

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

PART-III

CHEMISTRY- Honours

Paper- VI

(New and Old Syllabus)

Duration : 4 Hours

Full Marks : 100

*Candidates are required to give their answers in their own words as far as practicable.**The figures in the margin indicate full marks.*

(New Syllabus)

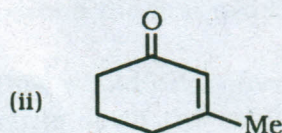
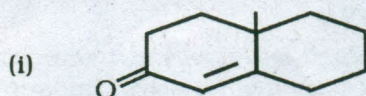
Use separate answer scripts for [CEMAT-36-OA & CEMAT-36OB]
and for CEMAT-36-PA & CEMAT-36PB]

CEMAT-36-OA

Answer two questions, taking one from each Unit.

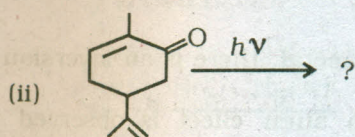
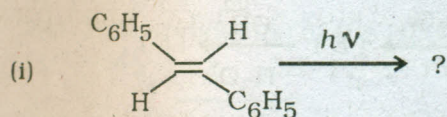
UNIT - I

1. a) Explain the terms 'synthetic equivalent' and 'functional group interconversion' with suitable examples. 3
- b) Mention two criteria for a good protecting group. 2
- c) Work backwards to devise synthetic route to the following molecules.

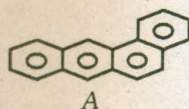


2 + 2

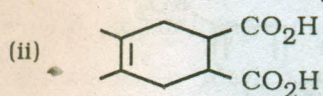
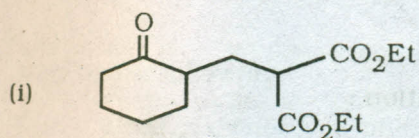
- d) Complete the following reactions from FMO considerations : $1 \frac{1}{2} + 1 \frac{1}{2}$



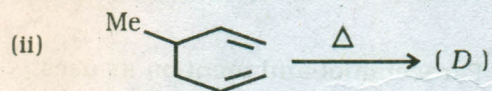
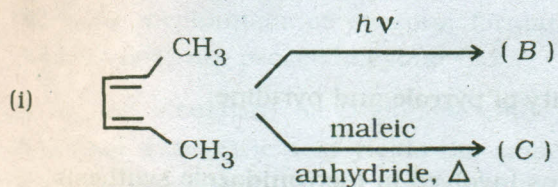
- e) Name the polynuclear hydrocarbon (A). 1



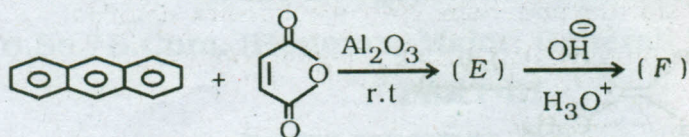
2. a) Give the retrosynthetic analysis and an efficient synthesis of the following compounds : $2 \times 1 \frac{1}{2}$



- b) Identify (B), (C) and (D) in the following reactions and explain their formation by FMO theory. 2×3



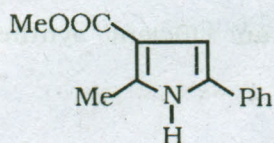
- c) Identify the products and explain the following sequences of reactions :



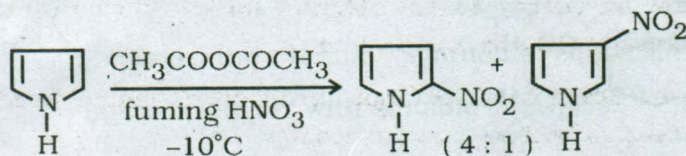
- d) In protecting an aldehyde to thioacetal, there is an inversion of polarity at the carbonyl carbon, but no such effect is observed in case of oxyacetal of the aldehyde. Explain.
- 2

Unit - II

3. a) Outline the synthesis of the pyrrole derivative.



- b) Explain the following observation :



What strategy would you take to get 3-nitropyrrole as the major product ?

- c) Compare the basicity of pyrrole and pyridine. 2
- d) Write down the steps involved in metronidazole synthesis. 2
- e) Outline the synthesis of Paracetamol and mention its uses. 3

4. a) How can you get pyrrole and furan rings by taking ethyl acetoacetate as one of the starting materials. Write mechanistic details. 3
- b) Identify the product(s) of the following reactions : 2 × 2
- (i) (ii)
- c) Carry out the following conversion with suitable mechanism (any one) :
- (i) Indole \longrightarrow Quinoline
- (ii) Pyridine \longrightarrow 4-nitropyridine. 2
- d) Write the synthesis of chloroquine and mention its use. 2 + 1

CEMAT-36-OB

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

Unit - I

5. a) Explain the following : 3 × 2
- (i) Draw an energy profile diagram for cyclohexane ring inversion maintaining a plane of symmetry.
- (ii) *cis*-4-*t*-Butyl cyclohexanol undergoes faster oxidation with chromic acid than its *trans* isomer.
- (iii) Both *cis*- and *trans*-1, 2-dibromocyclohexane, on treatment with I^- , gives cyclohexene.
- b) Give the mechanism of osazone formation from *D*-fructose. Why the reaction does not proceed beyond C-2 ? 3
- c) Write the structure of *D*-glucose and another aldohexose which on oxidation with nitric acid yields the same alderic acid. Would they form the same osazone ? 2
- d) How would you distinguish chemically between ribose and 2-deoxyribose ? 2

6. a) An aldohexose $C_6H_{12}O_6$ on reduction with Na/Hg gives *D*-sorbitol which on reaction with excess phenyl hydrazine forms one osazone, which is different from the osazone of *D*-glucose. Write the structure of the aldohexose explaining the reactions. 3
- b) Oxidation of *D*-fructose with Tollen's reagent yields a mixture of mannoic acid and *D*-gluconic acid. Account for the observation. 2
- c) Convert the following : 2 × 2
- (i) *D*-Arabinose \longrightarrow *D*-Glucose
- (ii) Glucose \longrightarrow 3-deoxyglucose.
- d) *Trans*-isomer of 4-*tert*butyl cyclohexane carboxylic acid is stronger acid than its *cis*-isomer. 2
- e) *Trans*-4-*t*-butyl cyclohexane-1-tosylate gives rise to 4-*t*-butyl cyclohexene with SPh^- rather than ^-OEt . Justify. 2

UNIT-II

7. a) Outline the chemical method for determination of C-terminal amino acid of a protein. 2
- b) Write any suitable method for synthesis of L-proline. 3
- c) Define the isoelectric point of an amino acid. 2
- d) What is special isoprene rule ? What happens when citral is heated with $KHSO_4$? 1 + 1
- e) Establish that (-) Nicotine has S-configuration. 3
8. a) How would you synthesise the tripeptide Phe-Gly-Ala applying Merrifield methodology and using *t*-butoxycarbonyl group as N-terminal protecting group ? 3
- b) Synthesise L-tryptophan by any suitable method. 3
- c) What happens when geraniol and nerol are separately treated with dil. H_2SO_4 ? Which one reacts faster and why ? 2 + 1
- d) Compare the basicities of ephedrine and ψ -ephedrine. 3

CEMAT-36PA

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

UNIT - I

9. a) Define thermodynamic probability.
- b) Deduce the relationship between entropy and thermodynamic probability.
- c) ΔG as a function of temperature for a reaction is given by $\Delta G = a + bT + cT^2$.
- (i) Show that in the limiting Zone of $T \rightarrow 0$, $b = 0$.
- (ii) Find ΔH as a function of temperature .
- (iii) Show schematically the variation of ΔG and ΔH with temperature on the same plot.
- d) Consider a system of non-interacting particles at constant temperature which are distributed in three non-degenerate energy levels in such a way that ϵ_1 , ϵ_2 and ϵ_3 energy levels consist of 4×10^{23} , 2×10^{23} and 1×10^{23} particles. Show that the energy levels are equispaced.
- $2 + 3 + (2 + 1 + 2) + 3$
10. a) Consider a system A consisting of sub-systems A_1 and A_2 , for which $\omega_1 = 1 \times 10^{20}$ and $\omega_2 = 2 \times 10^{20}$. What is the number of configurations available to the combined system ? Also compute the entropies S_1 , S_2 and S for the sub-systems A_1 , A_2 and the system A respectively. What is the significance of the result ?
- b) State and explain the third law of thermodynamics. Draw a curve showing the variation of entropy when a solid (at temperature T) is heated to form vapour at temperature T_1 ($T_1 >$ boiling point). How would you determine the absolute entropy of the substance in the vapour phase at temperature T_1 ?
- c) Show that $S = N.k_B \ln Q + E/T$. 4 + 6 + 3

UNIT - II

11. a) Which of the following molecules are IR active ? Give reasons.
 H_2 , CO_2 (symmetric stretching), HCl, HD.
- b) How does pure rotational spectrum provide information about the bond length of a diatomic molecule ? Discuss with the help of an example.
- c) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centred at 1876.06 cm^{-1} and 3724.20 cm^{-1} , respectively. Evaluate the equilibrium vibration frequency, the anharmonicity and force constant of the molecule. What will be the value of zero point energy ? $4 + 4 + 4$
12. a) Define a harmonic oscillator. Write down the value of its potential energy (U) as a function of displacement (q) from mean position. Draw U vs q curve. Show the effect of anharmonicity on the potential energy diagram.
- b) Establish the condition for a molecule to be Raman active. Define Stokes and anti-Stokes lines.
- c) State the 'rule of mutual exclusion'. $(2 + 1 + 1 + 1) + (3 + 2) + 2$

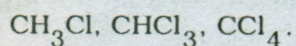
CEMAT - 36PB

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

UNIT-I

13. a) State Haüy's law of rational intercepts.
- b) Deduce Bragg's law $n\lambda = 2d \sin\theta$.
- c) Explain why the distance between two successive hkl planes for a cubic system cannot be $a/\sqrt{7}$ where a is the length of the edge of the cube.
- 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 of 26 : 34 : 37. $2 + 4 + 3 + 4$
14. a) Write down four differences between physisorption and chemisorption.
- b) Draw diagram showing variation of surface tension of aqueous solutions of the following substances with concentration :
- (i) Sodium chloride
- (ii) Sodium dodecyl sulphate.
- Explain using Gibbs adsorption isotherm.

- c) Arrange with explanation the following molecules in order of increasing dipole moments :



- d) Find the C.G.S unit of $\mu^2/3kT$.
- e) Write down BET isotherm for multilayer adsorption. $2 + 4 + 3 + 2 + 2$

UNIT-II

- a) Derive thermodynamically a relation between the depression of freezing point of a solvent and the concentration of a non-volatile solute dissolved in it, pointing out the assumptions and approximations.

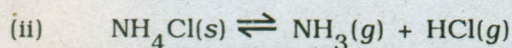
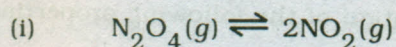
- b) What is van't Hoff factor ? Why is it introduced ?

- c) Define number of components and degrees of freedom of a system.

- d) At atmospheric pressure iodine sublimes but sulphur melts. Explain.

$6 + 2 + 2 + 2$

- a) Write down the number of components, number of phases and evaluate the degrees of freedom for the following equilibria :



when some $\text{NH}_4\text{Cl}(s)$ and $\text{NH}_3(g)$ is taken in a closed vessel and allowed to equilibrate.

- b) Explain eutectic point, eutectic temperature and eutectic composition with the help of a phase diagram.

- c) State Konowaloff rule and establish it from Duhem-Margules equation.

- d) 1 gm of urea [$M = 60$] dissolved in 100 gm of a solvent decreases its freezing point by 0.2°C . 1.6 gm of an unknown solute dissolved in 80 gm of the same solvent decreases the freezing point by 0.36°C . Calculate the molecular weight of the unknown solute. $3 + 2 + 3 + 4$

(Old Syllabus)

Duration : 4 Hours

Full Marks : 100

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

The figures in the margin indicate full marks.

Use separate answer scripts for Group A and Group B.

Group-A

(Full Marks - 50)

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

UNIT - I

1.
 - a) Give a scheme for isolation of Pt-metal or Ni-metal from its natural sources, stating the chemical reactions involved in different steps. 6
 - b) How are the following compounds prepared ? State their uses.
 - (i) Prussian blue
 - (ii) Sodium cobaltinitrite. $2 \times (2 + 1)$
 - c) Discuss the trends in the variation of the following properties across the period of 3d series :
 - (i) Complex formation for M^{2+} ions.
 - (ii) Redox potentials for $M/M^+(aq)$ system. $2 + 2$
2.
 - a) Explain the principle of separation of lanthanides by ion-exchange method. 4
 - b) Give example of one compound of transition metals in the negative oxidation state. 1
 - c) What happens when —
 - (i) gold chloride solution is treated with stannous chloride ? Give equation. 2

- (ii) Co(II) acetate is treated with ammonium thiocyanate in presence of HgCl_2 in aqueous solution ? 2
- d) Starting from hydrated nickel(II) chloride how will you prepare $\text{K}_2[\text{Ni}(\text{CN})_4]$? Give one example of its application in chemical analysis. 3
- e) Compare between the lanthanides and the actinides in respect of their electronic configuration. 4

UNIT-II

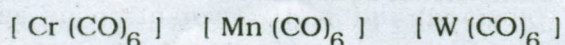
3. a) Which of the following pairs of complex has higher 10 Dq value and why ? 3
- (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Rh}(\text{NH}_3)_6]^{3+}$
- (ii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
- (iii) $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3+}$
- b) Draw all the optical and geometrical isomers of the following species : 4
- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{+2}$; $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
- (en \longrightarrow $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$)
- c) Diamagnetic complexes of cobalt (III) such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NO}_2)_6]^{3+}$ are orange-yellow. In contrast paramagnetic complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ are blue. Explain qualitatively the difference in colour. 2
- d) Room temperature magnetic moment of Cu(II) sulphate pentahydrate is almost equal to the spin only moment of Cu(II), whereas, that of Cu(II) acetate monohydrate is usually lower. Explain why. 4
- e) While $\text{Fe}^{3+}(\text{aq})$ ion reacts rapidly with EDTA at room temperature but $\text{Cr}^{3+}(\text{aq})$ reacts slowly. Explain why. 3

- f) The position of CO in the spectrochemical series is higher compared to CN^- . Explain. 2
4. a) Starting from $\text{K}_2[\text{PtCl}_4]$ design syntheses of *cis*- and *trans*-isomers of $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ explaining the principle involved therein. 4
- b) Explain the nature of Jahn-Teller distortion expected for an octahedral complex of d^9 system. 4
- c) Cr^{2+} and V^{2+} give intensely coloured complexes with dipyriddy (or bipyridyl) and 1, 10 phenanthroline and not with simple unsaturated π -acceptor ligands like CO, C_2H_4 etc. Explain why. 2 + 2
- d) The stepwise formation constants for complexes in general follow the order $k_1 > k_2 > k_3$ but for Fe^{2+} with 1,10-phenanthroline complex the order is $k_1 > k_2 < k_3$. Explain. 2
- e) Formulate expressions for CFSE for complex ions $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Mn}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$. 1 x 4

UNIT-III

5. a) Using 18-electron rule as a guide find the number of metal-metal bonds in the following :
- (i) $\text{Co}_4(\text{CO})_{12}$
- (ii) $\text{Os}_3(\text{CO})_{12}$
- (iii) $\text{Rh}_6(\text{CO})_{16}$. 3

- b) Explain the term 'co-operative effect' with respect to the oxygen transport in hemoglobin and point out the role of metal ion involved. 4
- c) Write a brief account on Na^+ and K^+ ions transport across biological membrane. 4
- d) What are fluxional molecules? Give one example. 2
- e) Explain the carbonyl stretching frequencies $[\bar{\nu}(\text{CO}), \text{cm}^{-1}]$ in the following compounds: 3



$[\bar{\nu}(\text{CO}), \text{cm}^{-1}]$	2000	1984	1960
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6. a) Write brief notes on any *two* of the following: 2 x 4
- Platinum complexes as anticancer drugs.
 - Biological nitrogen fixation
 - Cytochrome.
- b) Define oxidative addition reaction. What type of compounds generally undergo this type of reactions? 2
- c) How would you oxidise ferrocene to ferricenium ion? Show the structure of ferrocene and provide a chemical evidence that indicates free rotation of the cyclo-pentadiene rings about the metal axis. 2 + 4

Group-B

[Full Marks - 50]

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

7. a) Define systematic and random error in chemical analysis. Convert the binary number 10101 to its decimal equivalent. What are the functions of an operating system ? 2 + 1 + 2
- b) Write a short note on neutron activation analysis. 4
- c) State Nernst equation. Mention its use in potentiometric titrations. 3
- d) Describe the principle of the spectrophotometric estimation of phosphorus. 4
- e) Discuss the working principle of atomic absorption spectroscopy. 2
8. a) What do you mean by accuracy and precision in quantitative analysis ? Find the mean deviation and standard deviation of the following analytical results :
15.67, 15.69 and 16.03 2 + 2
- b) How is the pH of a solution measured ? Discuss the nature of the curve for the conductometric titration of a mixture of a weak acid and a strong acid by a strong base. 2 + 3
- c) State the principle of estimation of potassium in water sample by atomic emission spectroscopy. 3
- d) What are the input and the output devices of a computer ? Differentiate between hardware and software of a computer. 2 + 2
- e) Mention the common hazards of radiation. 2

UNIT-II

9. a) Describe the principle of gravimetric estimation of sulphate explaining gravimetric factor. 4
- b) Discuss in brief the principle of estimation of Fe^{3+} and Al^{3+} in a mixture by complexometric method. 4
- c) Describe the estimation of the following : 4
- (i) As in water
- (ii) NH_4^+ ion in soil.
- d) State the principle of Argentimetric estimation of chloride. Mention the indicator used for this estimation. 4
10. a) What is Zimmerman Reinhardt reagent ? Explain its function in the estimation of iron. 1 + 3
- b) Mention the composition of dolomite. How would you estimate its constituents ? 1 + 3
- c) Mention the constituents of the following and briefly discuss the basic principle to estimate them (any one) :
- (i) Dolomite
- (ii) Brass. 2 + 2
- d) Calculate the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$. Find the amount (ml) of conc. H_2SO_4 (36N) to prepare 250 ml of (N/10) H_2SO_4 solution. 2 + 2

UNIT-III

11. a) Compare the advantages and disadvantages of thin layer and column chromatography. 3

- b) State the principle of estimation of the following (any three) : 3×3
- (i) Glucose
 - (ii) Urea
 - (iii) BOD in water
 - (iv) CO in air.
- c) Write short note on any one of the following : 2
- (i) Partition co-efficient
 - (ii) Fractional distillation.
- d) What do you mean by R_f value in chromatographic separation ? 2
12. a) State the principle of ion-exchange chromatography. Give one example of cation exchange resin. $2 + 1$
- b) Give the scheme for recovery of coal-tar based chemicals by fractional distillation method. 4
- c) State the principle of estimation of the following (any three) : 3×3
- (i) Vitamin-C
 - (ii) Formalin
 - (iii) SPM in air
 - (iv) H_2S in air.
-