

CEMA(HN)-05

West Bengal State University
B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2015

PART-III

CHEMISTRY- Honours

Paper- V

(New and 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 (1) from each Unit.

UNIT - I

1. a) Define labile and inert complexes with examples. 2
- b) Of the two isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, one, (A) reacts with thio-urea (tu) to produce $[\text{Pt}(\text{tu})_4]^{2+}$, whereas the other isomer, (B) produces $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$ when treated with the same reagent. Which isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is cis- and which one is trans- ? Justify your answer. 1 + 1 + 2
- c) Show the splitting of the d^8 system in square planar and tetrahedral field. 4
- d) " Fe_3O_4 has an inverse spinel structure while Mn_3O_4 has a normal spinel structure." — Explain the observation from CFT. 3

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2. a) The KMnO_4 solution is deep purple in colour where the central metal is a d^0 system. — Explain. 2
- b) The position of I^- is lower than Cl^- in the spectrochemical series. Justify. 2
- c) Explain —
 whereas $\text{K}_3[\text{CoF}_6]$ is paramagnetic.
- d) Using an Orgel diagram explain the electronic spectrum of Cu^{2+} (aq.) ion. 3
- e) Aqueous cobalt (II) nitrate becomes deep green on addition of conc. HCl. — Explain. 2
- f) State the selection rules for electronic transitions in the spectra of metal complexes. 2

UNIT - II

3. a) Give the method of preparation of the following compounds with reactions and mention their uses :
- (i) H_2PtCl_6
- (ii) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ $2\frac{1}{2} + 2\frac{1}{2}$
- b) Why are the ionisation energies of 5d elements greater than those of 3d and 4d elements? 2
- c) Actinides have a greater tendency to form complexes than the lanthanides. Explain. 3

- d) The most stable oxidation state of Cu is +2. Compare the stability of +2 oxidation state of Au with that of Cu. 2
4. a) How would you prepare KMnO_4 from pyrolusite? Give one equation to establish the oxidising action of KMnO_4 in alkaline medium. 3 + 1
- b) Oxo-cations are common with the actinides, but not with the lanthanides. — Why? 2
- c) Explain why the structures of $[\text{MCl}_4]^{2-}$ ions change from Ni to Pt in their group. 3
- d) Why is the magnetic moment of copper acetate lower than the theoretical value? 2
- e) Why does yttrium resemble lanthanides? 1

CEMAT - 35-IB

Answer any two (2) questions taking one (1) from each Unit.

UNIT-I

5. a) Explain with example the different modes of bonding of CO molecule. Test the feasibility of the reactions on the basis of 18 electron rule :
- $$\text{Fe}(\text{CO})_5 + 2\text{NO} \longrightarrow \text{Fe}(\text{CO})_2(\text{NO})_2 + \text{CO}$$
- $$\text{Co}_2(\text{CO})_8 + 2\text{NO} \longrightarrow 2\text{Co}(\text{CO})_3(\text{NO}) + 2\text{CO} \quad 2 + 2 + 2$$
- b) Define oxidative addition reaction. What type of compounds generally undergo this type of reaction? 3
- c) Explain with example 'Aromatic character of ferrocene is more than that of benzene'. 2
- d) Metal—metal bonds in carbonyls are often shorter than metal atom diameters in pure metal. — Comment. 2

6. a) Cite example of a compound in which the cyclopentadienyl ring is bonded in the following mode : $\eta^1-C_5H_5$ and $\eta^5-C_5H_5$. Draw the structure. 2
- b) What is hydroformylation reaction ? Discuss the role of Co-organometallics as catalyst in the above reaction. 3
- c) Two different stretching vibrations of CO bonds are observed in $Fe_2(CO)_9$. Explain. 3
- d) Give an example of polymerisation of alkene mentioning the catalyst used. 2
- e) What do you mean by —
- (i) Insertion reactions
- (ii) Wilkinson's catalyst ? $2 \times 1 \frac{1}{2}$

UNIT-II

7. a) Briefly discuss the principle of gravimetric estimation of phosphate and explain the gravimetric factor. 3 + 1
- b) Give the principle of complexometric estimation of Mg ions present in a solution. 2
- c) Write the principle for estimation of copper in brass. Give the reactions. 2 + 1
- d) What are masking and demasking reactions ? Give examples. 3
8. a) State the principle of complexometric estimation of Fe and Al in a mixture. 3
- b) State the requirements and different steps of a gravimetric estimation procedure. 3
- c) How would you standardise an aqueous solution of iodine ? 2
- d) Give the principle of argentimetric estimation of chloride. What type of indicator is used in this method ? 2 + 1
- e) Mention the main constituents of portland cement. 1

CEMAT-35-AA

Answer any *two* (2) questions, taking *one* (1) from each Unit.

UNIT - I

1. a) Briefly discuss the roles of iron and copper in the biological system. $2\frac{1}{2} + 2\frac{1}{2}$
- b) Name one zinc containing enzyme and explain its biological function. 4
- c) Name two toxic metals and discuss their effects in the human body. 4
2. a) Discuss the structural features of $4\text{Fe} - 4\text{S}$ and $8\text{Fe} - 8\text{S}$ ferredoxins. 4
- b) Write the light phase and dark phase reactions related to photosynthesis. 3
- c) What are the essential and beneficial elements? What are essential trace elements? 3
- d) Write a short note on biological nitrogen fixation. -

Unit - II

3. a) What are nano-materials? How do the optical properties of metallic nano-particles arise? 2 + 2
- b) How can you synthesize gold-nanoparticles? Give suitable reactions with examples. 3
- c) What are natural polymers? Give two examples with their structure. 3
- d) What are monopolymer and copolymer? Give an example of each. 1 + 1
4. a) How do you differentiate between step growth polymerization and chain polymerization? Identify the salient features with suitable examples. 4

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- b) For a polymer solution at sufficient dilution $\frac{\eta_{sp}}{C} = 3.3 \times 10^{-5} M^{0.85}$ where M is the molecular weight of the polymer and η_{sp} is the specific viscosity of the polymer solution having concentration equal to C gm/100 cm³. What is the molecular weight of the polymer whose solution has a specific viscosity of 0.11 and concentration equal to 0.22 gm/100 cm³ ? 3
- c) Explain the structure of any chain silicate with example. 2
- d) Using 18-electron rule establish the possible structures of the following compounds : 3
- $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$, $HFe_3(CO)_{12}$

CEMAT-35-AB

Answer *two* (2) questions taking *one* (1) from each Unit.

Unit - I

5. a) How many amino acids are involved in the ten complete turns of α -helix ? 1
- b) What kind of bonding is largely responsible for the secondary structure of a protein ? 2
- c) Describe the three types of secondary structures of proteins. 3
- d) What are nucleotides ? Write the structures of nucleotides present in DNA. 1 + 4
- e) What is denaturation of protein ? 2

6. a) Describe important features of Houg-Steen model of double helical structure of DNA (for adenine only). 4
- b) What is a nucleoside ? Mention the difference(s) between the nucleosides of DNA and RNA. Show by writing structures. 1 + 3
- c) What is quaternary structure of protein ? Explain with an example. 2
- d) What kind of bonding is largely responsible for the tertiary structure of a protein ? 2
- e) How a denatured protein is re-natured ? 1

UNIT-II

7. a) Why are lyophilic sols more stable than lyophobic sols ? 2
- b) Why colloidal solutions do not settle down ? 3
- c) Find the condition for which the reaction rate of an enzymolysis that follows Michaelis-Menten kinetics is half its maximum value. 2
- d) Give elementary idea of PAGE and SDS-PAGE. What are their applications in biochemistry ? Define isoelectric focusing. 3 + 1 + 1
8. a) What is the significance of catalytic efficiency ? What is the criteria of a good enzyme ? 2 + 2
- b) Define isoelectric point. Name the technique which can be used to determine pI of a protein. 1 + 2
- c) Electrophoresis is a consequence of electrical double layer — comment. 3
- d) Explain how enzyme activity changes with change in pH. 2

(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.

Use separate answer scripts for Group A and Group B.

Group-A

(Full Marks : 50)

Answer any *three* questions, taking *one* from each Unit.

UNIT - I

1. a) What do you mean by thermodynamic probability in Statistical Mechanics ? Consider a system of six distinguishable particles. One of the macrostates has the following distribution of particles :

Energy	0 ϵ	1 ϵ	2 ϵ	3 ϵ	4 ϵ
No. of Particles	0	0	2	2	2

Calculate its thermodynamic probability.

4

- b) Derive the Boltzmann distribution law giving emphasis on the condition involved for a given system of N distinguishable particles where the energy levels $\epsilon_1, \epsilon_2, \dots, \epsilon_n$ are non-degenerate. [Assume : $\beta = \frac{1}{k_B T}$]

5

- c) Deduce barometric distribution formula using Boltzmann Distribution Law.

4

- d) The number of molecules in three consecutive energy levels are 1000, 100 and 10 respectively. Show that the distribution is according to Boltzmann statistics.

3

(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.

Use separate answer scripts for Group A and Group B.

Group-A

(Full Marks : 50)

Answer any three questions, taking one from each Unit.

UNIT - I

1. a) What do you mean by thermodynamic probability in Statistical Mechanics ? Consider a system of six distinguishable particles. One of the macrostates has the following distribution of particles :

Energy	0ε	1ε	2ε	3ε	4ε
No. of Particles	0	0	2	2	2

Calculate its thermodynamic probability.

4

- b) Derive the Boltzmann distribution law giving emphasis on the condition involved for a given system of N distinguishable particles where the energy levels $\epsilon_1, \epsilon_2, \dots, \epsilon_n$ are non-degenerate. [Assume : $\beta = \frac{1}{k_B T}$]

5

- c) Deduce barometric distribution formula using Boltzmann Distribution Law.

4

- d) The number of molecules in three consecutive energy levels are 1000, 100 and 10 respectively. Show that the distribution is according to Boltzmann statistics.

3

2. a) Derive Duhem-Margules equation stating clearly the assumptions. Show that if Raoult's law is applicable to one of the constituents of a binary liquid mixture, at all compositions, it must be equally applicable to the other constituent. 4
- b) Boiling point of acetone is 56.5°C and its latent heat of vaporization is $6920 \text{ cal mole}^{-1}$. Calculate the molal boiling point elevation constant of acetone. 3
- c) The normal boiling point of a binary solution of A and B with mole fraction of A, $x_A = 0.6589$ is 88°C . At this temperature, the vapour pressures of pure liquids A and B are 957 and 379.5 torr respectively. Is the binary solution ideal? Give reasons in favour of your answer. 4
- d) In an open container, on heating, sulphur melts, but iodide sublimes. Explain why. 2
- e) What is an azeotropic mixture? How would you ascertain that an azeotrope is a mixture and not a compound? 3

UNIT-II

3. a) What do you mean by Weiss indices and Miller indices for the crystallographic planes. Find out the Weiss indices and Miller indices for the plane having intercepts $2a$, b , $-2c$ on the respective crystallographic axes, where a , b and c are the primary intercepts on the axes. 4
- b) Potassium crystallises with a body-centered cubic lattice and has a density 0.856 gm.cm^{-3} . Calculate the length of the unit cell and distance between (110) planes. 4
- c) Using X-ray of wavelength, $\lambda = 1.79 \text{ \AA}$, a metal produces reflection at $2\theta = 47.2^{\circ}$. If this be the first order reflection from the (110) plane of b.c.c. unit cells, what is edge length of the cube? 3
- d) Estimate the void space in the face centered cubic lattice. 3
- e) State the assumptions of Einstein's theory of specific heat of solids. 2
- Molar polarisation values of O_2 and CH_4 are independent of temperature while those of HCl gas and CH_3Cl gas decrease with increase of temperature. Explain with proper reasons. 4

- b) Using Gibbs adsorption isotherm, explain the variation of surface tension with concentration of the aqueous solution of (i) NaCl, and (ii) Sodium dodecyl sulphate. 2 + 2
- c) Mention two ways how a pure solution differs from a colloid solution. 2
- d) What do you mean by weight average molecular wt. and number average molecular wt. of polymer. Suppose a protein exists under a particular condition as an equimolar mixture of a monomer form and a tetramer form. How would the average molar mass compare with that of the monomer, M if the average molar mass was obtained from (i) osmotic pressure measurement, and (ii) light scattering measurement? 3 + 3

UNIT-III

5. a) What are the essential conditions to get pure rotational spectra? Show that the rotational spectral lines of a rigid diatomic molecule are equispaced. 1 + 3
- b) The first line ($J = 0$) in the rotation spectrum of CO is 3.84235 cm^{-1} . Find out the value of I_{CO} (moment of inertia of CO) and the band distance $r_{\text{C-O}}$. 3
- c) Show diagrammatically the effect of isotopic substitution on the energy levels of rotational spectra of $\text{C}^{12}\text{O}^{16}$ when C^{12} is replaced by C^{13} . 3
- d) What do you understand by quantum yield? Give examples of reactions where it is equal to one, greater than one and less than one. 4
- e) State Stark-Einstein law of photochemical equivalence. 2
- f) Phosphorescence of aromatic hydrocarbons is usually observed at low temperature in rigid matrix. Explain. 2
3. a) Existence of Zero-point energy in a vibrating molecule is in agreement with the Heisenberg uncertainty principle. Comment. 2
- b) What are the essential conditions for a molecule to be Raman active? Explain what are Stokes and anti-Stokes lines in Raman scattering. 4
- c) Which factors influence the increase of population in the excited vibrational levels? What is the difference between overtones and hot bands in the IR spectra? 3

- d) A hetero-nuclear diatomic molecule of reduced mass 1.63×10^{-24} gm absorbs at 2880 cm^{-1} . Calculate the force constant assuming harmonic oscillator model. 3
- e) State the 'law of mutual exclusion'. Comment on the applicability of the law to the vibrations of CO_2 and H_2O molecules. 4
- f) What is the physical basis of separation of electronic and nuclear motion in molecules? 2

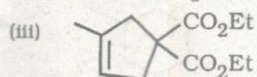
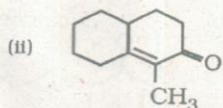
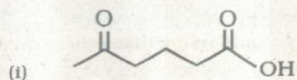
Group-B

[Full Marks : 50]

Answer any *three* questions, taking *one* from each Unit.

UNIT - I

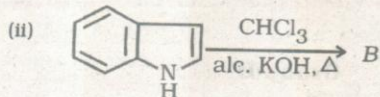
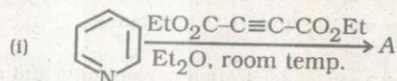
1. a) Describe the synthesis of the following compounds with proper retrosynthetic analysis (any *two*) : $2 \times 3 = 6$



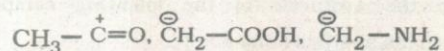
- b) Explain the following : $2 \times 2 = 4$

- (i) Furan and pyrrole have opposite directions of their dipoles.
- (ii) Indole undergoes electrophilic substitution at C-3 but pyrrole does so at C-2.

- c) Outline the synthesis of salbutamol and mention its medicinal use. 2 + 1
- d) How would you prepare malachite green or alizarin? 2
- e) Identify the products A and B : $2 \times 1 \frac{1}{2}$

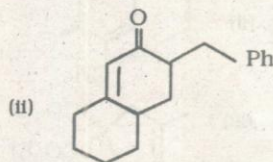
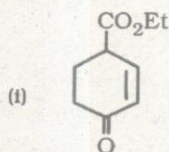


2. a) (i) Define illogical nucleophile with an example. 2
- (ii) Provide suitable synthetic equivalents for the following synthons (any two) : 2



- b) Synthesise the following compounds using disconnection approach :

2 × 3 = 6

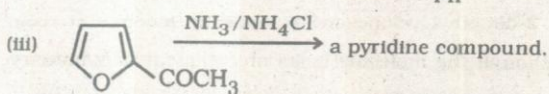
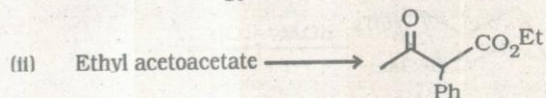
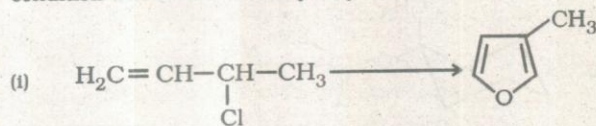


- c) Explain the mechanism of Favorskii rearrangement with a suitable reaction. 2

OR

- Give the mechanism for the nitration of furan with a mixture of Ac_2O and fuming nitric acid at -10°C . 2

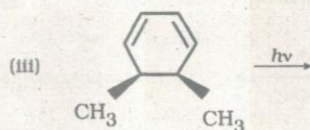
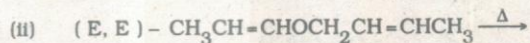
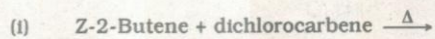
- d) Explain the following conversions indicating reagent(s) and reaction condition whenever necessary (any two) : 2 × 2 = 4



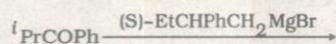
- e) Write the structure of chlorpromazine and mention one of its uses. 1 + 1

UNIT-II

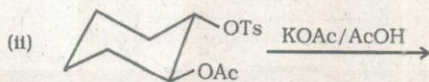
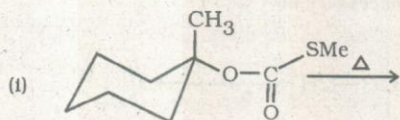
3. a) Between *trans*-1,2-dichlorocyclohexane and *cis*-1,3-dichlorocyclohexane, which would possess larger amount of (a, a) form in conformational equilibrium? Give reason. 2
- b) Predict the product(s) of the following reactions from FMO considerations (any two) : 2 × 3 = 6



- c) Predict with reason, the major product of following reaction. 2



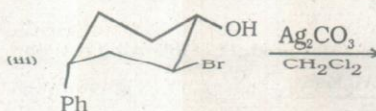
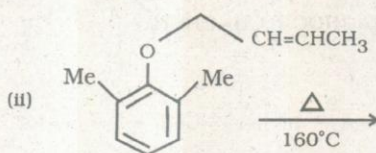
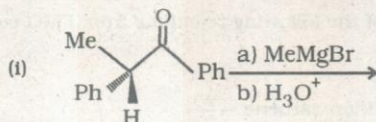
- d) Complete the following reactions with proper explanations : $2 \times 2 = 4$



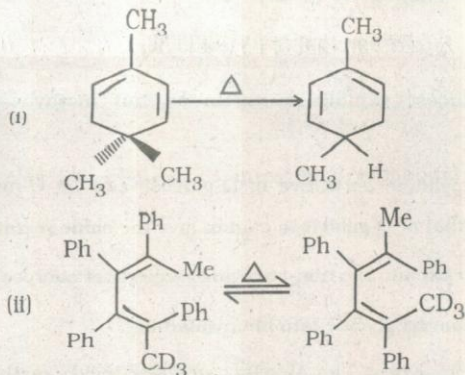
- (e) *cis*-1, 2-dimethylcyclohexane is optically inactive at room temperature even though the molecule lacks any element of symmetry. Explain this fact. 2

4. a) Draw the preferred conformation of 1-methyl-1-phenyl cyclohexane and justify your answer. 2

- b) Identify the product(s) and give mechanism for the following reactions (any two) : $2 \times 2 = 4$



- c) Explain the following facts (any three) : 3 × 2 = 6
- (i) Thermal dimerisation of ethylene is a symmetry forbidden process.
 - (ii) In cycloaddition reaction of cyclopentadiene with maleic anhydride, the less stable endo adduct predominates.
 - (iii) *trans*-4-*t*-butylcyclohexane carboxylic acid is a stronger acid than its *cis* isomer.
 - (iv) *cis*-4-*t*-butylcyclohexanol undergoes faster oxidation with chromic acid than its *cis* isomer.
- d) Suggest mechanism for the following transformations and depict the absolute stereochemistry of the chiral centres if any : 2 + 2 = 4



UNIT-III

5. a) Carry out the following transformations : 2 × 2 = 4
- (i) D-Arabinose → D-Mannose
 - (ii) D-Glucose → 3, 4, 6-tri-O-methyl-D-glucose.
- b) Oxidation of D-fructose with Tollen's reagent yields a mixture of ~~ammonium acid and D-glucosic acid~~. Account for this observation. 3
- c) How an (L)- α -amino acid can be detected by using ninhydrin ? Write with mechanism of the reaction. 4

- d) Write the names and structures of any one purine and any one pyrimidine base present in nucleic acids. 2
- e) Illustrate the application of 2, 4-dinitrofluorobenzene in the determination of N-terminal amino acid residue of a protein. How would you justify its choice over the much less expensive 2, 4-dinitrochlorobenzene? 2 + 1
- a) How would you distinguish chemically between ribose and 2-deoxyribose? 2
- b) Explain the following facts (any two): $2 \times 2 = 4$
- (i) The rate of oxidation of β -D-glucopyranoside by $\text{Br}_2 - \text{H}_2\text{O}$ is 250 times faster than that of its α -anomer.
- (ii) α -D-(+)-glucose exhibits mutarotation but methyl- α -D-glucoside does not.
- (iii) Di-isopropylidene derivative of D-glucose can be O-methylated at C-3, but that of D-galactose cannot give the same result.
- c) How would you explain the non-reducing property of sucrose? 2
- d) How can you convert glycine into phenylalanine? 2
- e) Synthesise the tripeptide Phe-Ala-Gly using Merrifield's method. 3
- f) Describe briefly the salient feature of the double helix structure of DNA. 3