

**West Bengal State University**  
**B.A./B.Sc./B.Com ( Honours, Major, General ) Examinations, 2014**

**PART - III**  
**CHEMISTRY — HONOURS**  
**Paper - V**  
**( NEW & OLD SYLLABUS )**

Duration : 4 Hours ]

[ Full Marks : 100

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

*The figures in the margin indicate full marks.*

**( NEW SYLLABUS )**

**Use separate answer scripts for [ CEMAT 35-IA & CEMAT 35-IB ]  
and for [CEMAT 35-AA & CEMAT 35-AB ].**

**CEMAT 35- IA**

Answer any *two* (2) questions taking *one* from each Unit.

**UNIT - I**

1. a) Explain why  $\text{OH}^-$  is a weaker field ligand than  $\text{H}_2\text{O}$  ? 2
- b) What do you mean by trans effect ? Predict the products expected if one mole of  $[\text{PtCl}_4]^{2-}$  is reacted successively with the following reagents :
- i) 2 moles of ammonia
- ii) 2 moles of pyridine
- iii) 2 moles of chloride
- iv) 1 mole of nitrite ( $\text{NO}_2^-$ ). 1 + 3
- c) What is CFSE ? From the view point of CFSE show whether  $\text{Co}_3\text{O}_4$  is a normal or an inverse spinel. 1 + 2
- d) For the  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion, the mean pairing energy,  $P$ , is found to be  $23,500 \text{ cm}^{-1}$ . The magnitude of  $\Delta_0$  is  $13,900 \text{ cm}^{-1}$ . Calculate the CFSE for this complex ion corresponding to high-spin and low-spin state. Which state will be more stable ? 1½ + 1½ + 1

2. a) Determine the ground state term symbol for the following ions : 3  
(i) Ni(II) and ii) Co(II).
- b) A metal forms two complexes in the same oxidation state. In one complex, the magnetic moment is 4.9 B.M. while in another it is 0 B.M. Which of the following metal(s) fits this behaviour and why ? 2  
Cr(III), Mn(II), Mn(III), Fe(II), Fe(III), and Co(II).
- c) Explain the nature of Jahn Teller distortion expected for an octahedral complex of a  $d^9$  system. 4
- d) What is spectrochemical series ? Justify the position of  $I^-$  and  $CN^-$  in it. 2 + 2

### UNIT - II

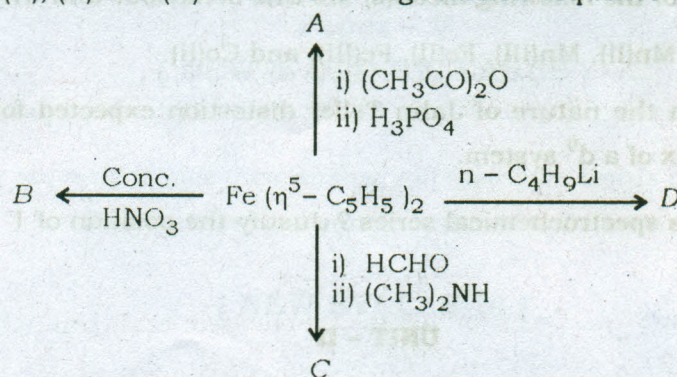
3. a) What do you mean by lanthanide contraction ? Explain the impact of lanthanide contraction on the chemical behaviour of the lanthanides. 2 + 2
- b) Discuss the trends in the stability of higher oxidation states of transition metals on gradually passing from 3d to 5d transition series. 4
- c) How does  $KMnO_4$  reacts in alkaline medium ? 1
- d) How would you prepare  $K_2Cr_2O_7$  from chromite ? Give balanced chemical equations. Give use of  $K_2Cr_2O_7$ . 3
4. a) Give a brief outline for the separation of lanthanides by ion-exchange method. 4
- b) Write the method of preparation of the following with chemical equations and give their uses :  $2\frac{1}{2} + 2\frac{1}{2}$   
(i)  $K_4[Fe(CN)_6]$  (ii)  $K_2[Ni(CN)_4]$
- c) Explain the relative advantages and disadvantages of using  $K_2Cr_2O_7$  and  $KMnO_4$  in quantitative estimation in acid medium. 3

## CEMAT 35- IB

Answer two (2) questions taking one from each Unit.

## UNIT - I

5. a) Give a method of preparation of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ . Identify the species (A), (B), (C) and (D) in the following reaction sequence : 2 + 4



- b) Explain with examples the different coordination modes of NO. 3
- c) What is Ziegler-Natta catalyst? What products do you expect when ethene and propene are individually treated with Ziegler-Natta catalyst? 1 + 3
6. a) The vanadium-carbon distance in  $\text{V}(\text{CO})_6$  is 200 pm, but in the anion  $[\text{V}(\text{CO})_6]^-$  it is only 193 pm. Explain. 2
- b) Assuming 18-electron rule to be valid, find the number of metal-metal bonds in (i)  $\text{Fe}_3(\text{CO})_{12}$  and (ii)  $\text{Os}_4(\text{CO})_{14}$ . 1½ + 1½
- c) Stability of ferrocene is greater than cobaltocene. Explain. 2
- d) Give short notes on the following : 2 × 2
- i) Fluxional molecules
- ii) Haptacity.
- e) How would you account the larger Pt-Cl distance in the  $\text{Cl}^-$  ion trans to ethylene than the other two Pt-Cl distances in Zeise's salt? 2

## UNIT - II

7. a) Briefly discuss the principle of gravimetric estimation of sulphate and hence explain gravimetric factor. 3 + 1
- b) With suitable example, discuss the role of pH in complexometric titration. 2

- c) Describe dissolution scheme of pyrolusite and hence write the principle for estimation of manganese in this solution. 2 + 2
- d) What do you mean by co-precipitation? 2
8. a) Outline a scheme (with equation) for the estimation of  $\text{CaCO}_3$  in dolomite. 3
- b) How does  $\text{KH(IO}_3)_2$  act as an oxidising agent? Discuss with suitable example. 3
- c) What is the composition of Zimmerman-Reinhardt solution? Why is it used in the estimation of  $\text{Fe(II)}$  by  $\text{KMnO}_4$  solution in presence of  $\text{Cl}^-$  ion? 4
- d) Explain with suitable example, the role of metal-ion indicator in complexometric estimation. 2

**CEMAT 35-AA**

Answer two (2) questions taking one from each Unit.

**UNIT - I**

1. a) Explain the biological function of hemoglobin stating the role of the metal ion present in its active site. 3
- b) Briefly explain the biofunction of the following : 2 + 2
- i) Ferredoxin
- ii) Carbonic anhydrase.
- c) What are the essential, trace and ultratrace elements? Explain with examples. 3
- d) What is chelation therapy? Give an example. 2 + 1
2. a) Define PS I and PS II and explain the role of metal ion involved in them. 4
- b) What is  $\text{Na}^+$  ion pump? How does it function? 3
- c) Name one Pt complex acting as drug and state its therapeutic applications. 2
- d) What is the biological function of cytochrome? 2
- e) What is the role of  $\text{Ca}^{2+}$  ion in human system? 2

**UNIT - II**

3. a) What is Buckminster Fullerene? Mention some of its unique properties with relation to its structure. 1 + 2
- b) Write two applications of gold nanoparticles. 3
- c) Define polymers. All polymers are macromolecules but all macromolecules are not polymers. Justify. 1 + 2

- d) A sample of polymer consists of 10% by weight of polymer of molecular weight 15,000 and 90% by weight of polymer of molecular weight 1,50,000. Determine the weight average and number average molecular weights of the polymer. 3
4. a) What are zeolites ? Give one example. How do they accommodate guest ions ? 3
- b) Explain metal surface catalysis with an example. 3
- c) What is meant by metal cluster structure ? Explain with an example. 3
- d) Nanoparticles behave differently from macro particles. Why ? 3

**CEMAT 35-AB**

Answer *two* (2) questions taking *one* from each Unit.

**UNIT - I**

5. a) Describe important features of the Watson and Crick double helical model of DNA. 4
- b) What is denaturation of proteins ? Mention the condition under which denaturation occurs ? 3
- c) Discuss the salient features of  $\alpha$ -helix structure of protein. 3
- d) What are the similarities and differences between nucleotides of DNA and RNA ? 3
6. a) i) How are enzymes classified ? Name the different classes of enzymes. 3 + 2
- ii) What is a coenzyme ? Give one example. 3 + 2
- b) What is the difference between nucleotides and nucleosides ? Explain with example. 3
- c) What is tertiary structure of protein ? 2
- d) What is the basic requirement for a protein to have quaternary structure ? Explain with one example. 3

**UNIT - II**

7. a) Discuss the mechanism of enzyme inhibition. Show that the equation for Lineweaver-Burk double reciprocal plot for competitive inhibition is
- $$\frac{1}{V} = \frac{K_m}{V_{\max}} \left( 1 + \frac{[I]}{K_i} \right) \times \frac{1}{[S]} + \frac{1}{V_{\max}} \quad 2 + 4$$
- b) What is Zeta potential ? Explain the stability of lyophobic colloids in the context of zeta potential. 2 + 2
- c) Discuss the effect of pH on enzyme activity. 2
8. a) What is turnover number ? 2
- b) What do you mean by electrophoresis ? How molecular weights of proteins can be determined by gel electrophoresis ? 2 + 3
- c) What is an autocatalytic reaction ? Explain with an example. 3
- d) Define isoelectric point. Give an example. 2

**( OLD SYLLABUS )**

Duration : 4 Hours ]

[ Full Marks : 100

**Use separate answer scripts for Group A and Group B.****Group - A**

[ Full Marks : 50 ]

Answer any *three* taking *one* question from each Unit.**UNIT - I**

1. a) Derive thermodynamically a relation between the osmotic pressure of a dilute solution of a solute and its molar concentration. State the assumptions and approximations involved. 4
- b) Calculate the van't Hoff factor and the degree of dissociation of a 0.1 molal aqueous solution of a monobasic acid, HA, which freezes at  $-0.3^{\circ}\text{C}$ . Given,  $K_f = 1.86 \text{ K kg mol}^{-1}$ . 2
- c) Prove that the phase rule  $F = C - P + 2$  remains unchanged even if one of the components is missing in some of the phases present at equilibrium. 3
- d) For a one-component system, the triple point is invariant, whereas the freezing point is variable. Explain. 2
- e) Explain, with  $S$ - $T$  diagram, the principle of cooling by adiabatic demagnetization of paramagnetic substances. 3
- f) The residual molar entropy of a crystalline substance at absolute zero is  $9.134 \text{ J K}^{-1}\text{mol}^{-1}$ . Find out the number of possible orientations that a molecule of the substance can adopt at this temperature. 2
2. a) Find an expression for  $\Delta S_{mix}$  for an ideal binary solution. 4
- b) A solution containing 1 g of urea in 1 kg of water freezes at the same temperature as another solution containing 1.5 g of a non-electrolyte 'S' in the same amount of water. Calculate the molar mass of the solute 'S'. 2
- c) Explain the phase diagram of a two-component system exhibiting liquid-liquid equilibrium with an upper critical solution temperature. 4
- d) Show that the internal energy ( $U$ ) of a system containing  $N$  non-interacting particles can be expressed in terms of its molecular partition function ( $Q$ ) as
- $$U = Nk_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V}$$
- The terms have their usual significance. 3
- e) Calculate the molecular partition function for a two-level (both non-degenerate) molecular system at 300 K with an excited state  $300 \text{ cm}^{-1}$  above the ground state ( $\epsilon_0 = 0$ ). 3

## UNIT - II

3. a) What is the lowest limit of the spacing of the lattice planes to produce X-ray diffraction spectra for a given radiation? 2
- b) An element occurs in two crystalline forms  $\alpha$  and  $\beta$ . The  $\alpha$ -form has FCC structure with  $a = 3.68 \text{ \AA}$  and the  $\beta$ -form has BCC structure with  $a = 2.92 \text{ \AA}$ . Calculate the ratio of their densities. 3
- c) The dipole moment of *p*-dichlorobenzene is zero, but that of *p*-dihydroxybenzene is non-zero. Explain. 2
- d) What is orientation polarization? How does it vary with temperature? 2
- e) What is zeta potential? How is it important for the stability of colloids? 4
- f) The mass-average molar mass is equal to the number-average molar mass of a monodisperse polymer. Explain. What is meant by polydispersity index of a polymer sample? 3
4. a) State the different factors on which X-ray scattering power of a crystal depends. Deduce the Bragg's equation for constructive interference in X-ray crystallography. 3
- b) Determine the Miller indices of the planes that intersect the crystal axes at (i)  $a, 2b, 3c$  and (ii)  $a, b, -c$ . 2
- c) Discuss the viscosity method for the determination of molar masses of macromolecules. 4
- d) What do you mean by CMC of a surfactant? Will there be any change in the value of CMC if hydrophobicity of the surfactant increases? 3
- e) Why does the molar polarization of a polar molecule decrease at high frequencies? 2
- f) The dielectric constant of a liquid at  $25^\circ\text{C}$  is 4.288. The molar mass of the liquid is  $112 \text{ gmol}^{-1}$  and its density at  $25^\circ\text{C}$  is  $1.108 \text{ gmol}^{-1}$ . Calculate the value of its molar polarization. 2

## UNIT - III

5. a) What are the different radiative and non-radiative paths by which the excited state of a molecule can decay? Explain with the help of Jablonsky diagram. 4
- b) Discuss with an example what is meant by photostationary state. 2
- c) What influences can be drawn if the quantum efficiency of a photochemical reaction is different from unity? 2
- d) State the effect of anharmonicity on the vibrational spectra of a heteronuclear diatomic molecule. 3
- e) The fundamental and the first overtone transitions of  $^{14}\text{N}^{16}\text{O}$  are centered at  $1876.06 \text{ cm}^{-1}$  and  $3724.20 \text{ cm}^{-1}$  respectively. Calculate the exact zero-point energy. 3

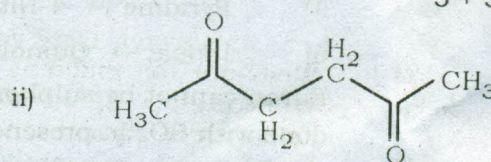
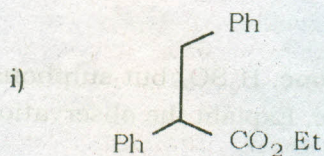
- f) The vibrational spectra of HCl shows the following :
- a very intense absorption at  $2886\text{ cm}^{-1}$
  - a weaker absorption at  $5668\text{ cm}^{-1}$  and
  - a very weak absorption at  $8347\text{ cm}^{-1}$ .
- Explain the observations. 4
6. a) State the difference observed in the rotational absorption spectra of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  with explanation. 3
- b) How would you determine the atomic mass of  $\text{C}^{13}$  accurately using rotational absorption spectroscopy? 3
- c) The symmetric stretching of  $\text{CO}_2$  is IR inactive but Raman active. Explain. 3
- d) Define 'quantum yield' of a photochemical reaction. How would you determine it experimentally? 4
- e) State and explain Franck-Condon principle. 3
- f) The molar absorption coefficient of a solute at  $440\text{ nm}$  is  $323\text{ L mol}^{-1}\text{cm}^{-1}$ . When light of that wavelength passes through a  $7.50\text{ mm}$  cell containing a solution of the solute,  $52.3\%$  of the light was absorbed. What is the concentration of the solution? 2

**Group - B**

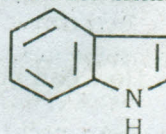
[ Full Marks : 50 ]

Answer any *three* taking *one* question from each Unit.**UNIT - I**

7. a) Give retrosynthetic analysis and an efficient synthesis of the following compounds : 3 + 3

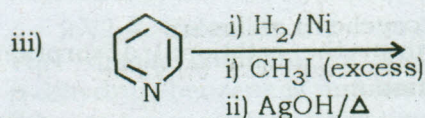
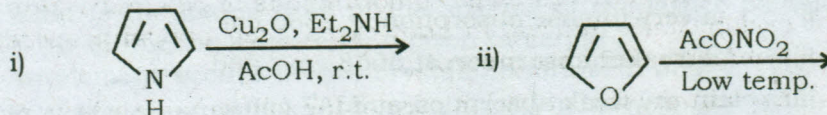


- b) Explain the following ( any one ) : 2
- Furan is an enol ether
  - Pyrrole undergoes electrophilic substitution faster than Furan.

- c) Using Fisher indole synthesis, how would you get  ? 2



d) Predict the products of the following reactions ( any two ) : 2 + 2



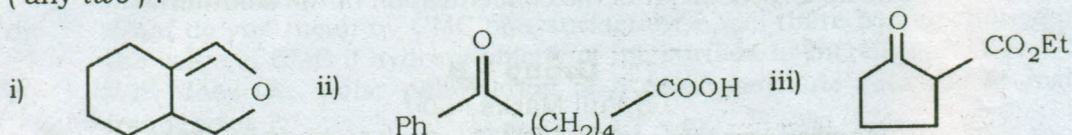
e) Outline the synthesis of metronidazole or chloroquine. State one common pharmaceutical use of it. 3 + 1

8. a) Give example of any two of the following : 2 × 2

- i) Two-group disconnection
- ii) Illogical disconnection
- iii) Disconnection of 1, 5-dicarbonyl compound.

OR

Design synthesis of the following compounds by disconnections and FGIs ( any two ) :



b) How can you synthesise pyrrole and furan by taking ethyl acetoacetate as the starting material ? Write mechanistic details. 4

c) Carry out the following conversions with mechanism in each case : 2 × 2

- i) Pyridine → 4-Nitropyridine
- ii) Indole → Quinoline.

d) Furan cannot be sulphonated with conc.  $H_2SO_4$  but sulphonation can be done with  $SO_3$  in presence of pyridine. Explain the observation. 2

OR

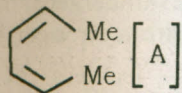
Pyrrole can act as both acid and base. Justify.

e) Outline the synthesis of paracetamol and mention its medicinal use. 2 + 1

f) How can you prepare congo red ? 1

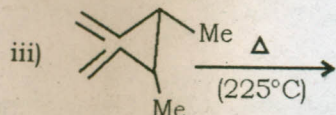
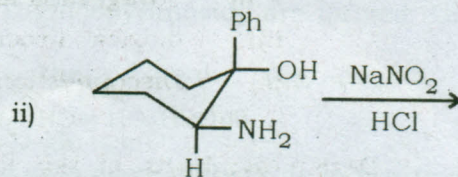
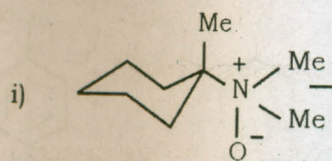
## UNIT - II

9. a) Draw the preferred chair conformations of *cis*- and *trans*-1, 3-dimethylcyclohexane. Indicate in both cases, their optical properties considering symmetry elements present. 4
- b) Explain the fate of [A] in case of the following pericyclic reactions :
- Photochemical electrocyclic ring closure
  - Thermal cycloaddition reaction with ethylene.



2 + 2

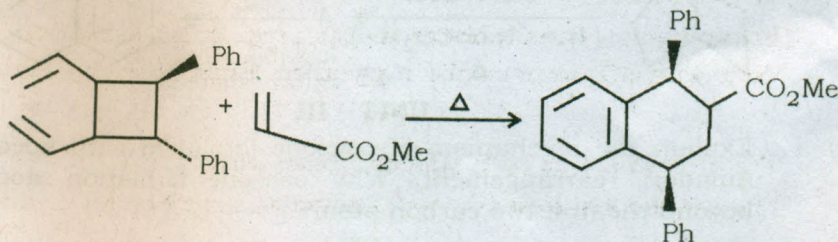
- c) Predict the products of the following with plausible mechanism in each case ( any two ) : 2 x 2



- d) i) Account for the preference for endo-addition in Diels-Alder cyclisation from symmetry considerations. 2
- ii) What are the symmetry allowed pathways for thermal [ 1, 3 ] sigmatropic rearrangement ? 2

OR

Rationalise the following reaction by FMO showing steps : 4



10. a) Solvolysis rate of the *cis*-isomer of 4-tert-butylcyclohexyltosylate is greater than that of the *trans*-isomer. Explain. 3

- b) Write the product of the thermal sigmatropic reaction of :

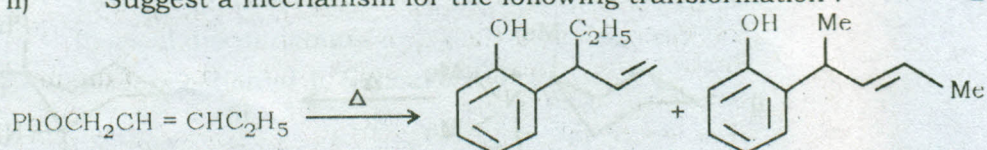


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- c) Explain the following observations :

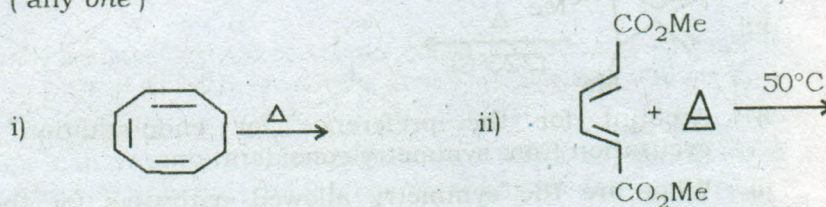
2 + 2

- i) For *trans*-2-bromocyclohexanol both the diequatorial and the diaxial conformers are almost equally populated.
- ii) *Trans*-4-tert-butyl tosylate undergoes bimolecular elimination with bromide rather than with a stronger base ethoxide ion.
- d) i) Between *cis*- and *trans*- isomers of 4-hydroxycyclohexane carboxylic acid, the former readily forms lactone while the other does not. Explain.
- ii) Suggest a mechanism for the following transformation :



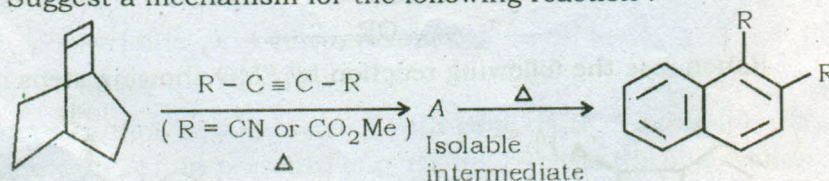
- e) Predict the products of the following reactions from FMO considerations : ( any one )

2



- f) Suggest a mechanism for the following reaction :

2



### UNIT - III

11. a) Explain the mechanism of osazone formation with special reference to Amadori rearrangement. Why osazone formation does not proceed beyond the first two carbon atoms ?

4

OR

How would you convert an aldose into its epimer ?

- b) Write down the conformations of  $\alpha$ - and  $\beta$ -D(+) glucopyranose. Which anomer predominates in an aqueous solution of D(+) glucose and why ?

3

- c) Mention the principle followed in the estimation of glycine. 1
- d) Give a brief account of the classification of enzymes. What are coenzymes? Give example. 4
- e) Draw the conformational structure of the aldohexose epimeric with glucose at C-3. 1
- f) Synthesise any *one* of the following amino acids as indicated : 3
- i) Aspartic acid (from diethylmalonate)
- ii) Tryptophan (by azlactone synthesis).
12. a) Define mutarotation. Give mechanism and show that amphoteric solvent is necessary for mutarotation. 3

OR

- Synthesise the dipeptide L-alanyl-L-phenylalanine using suitable protecting group.
- b) When D-glucose is treated with methanol in presence of acid under reflux, both the anomers of methyl D-glucopyranoside are formed. Give the mechanism of their formation. 4
- c) Show the reaction steps of the Edman degradation of  $\text{NH}_2\text{-CHR-CO-NH-pep}$ . 3
- d) How would you convert D-fructose to D-glucose? 3
- e) What happens when alanine is heated with acetic anhydride in pyridine? Give the mechanism involved. 3

OR

Identify compounds (A-D) in the following sequence of transformation. Suggest a mechanism for the conversion of (B) to (C).

