

WBCS MADE EASY

MWC(O)-CH-II/23

2023

CHEMISTRY

PAPER-II

Time Allowed — 3 Hours

Full Marks — 200

If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.

Answer may be given either in English or in Bengali but all answers must be in one and same language.

(Attempt any ten questions at least three from each group.)

Group-A

1. (a) In the phase diagram solid-liquid line slopes slightly to the right for carbon dioxide but that leans slightly to the left for water. Explain stating appropriate equation. 4
- (b) If a polymer sample contains an equal number of moles of species with degree of polymerization $X = 1, 2, 3, 4, 5, 6, 7, 8, 9$ and 10 . What are the number average and weight average degrees of polymerization? 4
- (c) The radioactive nuclide X has two decay modes (both first order): $X \rightarrow B$ and $X \rightarrow C$, with decay constant k_1 and k_2 respectively. Express $t_{1/2}$ of X in terms of k_1 and k_2 . 4
- (d) A first order reaction is 75% complete in 32 minutes. Calculate its half-life ($t_{1/2}$). 4
- (e) State the essential requirement for a molecule to be microwave active. Obtain an expression for the line spacing in the microwave spectra of a diatomic rigid rotor. 4
2. (a) Draw the labelled phase diagram of H_2O system and describe it. At atmospheric pressure, iodine sublimates but sulphur melts. Explain. 2+3+2
- (b) Write down the BET equation of adsorption explaining the terms involved and hence state the principle of determination of the surface area of a finely divided solid. 5
- (c) State the basic principles of Transition State Theory. If the activation energy for the gaseous reaction $H_2 + I_2 \rightarrow 2HI$ is 167 kJ and the ΔH for the reaction is -8.2 kJ, what is the activation energy for the decomposition of HI ? 4+4

WBCS MADE EASY

MWC(O)-CH-II/23

(2)

3. (a) The quantum yield of CO in the photolysis of gaseous acetone ($P < 6$ kPa) at wavelengths between 250-320 nm is unity. After 20 min irradiation with light of 313 nm wavelength, 18.4 cm^3 of CO (measured at 1008 Pa and 22°C) is produced. Calculate the number of quanta absorbed and the absorbed intensity in joules per second. 4
- (b) A polymer sample contain equal masses of particles with molecular weights 10,000 and 20,000. Calculate the number average (\overline{M}_n) and the weight average (\overline{M}_w) molecular weight of the polymer. How can you express the specific viscosity of a polymer solution (η_{sp}) in terms of η and η_0 , where η represents the viscosity of polymer solution and η_0 represents the viscosity of pure solvent? 4+2
- (c) The rotational constant B of ^{16}O molecule is $55.35 \times 10^9 \text{ s}^{-1}$ and the equilibrium bond length is $1.128 \times 10^{-10} \text{ m}$. Find the isotopic mass of ^{16}O atom. 5
- (d) With the help of Jablonski diagram, show the various photophysical processes through which a molecule in excited singlet state (S_2') can return to the ground singlet state (S_0). [v indicates vibrational level, other terms have their usual significance] 5
4. (a) In any solution for which Raoult's law is applicable to the solvent, Henry's law must hold for the solute, over the same concentration range. — Explain. Four phases of sulphur cannot exist simultaneously at equilibrium. — Justify or Criticize. 4+2
- (b) How can the molecular weight of macromolecules be determined by viscometry? 5
- (c) The gas phase reaction $2A \rightarrow B + C$ is bimolecular with an activation energy of $24000 \text{ cal mol}^{-1}$. The molecular weight and diameter of A are, respectively 60 and 3.5 angstrom. After deducing the necessary equation using the Collision theory of reaction rate, calculate the value of rate constant at 300 K (Assuming steric factor = 1). 4
- (d) What is the polydispersity index of a polymer sample containing 200 molecules each of molecular weight $10,000 \text{ g mol}^{-1}$, 300 molecules each of molecular weight $30,000 \text{ g mol}^{-1}$ and 500 molecules each of molecular weight $50,000 \text{ g mol}^{-1}$? 5
5. (a) Do the wavelength of light used and the width of the cell have any influence on (i) optical density and (ii) molar extinction coefficient? Explain photosensitized reactions and give an example of photosensitized reaction which is useful to mankind. 5+3
- (b) Write down the expression of temperature dependent Arrhenius equation on reaction rates, explaining the terms involved. How do you define 'energy of activation' for a chemical reaction? 2+2

For guidance of WBCS Prelims , Main Exam and Interview by WBCS Gr A Officers/ Toppers & Experts, WBCS Prelims and Main Mock Test (Classroom At Kolkata, Siliguri & Other Places & Online), Optional Subjects, Study Materials, Correspondence Course, etc. Call WBCSMadeEasy™ at 8274048710 / 85858543673 / 9674493673 (Sir) or mail us at mailus@wbcsmadeeasy.in. Download WBCS MADE EASY app from play store. Miscellaneous Service, Clerkship & other WBPSC Courses & Mock Test available from WBCS MADE EASY. Visit www.wbcsmadeeasy.in

WBCS MADE EASY

(3)

MWC(O)-CH-III/23

(c) Which of the following molecules are IR-active? Give reasons.

H₂, CO₂, HCl.

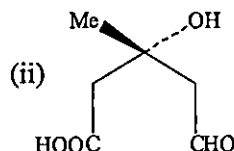
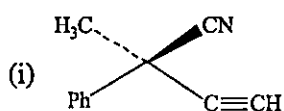
6

(d) Adsorption of a gas by solid is an exothermic process. — Justify or Criticize.

2

Group-B

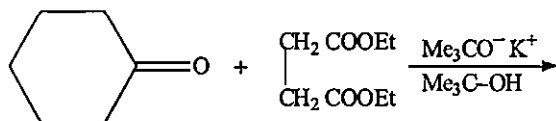
6. (a) Assign R/S descriptors of the following compounds indicating priority sequences. 2+2



(b) Pure (–) enantiomer of an optically active compound 'A' has a specific rotation of $[\alpha]_D^{20} = -44.8^\circ$. What is the optical purity of a sample of A, which shows a specific rotation of -26.88° ? How much of each enantiomer is present in the enantiomeric mixture? 4

(c) Predict the most stable conformation of 1-methyl-1-phenylcyclohexane. 4

(d) Predict the product and carry out the following Stobbe condensation reaction. 4



(e) 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? 4

7. (a) Draw the Fischer, Sawhorse and Newman projection formulae (Staggered) of CH₂OH–CHCl–CHBr–CHO. 3

(b) Draw the Newman projection formulae of 2,3-butanediols in their most stable conformations with proper reason. 5

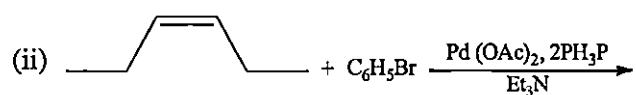
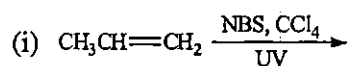
WBCS MADE EASY

MWC(O)-CH-II/23

(4)

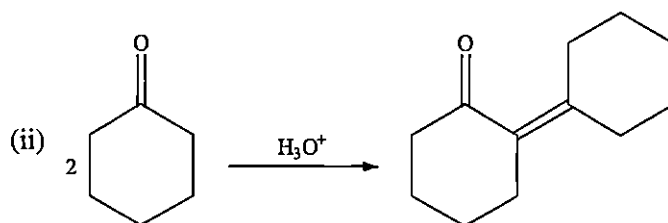
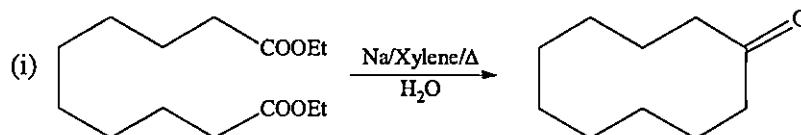
(c) Predict the product(s) with mechanism.

6+6



8. (a) Write down the mechanism of the following reaction.

5+5



For guidance of WBCS Prelims , Main Exam and Interview by WBCS Gr A Officers/ Toppers & Experts, WBCS Prelims and Main Mock Test (Classroom At Kolkata, Siliguri & Other Places & Online), Optional Subjects, Study Materials, Correspondence Course, etc. Call WBCSMadeEasy™ at 8274048710 / 85858543673 / 9674493673 (Sir) or mail us at mailus@wbcsmadeeasy.in. Download WBCS MADE EASY app from play store. Miscellaneous Service, Clerkship & other WBPSC Courses & Mock Test available from WBCS MADE EASY. Visit www.wbcsmadeeasy.in

WBCS MADE EASY

(5)

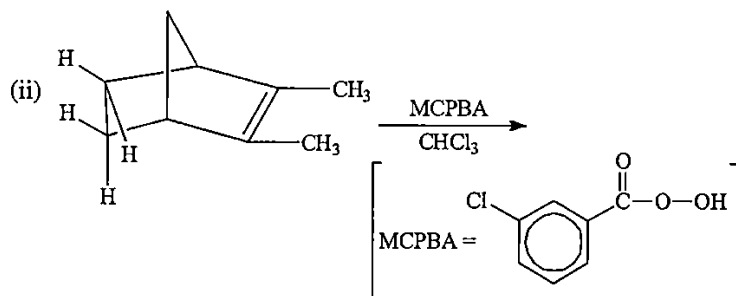
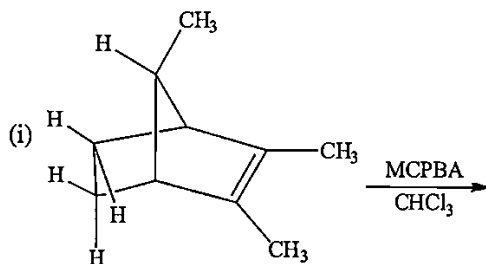
MWC(O)-CH-II/23

- (b) Using correlation orbital diagram show that thermal dimerisation of ethylene to cyclobutane is a disallowed interaction. 10

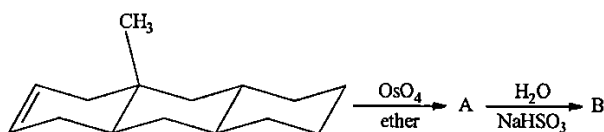
9. (a) Draw the two conformations of 1,3-butadiene. Which one of them is more stable? Give your reasoning. 3

- (b) Arrange the staggered conformations of 2,3-dimethylbutane in order of decreasing energy. 2

- (c) Predict the major and minor products in each of the following reactions and give the reasonings. 4



- (d) Identify the product (with Stereochemistry if appropriate) obtained in each step of the following reaction sequences: 3



For guidance of WBCS Prelims , Main Exam and Interview by WBCS Gr A Officers/ Toppers & Experts, WBCS Prelims and Main Mock Test (Classroom At Kolkata, Siliguri & Other Places & Online), Optional Subjects, Study Materials, Correspondence Course, etc. Call WBCSMadeEasy™ at 8274048710 / 85858543673 / 9674493673 (Sir) or mail us at mailus@wbcsmadeeasy.in. Download WBCS MADE EASY app from play store. Miscellaneous Service, Clerkship & other WBPSC Courses & Mock Test available from WBCS MADE EASY. Visit www.wbcsmadeeasy.in

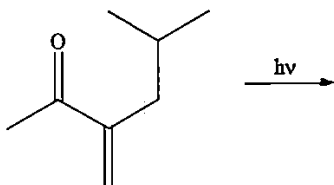
WBCS MADE EASY

MWC(O)-CH-II/23

(6)

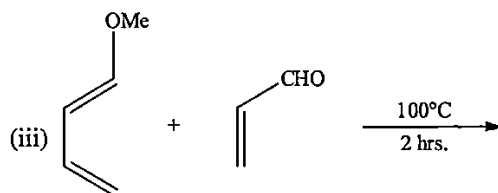
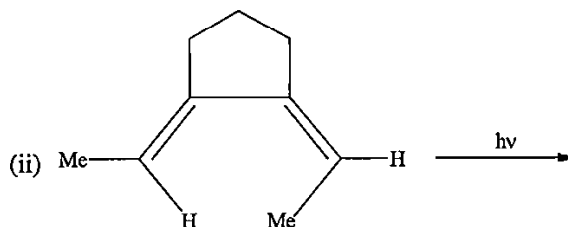
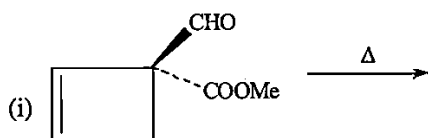
(e) Complete the following photochemical reaction with mechanism.

8



10. Predict the product(s) in the following reactions. Explain their formation.

4×5=20

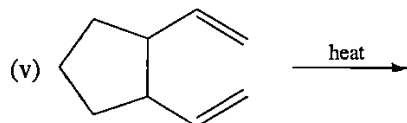
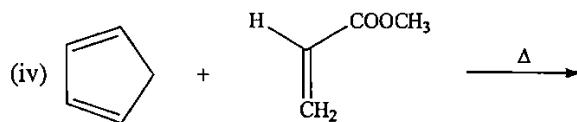


For guidance of WBCS Prelims , Main Exam and Interview by WBCS Gr A Officers/ Toppers & Experts, WBCS Prelims and Main Mock Test (Classroom At Kolkata, Siliguri & Other Places & Online), Optional Subjects, Study Materials, Correspondence Course, etc. Call WBCSMadeEasy™ at 8274048710 / 85858543673 / 9674493673 (Sir) or mail us at mailus@wbcsmadeeasy.in. Download WBCS MADE EASY app from play store. Miscellaneous Service, Clerkship & other WBPSC Courses & Mock Test available from WBCS MADE EASY. Visit www.wbcsmadeeasy.in

WBCS MADE EASY

(7)

MWC(O)-CH-II/23



Group-C

11. (a) What would be the spin only magnetic moment value of Mn^{2+} in $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2$? 4
 (b) Account for the observation that two separate water exchange rates are found for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution. 4
 (c) Draw the facial and meridional isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. 2+2
 (d) Give examples of one doubly bridging and one triply bridging nitrosyl compounds. 4
 (e) Write a short note on active transport across the membranes. 4
12. (a) F-Xe-O angle in XeOF_4 is nearly 90° . — Justify. 4
 (b) Explain the order of LMCT transition energies: $\text{MnO}_4^- < \text{TcO}_4^- < \text{ReO}_4^-$ 4
 (c) Draw the structures of the isomers of $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ and indicate the types of isomerism. 6
 (d) The mean pairing energy (p) of $[\text{Cr}(\text{H}_2\text{O})_6]^{+2}$ ion is found to be 23500 cm^{-1} . The magnitude of Δ_0 is 13900 cm^{-1} . Calculate the CFSE for this complex ion for both high spin and low spin state. 3+3
13. (a) Which of the following two complexes $[\text{Co}(\text{NH}_3)_6]^{+3}$ and $[\text{Fe}(\text{NH}_3)_6]^{+3}$ is labile and inert? Cite an example of coordination isomer. 2+2
 (b) Define the term 'oxidative addition reaction'. What condition must be met for such a reaction to occur? 4+2
 (c) Comment on the different V-C bond lengths in $[\text{V}(\text{CO})_6]$ and $[\text{V}(\text{CO})_6]^-$ compounds. 4
 (d) Give an example of each trace elements and ultratrace elements of metal ion in biological system. Mention any two biological function of redox-active transition metals such as copper (Cu) and iron (Fe). 2+2+2

For guidance of WBCS Prelims , Main Exam and Interview by WBCS Gr A Officers/ Toppers & Experts, WBCS Prelims and Main Mock Test (Classroom At Kolkata, Siliguri & Other Places & Online), Optional Subjects, Study Materials, Correspondence Course, etc. Call WBCSMadeEasy™ at 8274048710 / 85858543673 / 9674493673 (Sir) or mail us at mailus@wbcsmadeeasy.in. Download WBCS MADE EASY app from play store. Miscellaneous Service, Clerkship & other WBPS Courses & Mock Test available from WBCS MADE EASY. Visit www.wbcsmadeeasy.in

WBCS MADE EASY

MWC(O)-CH-II/23

(8)

14. (a) Explain why $\text{Ni}(\text{CO})_4$ is tetrahedral while $\text{Ni}(\text{CN})_4^{2-}$ is square planar? 3+3
(b) Explain why $[\text{Ni}(\text{en})_3]^{2+}$ is more stable than $[\text{Ni}(\text{NH}_3)_6]^{2+}$? 4
(c) Describe ambidentate ligand with proper examples. 4
(d) Write the formula of pentaammine(dinitrogen)ruthenium(III)chloride. The high-spin d^4 complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile, but the low-spin d^4 complex ion $[\text{Cr}(\text{CN})_6]^{4-}$ is inert. —Explain. 2+4
15. (a) Using 18 electron rule as a guide find the number of metal-metal bonds in the following compounds:
 $\text{Co}_4(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$ 2+2+2
(b) Compare C–C bond length in $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ and $[\text{PtCl}_3(\text{C}_2\text{F}_4)]^-$. 4
(c) Give one example of each non-heme electron transfer protein and heme electron transfer protein. Also comment on the number of metal centre(s) present in the active site structure of the proteins. 2+2
(d) What is the role of globin protein in hemoglobin? What are the effects of Zn deficiency? 4+2
-

For guidance of WBCS Prelims , Main Exam and Interview by WBCS Gr A Officers/ Toppers & Experts, WBCS Prelims and Main Mock Test (Classroom At Kolkata, Siliguri & Other Places & Online), Optional Subjects, Study Materials, Correspondence Course, etc. Call WBCSMadeEasy™ at 8274048710 / 85858543673 / 9674493673 (Sir) or mail us at mailus@wbcsmadeeasy.in. Download WBCS MADE EASY app from play store. Miscellaneous Service, Clerkship & other WBPSC Courses & Mock Test available from WBCS MADE EASY. Visit www.wbcsmadeeasy.in