2009

M.Sc. Part–II Examination

CHEMISTRY

PAPER—VI

Full Marks : 75

Time : 3 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *five* questions
taking at least *two* from each group.

Group—A

1. (a) Write down, without derivation, Planck's equation for spectral distribution of black body radiation and comparing this with Wien's equation, establish the fundamental equation $\varepsilon = h\nu$. 3

   (b) Obtain the expression for the rotational contribution to the molar entropy of a homonuclear diatomic gaseous molecule. 8

   (c) Calculate the translational molecular partition function for H_2 in a volume of $1 cm^3$ at $T = 300K$ ($h = 6.62 \times 10^{-34} JS$, $k = 1.38 \times 10^{-23} JK^{-1}$). 4

2. (a) Explain briefly the term 'Phase space'. 2

(b) What is meant by the Bose-Einstein condensation? Obtain the expression for the temperature at which such a phenomenon occurs. 13

3. (a) State the Ergodic hypothesis. 2

(b) Define the grand partition function Z and obtain the expression for pressure of an ideal gas in term of Z. 3+4

(c) Derive the relation between the Lagrangian multipliers α and β in term of chemical potential. 6

4. (a) What type of molecular weight is determined by osmometry method and why? Describe the method of molecular weight determination by osmometry method. 2+7

(b) How does molecular weight of a macromolecule is determined by sedimentation equilibrium method. 6

5. (a) What is an electro-capillary curve? What information can you obtain from such a curve? 2+2

(b) Show that the parallel plate condenser model can explain electro-capillary curve which is perfect parabola. 4

(c) Starting from equation :

$$d\gamma = -q_M dv - \frac{q_M}{Z_j F} d\mu_j - \sum \Gamma_i d\mu_i$$

derive

$$\left(\frac{d\gamma}{2RTd\ln a_\pm}\right)_{\text{const.}V_{-/+}} = -\Gamma_{+/-}$$

for 1:1 type of electrolyte, where γ = surface tension & Γ_i = surface excess for i-th type of species at the interface and all other terms bear usual significance. 7

Or

Show that at moderate concentration of an electrolytic solution, the simple Debye-Huckel law given by $\log f_\pm = -A(Z_+Z_-)I^{1/2}$ is modified as

$$\log f_\pm = \frac{-A(Z_+Z_-)I^{1/2}}{1+K^a}$$

where a = ion size parameter, $K = BI^{1/2}$ (B is a constant and k^{-1} = the thickness of ion atmosphere). Discuss the role of ion-size parameter to explain the deviation from simple D-H law at moderate concentration. Also show that the modified equation can explain in a better way the experimental behaviour of ionic solution at high concentration and that the equation reduces to the simple D-H law at low concentration of ions.

Also justify the statement that the simple D-H law is a limiting law. 15

Group—B

6. (a) Give a schematic representation of the Stern double layer and explain briefly its salient featues. 3

   (b) How would you express the total capacity at an electrode solution interface at high and low concentrations separately following Stern model? 4

   (c) How can you determine equilibrium exchange current density, transmission coefficients and stoichiometric number experimentally using low and high field approximations of Generalized Butler Volmer equation? 8

7. (a) What do you mean by Potential Energy Surface? Trace out the course of the reaction

$$H^{\alpha}-H^{\beta}+H^{\gamma}\longrightarrow H^{\alpha}+H^{\beta}-H^{\gamma}$$

   considering potential energy surface and explain the term saddle point. 1+10

   (b) The rate of a second order reaction between ionic species depend on ionic strength of the medium—Justify. 4

8. (a) "In a reaction between two ions entropy of activation always decreases after formation of activated complex due to electrostriction"—criticise the statement with the help of double sphere activated complex model. 10

   (b) The radii of two nonionic solutes A & B are 2·5A° and 3·5A° respectively. For a reaction between A & B in water at 25°C calculate the rate constant, if the reaction be diffusion controlled. Viscosity of the solvent is 0·9 CP. 5

9. (a) Without derivation of the equation describe the method of determination of average molecular weight of high polymers by light scattering method using Zimm plot. 6

(b) At 25°C, the density of glucose is 1·55g/cc ; its diffusion co-efficient is $6{\cdot}81\times10^{-6}$ cm^2s^{-1} and the coefficient of viscosity of water is $8{\cdot}937\times10^{-3}$ poise. Assuming that the glucose molecule is spherical, estimate its molar mass. 5

(c) A sample of serum globulin is placed in an ultracentrifuge which is operating at 40,000 rpm. If the sedimentation coefficient of this protein is $7{\cdot}1\times10^{-13}$s, how far will the solution boundary move in 20 minutes at a distance of 6·2cm from the axis of rotation? 4

10. (a) Write the final equation for $k_c/\Delta R_\theta$ in relation to light scattering from a polymer sample, explaining each term. Explain the steps involved in determining absolute $\overline{M}_w$ using Zimm plot. 3+4

(b) Write Flory-Huggins equation for free energy of mixing of a polymer solution explaining each term and mention the reason for non-ideality. Under what condition does this solution behave like an ideal solution? Write the important uses and drawbacks of Flory-Huggins equation. 3+1+4

(Inorganic Special)

Answer any *five* questions
taking at least *two* from each group.

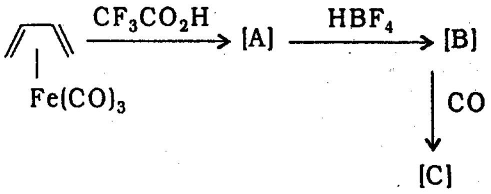
Group—A

1. (a) Discuss the bonding (with MO diagram) in transition metal-butadiene complex. 5

   (b) What do you mean by 'Piano-Stool' compound ? Cite example. 2

   (c) Give example of a complex where C_p-group acts as bridging ligand. Write down the synthesis procedure of the above complex. 2

   (d) Predict the product of the following reaction :

   (i) 

   (ii) $Na_2PdCl_4 \xrightarrow[\text{EtOH}]{2PhC \equiv CPh} [D]$

   (e) Complete the following reaction :

   $$\left[C_pMo(CO)_3\right]_2 \xrightarrow{h\nu} [E] \xrightarrow{CCl_4} [F]$$

   What is the final product formed in absence of Ccl_4 ? Write down the structure of that final product. 2+2

2. (a) 'Mono-capped octahedron' structure of $Os_7(CO)_{21}$ is consistent with its number of available valence electrons'—explain. 4

(b) Discuss 'Tetragonal prism' geometry in the light of metal-metal bonding. 3

(c) Write down the following synthetics : 4

(i) $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ from $Fe(CO)_3$

(ii) $Ru_3(CO)_{12}$ from $RuCl_3.xH_2O$.

(d) Predict the geometry of the metal core of the cluster $Fe_4C(CO)_{13}$ and $Os_5(CO)_{16}$. 2+2

3. (a) Explain with quantitative energy level diagram how lanthanides show luminescence property ? 6

(b) Establish the principle of separation of lanthanides in ion-exchange resin technique. 6

(c) Though the common oxidation state of lanthanides is +3, comment on the occurance of Tb(+4), Eu(+2) and Yb(+2). 3

4. (a) Discuss the active site structure, biofunction and modelling study of the enzyme superoxide dismutase. 2+3+2

(b) Write down the active site structure of 'Chlorophyl' and 'Cytochrome'. 4

(c) What are 'Ceruloplasmin' and 'Cytochrome P-450' ? 2+2

5. (a) Discuss the Catalytic Cycle related to the 'hydroformylation reaction'. 6

(b) Write a note on 'Insersion reaction'. 4

(c) What is 'Catalytic efficiency'? 2

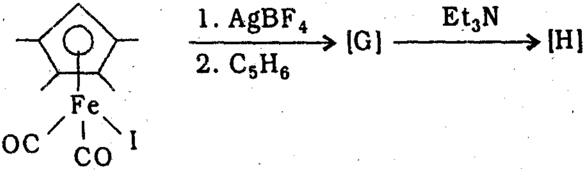
(d) Discuss 'Ziegler-Natta polymerization'. 3

Group—B

6. (a) (η^4–C_4H_4) Fe(CO)3 is diamagnetic—explain with MO-diagram. 5

(b) Identify [G] to [N] 4

(i)



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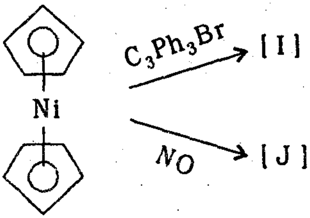

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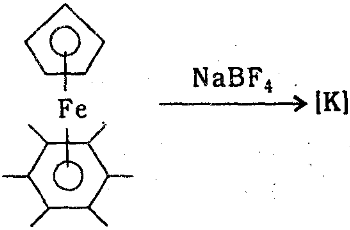
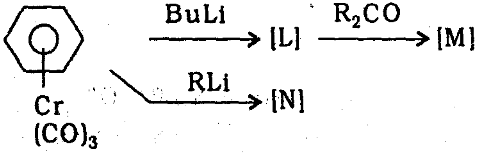
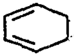


(iv) 

(c) Cite an example of a 'superferrocenophane'. 2

(d) How 'titanocene' can be synthesized by cocondensation reaction? 2

(e) Write down the final product with structure when $K[VCp_2]$ is reacted with . 2

7. (a) '$Os_5(CO)_{18}$ has a 'raft structure'. Is this consistent with its number of valence electrons available? 3

(b) How will you prepare $Fe_3(CO)_{12}$? Compare the structures of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$. 1+3

(c) Write down the synthesis, structure and bonding of a complex having five fold of metal-metal bonding. 4

(d) Predict the geometry of the metal core of $Ir_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. 2+2

8. (a) Among La and Lu which should have comparatively more basic character and why? 3

(b) Calculate the expected magnetic moment value for f^4 and f^{12} systems. 2+2

(c) At room temperature the experimental magnetic moment value for tris (acetylacetonato) europium (III) and tris (acetylacetonato) samarium (III) complexes are different from that of the expected magnetic moment values.—Explain. 5

(d) The lanthanides typically display weak but sharp absorption band whereas d-block element show strong and broad absorption band—explain. 3

9. (a) Write down the active site structure of 'hemocyanin'. Explain O_2 binding in 'hemocyanin'. Discuss its magnetic behaviour. 3+2+2

(b) What is 'hypoferremia'? 2

(c) Write notes on the enzyme 'urease' and 'peroxidase'. 3×2

10. (a) Explain the Pd-catalyzed oxidation of ethylene to acetaldehyde. Why Cu^{2+} is used during the process. 6+2

(b) What do you mean by "reductive elimination"? 2

(c) Write down the catalytic cycle for the following reaction

$$CH_3OH + CO \xrightarrow{[Rh(CO)_2I_2]^-} CH_3COOH \cdot \qquad 5$$

(Organic Special)

Answer any *five* questions
taking at least *two* from each group.

Group—A

1. (a) Define gels. Classify different types of gels. Give some examples of low molecular mass organogelators. What are the techniques used for studying gel morphologies? 2+2+2+2

(b) How can one design a protease enzyme mimic? Illustrate a protease enzyme mimic based on modified barbitol. 2+5

2. (a) Answer any *two* of the following : 4×2

(i) Chlorobenzene chromiumtricarbonyl complex is allowed to react with the following three nucleophiles and the reactions are oxidatively quenched after they have proceeded for their half lives.

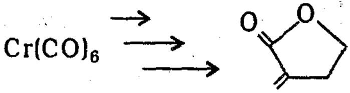
$NaCH(CO_2Et)_2$, $LiCMe_2CH_2CN$ and 2-lithio-2-methyl-1, 3-ditheane

What are the products obtained in each case?

(ii) "Acidities of both the ring protons and benzylic proton of an aromatic compound are enhanced upon complexation with $Cr(CO)_3$, but the mechanisms are different". Elucidate.

(iii) Account for the formation of diastereomeric products when chromiumtricarbonyl complexes of benzylidene derivatives of *alpha*-tetralone are treated with (a) nitromethane (b) ethyl acetoacetate.

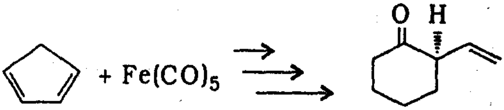
(iv) Complete the following sequence of reactions :



(b) How would you account for the regiocontrole of the nucleophilic substitution of the chromiumtricarbonyl complex of a monosubstituted benzene when the substituent is an electron donor and an electron acceptor respectively? 4

Or

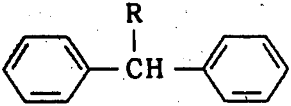
Complete the following sequence of reaction :



(c) Account for the difference in stereochemistry of the products obtained when monochromiumtricarbonyl complex of fluorene is cooled to −78°C followed by treatment with methyl iodide and when the same reaction mixture is warmed to room temperature. 3

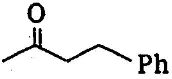
3. (a) Name one each of palladium (II) and palladium (O) catalysts used in C–C bond formation. What is the essential point of difference in the palladium catalysed Heck olefination and Suzuki cross-coupling? Describe the catalytic cycle of Heck olefination stressing the role of the base used in this cycle. 1+1+7

(b) The difference in the rates of deprotonation of the following compound and its monochromium tricarbonyl complex with a base is much larger when R =H in comparison to when R = Ph. How would you explain this phenomenon? 6



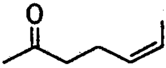
4. (a) Define : (i) Synthon ; (ii) Synthetic equivalent ; (iii) Functional group interconversion. Give examples in each case. 4

(b) Illustrate the necessity for the use of functional group activation in the retrosynthetic analysis of the following compound : 3

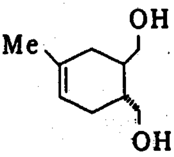


(c) Work backwards using the principles of retrosynthetic analysis to find out the suitable starting materials for any *two* of the following compounds and give the forward synthesis in each case : 2×4

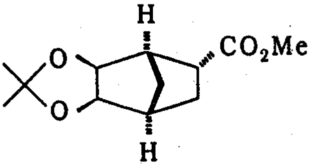
(i)



(ii)



(iii)



5. (a) Why proline is known as "helix breaker"? Illustrate the following secondary structural element of a peptide : α-helix, β-pleated sheet, β-turn, 3·10 helix. 2+2+2+2+2

(b) What is Ramachandran plot? Locate the following secondary structural element in the Ramachandran plot : right-handed α-helix, β-pleated sheet (bath parallel and anti-parallel). 3+2

Group—B

6. (a) Write the names of different penicillins isolated from the culture medium of penicillium group of fungus. 2

(b) Write all steps for the synthesis of benzyl penicillin starting for Phthalimide and d-penicillamine as applied by Sheehan et.al. Explain the conditions used in each step. 5+3

(c) What are the different paths through pathogenic microbes? How penicillin inhibits the cell wall synthesis of gram-negative bacteria? 2+3

7. (a) The following Vitamin shows the property as :

$$\underset{(\underline{A})}{C_{12}H_{14}Cl_2N_4OS} \xrightarrow[\text{saturated with } SO_2]{Na_2SO_3\text{solu}} \underset{(\underline{B})}{C_6H_9NOS} + \underset{(\underline{C})}{C_6H_9N_3O_3S} + NaCl$$

Chemical and spectral evidence showed that compound $(\underline{C})$ is a thiazole and compound $(\underline{D})$ is a pyrimidin derivative.

Identify $(\underline{C})$ and $(\underline{D})$ and establish the structure of $(\underline{A})$. 10

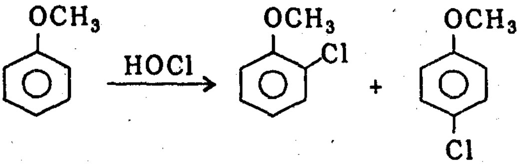
(b) How vitamin A and B react in the biological system? Write all the steps involved in cocarboxylase action in biological system. 5

8. (a) Define Molecular Recognition. What are the forces involved in molecular recognition process? Design a receptor for adipic acid and illustrate the complexation. Write the applications of crown ethers. 2+2+2+2+2

(b) What are cryptands? How can cryptates be used in light conversion and energy transfer devices? 2+3

9. (a) What is hydrophobic effect? Illustrate hydrophobic effects on simple organic reactions in water. 3+4

(b) What are cyclodextrins? What are the major driving forces for cyclodextrin complexation? Write some applications of cyclodextrins. What is the effect of added α-CD on the following chlorination reaction : 2+2+2+2

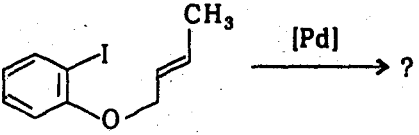


10. (a) When 1-bromo-2-methoxynapthalene is treated with phenylmagnesium bromide in presence of a Ni(O) catalyst a new carbon-carbon bond is formed. Can you write down the mechanistic steps? 6

(b) Clearly identify the oxidative addition, transmetalation & reductive elimination steps involved. 3

(c) Complete the following transformations : 2×3

(i)



(ii)