

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 2nd Semester Examination, 2023

CEMACOR04T-CHEMISTRY (CC4)

ORGANIC CHEMISTRY-II

Time Allotted: 2 Hours

Full Marks: 40

2

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.

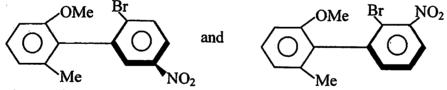
Answer any three questions taking one from each unit

Unit-I

- 1. (a) All compounds having enantiotopic ligands are achiral, justify.
 - (b) Write down the structure of the alcohol produced by the attack of hydride (H⁻) 3 ion on 2-butanone from its *si*-face and find the absolute configuration.
- (c) Designate (R/S) configuration to the following compounds.

(i) Me CO₂Et (ii) Br C=C=C H (iii)
$$\frac{Me}{H}$$
 COOH (iii) $\frac{Me}{H}$ $\frac{Me}{H}$ COOH

(d) Which of the compound will undergo faster racemisation and why?



- (e) Draw the qualitative potential energy profile of 2-chloroethanol and identify the most stable conformer with reasoning.
- 2. (a) Identify H_a and H_b as homotopic, enantiotopic or diastereotopic ligands with proper reason.

(i)
$$H_a$$
 (iii) H_a (iii) H_b (iiii) H_b (iii) H_b H_b H_b H_b H_b H_b H_b H_b

- (b) Draw the *anti*, gauche and eclipsed conformations of 1, 2-dichloroethane.
- (c) What is atropisomerism?
- (d) Define torsional angle. What is the basic difference between dihedral angle and torsional angle?
- (e) What is the most stable conformation of 1, 3-butadiene and why?

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Unit-II

- 3. (a) Salicylic acid is much stronger than p-hydroxy benzoic acid but acidity of o-nitrophenol and p-nitrophenol is almost same — Explain.
- 3

(b) Which one of the following is more basic and why?

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(c) Qualitatively compare and explain the acidity of following compounds:

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(i) $HC \equiv C - COOH$ (ii) $CH_2 = CH - COOH$ (iii) CH_3CH_2COOH

- 3
- (d) Heat of formation, ΔH of the following two reactions are almost same, but the second reaction is more facile, why?

- (i) $CH_3COOH + EtOH \xrightarrow{\Delta} CH_3COOEt + H_2O$
 - OH = Dry HCI OH = OO OOO

(e) Which one of the following pairs has got higher enol content? Explain.

(ii) HO

4. (a) $CH_3COCH_3 + Br_2 \xrightarrow{OH^-} BrCH_2COCH_3$ $CD_3COCD_3 + Br_2 \xrightarrow{CD_3} BrCD_2COCD_3$

- 3
- Given $k_H/k_D \simeq 7.0$. Explain the above reaction indicating the rate determining step. (b) Acetamide is weakly basic but phthalimide is sufficiently acidic, justify your
- 2

answer with relevant resonating structures.

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(c) What is nucleophilic catalyst? Give example and application.

- (d) "(E)-HO₂CC = CHCO₂Na is a stronger base than it's (Z)-isomer" Explain. (e) What is secondary kinetic isotopic effect? Give an example.
- 2 2

(f) Calculate ΔH (Enthalpy change) for the following reaction:

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- $H_3C C = C CH_3 H_3C C CH_3$ $CH_3 CH_3 CH_3 CH_3$ $CH_3 CH_3 CH_3$
- C = C bond energy = 145 kcal / mole
- C C bond energy = 83 kcal / mole
- C H bond energy = 99 kcal / mole
- H H bond energy = 103 kcal / mole

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Unit-III

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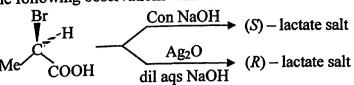
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5. (a) Account for the following observations with mechanism:



- (b) Write down the structure of the products when (S)-1-phenylethanol is separately treated with SOCl₂/Et₂O and SOCl₂/pyridine. Explain the formation of the product(s).
- (c) Give the mechanistic interpretation of the following observation: (+) $-C_6H_{13}CH(CH_3)Cl$ $20\% H_2O$ (±) $C_6H_{13}CHMeOH$ Racemic-2-Octanol
- (d) Explain the following reactions with mechanism: Explain the folio $\frac{Cl_2}{ClCH_2CH(CH_3)_2} + \frac{Cl_2}{300^{\circ}C} (CH_3)_3C - Br + \frac{Br_2}{127^{\circ}C} (CH_3)_3C - Br + (CH_3)_2CHCH_2Br$ $\sim 98\% \sim 2\%$

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(e) Write down the structure of product [X] of the following reaction with proper 2 stereochemistry and reaction mechanism.

- 6. (a) Reaction of alkyl halide with NaCN yields mainly alkylcyanide (RCN) whereas reaction with AgCN yields isocyanide compounds (RNC) — Explain.
 - (b) Write the product(s) in the following reaction with proper mechanism. 2

- (c) Indicate the products obtained from the following reactions showing the $2\frac{1}{2} \times 2 = 5$ mechanism involved:
 - (i) $Me_2CH CHBrMe \xrightarrow{\Theta OH}$ (ii) $Me_2CH CH Me \xrightarrow{\Theta OH}$
- (d) The rate of reaction of EtCl with KI-acetone mixture decreases with increased 2 percentage of water in the mixture — Give reason for the fact.
- (e) What is the advantage of using crown ether in a substitution reaction? Explain 2 with any suitable example.



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B.Sc. Honours 2nd Semester Examination, 2023

CEMACOR03T-CHEMISTRY (CC3)

INORGANIC CHEMISTRY-I

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

<u>Unit-I</u>				
1.	(a)	Compare the radial distribution plots for $2s$ and $2p$ orbitals and hence comment on their relative penetrating power.	3	
	(b)	Find out the ground state term symbol for Co ²⁺ and Cr ²⁺ ions.	2	
	(c)	Identify the possible Bohr-Sommerfeld orbits for $n = 1$.	2	
	(d)	In an atom the angular momentum of an electron is $\sqrt{6} h/2\pi$. What will be the minimum value of the principal quantum number of the electron?	2	
	(e)	Calculate the uncertainty in position of an electron whose velocity is 3.0×10^4 cm s ⁻¹ and accuracy upto 0.001%. Mass of an electron = 9.1×10^{-28} g.	2	
2.	(a)	Apply Pauli's exclusion principle to predict the maximum capacity of <i>p</i> -subshell for accommodating electrons.	2	
	(b)	Why de Broglie's wave equation has no significance for a macroscopic particle?	1	
	(c)	Show that the de-Broglie wavelength of the electron in the first Bohr orbit of the hydrogen atom is $2\pi a_0$ (where a_0 = First Bohr radius).	2	
	(d)	"Though the $(n+1)$ rule to determine the order of energy of different subshells is useful in most cases, there are some exceptions" — Justify the statement with an example.	2	
	(e)	Calculate the frequency of radiation emitted when an electron jumps from the third to the first Bohr orbit. [Rydberg Constant = 109677 cm ⁻¹].	2	
	(f)	Deduce the expression for energy of a Hydrogen like atom in SI unit.	2	
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<u>Unit-II</u>				
3.	(a)	Rationalize the electron affinity trend of C, N and O atoms:	2	
		C N O		
		122 –20.3 141 (in KJ mole ⁻¹)		
		•		

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(b) Calculate the oxidation state of Tl in Tll ₃ and justify your answer.		
(c) Atomic radii of Nb and Ta are almost identical. Comment	2	
(d) The Cl-O bond length in ClO ₂ is 141 pm while that in ClO ₂ is 148 pm. Explain.	2	
	2	
4. (a) What is meant by ionic radius? Discuss with example the Pauling's method of determination of univalent radii applicable for isoelectronic ion pairs.(b) Rationalise the trends in ionization energy in the following cases:	1+2	
Elements r: 5	2	
First ionisation energy (ey) 5.20	2	
(c) The F-F bond distance in F ₂ is 141.2		
(c) The F-F bond distance in F ₂ is 141.3 pm. Calculate Allred-Rochow electronegativity of fluorine using Slater's rule.	3	
<u>Unit-III</u>		
5. (a) What is Hammett acidity function, H_0 ? How can you define super-acid on its basis? What happens when SbF ₅ is added to HSO ₃ F?	3	
(b) What will be the pH of the solution obtained by mixing 10 ml of 0.2 (N) KOH with 30 ml of 0.1 (N) CH ₃ COOH? $K_a = 2 \times 10^{-5}$.	3	
(c) Predict which way the reactions will go in the gas phase with explanation		
(F) III I IVal	2	
(ii) $TiF_4 + 2TiI_2 \rightarrow TiI_4 + 2TiF_2$		
(d) When 0.05 mole of NaOH was added to one litre of a buffer solution, its pH changed from 5.70 to 5.85. Find the buffer capacity.	2	
6. (a) Draw the acid-base neutralization curves for the titration of(i) HCl Vs. NaOH		
(ii) CH ₃ COOH Vs. NaOH	3	
Evaloin your chairs of the		
(b) What is the pH of 10^{-3} M agueous solution of $\lambda V = 0$		
(b) What is the pH of 10 ⁻³ M aqueous solution of NH ₄ OH? Given K _b = 1.85×10 ⁻⁵ M (c) Arrange RF ₂ RCl ₂ RP ₃ RU is at 2.5°C.		
 (c) Arrange BF₃, BCl₃, BBr₃, BI₃ in order of their Lewis acidity with justification. (d) Identify the structural difference between H₃PO₃ and H₂A₂O₃. 	2	
 (c) Arrange BF3, BCI3, BBr3, BI3 in order of their Lewis acidity with justification. (d) Identify the structural difference between H3PO3 and H3AsO3 using Pauling's rule. [Given pKa (H3PO3) ~ 2.0; pKa (H3AsO3) ~ 9.0] 		
[Given pk _a (H ₃ PO ₃) ~ 2.0; pK _a (H ₃ AsO ₃) ~ 9.0] using Pauling's rule.	3	
	2	
<u>Unit-IV</u>		
7. (a) What is comproportionation reaction? Give example.	·	
 (a) What is comproportionation reaction? Give example. (b) "Addition of phosphoric acid is essential in the titration of Fe²⁺ ion with (Given: E⁰ and the E = 1.33 years E⁰ 	1	
(Given: $E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0 = +1.33 \text{ volt}, E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = +0.77 \text{ volt},$	2	
E^0 for $Ind_{ox}/Ind_{red} = +0.76 \text{ V}$		

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(c) Discuss the role of Zimmerman-Reinhardt reagent in the titration of Fe2+ by KMnO₄ in HCl medium.

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(d) Calculate the redox potential values at the following three stages of titration of 0.1 (N) Fe²⁺ and 0.1 (N) KMnO₄ in 1 (N) H₂SO₄ medium

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- (i) $25 \text{ ml Fe}^{2+} + 24.90 \text{ ml KMnO}_4$
- (ii) $25 \text{ ml Fe}^{2+} + 25 \text{ ml KMnO}_4$
- (iii) $25 \text{ ml Fe}^{2+} + 25.10 \text{ ml KMnO}_4$

Given: $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77 \text{ V} \text{ and } E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.51 \text{ V}$

(e) What do you mean by common ion effect? In qualitative group analysis, Cu²⁺ is precipitated as sulphide in Gr IIA but Zn²⁺ does not — Explain.

1+2

8. (a) What are redox indicators? Give one example with structure both in oxidised and reduced states.

2

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 $Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$ $E^0 = 0.36 \text{ V}$ (b) $E^0 = 0.54 \text{ V}$ $I_2 + 2e = 2I^-$

A solution of potassium ferricyanide cannot oxidise iodide to iodine but it can do so in presence of Zn²⁺ ion — Explain.

3

(c) Construct a Frost diagram for mercury in acid solution from the following Latimer diagram:

 $Hg^{2+} \xrightarrow{+0.911 \text{ V}} Hg_2^{2+} \xrightarrow{+0.796 \text{ V}} Hg$

Hence work out the possibility of disproportionation or comproportionation of Hg_2^{2+} .

3

(d) The solubility of CaF_2 in water at 18°C is 2.04×10^{-4} mol/lit.

- Calculate: Solubility product and (i)
- The solubility of CaF₂ in 0.01 M NaF solution.