M.Sc. 4th Semester Examination, 2012

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 taking at least *two* from each Group

GROUP –A

1. (*a*) What are liquid crystals ?

   (*b*) Write the classification of liquid crystals.

   (*c*) What are discotic liquid crystals ?

   (*d*) How do you synthesize the hexa esters of benzene starting from glyoxal ? 2 × 4

2. (*a*) What is a gel ?

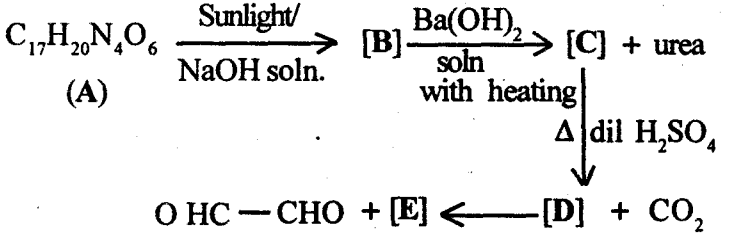
   (*b*) Classify the different types of gels.

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

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

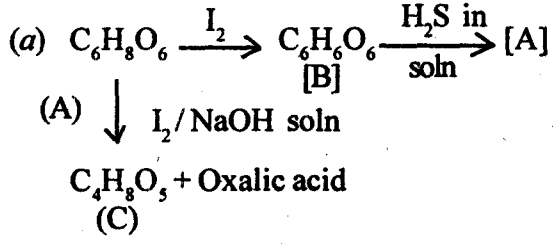
(*e*) What are the techniques used in studying gel morphologies ? 2 + 2 + 1 + 2 + 1

3. Complete the transformation : 8



Identify *B*, *C*, *D* and *E* and hence deduce the structure of (**A**).

4. The following compound (**A**) exhibits the properties as shown below : 8



(*b*)

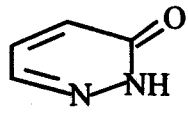
$$C_6H_8O_6 \xrightarrow[(ii)\,CH_3I/Ag_2O]{(i)\,CH_2N_2} C_{10}H_{10}O_6 \xrightarrow[(ii)\,Ba(OH)_2]{(i)\,O_3} C_6H_{12}O_5$$

(A) **(D)** **(E)**

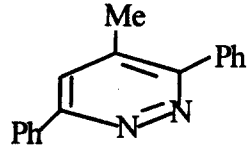
Compound (**A**) can reduce Tollens reagent and gives violet colouration with neutral $FeCl_3$ solution Hence identify *A*, *B*, *C*, *D*, and *E*.

5. Logically develop the synthesis of the following (any *four*) : 2 × 4

(*i*)



(*ii*)



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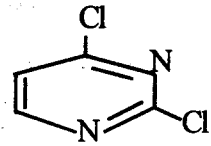
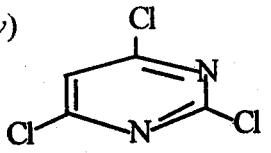
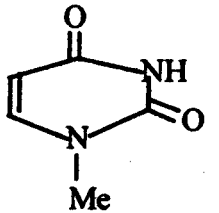


(*iv*)



(*v*)



GROUP –B

6. (*a*) Elaborate on the following secondary structural elements of proteins : α-helix, β-pleated sheet, β-turn.

(*b*) Define Ramachandran plot and locate the above secondary structural elements. 4 × 2

7. (*a*) What is green chemistry ?

(*b*) Write the principles of green chemistry.

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

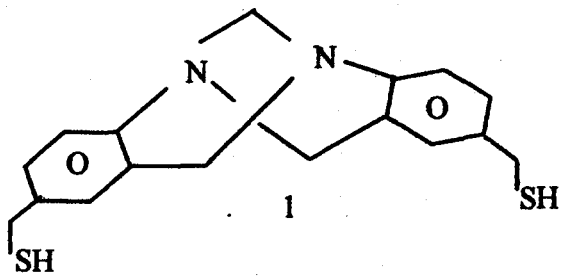
(*d*) Give examples of (*i*) a green synthesis of gold nano particles and (*ii*) a green organic synthesis.

2 + 2 + 1 + 3

8. (*a*) What is self-replication ?

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

(*c*) Propose a self-replicating scheme based on the Tröger's base analogue1.



1

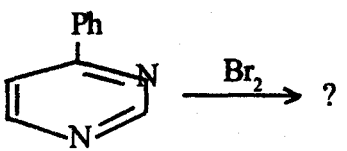
(*d*) Write a possible synthesis of compound 1.

2 + 1 + 2 + 3

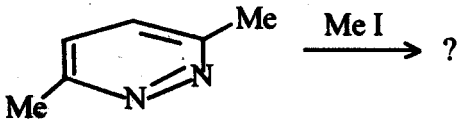
9. (*a*) "Electrophilic substitution is less common in diazines system." Why ? Explain.

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

(*i*)



(*ii*)



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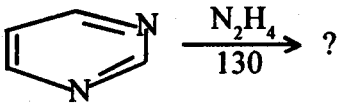
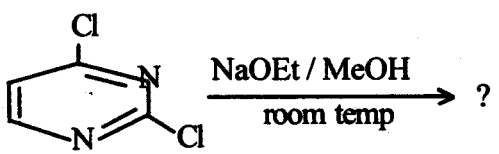


(*iv*)



8

10. (*a*) What are coenzymes ? Explain the reactions where the coenzyme thiamine Pyrophosphate and Flarium mononucleotide take part in biological processes.

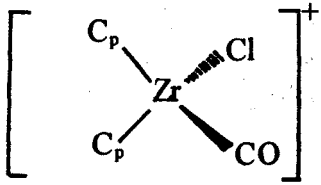
(*b*) Explain the different steps involved in the carbohydrate metabolism where end product is pyruvic acid for glucose. 8

(*Inorganic Special*)

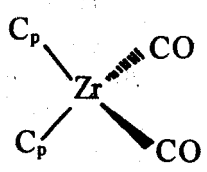
Answer any **four** questions

1. (*a*) The infra-red spectrum of $[\eta^5 - C_pFe(CO)_2]_2$ When measured at room temperature indicated three bands at 2005, 1961 and 1795 cm^{-1} and when measured at high temperature gave a different spectrum with three bands at 2015, 1973 and 1938 cm^{-1}. In contrast, the infra-red spectrum of $[\eta^5 - C_pO_s(CO)_2]_2$ gave bands at 2040, 1986 and 1948 when measured both at room temperature and high temperatures. Both the compounds obey the 18 electron rule. Draw possible structures of the compounds explaining this phenomenon. 4

(*b*) Among the given two complexes (*i*) and (*ii*) which will show lower carbonyl stretching frequency ? Give reasons for your answer. 2



(*i*)

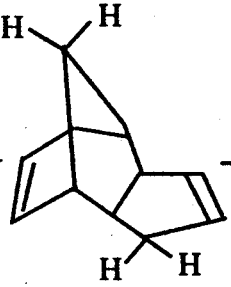


(*ii*)

(*c*) Complete the reactions : 4

(*i*) $VCl_3 + 4Na + 6CO \xrightarrow[300\ bar]{diglyme} ? \xrightarrow{H_3PO_4} ?$

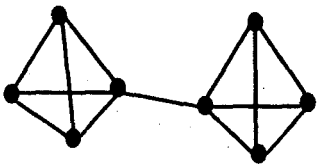
(*ii*) $Fe(CO)_5 + NaOH \longrightarrow ? \xrightarrow{MnO_2} ?$

(*iii*) $Mo(CO)_6 +$  $\xrightarrow[\text{microwave}]{750\ W} ?$ diglyme, 1hr

(*iv*) $PtCl_2 + CO \longrightarrow ?$

2. (*a*) $[\eta^5 - C_pFe(CO)]_4$ is a dark green solid compound. Its infra-red spectrum shows a single CO stretching band at 1640 cm^{-1}. The ^1H-NMR spectrum shows a single line even at low temperature. Propose a structure for this compound based on the given data. 4

(*b*) How $[Fe_3CO_{11}]^{2-}$ can be synthesized ? Draw its structure. 2

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

(*d*) $Os_5(CO)_{19}$ has a 'bow-tie' geometry. Is this consistent with the number of valence electrons available? 2

3. (*a*) An EPR instrument is operating at a frequency of 9·1 GHz and measurements are made with atomic hydrogen. Resonance is observed at a magnetic flux density of 0·3247 T. Calculate the *g*-value for the electron in the hydrogen atom. 3

(*b*) What do you mean by 2 + 2

(*i*) Zero field splitting

(*ii*) Hyperfine splitting.

(*c*) Name the best known free radical used in calibrating ESR spectra. 1

(*d*) Determine the number of ESR lines possible for triphenylmethyl radical. 2

4. (*a*) Explain the ESR spectrum of $[NO(SO_3)_2]^{2-}$ ion. 4

(*b*) The interaction of an unpaired electron with ^{14}N causes a splitting of three lines while with ^{55}Mn it gives six lines. Why. 3

(*c*) 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

5. (*a*) What do you mean by Replication, Transcription and Translation processes in biological system ? 4

(*b*) Explain PS I and PS II 2 + 2

(*c*) Briefly discuss Cytochrome P_{450}. 2

6. (*a*) How do you determine correct geometrical structure of an inorganic compound by Mossbauer spectroscopy ? 3

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

(*c*) Explain the variable temperature ^{57}Fe Mössbauer spectra of

$$[Fe(II)\ Fe_2(III).(OAc)_6(H_2O)_3]$$ 2

(*d*) What is Gamma ray spectroscopy ? 2

7. (*a*) Discuss the catalytic cycle of the enzyme nitrate reductase. 4

(*b*) Draw the active site structure of the enzyme superoxide dismutase. 2

(*c*) What are the role of the enzymes Xanthine oxidase and catalase in biological system ? 2

(*d*) Write down the applications of vanadium containing proteins. 2

(*Physical Special*)

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

GROUP – A

Answer any *one* of the following :

1. (*a*) Write the thermodynamic equations of motion for a two-force, two-flux irreversible process, explain the terms, state the Onsager reciprocity relations and explain its significance .

(*b*) Establish Prigogine's principle of minimum entropy production. 10

2. Obtain the expression for the rate of entropy production for a process where the application of an electric field $\Delta\phi$ causes a pressure difference Δp and utilising this expression define streaming potential and electroosmosis in terms of the phenomenological coefficients. 10

GROUP – B

Answer any *one* of the following :

3. (*a*) Define particle scattering factor of a macromolecule ?

(*b*) Equal numbers of molecules with $M_1 = 10{,}000$, $M_2 = 50{,}000$ and $M_3 = 1{,}00{,}000$ are mixed. Calculate the polydispersity index (PDI) of the polymer sample and comment on your result.

(*c*) At 25°C, the density of glucose is $1{\cdot}55\ g\ cm^{-3}$; its diffusion coefficient 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 its molar mass.

3 + 3 + 4

4. (*a*) Derive the Flory-Huggins equation for a polymer solution.

(*b*) Write and explain the relation by which you can say that diffusion method is a helpful tool for determination of average molecular weight of a polymer solution.

(*c*) The intrinsic viscosity of myosin is 217 $cm^3 g^{-1}$. Calculate the approximate concentration of myosin in water which would have a relative viscosity of 1·5. 6 + 2 + 2

GROUP – C

Answer any *one* of the following :

5. (*a*) What do you mean by Mössbauer spectroscopy ? State its principles. 2 + 3

(*b*) Write down the equation of chemical shift for Mössbauer spectroscopy. 2

(*c*) How do you determine the structure of $I_2Br_2Cl_4$ with the help of Mössbauer spectroscopy ? 3

Or

(*a*) Describe Temperature dependent Mössbauer Spectroscopy with one example. 5

(*b*) Draw and explain the Mössbauer Spectra of $[Fe(CN)_6]^{4-}$. 2

(*c*) Write down three major conditions for Gamma Ray spectroscopy. 3

6. Write a short note on primary, secondary, tertiary and quaternary structure of protein. Describe Rama chandran plot. 2 + 2 + 2 + 2 + 2

Or

What is the basic principle of chromatographic method? Describe ion exchange chromatographic separation of protein mixture. Write the basic principle of circular dichroism. Mention about the different forms of DNA. 2 + 3 + 3 + 2

GROUP – D

Answer any *one* of the following :

7. What do you understand by Nano-materials? How does the nano-materials for a given substance differ from their bulk counterpart? Define the term dispersion (F) for a nano crystal. Show that for a cubic nano-crystal having 'N' number of atoms

$$F \cong \frac{6}{N^{1/3}}$$

Why are the corner atoms often missing on nano-crystals even in thermodynamic equilibrium ?

1 + 2 + 2 + 3 + 2

8. Write down the steps involved for the synthesis of metal nanoparticles in solution. Describe a method for the solution phase synthesis of silver nanoparticle. What do you mean by surface plasmon Resonance ? How do you explain the appearence of two absorption band for rod shaped silver nanoparticles ? 2 + 3 + 2 + 3