WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2024-25

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

1. (a) Name three types of systematic error. How are these errors caused? 3

   (b) What is the function of a monochromator? Which compounds are used for making prism in IR spectrometer? 2

   (c) Calculate the molar absorptivity of 0.4×10^{-3} M solution which has an absorbance of 0.15 when path length is 1.3 cm. 2

   (d) Write a short note on Zeeman background correction used in flame atomic absorption spectroscopy. 3

   (e) Point out the basic difference between absorbance and emission spectrum. 2

   (f) What are auxochromes? Give an example of your choice. 2

   (g) Write down the different types of interferences encountered during analysis with AAS. 2

2. (a) The set of data received during a quantitative analysis is 19.4, 19.5, 19.6, 19.8, 20.1 and 20.3 respectively. Calculate the mean and median from the above set. 3

   (b) What are stretching and bending vibrations? 3

   (c) Differentiate between: 4

   Absolute error and relative error

   Random error and systematic error

   (d) What is cold or flameless technique in AAS? Why is it so called? Name the elements that can be analyzed by this method. 2+1+1

   (e) What are the methods of removal of chemical interferences in AAS? 2

GROUP-B

3. (a) What is the principle behind conductometric titration? 2

   (b) What is the function of salt bridge in an electrochemical cell? 2

   (c) What is the difference between potentiometric titration and conductometric titration? What is dilution effect in conductometric titration? 2+1

(d) The TG curve of a 2.92 mg sample containing $MgSO_4.7H_2O$ (molecular weight 246) exhibited a weight loss of 0.59 mg at a temperature of 105°C corresponding to the reaction 2

$$MgSO_4.7H_2O\,(s) \rightarrow MgSO_4.H_2O\,(s) + 6H_2O\,(g)$$

Calculate the percentage of $MgSO_4.7H_2O$ in a sample.

(e) What is liquid junction potential? How can it be minimised? 3

4. (a) What is a derivative thermogravimetry? 2

(b) Why is the glass used in pH-sensitive electrode should be appreciably hygroscopic? 2

(c) What are the different kinds of potentiometric titrations? 2

(d) Draw the titration curve for acid base titration of a diprotic acid H_2A with NaOH and mention the species present at the two equivalence points. 3

(e) The TGA analysis of the CaO and $CaCO_3$ mixture reveals a mass decrease from 250.6 mg to 190.8 mg between 600°C and 900°C. Calculate the percentage of calcium carbonate in the mixture. 3

GROUP-C

5. (a) In TLC analysis of an organic sample the solvent front is 18 cm and fronts due to compounds A, B, C and D are 16.6, 14.3, 10.2 and 5.7 cm respectively. If the R_f value of an unknown compound is 0.79, identify the compound as A, B, C or D. 3

(b) What are stationary and mobile phases in gas chromatography? 2

(c) Define ion exchange capacity of a resin. 2

(d) Mention one advantage and one disadvantage of TLC over paper chromatography. 2

(e) Discuss the basic principle of solvent extraction method. 3

6. (a) Write down the advantages of thin layer chromatography over paper chromatography. Why spraying agent is required in the separation of ions through paper chromatography? 1+1

(b) Describe the basic principle of gas chromatography (GC) instrument. Identify the carrier gas used in GC. 3+1

(c) Mention the major components of HPLC. 2

(d) Define R_f value. What are the largest and smallest R_f values possible? — Explain. 2+2

——×——

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2024-25

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 $12\times 2 = 24$

1. (a) Predict the type of spinel structure adopted by Fe_3O_4 and Co_3O_4 with proper justification. 3

   (b) Electronic absorption spectrum of CoF_6^{3-} shows two maxima in the visible region at 11,500 and 14,500 cm^{-1}. Account for the cause of bands and expected colour of the complex ion. 3

   (c) Give reasonable explanations to the following facts: 2+2

   (i) FeF_6^{3-} ion is colourless, whereas $FeCl_4^{-}$ ion is coloured.

   (ii) Room temperature magnetic moment of Cu(II) acetate monohydrate is usually lower.

   (d) Find out the ground state term symbol for Mn^{+3} ion. 2

2. (a) H_2O is in lower position than CO in spectrochemical series though the μ (dipole moment) of H_2O is higher than CO. — Explain. 3

   (b) Between *cis*- and *trans*- $[Co(en)_2Cl_2]^+$ which one will give more intense d-d transition and why? 3

   (c) Discuss the structural variation of $[NiCl_4]^{2-}$, $[Ni(NH_3)_6]^{+2}$, $[Ni(CN)_4]^{-2}$. 4

   (d) What is Nephelauxetic effect? Explain it with example. 2

3. (a) 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 $[Fe(C_2O_4)_3]^{3-}$

   (b) Octahedral Ni(II) complexes have magnetic moment in the range 2.9-3.4 B.M. Tetrahedral complexes of Ni(II) have magnetic moment up to 4.1 B.M. Rationalize the observation. 3

   (c) Consider the octahedral complex of $[Mn(H_2O)_6]^{3+}$. If Orgel diagram of this high-spin complex is drawn, explain the *d*-orbital splitting. 3

   (d) How the Laporte selection rule is relaxed? State with a suitable example the consequence of the relaxation in electronic spectrum. 3

4. (a) The observed magnetic moment for K_3TiF_6 is 1.70 μB. Calculate magnetic moment (spin only) for this Complex. Why is there a difference between calculated and observed values? 3

   (b) Though Cr^{2+} and Mn^{3+} are isoelectronic, $[Cr(OH_2)_6]^{2+}$ is highly reducing but $[Mn(OH_2)_6]^{3+}$ is highly oxidizing. — Explain. 3

   (c) Using the qualitative Orgel diagram, explain the electronic spectral transition for $3d^9$ ion in weak octahedral field. 3

   (d) $[Ni(H_2O)_6]^{2+}$ has an absorption band at 1176 nm in near IR region and two visible absorption bands at 649 and 385 nm. Calculate 10 Dq value in cm^{-1} with proper justification. 3

UNIT-II

Answer any *one* question from the following $16 \times 1 = 16$

5. (a) What are the basis of Lanthanide separation? Give a brief outline of the separation of the lanthanide elements by the Ion-exchange method. 4

   (b) (+3) oxidation state is common for lanthanides in general while actinides can show variable oxidation states. — Explain. 3

   (c) Write down the ground state electronic configurations of U. 1

   (d) Spectral features of 4*f* complexes have a marked difference from their 3*d* counterpart. Mention the differences. 3

   (e) Explain why La(+3) and Lu(+3) are diamagnetic while Sm(+3) has low paramagnetism. 3

   (f) Comment on the statement — 'Nb' and 'Ta' are difficult to separate. 2

6. (a) Usually colourful complexes are observed in actinide series while most of the lanthanide complexes are colourless. Justify the statement with suitable examples. 3

   (b) 'Higher coordination number complexes are more frequent for 4*d* and 5*d* series compared to 3*d* series of transition metals.' Explain with suitable example. 3

   (c) What is Lanthanide contraction? How does it influence the chemical behaviour of lanthanides? 3

   (d) Actinides have a greater tendency to form complexes than lanthanides. — Explain. 3

   (e) The electronic absorption spectra of tri-positive lanthanide ions give rise to multiple sharp peaks. — Explain. 2

   (f) Discuss the trend in variation of Redox Potentials for M/M^{+2} (aq) system across the period of 3*d* series. 2

——×——

$\frac{10^7}{1176}$

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2024-25

CEMACOR12T-CHEMISTRY (CC12)

Time Allotted: 2 Hours Full Marks: 40

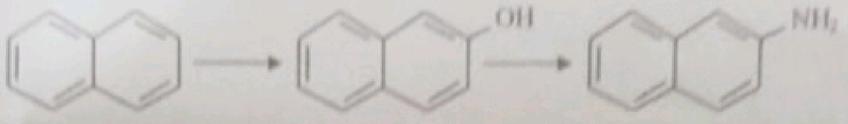
The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

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

UNIT-I

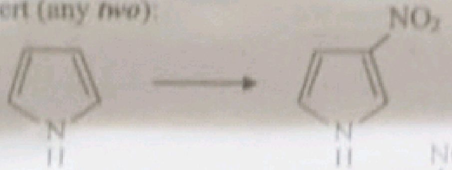
1. (a) Outline Bogert-Cook synthesis of Phenanthrene. 2

(b) Carry out following conversion. 2

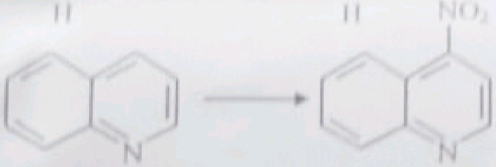


(c) Convert (any *two*): 2+2

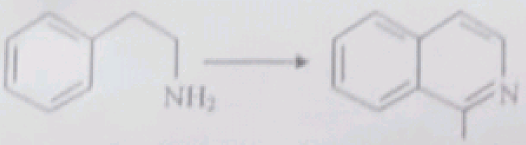
(i)



(ii)



(iii)

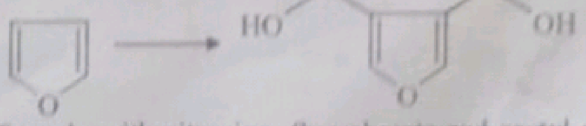


(d) Compare the rate of nitration of benzene, pyrrole and pyridine with reasons. 2

2. (a) Anthracene acts as a diene whereas phenanthrene acts as a dienophile — Explain with example. 2

(b) Indole cannot be synthesised from acetaldehyde and phenylhydrazine by Fischer's method. — Why? How would you modify the starting materials to synthesise N-methylindole? $1\frac{1}{2}+1\frac{1}{2}$

(c) How can you accomplish the following transformation? 2



(d) Furan reacts differently with nitronium fluoroborate and acetyl nitrate (in pyridine) to give 2-nitrofuran. Explain with suitable mechanism. 3

UNIT-II

3. (a) Draw all possible conformations of *cis* and *trans*-1,3-dimethylcyclohexane. Comment on the relative stability of conformers based on steric interaction. Are the compounds resolvable? 1+2+1

   (b) Both *cis* and *trans*-1,2-dibromocyclohexane give the same product when heated with iodide ion. Identify the product and explain the reaction. 2

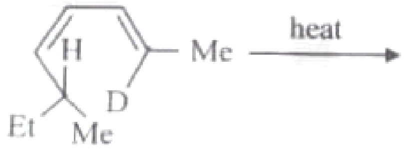
4. (a) Draw the energy profile for ring inversion of cyclohexane through the energetically most favourable pathway. Identify the chiral conformations involved in the process. 3

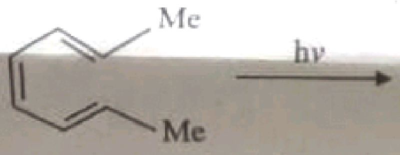
   (b) What happens when both *cis*- and *trans*-2-chlorocyclohexanols are separately treated with alcoholic alkali? Explain the pathways in each case. 3

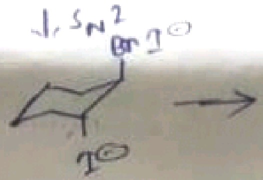
UNIT-III

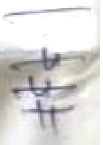
5. (a) What happens when *cis*-3,4-dimethylcyclobutene is heated with maleic anhydride? Show FMO interactions involved in the reaction. 2

   (b) Predict the product(s) with stereochemistry of the following reactions. Designate the pericyclic steps involved therein. 2+2

(i) 

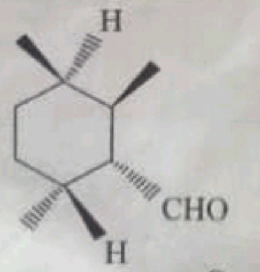
(ii) 





6. (a) 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

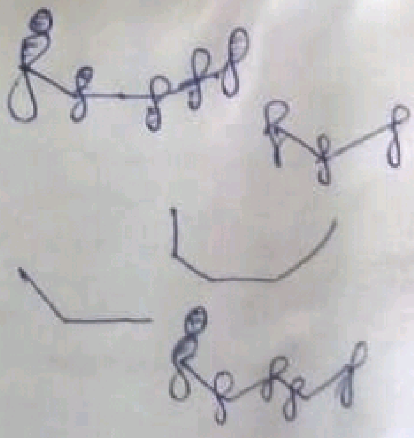
   (b) How can you synthesise the following compounds as directed? 2+2

(i) 

(By Diels-Alder reaction)

(ii) 

(By Claisen rearrangement)



UNIT-IV

7. (a) β-D-glucopyranose undergoes oxidation by bromine water 250 times faster than α-D-glucopyranose. — Explain. 2

   (b) Convert D-arabinose to D-glucose. 2

   (c) Explain why mutarotation of glucose occurs rapidly in the presence of 2-pyridinol. 2

(d) Glucose and fructose cannot be differentiated by Tollens' reagent even though only one of them contains aldehydic group. — Explain. 2

8. (a) Diisopropylidene derivative of D-glucose can be O-methylated at C-3; but that of D-galactose cannot give the same result. — Explain. 2

(b) What is anomeric effect? Comment on the effect of solvent on anomeric effect. 2

(c) An aldose 'B' and D-altrose produces identical osazone. Show the detailed mechanism of osazone formation from 'B'. 2

(d) Sucrose does not show any change in specific rotation when dissolved in water. — Explain. 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) Write down the structure of L-proline. 1

(c) How can you synthesise proline by Gabriel's phthalimide synthesis? 2

(d) Explain the following: (any *two*) 2+2

(i) Edman method is preferred over Sanger method in determination of N-terminal amino acid in a peptide.

(ii) Acetyl group cannot be used as N-protecting group during peptide synthesis.

(iii) 2,4-DNFB is used in Sanger method though 2,4-dinitrochlorobenzene is cheaper reagent.

10. (a) Write down the structures of adenosine and guanosine. Explain why guanosine is hydrolysed more rapidly than adenosine. 2

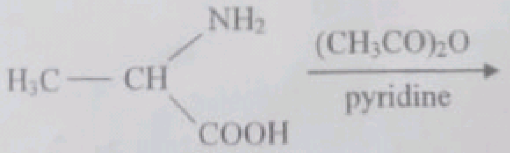
(b) Why is DNA more stable than RNA under alkaline condition? 2

(c) Show with mechanism how methionine residue in a polypeptide can be selectively cleaved by cyanogen bromide. 2

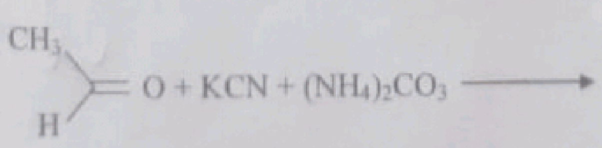
(d) How would you differentiate chemically between the following peptides? 2

gly-ala-ala and ala-gly-ala

(e) Predict the product with mechanism: (any *one*) 2

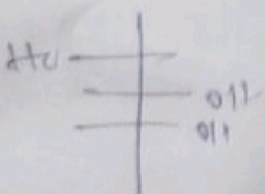
(i) 

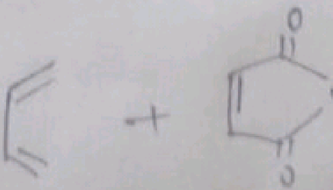
$$H_3C-CH(NH_2)(COOH) \xrightarrow[\text{pyridine}]{(CH_3CO)_2O}$$

(ii) 

$$(CH_3)(H)C{=}O + KCN + (NH_4)_2CO_3 \longrightarrow$$

—×—





No of atoms per unit

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2024-25

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

4

n =?

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

UNIT-I

1. (a) State and explain the Law of reciprocal indices. Find the Weiss indices and Miller indices of the plane that intersects the crystallographic axes at $2a,\ \infty b - 3c$. 2+1+1

(b) Show that for a cubic lattice of edge-length 'a' the spacing between (hkl) planes is given by $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$. 4

(c) A solid 'A' crystallizes as a face centered cube (fcc) with side-length, a = 3Å. Another solid 'B' crystallizes as a body centered cube (bcc) with side-length, a = 6Å. Find the ratio of the densities of the two solids, i.e., (d_A/d_B). 3

(d) Calculate the percentage of void space in I-type (body centered cubic) cubic systems. 3

2. (a) Prove that 5-fold rotational axis of symmetry is not possible in a crystal lattice. 4

(b) Cubic lattice of metallic Al ($\rho = 2.70$ gcm^{-3}) exhibits first four X-ray (λ = 154.2 pm) reflections at θ = 19.25°, 22.38°, 32.58° and 39.15°. Determine (i) the type and edge-length of cubic unit cell, (ii) the atomic mass and atomic radius of Al. 2+2

(c) The characteristic k_α line of Cr, Fe and Ni have wavelengths 2.29, 1.94 and 1.66 Å respectively. Which of these rays can be used for X-ray diffraction study of the interplanar spacing of 0.971 Å? What will be the corresponding glancing angle for first order reflection? 3

(d) NaCl (M = 58.45) has a f.c.c. structure and its density is 2.17 gm/c.c. Find out the interionic separation between Na$^+$ ions and Cl$^-$ ions. 3

UNIT-II

3. (a) Explain the third law of thermodynamics with the help of Boltzmann-Planck's equation $S = k_B \ln W$. 2

(b) Calculate the relative Boltzmann population of two nondegenerate vibrational energy levels that are separated by 1000 cm^{-1} at 27°C. 3

(c) Some noninteracting distinguishable particles are distributed in three energy levels $\varepsilon_0 = 0$, $\varepsilon_1 = k_B T$ and $\varepsilon_2 = 2k_B T$ at T K, which are respectively nondegenerate, 2-fold degenerate and g-fold degenerate. If the partition function for this distribution is 2.1417. Calculate the value of 'g'. 3

(d) Show that the entropy, $S = Nk_B \ln Z + (\frac{U}{T})$, where Z is the partition function, U is the average internal energy and the other terms have their usual meaning. 3

(e) What is Stirling's approximation? 2

4. (a) What do you mean by the most probable **macro-state**? Consider a system with four nondegenerate energy states with the energy gap between the successive levels is ε. Find out the most probable macro-states having total energy, 12ε with 8 particles. Assume that the energy of the ground level is zero. 1+3

(b) One mole distinguishable molecules are equally distributed in two nondegenerate energy levels. Show that molar entropy for this distribution is given by $S_m = R \ln 2$ 3

(c) Show that as T approaches 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 equal 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

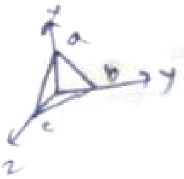
(d) The molecular partition function is defined as the reciprocal of mole fraction of molecules in nondegenerate ground level ($\varepsilon_0 = 0$). — Justify the statement. 2

UNIT-III

5. (a) Find out the unit of $\left(\frac{h\nu}{k_B}\right)$. What is its significance in Einstein's heat capacity equation for monoatomic solid? 1+1

(b) ΔG for a reaction as a function of temperature (T) near $T \to 0$ is given by: 1+2+2

$$\Delta G = a + bT + cT^2$$



(i) Show that $b = 0$;

(ii) Express ΔH and ΔC_p as function of temperature.

(iii) Show schematically the variation of ΔG and ΔH with T in the same plot.

(c) A solution contains equal number of polymeric particles with molar masses 1000 g mol^{-1} and 2000 g mol^{-1}. Calculate $\overline{M}_n$ and $\overline{M}_m$. 2

(d) Show that the molar entropy of a perfect crystalline substance obeying Debye's law of heat capacity at low temperature is equal to $\frac{1}{3}C_{v,m}$. 2

(e) Explain why the melting point and the density of the linear polymer are higher than that of the polymers with side chains. 2

6. (a) Show that the average molar energy of a solid according to Einstein's theory is $U = 3N_0 \cdot \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$, where $\beta = \frac{1}{k_B T}$ and the other terms have their usual meaning. Hence, derive the expression of molar heat capacity of the solid. 3+2

(b) Construct with suitable explanation the S *vs.* T curve for a paramagnetic substance. Using this curve explain the working principle of adiabatic demagnetization. Comment on unattainability of absolute zero of temperature by this technique. 2+2+2

(c) A spontaneous polymerization reaction is exothermic in nature. — Justify or contradict. 2

——×——