



WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2022-23



CEMACORIIT-CHEMISTRY (CC11)

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

UNIT-I

Answer any two questions from the following

12×2 = 24

- ✓ (a) Find CFSE for d^6 systems in terms of Dq and pairing energy for high spin complexes. 2
- (b) CrF_6^{3-} shows absorption bands at 14900, 22700 and 34400 cm^{-1} respectively. Assign the bands. Find $10Dq$ value. 2+2
- (c) Give reasonable explanations to the following facts. 2
- (i) FeF_6^{3-} ion is colorless, whereas, $[Fe(CN)_6]^{3-}$ ion is colored. 2
- (ii) Room temperature magnetic moment of Copper(II) sulfate pentahydrate is almost equal to the spin only moment of Cu(II) whereas that of Cu(II) acetate monohydrate is usually lower. 2
- (d) What is Nephelauxetic effect? 2
2. (a) 'Octahedral Cu(II) complexes are distorted' — Explain in the light of CFT using approximate energy diagram. 3
- (b) OH^- ion is in lower position than H_2O in spectrochemical series. Explain. 3
- (c) Explain with examples, how super-exchange and anti-ferromagnetic interactions influence the magnetic behaviour of co-ordination complexes. 3
- (d) Between cis- and trans- $[Co(en)_2 Cl_2]^+$. Which one will give more intense d-d transition? Why? 3
3. (a) Diamagnetic complexes of cobalt(III) such as $[Co(NH_3)_6]^{3+}$ and $[Co(NO_2)_6]^{3-}$ are yellow orange. In contrast paramagnetic complexes $[CoF_6]^{3-}$ and $[Co(OH_2)_3F_3]$ are blue. Explain qualitatively the difference in color. 3
- (b) Which of the following complexes would you expect to suffer from a Jahn-Teller distortion: $[CrI_6]^{4-}$, $[Cr(CN)_6]^{4-}$, $[CoF_6]^{3-}$ and $[Mn(ox)_3]^{3-}$? Give reasons for your answers. 2
- (c) Which of the following pairs of complexes has higher Dq value and why? 3
- (i) $[Co(NH_3)_6]^{3+}$ and $[Rh(NH_3)_6]^{3+}$
- (ii) $[Fe(C_2O_4)_3]^{4-}$ and $[Fe(C_2O_4)_3]^{3-}$
- (iii) $[Cr(en)_3]^{3+}$ and $[Cr(C_2O_4)_3]^{3-}$



- (d) How does pi bonding in metal ligand complexes influence the stability of oxidation states of transition metals? Give two examples with explanations. 2+2
4. (a) Pick up the ions which will undergo tetragonal distortion in octahedral field. Give reason of your choice. 3
 Fe^{+3} (High Spin), Co^{+2} (Low Spin) and Ni^{+2}
- (b) Chromium(II) acetate mono-hydrate is diamagnetic at room temperature. Explain. 3
- (c) Using an approximate Orgel diagram, explain the electronic spectrum of $Ni^{2+}(aq)$ ion. 3
- (d) The observed magnetic moment for $K_3[TiF_6]$ is $1.70\mu_B$. Calculate μ (spin-only) for this complex. Why is there a difference between calculated and observed values? 1+2

UNIT-II

Answer any *one* question from the following

16×1 = 16

5. (a) What is Lanthanide contraction? How does it influence the chemical behaviour of lanthanides? 3
- (b) Discuss the trend of variation of two important chemical properties in passing from 3d through 4d to 5d transition elements. 3
- (c) Actinides have a greater tendency to form complexes than lanthanides — Explain. 3
- (d) Why are the ionisation energies of 5d elements greater than those of 3d and 4d elements? 3
- (e) Although lanthanides usually exhibit +3 oxidation states, Eu^{2+} and Ce^{4+} have special stability. Give reason. 2
- (f) Bands from f-f transitions are sharp but those from d-d transitions are broad. Explain why. 2
6. (a) What are the basis of lanthanide separation? Give a brief outline of the separation of the lanthanide elements by the ion-exchange method. 1+3
- (b) Make critical comments on common and stable oxidation states of Cu, Ag and Au. 3
- (c) Oxo-cations are common with the actinides, but not with the lanthanides. Why? 3
- (d) ' La^{3+} and Lu^{3+} are diamagnetic while Sm^{3+} shows low magnetic moment' — Comment. 3
- (e) (+3) oxidation state is common for lanthanides in general while actinides can show variable oxidation states — Explain. 3

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CEMACOR12T-CHEMISTRY (CC12)

Time Allotted: 2 Hours

Full Marks: 40

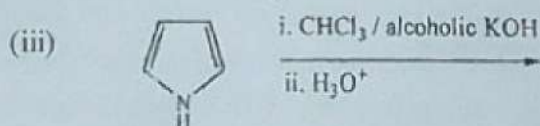
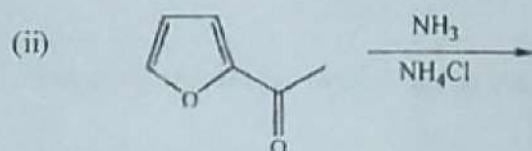
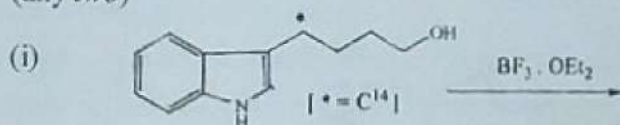
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Answer any five questions taking one from each unit

UNIT-I

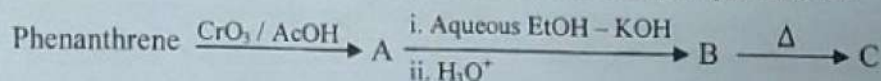
1. (a) Indole cannot be synthesised from acetaldehyde and phenyl hydrazine by Fischer's method — Why? How would you modify the starting materials to synthesise N-methylindole? 1½+1½

- (b) Predict the product(s) in the following reactions with plausible mechanism. (any two) 2×2 = 4

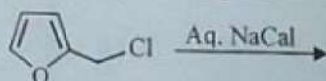


- (c) 2-Methyl-1-naphthol easily couples with benzene diazonium chloride in alkaline medium but 1-methyl-2-naphthol fails to couple with benzene diazonium chloride under identical conditions. Explain. 3

2. (a) Complete the following reaction sequence with necessary explanations: 3



- (b) Write down the product of the following reaction with plausible mechanism. 2



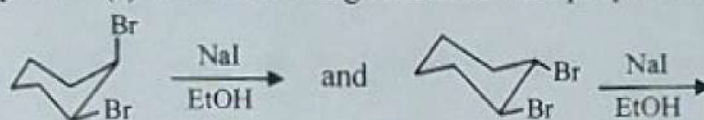
- (c) How can you convert naphthalene into 9-methyl anthracene? 3

- (d) How can you convert pyridine into 4-nitropyridine? 2



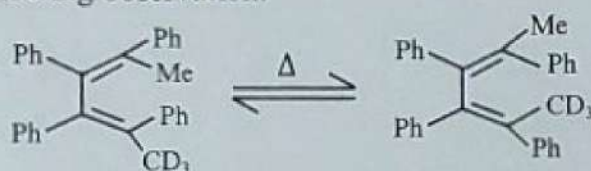
UNIT-II

3. (a) Count the number of destabilising interactions in (1R,2S)-1,2-dimethylcyclohexane. Is the molecule chiral? Will it show any optical rotation at room temperature? Explain your answer. 3
- (b) Draw energy profile diagram for ring inversion of cyclohexane through the energetically most favourable pathway. Identify the chiral conformations involved in this process. 3
4. (a) Cite an example of a substituted cyclohexane system where the conformation with the axial substituent is more stable than the equatorial one. Explain the reason behind it. 2
- (b) Identify the product(s) in the following reactions with proper mechanism: 2+2

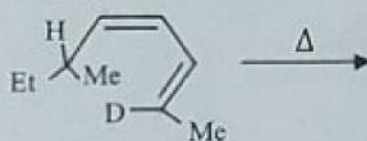


UNIT-III

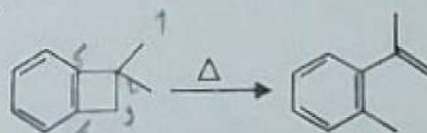
5. (a) Compare the rates of Diels-Alder reaction of isoprene and 2-t-butyl-1,3-butadiene separately with tetracyanoethylene. 2
- (b) Explain the following observation: 2



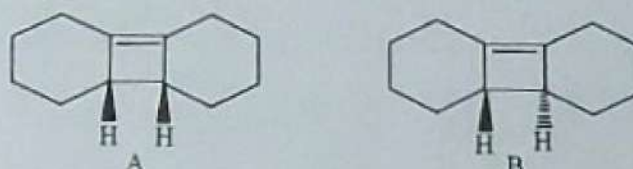
- (c) Predict the product(s) with stereochemistry of the following reaction. Designate the pericyclic step involved. 2



6. (a) Suggest a mechanism for the following reaction clearly indicating the pericyclic process involved therein. 2



- (b) Which of the following compounds will undergo thermal electrocyclic ring opening at a faster rate? — Explain. 2



- (c) Thermal [1,5] hydrogen shift is facile, but [1,3] hydrogen shift is not observed. Explain. 2



UNIT-IV

7. (a) How would you distinguish chemically between D-glucose and D-fructose? 3
- (b) An aldopentose 'A' can be oxidised to an optically active aldaric acid 'B'. Degradation of 'A' gives 'C'. Oxidation of 'C' produces an optically inactive aldaric acid 'D'. 'A' belongs to 'D'-family. Give the structures of '(A-D)' with reasons. 3
- (c) What is anomeric effect? How does it vary with solvent polarity? 3
8. (a) Between $\text{Br}_2\text{-H}_2\text{O}$ and Tollens' oxidation which one do you think to be superior for conversion of D-glucose to D-gluconic acid? Justify your choice. 2
- (b) How can you prove that all methylpyranosides of the α -D-hexose series have identical configurations at C-1 and C-5? 2
- (c) Sucrose does not show any change in specific rotation when dissolved in water. Explain. 2
- (d) Convert D-Glucose to $\text{CH}_2\text{OAc}-(\text{CHOAc})_4-\text{CHO}$. 2

UNIT-V

9. (a) Write down the structure of L-proline. How can you synthesise proline by Gabriel's phthalimide synthesis? 4
- (b) Between A-T and G-C which base pair is stronger and why? 2
- (c) Alkaline hydrolysis of RNA occurs faster than that of DNA. Explain. 2
- (d) How can you separate the components of the mixture of glycine, lysine and glutamic acid? (Isoelectric points of glycine, lysine and glutamic acids are 6.0, 9.5 and 3.1, respectively). 2
- 10.(a) How can you achieve the synthesis of gly-phe using Merrifield resin? 3
- (b) Acid hydrolysis of guanosine occurs faster than that of adenosine. Explain. 2
- (c) Activation of the $-\text{COOH}$ of an amino acid through its conversion into COCl may not be useful for peptide bond formation when the amino group is protected in the form of benzyl urethane. Offer an explanation. 3
- (d) What happens when the tripeptide ala-val-phe is heated with anhydrous hydrazine at 100°C ? 2

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2022-23

CEMADSE011-CHEMISTRY (DSE-I/2)
ADVANCED PHYSICAL CHEMISTRY

Time Allowed: 2 Hours

Full Marks: 40

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Answer any *three* questions taking *one* from each unit

UNIT-I

1. (a) (i) State Haüy's law of rational intercepts. 2
(ii) Determine the Miller indices of the planes that intersect the crystal axes at a , $2b$, ∞c and $\frac{1}{2}a$, $\frac{1}{3}b$, $-c$. 2
- (b) There exists long range order in crystals. Justify or criticize. 2
- (c) What is the highest order that can be observed in Bragg's reflection from a crystal of interplanar distance 2Å by X-ray having wavelength 100 pm ? 2
- (d) A metal has a body centred cubic lattice and length of a unit cell is 2.95Å . If the density of the metal is 9.95 gm/cc , calculate the atomic weight of the metal. 3
- (e) The molar volume of KCl is 1.3 times that of NaCl. If the glancing angle for the first order Bragg reflection from the 100 plane of NaCl is 5.9° , calculate the same for KCl. 3
2. (a) (i) Deduce Bragg's law $\lambda = 2d \sin \theta$. 3
(ii) On what factors does the intensity of the diffracted beam from different sets of planes depend? 2
- (b) The characteristic K_α lines of Cr, Fe and Ni have wavelengths of 2.2009 , 1.9373 and 1.6591Å respectively. (i) Can all be used to determine a lattice spacing of 1 Å ? 3
(ii) What will be the largest value of diffraction angle θ ?
- (c) The unit cell dimension ' a ' of NaCl lattice is 5.63 Å . If X-ray beam of wavelength 1.1 Å falls on a family of planes with a separation of $\left(\frac{a}{\sqrt{5}}\right)$; how many orders of diffraction are observable? 3
- (d) Show that the maximum proportion of available volume which may be filled by hard spheres in simple cube, body centred cube and face centred cube is in the ratio $26:34:37$. 3

UNIT-II



3. (a) Consider a system of n molecules distributed among non-degenerate energy levels represented by $\epsilon_0, \epsilon_1, \epsilon_2, \dots$ etc. Write down the expression for molecular partition function for the system. Show that internal energy (U) of the system can be expressed as

$$U = nkT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

where k is the Boltzmann constant, T and V being the temperature and volume of the system respectively.

- (b) What is meant by most probable macrostate? 1
- (c) In a six particle system four energy states are available and energy levels are nondegenerate. The gap between the successive levels is ϵ . Find out the most probable configurations of the states having energy 10ϵ and 6ϵ . 2+2
- (d) Calculate the relative number of microstates in water with respect to ice at 0°C . Given $\Delta H_{\text{fus}} = 1440 \text{ cal mol}^{-1}$. 3
- (e) Entropy is a function of thermodynamic probability. How can one conclude that the function is logarithmic? 2
4. (a) Define partition function. What is its physical significance? 2
- (b) A system consisting of 4 identical and distinguishable particle, each possessing three available states of 1, 2 and 3 units, has a total of 10 unit energy. Calculate the number of ways, W , in which these conditions are satisfied. 3
- (c) If N molecules are distributed among the possible nondegenerate energy levels $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ etc in an isolated system, show that the entropy of this system can be represented as $S = k\beta E + Nk \ln Q$ (here symbols have their usual meaning). Find the value of β in terms of T . 3
- (d) The relative population in two states with energies E_1 and E_2 satisfying Boltzmann distribution is given by $\frac{n_1}{n_2} = \frac{g_1}{g_2} e^{-(E_1 - E_2)/k_B T}$. What is the relative degeneracy g_2/g_1 ? 2
- (e) State Sterling's approximation and mention the condition of its validity. 1
- (f) Express Helmholtz free energy (A) in terms of partition function. 2

UNIT-III

5. (a) ΔG for a reaction as a function of temperature (T) for low value of T (T approaching zero Kelvin) is given by: 2+1+2
- $$\Delta G = a + bT + cT^2$$
- (i) Show that $b = 0$; (ii) Find ΔH as a function of temperature and (iii) show schematically the variation of ΔG and ΔH with T on the same plot.
- (b) What is residual entropy? Calculate the residual entropy of two moles of CO molecules from the Boltzmann equation. Which has a higher residual entropy water or methane? Explain. 1+2+1



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- (c) A solution contains equal number of particles with molar masses 10000 g mol^{-1} and $20000 \text{ gm mol}^{-1}$ respectively, Calculate \bar{M}_n and \bar{M}_m . 2
- (d) What is functionality? The functionality of glycerol is three. Comment. 1+1
- (a) (i) Evaluate the values of the constants 'x' and 'y' in the equation $C_p - C_v = TV\alpha^x\beta^y$ from dimensional considerations. Terms have their usual significances. 1
- (ii) From Debye's equation for heat capacity of solids calculate the atomic heat of copper at 0°C . 2
- (b) (i) Arrange the following molecules in order of increasing standard molar entropy: $\text{C}_2\text{H}_2(\text{g})$, $\text{C}_2\text{H}_4(\text{g})$ and $\text{C}_2\text{H}_6(\text{g})$. Explain your answer. 3
- (ii) Explain with $S-T$ diagram the process of cooling by adiabatic demagnetisation of paramagnetic substances. 3
- (c) (i) Deduce the relation between number average degree of polymerisation, ' $\langle x_n \rangle$ ' and extent of polymerisation, ' p '. Hence show that near the completion of polymerisation reaction a small increase in ' p ' leads to a large increase in ' $\langle x_n \rangle$ '. 2
- (ii) What are conducting polymers? Give examples and account for their conducting properties. 2



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CEMADSE02T-CHEMISTRY (DSE1/2)

Time Allotted: 2 Hours

Full Marks: 40

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Answer any three questions taking one from each GROUP

GROUP-A

(Units 1 and 2)

1. (a) Why use of premix chamber burner is preferable than total consumption burner in AAS? 2
- (b) A sample in a 1.0 cm cell in a spectrometer transmit 80% light at a certain wavelength. If the absorptivity of the substance at this wavelength is $2.0 \text{ g}^{-1}\text{cm}^{-1}\text{L}$, what is the concentration of the substance? 2
- (c) Discuss the principle of operation of a single-beam spectrophotometer and a double-beam spectrophotometer. 2
- (d) Name the radiation sources and detectors used in UV, visible and IR regions of the spectrum. 3
- (e) A high concentration of a potassium salt is sometimes added to standards and samples in flame absorption or emission methods — Discuss. 2
- (f) Why a high-temperature nitrous oxide-acetylene flame is sometimes required in AAS? 2
- (g) Calculate the uncertainty in the number of millimoles of chloride contained in 250.0 mL of a sample when three equal aliquots of 25.00 mL are titrated with silver nitrate with the following results: 36.78, 36.82, and 36.75 mL. The molarity of the AgNO_3 solution is $0.1167 \pm 0.0002\text{M}$. 3
2. (a) The zinc and tin contents of a brass sample are analyzed giving the following results (i) Zn 33.27, 33.37 and 33.34% (ii) Sn 0.022, 0.025 and 0.026%. Calculate the standard deviation and the coefficient of variation for each analysis. 3
- (b) Discuss the principle of spectrophotometric determination of manganese. What kind of flame would you use in the AAS method of determination of metal ions that form refractory oxides and why? 3+2
- (c) 'The UV absorption peaks are usually broader than IR absorption peaks' — Explain. 2
- (d) Atomic absorption is preferable to atomic emission spectrometry for identification of unknown elements. 2
- (e) What are the methods of removal of chemical interferences in AAS? 2
- (f) Good precision does not guarantee accuracy — Why? 2



GROUP-B

(Units 3 and 4)

3. (a) What is thermogram? Mention two sources of errors in TGA. 1+2
(b) How could you quantitatively analyze calcium carbonate and magnesium carbonate from their mixture using TGA? 3
(c) Draw to show the first and second derivative potentiometric titration curve for chloride by AgNO_3 and indicate the equivalence point in each of them. 2
(d) Mention one advantage and one disadvantage of glass electrode for pH measurement. 2
(e) Cite one example where conductometric titration is more advantageous over potentiometric titration. 2
4. (a) What is dilution effect in conductometric titration? How could you avoid it during conductometric titration? 2
(b) What are the basic requirements of a reference electrode in potentiometric measurements? 2
(c) Why should the glass electrodes be calibrated using standard buffer solutions before use? 2
(d) What is liquid-junction potential and residual liquid-junction potential? How can this be minimised? 3
(e) Discuss pH metric titration curve of a tribasic acid and NaOH. Identify the equivalence point and how pKa can be calculated. 3

GROUP-C

(Unit 5)

5. (a) For a solute with distribution ratio of 25.0, show by calculation which is more effective, extraction of 10 ml of an aqueous solution with 10 ml organic solvent or extraction with two separate 5.0 ml portion of solvent. 3
(b) Explain the difference between a cation exchange resin and an anion exchange resin. 2
(c) Why paper chromatography can be considered as a liquid-liquid partition chromatography? Name the spraying agent used for detection of amino acids in paper chromatography. 2+1
(d) Describe the basic principle of GC instrument. Identify the carrier gas used in GC. 4
6. (a) What is R_f ? On what factor does it depend? 2
(b) What are synergistic agents and what is their function in solvent extraction process? 2
(c) How cation and anion exchangers are regenerated? 2
(d) What do you mean by reversed phase chromatography? 2
(e) How could you separate Cu^{+2} and Zn^{+2} by ion exchange chromatography? 2
(f) Mention one application of HPLC technique. 2

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CEMACOR11T-CHEMISTRY (CC11)

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UNIT-I

Answer any two questions from the following

12×2 = 24

1. (a) Explain the nature of Jahn-Teller distortion expected for an octahedral complex of Cu(II) ion. 3
- (b) $[\text{NiCl}_4]^{2-}$ is paramagnetic, whereas $[\text{PtCl}_4]^{2-}$ is diamagnetic, although both Ni(II) and Pt(II) are d^8 ions. — Explain. 3
- (c) With the help of approximate Orgel diagram explain the electronic spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$. 3
- (d) Crystal field splitting of the d -orbital is more pronounced in the octahedral field than that in the tetrahedral field. — Explain. 3

2. (a) Between the two redox couple, $[\text{Co}(\text{OH}_2)_6]^{3+}/[\text{Co}(\text{OH}_2)_6]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}$ which one is more oxidizing and why? 3
- (b) $\text{K}_2\text{Ca}[\text{Cu}(\text{NO}_2)_6]$ and $\text{K}_2\text{Ba}[\text{Cu}(\text{NO}_2)_6]$ exhibit static Jahn-Teller distortion while $\text{Tl}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$ shows dynamic Jahn-Teller distortion. — Explain. 3
- (c) Ni(II) is smaller in size in the square planar environment as compared to that in tetrahedral environment, but reverse is the case with Ag(I). — Explain. 3
- (d) Mn^{2+} (aq) is pale in colour whereas aqueous solution of MnO_4^- is intense in colour. — Explain. 3

3. (a) Account for the following order of lattice enthalpies of the octahedral fluorides of $3d$ (M^{2+}) ions: 3

$$\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$$
- (b) Explain why $\text{Ni}(\text{CO})_4$ is tetrahedral while $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar. 2
- (c) Electronic spectrum of $[\text{CoF}_6]^{3-}$ shows two maxima in the visible region. — Explain. 3
- (d) Co^{2+} (d^7 , high spin) has a magnetic moment in the range 4.8-5.2 BM in octahedral field, while in tetrahedral environment the value is in the range 4.0-4.4 BM. The reverse type of observation is true for Ni^{2+} ion. — Explain. 2+2



4. (a) Use Jahn-Teller theorem to decide if $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ will have an un-distorted octahedral structure. 3
- (b) State the selection rules for electronic transition in the spectra of metal complexes. 2
- (c) Fe_3O_4 has an inverse spinel structure whereas Mn_3O_4 has a normal spinel structure. — Explain the observation from CFT. 3
- (d) Find out the ground state term for V^{3+} ion. 2
- (e) Calculate the spin-only magnetic moment in Bohr Magnetons for $\text{K}_3[\text{CuF}_6]$. 2

UNIT-II

Answer any one question from the following

16×1 = 16

5. (a) What is the common oxidation state of lanthanide elements? Why is it so? 1+2
- (b) Give the general electronic configuration of lanthanides and explain the trends in ionic radii of M^{3+} ion of this class. 1+2
- (c) $4s$ orbitals are filled before the $3d$ orbitals but during ionization $4s$ electrons are removed before $3d$ electrons. — Comment. 2
- (d) Discuss how the stability of the oxidation states changes from $3d$ to $4d$ to $5d$ transition metals. 3
- (e) Lanthanides have more or less identical chemical properties while d -block elements differ widely in this respect. — Explain. 3
- (f) The electronic absorption spectra of tri-positive lanthanide ions give rise to multiple sharp peaks. — Explain. 2
6. (a) What are the common oxidation states of Cu, Ag and Au? — Explain. 3
- (b) Why do actinides show larger number of oxidation states compared to lanthanides? 3
- (c) Which one of the following are diamagnetic and which are paramagnetic?
 Yb^{2+} , Ce^{4+} and Sm^{3+} 3
- (d) Cu^{2+} ions are coloured and paramagnetic whereas Zn^{2+} ions are colourless and diamagnetic. — Explain. 3
- (e) Compare the properties of lanthanides and actinides with respect to the following properties: 4
- (i) colour and (ii) absorption spectra.

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

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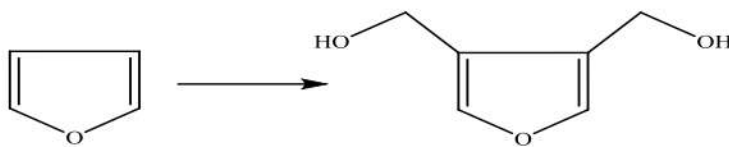
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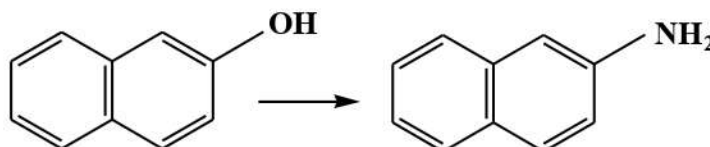
Answer any five questions taking one from each unit

UNIT-I

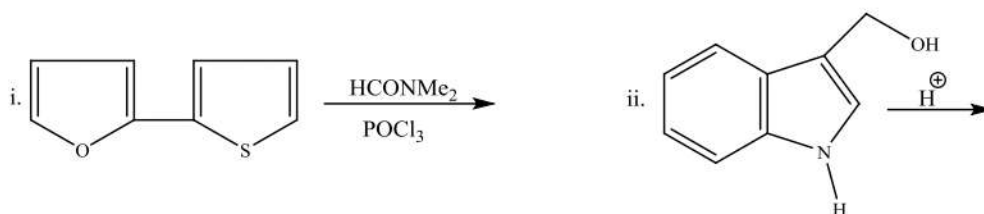
1. (a) Outline Bogert-Cook Synthesis of Phenanthrene. How can you minimize the formation of the undesired spirocyclic product in this reaction? 2+1
- (b) (i) How can you accomplish the following transformation? 2+2



- (ii) Carry out the following transformation with plausible mechanism.



- (c) (i) Compare the basicity of 2-methyl indole and 3-methyl indole. 1 1/2 + 1 1/2
- (ii) State, with mechanism, how can you convert benzaldehyde into 1-methylisoquinoline.
2. (a) What happens when 2-naphthol is treated with ferric chloride? 1
- (b) Predict the product(s) in the following reactions and suggest mechanism in each case. 2 1/2 + 2 1/2



- (c) Furan reacts differently with nitronium fluoroborate and acetyl nitrate (in pyridine) to give 2-nitrofuran. — Explain. 2
- (d) How 2-bromonaphthalene is prepared from naphthalene? 2



UNIT-II

3. (a) Predict the product(s) and give mechanism for the following reaction.



1½

- (b) What happens when *cis*-1,3-cyclohexane dicarboxylic acid is heated? Comment on the chirality of the product.

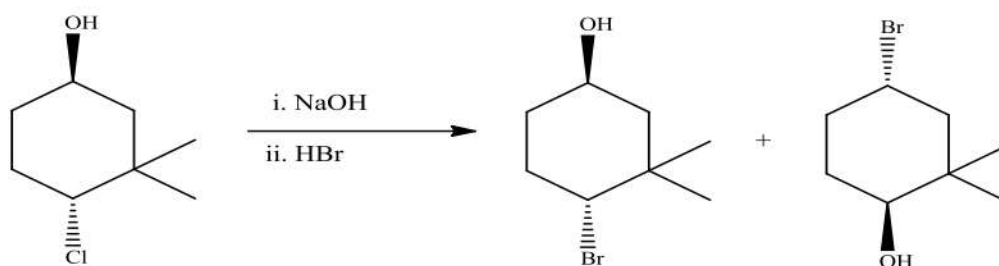
2

- (c) Explain the fact that *trans*-4-*tert*-butylcyclohexyl tosylate undergoes bimolecular reaction with the base bromide and thiophenolate, although not with the much stronger base ethoxide.

2½

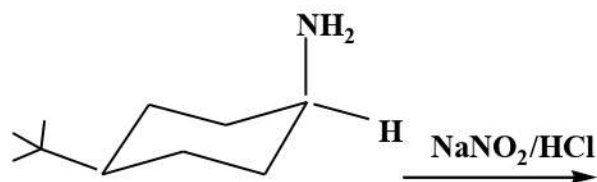
4. (a) Provide a mechanistic rationalisation to explain the stereochemical aspects of the following reaction.

3



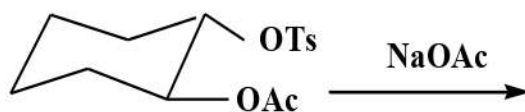
- (b) Write the product with proper stereochemistry for the following reaction and explain:

1½



- (c) Predict the product of the following reaction with suitable mechanism:

1½



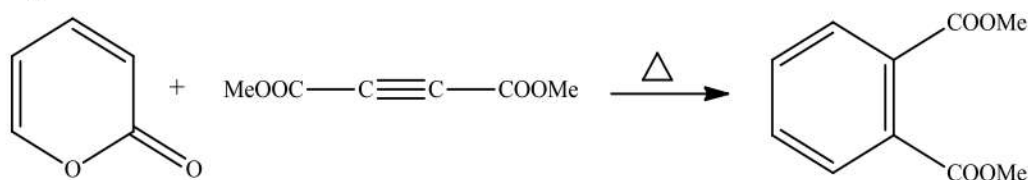
UNIT-III

5. (a) In the thermal ring opening of *trans*-3,4-dimethylcyclobutene, two products can be formed by conrotatory mode, but only one is actually formed. Identify the possible products. Which one is observed and why?

2

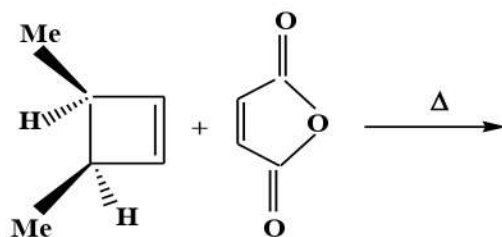
- (b) Propose a mechanism for the following reaction clearly indicating the pericyclic steps involved therein.

2

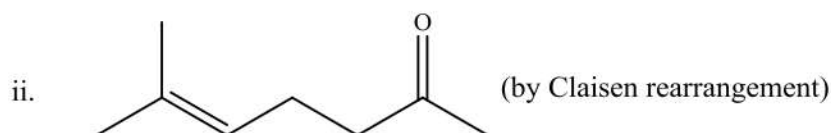
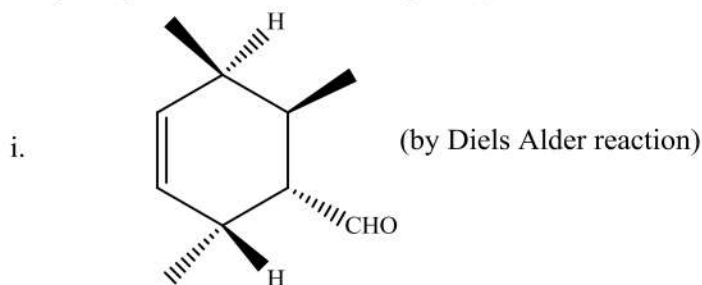




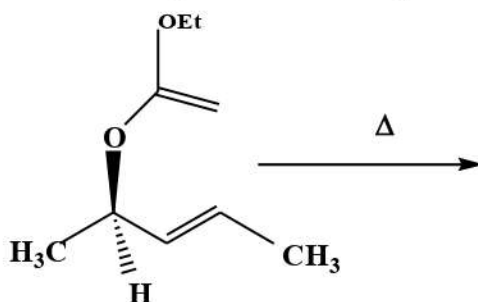
- (c) Predict the product with stereochemistry in the following reaction and indicate the reaction pathways:



6. (a) How can you synthesise the following compounds as directed? 2



- (b) Predict the product of the following reaction with explanation: 2



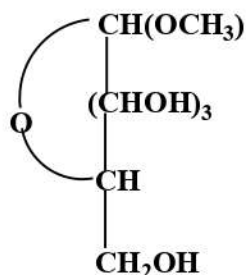
- (c) Thermal 1,3-sigmatropic shift of hydrogen is symmetry forbidden but thermal 1,3-sigmatropic shift of an alkyl group may be symmetry allowed. Explain in terms of FMO theory. 2

UNIT-IV

7. (a) β -D-Glucopyranose is oxidized at 250 times faster rate than α -D-Glucopyranose using $\text{Br}_2/\text{H}_2\text{O}$. — Explain. 2
- (b) How can you convert D-glucose into: 2
- (i) *meso* tartaric acid and (ii) D-glucuronic acid?
- (c) D-Glucose and another aldohexose (A) give the same product when treated with sodium amalgam. Find out the structure of (A). To which family between D and L, does (A) belong? 2
- (d) How would you distinguish chemically between ribose and 2-deoxyribose? 2



8. (a) How many moles of HIO_4 will be required for the oxidation of one mole of the following compound? Write down the products.



- (b) Why osazone formation doesn't proceed beyond C-2 of an aldohexose? 2
- (c) Clearly represent the most stable conformation of the β -pyranose form of the following sugars and justify. 2
- (i) β -D-allopyranose (ii) β -L-glucopyranose
- (d) Diisopropylidene derivative of D-glucose can be O-methylated at C-3, but that of D-galactose cannot give the same result. — Explain. 2

UNIT-V

9. (a) Specific rotation of an amino acid is pH-dependent. — Justify. 2
- (b) Name one amino acid that produces yellow colour with ninhydrin. Write down the pertinent reaction. 1+2
- (c) A tripeptide X on hydrolysis gives two amino acids, Glu (2 equivalent) and Ala (1 equivalent). X does not react with 2,4-dinitrofluorobenzene. Ala is released first when X is incubated with carboxypeptidase. Deduce the structure for X. 3
- (d) Define the isoelectric point of an amino acid. How can lysine (pI 9.6) be separated from glycine (pI 5.97) by electrophoresis? 2
- 10.(a) Explain the role of cellular water in the stabilisation of a DNA duplex. Show the G-C base pairing in DNA. 1+2
- (b) In deionised water, isoelectric and isoionic points of an amino acid are identical. — Why? 1
- (c) Trace the route of synthesis of $\text{Ph-CH(NH}_2\text{)-CO}_2\text{H}$ from phthalimide. 2
- (d) Predict the product with mechanism when leucine is heated with acetic anhydride in presence of pyridine. 2
- (e) How can you synthesise L-tryptophan using azlactone method? 2

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2021-22

CEMADSE01T-CHEMISTRY (DSE1/2)

ADVANCED PHYSICAL CHEMISTRY

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

Answer any three questions taking one from each unit

UNIT-I

1. (a) (i) A lattice point in a crystal structure must be occupied by atoms or ions. Justify or criticize. 2+2+
1+2
- (ii) The unit cell has orientation but no position. Justify or criticize.
- (iii) State two reasons why Miller indices are preferred to Weiss indices.
- (iv) X-ray diffraction method cannot distinguish between two atoms differing only by the possession of one extra electron. Explain why.
- (b) Explicitly justify that a five-fold rotational axis of symmetry is not possible in a crystal system. 3
- (c) For a given crystal the first-order reflection with a monochromatic beam of X-ray is observed at $10^{\circ}12'$. Find the angle at which the third-order reflection will be observed from the same plane. 2
- (d) The K_{α} lines of chromium, iron and nickel are observed at 2.28, 1.96 and 1.68 Å, respectively. Justify which of these radiations can be suitable for determination of a lattice spacing of 1.0 Å. 2
2. (a) (i) Write the conditions for constructive interference in Bragg diffraction. Why is constructive interference necessary for determination of crystal structure? 2+1+2
- (ii) X-ray radiation is preferred instead of IR in the determination of crystal structure. — Comment.
- (iii) In Bragg diffraction method monochromatic X-ray is customarily used. Justify whether a polychromatic beam of X-ray is suitable for determination of crystal structure.
- (b) What do you understand by the term 'space lattice'? Show that the interplanar distance in cubic system is given as $d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}$, where, a is the edge-length of the cube and (hkl) are the Miller indices. 1+3
- (c) The first-order reflection of a beam of monochromatic X-ray from the (100) planes of sodium chloride crystal is observed at an angle of $6^{\circ}35'$. Find the wavelength of the X-ray used in the experiment. Also calculate the angle of reflection if X-ray of wavelength 154 pm is used. 3
Given: Density of NaCl is 2.17 g cm^{-3} .



- (d) State the criteria for obtaining sharp diffraction lines of uniform thickness in powder X-ray diffraction method.

UNIT-II

3. (a) The Boltzmann distribution may be represented by expressing the number of molecules (N_i) in the level ϵ_i (under isothermal conditions) as $N_i = A \exp(-b\epsilon_i)$ where A and b are constants. 2+2

Answer the following questions taking $b = 1/k_B T$:

- (i) Show that $N_{i+1} < N_i$ for any finite temperature, with $\epsilon_1 < \epsilon_2$.
 (ii) Obtain an expression for A in terms of b and show that it is related to the partition function.

- (b) Consider a system of six distinguishable particles. One of the macrostates has the following distribution of particles: 3

Energy	0	ϵ	2ϵ	3ϵ	4ϵ
No. of particles	0	0	2	2	2

Calculate its thermodynamic probability.

- (c) If the work function, A , is $A = -Nk_B T \ln Q$ 3

Then show that $P = Nk_B T \left(\frac{d \ln Q}{dV} \right)_T$

where N = number of molecules, Q = molecular partition function.

- (d) The degeneracy of the 1st and 2nd energy levels are respectively 2 and 5. Find out the ratio $\frac{n_2}{n_1}$ when $\epsilon_2 - \epsilon_1 = 10^{-21}$ J and temperature is 400 K. 3

4. (a) Define configuration entropy and thermodynamic probability. Entropy is a logarithmic function of thermodynamic probability. — Justify. 2+2

- (b) For a system, the energy levels are 0, ϵ , 2ϵ , 3ϵ where $\epsilon = 4.14 \times 10^{-21}$ and the degeneracy of the levels are respectively 1, 1, 3, 5. Find the molecular partition functions at 300 K. 3

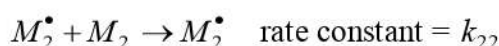
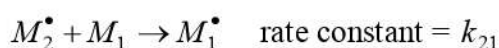
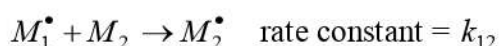
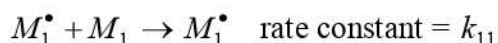
- (c) Three identical but distinguishable particles are distributed among three energy levels 0, E , $2E$. Write down the different possible distributions of the particles for total energy (i) E and (ii) $2E$. Also, obtain the thermodynamic probability for each distribution and hence the change in entropy for increasing the total energy from (i) to (ii). 2+2+2

UNIT-III

5. (a) (i) The Einstein's heat capacity model can successfully explain the lowering of heat capacity of solids with lowering of temperature. Discuss about the physical reasons underlying the success of the model. 2+2
 (ii) State the physical reasons for failure of the model in the limit of very low temperature, and comment on Debye's modification.



- (b) (i) The residual entropy of a substance is found to be $9.2 \text{ JK}^{-1}\text{mol}^{-1}$. Show that the number of possible orientations that a molecule of the substance can have at absolute zero is 3.024. Is this fractional value permissible? Justify your answer. 2+(2+1)
- (ii) Deduce the magnitude of coefficient of thermal expansion of a pure crystalline substance in the limit of absolute zero and hence show that $C_{p,m}$ and $C_{v,m}$ of a pure crystalline substance become almost equal in the limit of absolute zero.
- (c) All polymers are macromolecules, but all macromolecules are not polymers. — Justify. 2
- (d) Briefly discuss about how you can monitor the progress of a step-growth polymerization reaction. 2
6. (a) Calculate the molar residual entropy of NO crystal. Compare the result with the experimental value of $2.78 \text{ JK}^{-1}\text{mol}^{-1}$ and comment. 2
- (b) Provide a justification of the third law of thermodynamics from the probabilistic interpretation of entropy and hence justify the concept of origin of residual entropy. 2
- (c) (i) In adiabatic demagnetization method $dq_{rev} = 0$, hence the demagnetization step is isentropic; then how does it lead to a drop in temperature? — Explain. 1+1
- (ii) Gadolinium(III) sulfate octahydrate is a preferred material to the anhydrous salt for application in attainment of low temperature by adiabatic demagnetization. — Justify.
- (d) Briefly discuss about the influence of the presence of polar functional moieties in the polymeric chain on the melting point/boiling point of the polymer. 2
- (e) Consider the following kinetic mechanism of copolymerization: 3+1+1



Based on the given mechanism show that the 'copolymer equation' can be given as $\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$ where r_1 and r_2 denote the reactivity ratios.

Use the above expression to answer the following questions:

- (i) Comment on the type of copolymer formed when both the reactivity ratios are equal.
- (ii) Comment on the type of polymer formed when one of the reactivity ratios is significantly greater than the other.

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2021-22

CEMADSE02T-CHEMISTRY (DSE1/2)

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

Answer any three questions taking one from each GROUP

GROUP-A

(Units 1 and 2)

1. (a) What are determinate errors? Name the different types of determinate errors. 2
- (b) The amounts of the component A present in the compound AB are given in percent. 2
Results of A in %: 48.32, 48.36, 48.23, 48.11 and 48.38.
Calculate the mean and relative mean deviation.
- (c) Define molar absorptivity. Mention its unit. 2
- (d) What are the basic structural units of a spectrometer? 2
- (e) What special technique is used to determine mercury in water sample below the level of $\mu\text{g/L}$ by AAS? Discuss. 2
- (f) Discuss the basic principle of Job's method of continuous variation. 2
- (g) Name two IR sources and mention their composition. 2
- (h) What are spectral interferences in AAS? Mention few ways to minimize them. 2
2. (a) During standardization of KMnO_4 solution by standard oxalic acid, the volume (mL) of KMnO_4 required for four titrations were 20.5, 20.8, 20.7 and 20.4. From those data calculate average deviation, relative error (%) and error in ppm of that analysis. 3
- (b) Why ionization suppressor is used in estimation of metal ion by atomic emission spectroscopy? 2
- (c) State one advantage and one disadvantage of atomic absorption spectroscopy over atomic emission spectroscopy. 2
- (d) Discuss the characteristics of normal error curve. 2
- (e) For which purpose graphite furnace atomic absorption spectroscopy is used? What do you mean by atomic absorption analysis by cold vapour technique? 3
- (f) Give one example of isotopic substitution for structure elucidation of compound in analytical chemistry. 2
- (g) The absorption of ultraviolet and visible radiation can be conveniently studied together, but infrared absorption studies are made separately. Explain. 2

**GROUP-B****(Units 3 and 4)**

3. (a) What basic information can be obtained from the measured weight loss in a TGA curve? 2
- (b) Show graphically (qualitatively) the different steps in thermogravimetric separation of CaCO_3 and MgCO_3 . 2
- (c) State two limitations of TGA. 2
- (d) Show how the boundary potential is a measure of the pH of the external solution in a pH meter. 2
- (e) How can you determine the pKa value of acetic acid by using a conductivity meter? 2
- (f) What is cell constant? How it is determined? 2
4. (a) What are the main factors that affect the thermogram of a compound? 3
- (b) What is derivative thermogravimetry? 2
- (c) Why is it necessary for the glass in the membrane of a pH-sensitive electrode to be appreciably hygroscopic? 2
- (d) Identify the different kinds of potentiometric titrations. 2
- (e) What will be the nature of the conductometric titration curve of oxalic acid by NaOH? How will you determine the equivalence points? 3

GROUP-C**(Unit 5)**

5. (a) What do you mean by ion exchange capacity of a cation exchange resin? Explain the factors on which one cation is preferentially adsorbed over another by a cation exchange resin. 2+2
- (b) Why thin layer chromatography is superior to paper chromatography? What do you mean by the term "Chromatogram"? 2+2
- (c) Mention two detectors which are often used in gas chromatography. Why retention time is the basis for gas chromatographic analysis? 2+2
6. (a) What is the basic principle of solvent extraction? 3
- (b) How does chelation help in metal ion extraction? Give example of two chelating agents. 3
- (c) Gel permeation chromatography is a type of size-exclusion chromatography. Justify or criticize the statement. 2
- (d) What is cation exchange resin? Give one example. 2
- (e) What are the mobile and stationary phases in gas-liquid chromatography? 2

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2020, held in 2021

CEMACOR11T-CHEMISTRY (CC11)

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

UNIT-I

Answer any two questions from the following

12×2 = 24

1. (a) Calculate CFSE of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Predict the most Stable ion. 3
- (b) The magnetic moment of the brown ring compound formed in the ring test of nitrate is 3.89 BM. Find out the oxidation state and the type of hybridisation of the central metal ion. 3
- (c) 'Octahedral Cu(II) complexes are distorted' — Explain in the light of CFT using approximate energy diagram. 4
- (d) The aqueous solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows a maximum absorption around 20300 cm^{-1} in its electronic spectrum. Express the band position in nm. Will the complex give colour in visible region? 2
2. (a) Although both Co(III) and Ni(IV) are d^6 systems yet $[\text{NiF}_6]^{2-}$ is diamagnetic but $[\text{CoF}_6]^{3-}$ is paramagnetic. Explain. 3
- (b) Explain why Cr(II) is strong reducing agent but Mn(III) is strong oxidising agent, although both are d^4 ions. 3
- (c) Give expression for CFSE of Fe(II) ion in weak and strong octahedral crystal fields. 2
- (d) Room temperature magnetic moment of Copper(II) sulfate pentahydrate is almost equal to the spin only moment (1.73 BM) of Cu(II), whereas, that of Copper(II) acetate monohydrate is unusually lower (1.4 BM). Explain. 4
3. (a) Find out spin only magnetic moment (μ_s) in 4
 - (i) $[\text{Fe}(\text{OH}_2)_5\text{NO}]\text{SO}_4$
 - (ii) $\text{K}_4[\text{Ni}(\text{CN})_4]$.



- (b) Which of the following pairs of complex has higher 10 Dq value and why?
- $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Rh}(\text{NH}_3)_6]^{3+}$
 - $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
 - $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$.
- (c) Show with calculation, whether NiFe_2O_4 will show normal or inverse spinel structure. 3
- (d) From electronic spectrum, 10 Dq of $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is found to be 21000 cm^{-1} . The pairing energy of Mn(III) is 28800 cm^{-1} . Predict whether the complex will be high or low spin. 2
4. (a) Arrange the following pairs on the basis of crystal field splitting parameter (10 Dq): 2
- $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Os}(\text{CN})_6]^{4-}$.
- (b) Though Cr^{2+} and Mn^{3+} are isoelectronic, $[\text{Cr}(\text{OH}_2)_6]^{2+}$ is highly reducing but $[\text{Mn}(\text{OH}_2)_6]^{3+}$ is highly oxidizing. Explain. 3
- (c) OH^- ion is in lower position than H_2O in spectrochemical series — Explain. 3
- (d) Among CrF_2 and MnF_2 , one is octahedral while the other is distorted octahedral. Explain. 2
- (e) “Low spin tetrahedral complexes are rare, though there are many low spin octahedral complexes” — Explain the observation. 2

UNIT-II

Answer any one question from the following

16×1 = 16

5. (a) What do you mean by lanthanide contraction? Explain the impact of lanthanide contraction on the chemical behaviour of the lanthanides. 4
- (b) ‘Oxo-cations are common with the actinides, whereas in case of lanthanides these are not common’. Explain. 2
- (c) ‘Absorption spectra of lanthanides in acidified solution are line like’ — Explain. 2
- (d) Explain why La^{3+} and Lu^{3+} are diamagnetic while Sm^{3+} has low magnetic moment. 3
- (e) ‘Lanthanides normally do not form complexes’ – Explain. 2
- (f) “Lanthanides exhibit +3 oxidation state in general while actinides can show variable oxidation states.” — Explain. 3



6. (a) Discuss the separation of lanthanides by ion-exchange method. 4
- (b) Nobelium(II) is more stable and non-reducing while Ytterbium(II) is a stronger reducing agent. Explain. 2
- (c) What is the correct order of basicity among the following lanthanide(III) hydroxides? $\text{Pr}(\text{OH})_3$, $\text{Sm}(\text{OH})_3$, $\text{Dy}(\text{OH})_3$, $\text{Yb}(\text{OH})_3$ — Explain. 2
- (d) Write the names of the lanthanides each of which have a stable oxidation state which is (i) higher than usual (ii) lower than usual. Explain your answer. 2+2
- (e) Qualitatively discuss the magnetic properties of the lanthanides. 4

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester supplementary Examination, 2021

CEMACOR12T-CHEMISTRY (CC12)

ORGANIC CHEMISTRY-V

Time Allotted: 2 Hours

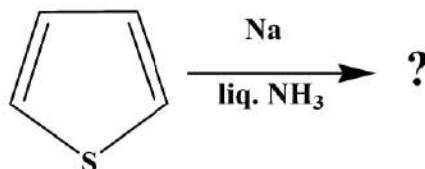
Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

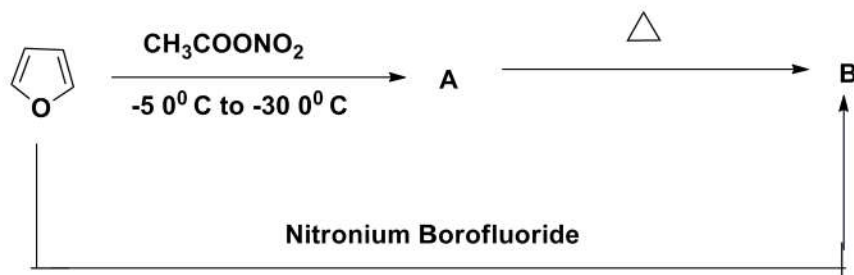
Answer any four questions taking one from each unit

UNIT-I

1. (a) Describe Fischer indole synthesis of 2-methylindole. Write plausible mechanism. 2+1
How would you demonstrate which nitrogen is lost during cyclisation?
- (b) How could you synthesize anthracene starting from naphthalene using Diels Alder reaction as one of the key steps? 2
- (c) Arrange furan, pyrrole and thiophene in order of increasing aromaticity. 2
- (d) Predict the products in the following reaction with plausible mechanism. 3



2. (a) Identify A and B and explain all the steps. 3



- (b) Unlike pyrrole indole undergoes electrophilic substitution at C-3. Explain. 2
- (c) How can you convert toluene into 1,4,6-trimethyl naphthalene? 3
- (d) Compare the basicity of pyrrole and pyridine. 2



UNIT-II

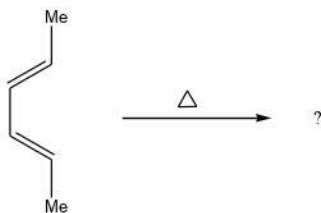
3. (a) Acetolysis of both cis- and trans-tosylate shown below give the same diacetate. Explain.



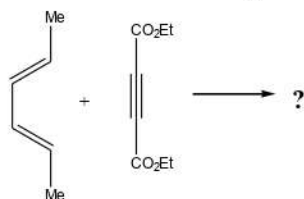
- (b) The cis-1,2-dimethylcyclohexane is less stable than its trans isomer, but cis-1,3-dimethylcyclohexane is more stable than its trans isomer. Draw the most stable conformations of both and explain. 3
4. (a) Compare the rate of hydrolysis of cis and trans isomer of ethyl 4-*t*-butylcyclohexane carboxylate. 3
- (b) Write down the preferred conformation of cis-4-hydroxyl cyclohexane carboxylic acid. What happens when it is heated? 2+1

UNIT-III

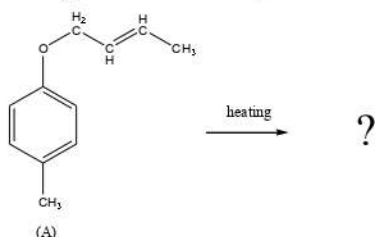
5. (a) Write down the characteristics of pericyclic reaction. 2
- (b) Write down the product of the following reaction. 2



- (c) Dimerisation of cyclopentadiene in thermal condition gives preponderantly the *endo* cycloadduct under kinetically controlled conditions. — Explain. 2
6. (a) Define stereoselectivity of 4 pi system under photochemical and thermal condition. 2
- (b) Write down the product of the following reaction. 2



- (c) What happens when compound A is subjected to heating? 2





UNIT-IV

7. (a) Write down pyranose structure of D – Glucose. 1
- (b) How can you selectively methylate C₃-OH of D-glucose? 2
- (c) E, F and G are the three aldohexoses. E and F yield D-sorbitol when they are catalytically hydrogenated. E and F yield different osazones when treated with excess phenyl hydrazine. F and G give the same osazone but different alditols. Give structures of E, F and G assuming that F and G are D-aldohexoses. 3
- (d) What happens when D- glucose is subjected to HNO₃ oxidation? 2
8. (a) What are epimers? 1
- (b) Describe mutarotation of glucose. 2
- (c) An aldpentose [P] can be oxidized with dil HNO₃ to an optically active aldaric acid. Kiliani- Fisher synthesis starting with [P] gives two new aldoses [Q] and [R]. Aldose [Q] can be oxidized to an optically inactive aldaric acid, but aldose [R] is oxidized to an optically active aldaric acid. Assuming the D-configuration, give the structures of [P], [Q] and [R] and also justify the assignments. 3
- (d) State with mechanism what happens when D-fructose is heated with Tollen's reagent. 2

UNIT-V

9. (a) Write down the steps for the synthesis of a tripeptide Gly-Ala-Phe in the solid phase with the help of Merrifield resin. 3
- (b) Describe Sanger degradation method for N-terminal amino acid determination of peptide. 3
- (c) Between A-T and G-C, hydrogen bonding in which pair is stronger? Why? 2
- (d) RNA undergoes alkaline hydrolysis at a faster rate than DNA. Explain. 2
- 10.(a) Describe synthesis of tripeptide Leu-Val -Pro using chemical method. 3
- (b) Outline the Gabriel synthesis of glycine. 3
- (c) Briefly explain the factors responsible for the stabilisation of a DNA duplex. 2
- (d) Differentiate between nucleosides and nucleotides. 2

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2020, held in 2021

CEMADSE01T-CHEMISTRY (DSE1/2)

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

Answer any three questions taking one from each unit

UNIT-I

1. (a) (i) For different reflections from the same face of a crystal the glancing angle is a constant multiplier of the order of diffraction. Justify or criticize. 2
- (ii) In the context of Bragg diffraction justify whether radio-wave is suitable for determination of crystal structure. 2
- (b) (i) Show that for a square lattice of side-length = a the spacing between the $(hk0)$ planes is $a/\sqrt{h^2 + k^2}$. 3
- (ii) The spacing between two consecutive parallel $(hk0)$ planes is $a/\sqrt{11}$. Comment on the possibility of this result. 2
- (c) For a unit cell having $a \neq b \neq c$ (and $\alpha = \beta = \gamma = 90^\circ$) show that the inter-planar distance between the (hkl) planes is reduced by a factor of n when the Miller indices are multiplied by the same factor. 2
- (d) An element exists in two crystalline forms- a α -form that crystallizes in fcc lattice having edge-length of 370 pm, and a β form that crystallizes in bcc lattice having edge-length of 290 pm. What is the ratio of densities of the two crystalline forms? 3

2. (a) (i) Find the lower limit of interplanar spacing to produce a first-order Bragg diffraction. 2
- (ii) Find the highest order of Bragg diffraction that can be observed from a crystal of interplanar distance of 2.3 Å by X-ray of wavelength 120 pm. 2
- (b) Determine the Miller indices of the plane that intersects the crystal axes at 2
- (i) $(-a, b, \infty)$ and (ii) $\left(\frac{3}{2}a, \frac{3}{2}b, 2c\right)$.
- (c) For packing of a cubic crystal with identical atoms the edge-length of the unit cell is found to be $2/\sqrt{3}$ times the diameter of the atoms. Identify the type of the cube and calculate the percentage of void space. 3



- (d) Sodium chloride and potassium chloride are known to have the same crystalline structure, but the reflection from (111) plane is observed from sodium chloride while the same is absent in potassium chloride. Explain.
- (e) A metal (atomic weight 23.02) crystallizes in bcc lattice having edge-length of 412 pm. Calculate the density of the metal and the radius of atom.

UNIT-II

3. (a) Calculate the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 8, 0, 3, 2, 0, 1. 2
- (b) (i) What is partition function? What is its unit? 1
- (ii) Show that as T approaches the absolute zero of temperature the degeneracy of the ground state becomes equal to the partition function. Evaluate the partition function for a molecule with an infinite number of equally spaced nondegenerate energy levels having energy separation ε . What is the fraction of molecules in the i -th energy state possessing an energy ε_i . 1+2+1
- (c) (i) For a system of N independent and distinguishable particles show that 3
- $$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_{V, N}$$
- (where $\langle E \rangle$ is a average energy, k_B is Boltzmann constant, q is molecular partition function).
- (ii) Consider the molecular partition function of an ideal monatomic gas as $q = \exp(a + b \ln T)$ where a, b are constants. Find an expression for b and the molar heat capacity of the gas. 3
4. (a) The total number of microstates of a system comprised of N number of particles distributed in two energy states is given as $\Omega_{tot} = 2^N$. Using Stirling's approximation, find the number of microstates (Ω_{eq}) for the distribution in which the two energy states are equally populated. Compare Ω_{tot} and Ω_{eq} comment on the result. 2+2
- (b) (i) Two non-degenerate energy states are separated by 200 cm^{-1} . At what temperature will the population of the higher state be one-third to that of the lower state? 1 $\frac{1}{2}$
- (ii) Using the Boltzmann distribution law show that $n_{i+1} < n_i$ at any finite temperature (n_i is population of the i -th state). 1 $\frac{1}{2}$
- (c) (i) State the physical significance of partition function. 1
- (ii) The molecular partition function of an ideal gas is given as $q = (aT/b)^{3/2} V$, where a and b are constants. Find an expression for pressure of the gas. 3
- (d) Starting from the expression of Helmholtz energy $A = -Nk_B T \ln q(N, V, T)$ find an expression for entropy of the system (q is molecular partition function). 2



UNIT-III

5. (a) According to the Einstein's model the molar heat capacity of monatomic crystal can be expressed as 1+3+2

$$C_{v,m} = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

where θ_E is the characteristic Einstein temperature.

- (i) Write down the defining equation for θ_E and state its physical significance.
- (ii) Find the proper expressions for $C_{v,m}$ in the limits of very low and very high temperature.
- (iii) Argue on the applicability of the equation in the two limits of temperature.
- (b) ΔG for a reaction is given as $\Delta G = \alpha + \beta T + \gamma T^2$. 3
- (i) Show that $\beta = 0$ when $T \rightarrow 0$.
- (ii) Find an expression for ΔH and ΔC_p .
- (c) (i) An spontaneous polymerization reaction must be exothermic. Justify or contradict. 2+2
- (ii) For a polymerization reaction show that $\langle DP \rangle_n = \frac{2}{2 - f\xi}$, where $\langle DP \rangle_n$ is the number-averaged degree of polymerization, ξ is the extent of polymerization, f is the average degree of functionality.
6. (a) Show that the molar entropy of a perfect crystalline substance obeying the Debye's law of heat capacity at low temperature is equal to $C_{v,m}/3$. 2
- (b) Adiabatic demagnetization with a paramagnetic substance is a technique for attainment of low temperature. 2+3+2
- (i) Construct with suitable explanation the S vs. T curve for a paramagnetic substance.
- (ii) Using the S vs. T curve, explain the working principle of adiabatic demagnetization.
- (iii) Comment on unattainability of the absolute zero of temperature by this technique and hence argue that unattainability of absolute zero is consistent with the third law of thermodynamics.
- (c) Derive the integrated rate law equation for the kinetics of step-growth polymerization using a suitable example. Using your rate law equation plot the variation of $\langle DP \rangle$ with the progress of reaction (where $\langle DP \rangle$ is average degree of polymerization). 3+1

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2020, held in 2021

CEMADSE02T-CHEMISTRY (DSE1/2)

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

Answer three questions taking one from each unit

UNIT-I

1. (a) Define accuracy and precision. 3
- (b) Calculate the mean and the standard deviation of the following set of analytical results 15.67g, 15.69g and 16.03g. 2
- (c) What is the basic principle of mole ratio method for determining stoichiometry of metal ligand complexes? 3
- (d) What are the advantages of a double beam spectrophotometer over a single beam spectrophotometer? 3
- (e) Differentiate between total consumption burner and premix chamber burner. 3
- (f) What is the use of chopper in AAS? 2

2. (a) Good precision does not guarantee accuracy — Explain. 2
- (b) What do you mean by 'systematic error' and 'random error'? 2
- (c) What is the role of flame in atomic absorption spectrometry? Mention two fuel-oxidant gas mixture used for producing flame in atomic absorption spectrometer. 2+2
- (d) What is the function of monochromator used in various spectrophotometer? 2
- (e) Which is the most common light source used in atomic absorption spectrometer? 1
- (f) Describe the structure of a hollow cathode lamp used as a source of Atomic Absorption Spectroscopy. 2
- (g) What is the main difference between Flame Emission Spectrometry and Atomic Absorption Spectroscopy? 1
- (h) What are the methods of removal of chemical interferences in AAS? 2



UNIT-II

3. (a) What is thermogravimetric analysis? Describe the different steps in thermogravimetric analysis of calcium oxalate monohydrate. 2+2
- (b) What are the basic requirements of a reference electrode in potentiometric measurements? 2
- (c) Mention two errors that affect pH measurements with glass electrodes. 2
- (d) What is liquid junction potential? How can we minimize the liquid junction potential? 2+2
4. (a) What type of information can be obtained from thermogravimetric analysis? What are the main components of TGA apparatus? Discuss. 2+2
- (b) What are the indicator electrode and reference electrode in a typical pH measuring cell? Describe the basic constituents of the indicator electrode. 2+2
- (c) Discuss the nature of curve for the conductometric titration of a mixture of acetic acid and hydrochloric acid by sodium hydroxide. What is dilution effect and mention steps taken to avoid the same. 2+2

UNIT-III

5. (a) How can you classify chromatographic techniques on the basis of the type of equilibrium process involved? Give examples of each type. 2
- (b) What do you mean by 'R_f value'? What are the maximum and minimum R_f values possible? Justify your answer. 2+2
- (c) Why masking agents are used in solvent extraction by chelation process? 2
- (d) What is HPLC? Discuss. 2
- (e) Why in solvent extraction distribution ratio is more meaningful term than distribution coefficient? 2
6. (a) Define stationary phase and mobile phase in chromatography. 2
- (b) What is partition coefficient of a solute in chromatography? 2
- (c) Name the basic components of gas chromatography instrument. Which gases are used as carrier gases? 3
- (d) R_f values of three amino acids X, Y and Z are 0.14, 0.38 and 0.72 respectively. Which one of these amino acids in their TLC separation will occur on the top and which one at the bottom? Explain your choice. 2
- (e) Explain in detail the mechanism of extraction by solvation process. 3

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