WEST BENGAL STATE UNIVERSITY
B.Sc. Honours PART-III Examinations, 2018

CHEMISTRY-HONOURS
PAPER- CEMA-V

Time Allotted: 4 Hours   Full Marks: 100

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.

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* questions taking *one* from each unit.

UNIT-I

1. (a) Of the two isomers of $[Pt(NH_3)_2Cl_2]$, one isomer 'A' reacts with thiourea (tu) to produce $[Pt(tu)_4]^{2+}$, whereas the other isomer 'B' produces $[Pt(NH_3)_2(tu)_2]^{2+}$. Predict the isomers 'A' and 'B'. Justify your answer.   2+1

    (b) Calculate CFSE of $Mn(H_2O)_6^{2+}$, $Fe(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$ and predict most stable complex ion.   2

    (c) Explain the nature of Jahn-Teller distortion expected for an octahedral complex of $Cu(II)$ ion.   3

    (d) Observed magnetic moment value of $Co(II)$ complexes in octahedral field is higher than spin only moment. Explain.   3

    (e) $[NiCl_4]^{2-}$ is paramagnetic, whereas $[PtCl_4]^{2-}$ is diamagnetic although both $Ni(II)$ and $Pt(II)$ are d^8 ions. Explain.   2

2. (a) With the help of approximate Orgel diagram explain the electronic spectrum of $[V(H_2O)_6]^{3+}$.   3

    (b) Although $Co(III)$ and $Ni(IV)$ are d^6 systems yet $[NiF_6]^{2-}$ is diamagnetic but $[CoF_6]^{3-}$ is paramagnetic. – Explain.   3

    (c) Rationalise the given order of stability constants of crystal lattice energies of anhydrous chlorides of the metal ions: 3+1

    $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$.

    Why does Cu^{2+} reluctant to synthesize $[Cu(en)_3]^{2+}$ complex?

    $(en = NH_2 - CH_2 - CH_2 - NH_2)$

    (d) The ions Cr^{2+} and Mn^{3+} are isoelectronic yet $[Cr(H_2O)_6]^{2+}$ is highly reducing while $[Mn(H_2O)_6]^{3+}$ is highly oxidizing – How would you reconcile?   3
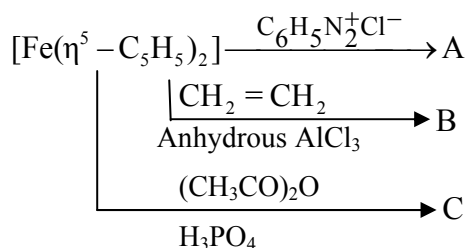
UNIT-II

3. (a) How will you prepare $K_2[Ni(CN)_4]$? On calculating its magnetic moment, explain the structure of the complex.   **3**

   (b) Explain why (any *one*):   **2**

      (i) Actinides have greater tendency to form complexes than that of lanthanides.

      (ii) Nobelium(II) is more stable and non-reducing while Yb^{2+} is a stronger reducing agent.

   (c) Although lanthanides usually exhibit +3 oxidation state, Eu^{2+} and Yb^{2+} have special stability. Explain.   **3**

   (d) What is lanthanide contraction and what is its influence on the chemistry of post lanthanide elements?   **2+2**

4. (a) How would you prepare $KMnO_4$ from pyrolusite? Explain with reason the oxidising property of $KMnO_4$ in acid and alkali medium.   **2+2**

   (b) Oxo cations are common with the actinides, whereas in case of lanthanides these are not common. Explain why?   **2**

   (c) Absorption spectral characteristics of lanthanides in acidified solution are line like while transition metal complexes show broad band. – Explain.   **3**

   (d) What happens when aqueous solution of Na_2S is added to alkaline solution of sodium nitroprusside? Draw the structure of reactants and products. Explain the origin of color change.   **3**

CEMAT–35 –IB

Answer any *two* questions taking one from each unit

UNIT-I

5. (a) Define haptocity of non-Werner type complexes. What will be haptocity of ligand in $[Ni(C_5H_5)_2]$? Draw the structure of the complex.   **3**

   (b) Write short notes on Hydrogenation of Olefins (Including mechanism).   **4**

   (c) How is Zeigler Natta Catalyst prepared?   **2**

   (d) Identify the species A, B and C in the following reaction: **3**

   $$[Fe(\eta^5-C_5H_5)_2] \xrightarrow{C_6H_5N_2^+Cl^-} A$$
   $$\xrightarrow[\text{Anhydrous AlCl}_3]{CH_2=CH_2} B$$
   $$\xrightarrow[\text{H}_3\text{PO}_4]{(CH_3CO)_2O} C$$

   (e) Using EAN rule determine number of M–M bond(s) in $Mn_2(CO)_{10}$.   **1**

6. (a) In Zeise's salt the chloride ion trans to ethylene has the larger Pt-Cl distance than the other two Pt-Cl distances — Rationalise.   **2+3**

   Do you expect free rotation of C_2H_4 molecules in Zeise's salt without hampering the stability of the species?

   (b) Define 'Hydroformylation reaction'. Explain the role of cobalt organometallics as catalyst in it.   **3**

   (c) How would you prepare Vanadium hexacarbonyl? Does it obey 18-electron rule? Give reasons for your answer.   **2+1**

   (d) What are fluxional molecules? Cite one example.   **1+1**

UNIT-II

7. (a) What is Zeimmermann-Reinhardt reagent? Explain the function of its constituents in permanganometric estimation of Fe^{3+} ion.   1.5+1.5

   (b) What are co-precipitation and post-precipitation? How is post-precipitation avoided during gravimetric analysis?   1+1+1

   (c) Write the principle of estimation of Cu^{2+} ion iodometrically. How is thiosulphate solution standardized? What is the function of thiocyanate in this titration?   2+1+1

   (d) What are masking and demasking agents? Give examples.   2

8. (a) Give the principle of argentometric estimation of chloride using adsorption indicator.   3

   (b) Find the oxidimetric equivalent weight of $KBrO_3$.   2

   (c) Why in iodometric titration addition of starch indicator is suggested near the end point of titration?   2

   (d) Briefly describe the dissolution process of chalcopyrites and hence write the principle for estimation of copper in the solution.   2.5+2.5

CEMAT–35 –AA

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

UNIT-I

9. (a) What is Na^+ ion pump? Explain the mechanism of this.   3

   (b) Give example of a toxic metal and discuss its toxic effects on human body.   3

   (c) What are the biological functions of (i) Myoglobin and (ii) Ferridoxin?   3

   (d) What are photosystems -I and -II? Explain the role of metal ion involved in them.   4

10. (a) Write a brief note on biological nitrogen fixation.   3

    (b) Name an Au complex used as drug and state its therapeutic applications.   1+2

    (c) How can you differentiate the oxygen carrier and oxygen transport proteins? Explain with examples.   3

    (d) Mention two diseases caused by metal deficiency in the human body. Explain the role of the metals in the metabolic process.   2+2

UNIT-II

11.(a) Briefly discuss the viscosity method for determination of molecular weight of polymers.   3

   (b) Mention two differences between: 2+2

   (i) Step growth polymerization and chain polymerization.

   (ii) Carbon nanotubes and graphene.

   (c) Find the value of *n* assuming the validity of the 18 electron rule in the following compounds: 2+2

   (i) $Ru_3(CO)_n$ (ii) $Fe_4(\eta^5 - Cp)(\eta^1 - Cp)(CO)_n$

   (d) Give an example of a metal surface catalysis reaction.   1

12.(a) Explain the structure of fullerene-C_{60}. Reduced fullerene has many practical applications. – Comment. 3

(b) Zeolites play an important role in heterogeneous catalysis. Explain with an example. 3

(c) A sample of polymer contains 5, 25, 40 and 30 per cent molecules of the polymer with molecular weights 10,000; 12,000; 13,000 and 15,000. Determine the weight average and number average molecular weights of the polymer sample. 3

(d) Describe in detail any chemical method for the synthesis of Au nanoparticles. Explain the role of the different chemicals used in the synthetic process. 3

CEMAT–35 –AB

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

UNIT-I

13.(a) What are nucleosides and nucleotides? Show the structure of nucleotide containing the base which occurs only in RNA, but not in DNA. 4

(b) Explain the differences between secondary and tertiary structures of protein. What types of bonding interaction are present in each case? 5

(c) What do you mean by protein renaturation? 2

(d) Name one amino acid residue which is rarely found in alpha helix. Give reason. 2

14.(a) Describe the salient features of Watson and Cricks double helical model of DNA. 4

(b) What forces stabilize α helices? Which amino acids have highest propensity to form α helices? 2+2

(c) How are enzymes classified? Name the different classes of enzymes. 3

(d) A sample of DNA contains 30% cytosine **(C)** as a base. Calculate the % of other bases present in the sample. 2

UNIT-II

15.(a) What is meant by electrophoresis? How would you determine the molecular weight of a protein by gel electrophoresis? 5

(b) What is turnover number of an enzyme? 2

(c) Derive the *Michaelis-Menten equation* for an enzyme-catalyzed reaction and from therein deduce the Lineweaver-Burk form. 5

16.(a) Discuss the principle characteristics of competitive inhibition. What is turnover number? 3+2

(b) How do lyophilic colloids differ from lyophobic colloids? Lyophilic sols are more stable than lyophobic sols. Explain. 2+2

(c) Define autocatalysis. What is the nature of a rate equation of such reactions? Explain with an example. 3

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B.Sc. Honours PART-III Examinations, 2018

CHEMISTRY-HONOURS

PAPER-CEMA-VI

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and adhere to the word limit as practicable. Use separate answer scripts for Organic and Physical sections.
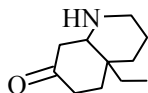*All symbols are of usual significance.*

Use separate Answer Scripts for **[CEMAT-36-OA & CEMAT-36-OB]**
and for **[CEMAT-36-PA & CEMAT-36-PB]**

CEMAT-36-OA

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

Unit-I

1. (a) Write two synthetic equivalents of $CH_3 - \overset{\ominus}{C} = O$.   1

   (b) Give retrosynthetic analysis of the following molecule –   2


   (c) Carry out the following conversion indicating proper reagents.   2
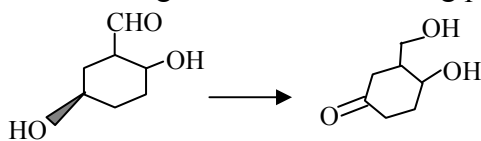
   (d) Alkaline solutions of 1-methyl-2-naphthol and 2-methyl-1-naphthol react   2
   with benzene diazonium chloride in different manner – Explain.

   (e) Predict the product of the following reaction indicating FMO interactions.   3
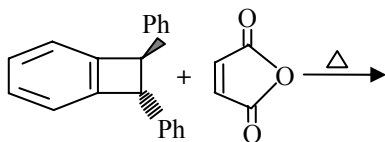
(f) Draw the structure of the major diastereoisomer in the following and justify the diastereoselectivity with appropriate model.   3
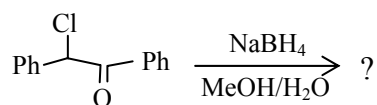
2. (a) What do you mean by illogical electrophile and illogical nucleophile? Give one example of each.   2

   (b) Mention two criteria for a good protecting group. Using protection and deprotection techniques outline the following transformations.   2+2
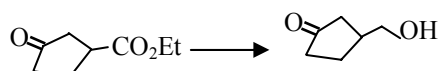

   (c) Thermal [1, 5] hydrogen shift is facile but [1, 3] hydrogen shift is not observed. Explain.   2

   (d) How will you prepare anthracene from naphthalene?   2
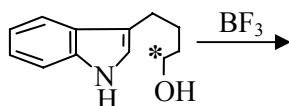   (e) How would you account for the following transformation?   3
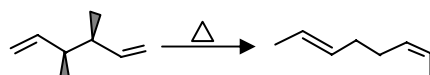
Unit-II

3. (a) How would you synthesize 2-chloro-4-methylquinolene and 4-chloro-2-methylquinoline separately from the same starting material? Explain with mechanism.   2+2

   (b) Carry out the following transformations (any *two*):   2+2

   (i) 4-methylpyridine ⟶

   (ii)

   (iii)
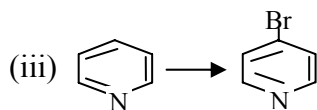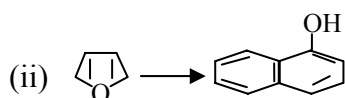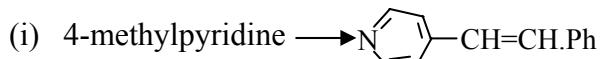
   (c) Complete the reaction and explain with mechanism.   2

(d) Arrange the following species in order of decreasing delocalization energies. Justify your choice.   2

Pyrrole, Furan, Thiophene, Benzene.

4. (a) Write down the synthesis of Sulphadiazine and mention one important use of this compound.   2+1

(b) Predict with proper justification the product(s) in the following reactions.   3

(i) $\xrightarrow[\text{NaOH}]{\text{CHCl}_3}$

(ii) $\xrightarrow{\text{NaCN}}$
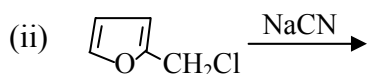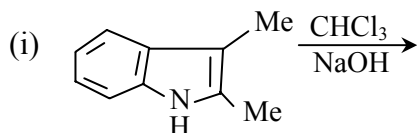
(c) What happens when quinoline and pyridine are treated with Na in liq ammonia separately? Explain with suitable mechanism.   3
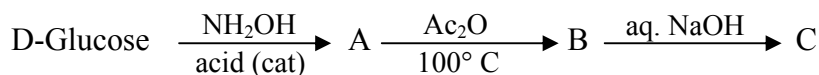
(d) Describe Fischer indole synthesis of 2-methylindole. Write plausible mechanism. How would you demonstrate which nitrogen is lost during cyclisation?   2+1

CEMAT-36-OB

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

Unit-I

5. (a) Draw the structure of L-arabinose and explain why it shows abnormal mutarotation.   1+2

(b) What is anomeric effect? Explain the fact that in dry methanol α- and β-D(+) glucose exist in equal amounts.   1+2

(c) Draw the preferred pathway of ring inversion of cyclohexane with appropriate conformations. Which symmetry element is retained along this pathway? Explain.   4

(d) Write the structures for A, B and C in the following transformation.   3

D-Glucose $\xrightarrow[\text{acid (cat)}]{\text{NH}_2\text{OH}}$ A $\xrightarrow[\text{100° C}]{\text{Ac}_2\text{O}}$ B $\xrightarrow{\text{aq. NaOH}}$ C

6. (a) Arrange the following dichlorocyclohexanes in order of decreasing amount of (a, a) form present in their conformational equilibrium. Give reasons.   3

trans-1, 4-dichlorocyclohexane, *cis*-1,3-dichlorocyclohexane, *trans*-1, 2-dichlorocyclohexane.

(b) Explain the formation of the products when D-glucose is separately allowed to react with acetone/dry HCl and benzaldehyde/dry HCl.   3

(c) β-D-glucose is oxidized to gluconolactone with bromine-water at a much faster rate than α-D-glucose. Explain.   2

(d) Which diastereomer of 4-*tert*-butylcyclohexanol undergoes faster chromic acid oxidation and why?   2

(e) How would you justify the fact that all the methyl pyranosides of α-D-hexose series have the same configuration at C–1 and C–5?   3

Unit-II

7. (a) Draw the stereoisomers of citral. Device a chemical method for the determination of the configuration of the stereoisomers of citral.   3

(b) Most amino acids form a purple product when heated with ninhydrin. Draw the mechanism for the formation of a coloured product when valine is treated with ninhydrin.   3

(c) Synthesise the tripeptide gly.phe.ala by solid phase peptide synthesis methodology. Explain the choice of protecting groups in this synthesis.   3

(d) How will you prepare phenylalanine by Erlenmeyer Azlactone synthesis?   2

(e) Give the CIP configurational descriptor of L-cysteine.   1

8. (a) What happens when ephedrine and ψ-ephedrine are heated separately with diphenylboronic acid? What structural information do you get from the above reactions?   2

(b) How would you establish by chemical reaction that geraniol and nerol have *trans*-and *cis*-configurations, respectively?   2

(c) Explain with mechanism the role of 2, 4-DNFB for the determination of N-terminal residue of a protein.   2

(d) Show how methionine residue in a polypeptide can be selectively cleaved by cyanogen bromide.   3

(e) What is isoelectric point of an amino acid? Explain why the isoelectric point of glycine is 6.0, while that of lysine is 9.5.   1+2

CEMAT-36-PA

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

Unit-I

9. (a) Consider a system following Boltzmann distribution, having two energy levels at energies zero and β^{-1}. If the lower level is non-degenerate and the upper one is doubly-degenerate, then find the probability of occupying a state of energy β^{-1}. [Given: $\beta = \dfrac{1}{k_b T}$, k_b = Boltzmann constant]   3

(b) If internal energy of a system of N molecules is U, then show that $U = Nk_b T^2 \left(\dfrac{d \ln f}{dT} \right)$ [Given : f = molecular partition function].   4

(c) At absolute zero H_3CD has residual entropy as 11.7 $JK^{-1} mol^{-1}$. Explain.   3

(d) Evaluate Einstein temperature θ_E, for diamond, for which frequency of oscillation of the atoms, ν, is 46.5×10^{12} Hz.   3

10. (a) For a system, which follows Boltzmann distribution, with one state at zero energy and another state at the energy, ε, the populations in the states tend towards equality as $T \to \infty$. Justify.   3

(b) Entropy, S, is expressed as, $S = k_b (N \ln N + \alpha' N + \beta E)$ where N = number of molecules, α' is a number and β is constant at a particular temperature. Find β.   4

(c) If the work function, A, is

$A = -Nk_b T \ln f$

then show that

$P = Nk_b T \left(\dfrac{\partial \ln f}{\partial V} \right)_T$

where N = number of molecules, f = molecular partition function.   3

(d) In adiabatic demagnetization during demagnetisation step entropy is supposed to be increased. Justify/criticise.   3

Unit-II

11. (a) Consider the first line (J = 0) in the rotational spectrum of carbon monoxide as 3.84 cm^{-1}. Find the moment of inertia and the equilibrium inter-nuclear distance.   3

(b) For the rigid diatomic molecule, the infra-red spectral absorption occurs exactly at the classical vibrational frequency. Explain. 3

(c) Calculate the relative population in the J = 1 state with respect to J = 0 state at 300 K considering B = 2 cm^{-1}. Comment on how the relative population changes with increase of J and B value. 3+1

(d) If a' vibrational mode of a molecule is Raman active then it should be infra-red inactive. Justify / criticise. 2

12.(a) In pure rotational Raman spectrum of a diatomic molecule the separation of the first line from the exciting line is 6B cm^{-1}, while that between successive lines is 4B cm^{-1}. Explain. [Given: B = rotational constant] 3

(b) For a diatomic molecule, behaving as anharmonic oscillator, the maximum vibrational quantum number, v_{max}, is given by, $v_{max} = \dfrac{1}{2\tilde{x}_e} - 1$.

($\tilde{x}_e$ is anharmonicity constant). 3

(c) The spectrum of HCl shows very intense absorption at 2886 cm^{-1}, a weaker one at 5668 cm^{-1}, and a very weak one at 8347 cm^{-1}. Calculate the fundamental frequency, ω_e and the anharmonicity constant, x_e. 3

(d) Explain the Stokes and anti-Stokes lines in Raman spectra according to the classical theory of Raman effect. 3

CEMAT-36-PB

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

Unit-I

13.(a) Define primitive unit cell. State the law of rational indices. Find out the Weiss indices and Miller indices for the plane having intercepts 2*a*, *b*, −2*c* on the respective crystallographic axes, where *a*, *b* and *c* are the primary intercepts on the axes. 1+1+1+1

(b) Using X-ray of wavelength $\lambda = 1.79 \times 10^{-8}$ cm, a metal produces reflection from the (110) plane of B.C.C. unit cells, what is edge length of the cube? 3

(c) Mention the properties of liquid crystal. 2

(d) At 0°C, the molar polarization of a liquid is 32.16 cm^3 mol^{-1} and its density is 1.92 g cm^{-3}. Calculate the relative permittivity of the liquid. 4

[Given: Molar mass of the liquid, M = 55.0 g mol^{-1}]

6

14.(a) Define 'surface excess'. Derive an equation to show the dependence of surface excess on surface tension of a two component system, stating the assumptions made. **1+4**

   (b) If the dipole moment of chlorobenzene is 1.57 D then find that for m-dichlorobenzene. **2**

   (c) The polarizability volume of NH_3 is 2.22×10^{-30} m^3; calculate the induced dipole moment of the molecule by an applied electric field of strength, 15.0 kVm^{-1}. **3**

   [Given: $\varepsilon_0 = 8.854 \times 10^{-12}$ $C^2J^{-1}m^{-1}$; 1 D $= 3.33564 \times 10^{-30}$ cm].

   (d) Molar polarization values of O_2 and CH_4 are independent of temperature while those HCl gas and CH_3Cl gas decrease with increase of temperature. Explain with proper reasons. **3**

Unit-II

15.(a) Derive thermodynamically using chemical potentials a relation between the depression of freezing point of a solvent and the molal concentration of nonvolatile solute dissolved in it pointing out the assumptions and approximations involved if any. **4+2**

   (b) Liquid carbon dioxide cannot exist at normal atmospheric pressure whatever be the temperature. Justify. **2**

   (c) The normal boiling temperature of benzene is 353.24 K, and the vapour pressure of liquid benzene is 1.19×10^4 Pa at 20.0°C. If the triple point temperature is 278 K then find the triple point pressure. **4**

16.(a) Explain Eutectic point, Eutectic temperature and Eutectic composition with the help of a phase diagram. **3**

   (b) What is an azeotropic mixture? How would you ascertain that an azeotrope is a mixture, not a compound? **3**

   (c) The molecular origin of Raoult's law is the effect of solute on the entropy of the solution. Explain qualitatively. **2**

   (d) A mixture of 100 g water and 80 g of phenol separates into two layers at 60°C. One layer, L_1, consists of 44.9% water by mass; the other L_2, consists of 83.2% water by mass. Calculate the total number of moles in L_1 and L_2. [Given: molar mass of phenol $= 94.11$ g mol^{-1}] **4**