 3

(*c*) Predict the number of lines in the ESR spectrum of the $[^{13}CF_2H]$ radical. [I (^{19}F) = 1/2]. 2

(*Physical Special*)

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

GROUP – A

Answer any *two* questions

1. (*a*) How does diffusion is helpful for determination of number average molecular weight ? 6

(*b*) At 25°C, the density of glucose is $1{\cdot}55\ gcm^{-3}$; it's diffusion co-efficient is $6{\cdot}81 \times 10^{-6}\ cm^2\ s^{-1}$ and the co-efficient of viscosity of water is $8{\cdot}937 \times 10^{-3}$ Poise. Assuming that the glucose molecule is spherical, estimate it's molar mass. 4

2. (*a*) What do you understand by the term "light Scattering" ? 2

(*b*) Define 'Particle Scattering factor' of a macromolecule ? 2

(*c*) Define sedimentation co-efficient. How does it determine. 1+ 2

(*d*) Calculate the time required for glucose molecule to diffuse through a distance of 10,000 Å. The diffusion co-efficient of glucose is $0{\cdot}462 \times 10^{-9}\ m^2\ s^{-1}$. 3

3. (*a*) How can you differentiate between $FeSO_4$ and $FeCl_3$ with the help of Mössbauer spectra ? 3

(*b*) A free Mössbauer nucleus of mass 99·5 amu emits radiation of wavelength 0·1 nm. Calculate the recoil velocity and Doppler shift. 4

(*c*) Predict the variation of isomer shift in Sn^{4+}, Sn^{2+} and Sn, covalently bonded to four groups. Explain the cause of this variation. 3

4. (*a*) Explain each term involved in the equation for a two-flux, two-force irreversible process, and explain its significance. 5

(*b*) Write down, without derivation, the expression for the rate of entropy production for a process where a potential difference 1 φ causes a pressure difference 1p and using this expression obtain the Saxen's relations. 5

GROUP – B

Answer any *two* questions

5. (*a*) The energy difference between $^{57}Fe^*$ and ^{57}Fe is 14·4 KeV. In a Mössbauer experiment if the relative velocity of the source and the absorber is 99 ms^{-1}, calculate the shift in frequency. 2

(*b*) A particular Mössbauer nucleus has spins 5/2 and 3/2 in its excite 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 applied, and (*iii*) both an internal electric field gradient and an external magnetic field are pressent ? 3

(*c*) What are the essential criterion of a nucleus for Mössbauer spectroscopy ? 3

(*d*) How do you determine the structure of $I_2Cl_4Br_2$ with the help of Mössbauer spectroscopy ? 2

6. (*a*) Describe one method for the synthesis of anisotropic gold nanoparticle. Explain the origin of two absorption maxima of rod shaped gold hydrosol. 3 + 3

(*b*) Explain the following : 2 + 2

(*i*) Melting temperature of nanomaterials are generally lower than its bulk phase.

(*ii*) Corner atoms of nanocrystals are generally missing.

7. (*a*) Define nanomaterial. How does nanomaterial differ from its bulk counterpart ? 1 + 2

(*b*) Considering the nanoparticles to be spherical, the expression for the overall potential is given by,

$$V = \frac{B}{R^n} - \frac{C}{R^6} + \frac{N^2 \cdot e^2}{\in_m \cdot R}$$

where 'R' is the centre to centre distance of two spherical nanoparticle. 'B' and 'C' are the characteristic constant. 'N' is the number of species carring electronic charge 'e' at the surface of nanoparticle and $\in_m$ is the medium dielectric constant. Give a schematic plot of the potential as a function of 'R'.

Deduce the following expression for potential maxima (V_{max}),

$$V_{max} = 0 \cdot 5823 . C^{-1/5} \left(\frac{N^2 e^2}{\in_m} \right)^{6/5}$$

Comment on your result. 6 + 1

8. Write the major structural differences between DNA and RNA. What are the driving forces for the stabilization of DNA double helical structures. 5 + 5
