**2021/TDC/CBCS/ODD/
CHMHCC–301T/288**

**TDC (CBCS) Odd Semester Exam., 2021
held in March, 2022**

CHEMISTRY

(3rd Semester)

Course No. : CHMHCC–301T

(s-, p-block Elements and Metallurgy)

Full Marks : 50
Pass Marks : 20

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

SECTION—A

Answer any *ten* questions :   2×10=20

1. What is inert pair effect? Illustrate with an example.

2. Draw and discuss the resonance structures of chlorine dioxide.

(2)

3. What do you mean by interhalogen compounds?

4. State with equations, what happens when XeF_6 is treated with aqueous NaOH.

5. Which of the noble gases is most abundant in the universe? Mention two uses of the gas.

6. Explain the shape of XeF_4.

7. Arrange the following in order of increasing base strength and explain reasons :

$$NH_3, NCl_3, NF_3$$

8. What is soft base? What are its characteristics?

9. Which of the following is Bronsted acid and/or Bronsted base?   1+1=2

   (a) NH_3

   (b) $H_2PO_4^-$

10. What are inorganic chain compounds?

11. What are phosphazenes? Give one example.

12. What is the valence state of P in P_4O_6? Depict its structure.

(3)

13. Define gangue.

14. Write an application of Ellingham diagram.

15. What is meant by the term 'concentration of the ore'?

SECTION—B

Answer any *five* questions :   6×5=30

16. (a) Arrange the oxyacids of chlorine in the increasing order of their acidity and oxidizing power. Justify your answer.   3

    (b) Discuss the structure of diborane molecule.   3

17. (a) How is IF_5 prepared? Explain its structure on the basis of hybridization of I-atom.   2+2=4

    (b) How is Caro's acid synthesized?   2

18. (a) Name the first real compound of any of the noble gases. Discuss the preparation and properties of XeF_2 and establish its linear structure with the help of hybridization of orbitals of xenon and fluorine.   1+1+1+1=4

    (b) Write the important uses of clathrates.   2

(4)

19. *(a)* Draw and discuss the structure of xenon oxide difluoride ($XeOF_2$).   3

(b) The 'xenate' ion disproportionates in basic solution to yield xenon, perxenate ion and oxygen. Give a balanced equation for this reaction.   3

20. *(a)* Explain why hard acids coordinate with hard bases and soft acids coordinate with soft bases.   3

(b) Discuss Cady and Elsey concept of acids and bases citing illustrative examples.   3

21. *(a)* What are protic and aprotic solvents? Is liquid NH_3 a protic or an aprotic solvent? Give reasons.   1+1=2

(b) Applying the HSAB principle, complete the following reactions and give reasons :   2+2=4

    (i) $CuI_2 + CuF \longrightarrow$?

    (ii) $CdCl_2 + H_2S \longrightarrow$?

22. *(a)* How SiH_4 may be synthesized? What is its structure? How does it react with *(i)* O_2 and *(ii)* heat?   2+1+1=4

(b) How is P_4O_4 prepared? What happens when it reacts with water?   2

         (Continued)

(5)

23. *(a)* Write the preparation and structure of a cage compound of each of P and B.   4

(b) Draw the open and closed structures of silicons.   2

24. *(a)* Explain the electrolytic process for the extraction of zinc.   3

(b) Discuss the principle of extraction of nickel by Mond's process from purified matte.   3

25. Name the principal ore of chromium and give its chemical formula. Give an outline of extraction of chromium from its ore.   2+4=6

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         2021/TDC/CBCS/ODD/
                               CHMHCC–301T/288

2021/TDC/CBCS/ODD/
CHMHCC–302T/289

TDC (CBCS) Odd Semester Exam., 2021
held in March, 2022

CHEMISTRY

(3rd Semester)

Course No. : CHMHCC–302T

(Organic Chemistry)

$$\frac{\textit{Full Marks} : 50}{\textit{Pass Marks} : 20}$$
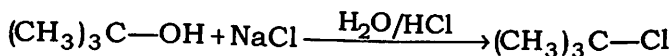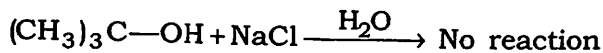
Time : 3 hours

The figures in the margin indicate full marks
*for the questions*

SECTION—A

Answer any *ten* questions :   2×10=20

1. Suggest an explanation for the following results :

$$(CH_3)_3C—OH + NaCl \xrightarrow{H_2O} \text{No reaction}$$

$$(CH_3)_3C—OH + NaCl \xrightarrow{H_2O/HCl} (CH_3)_3C—Cl$$

(*Turn Over*)

(2)

2. The rate of formation of 2-ethoxy-2-methyl-propane from the reaction of 2-bromo-2-methylpropane with ethanol does not increase, if the better nucleophile sodium ethoxide is added. Explain this observation.

3. Identify the better nucleophile in the following pairs and give reasons for your choice : 1×2=2

   (a) $\overset{(-)}{RO}$ or $\overset{(-)}{RS}$

   (b) $\overset{(-)}{NH_2}$ or NH_3
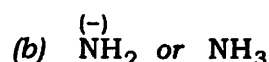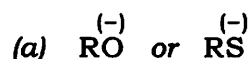
4. Propose mechanism for the following conversion :
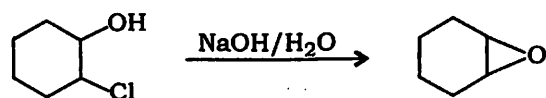
5. An unsymmetrical ether can cleave to give two different alcohol-haloalkane mixtures.

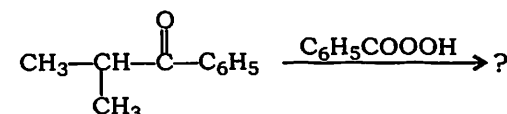$$ROR' \xrightarrow{HI} \begin{array}{c} ROH + R'I \\ or \\ R{-}I + R'OH \end{array}$$
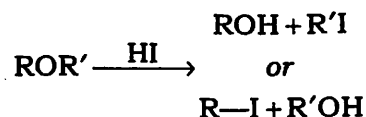
   Predict the major pathway in the cleavage of benzyl methyl ether (PhCH$_2$OCH$_3$) and explain the basis of your choice.

(3)

6. The carbon-oxygen bond in phenol is slightly shorter than that in methanol. Explain why.

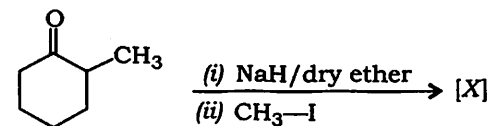7. (a) Arrange acidity of given compounds in decreasing order :
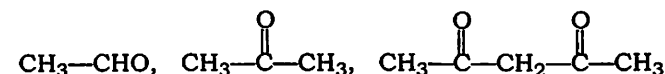
   (b) Predict the major product of the following reaction :
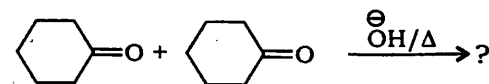

   1+1=2

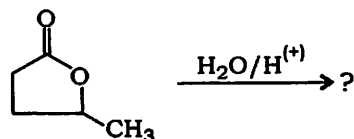8. In the given reaction, identify [X] and write a mechanism for the reaction :

9. Predict the major product of the following reaction and propose a reasonable mechanism :
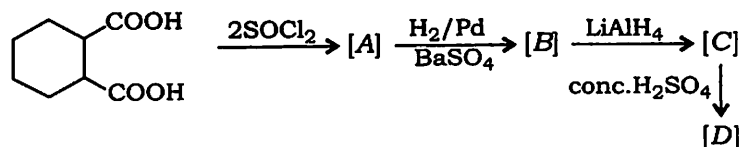
(4)

10. Predict the product of the following hydrolysis and propose a reasonable mechanism :

$$\xrightarrow{\text{H}_2\text{O}/\text{H}^{(+)}} ?$$

11. Identify the A, B, C and D in the following reaction sequence : $\frac{1}{2} \times 4 = 2$

$$\xrightarrow{2\text{SOCl}_2} [A] \xrightarrow[\text{BaSO}_4]{\text{H}_2/\text{Pd}} [B] \xrightarrow{\text{LiAlH}_4} [C]$$

$$\downarrow \text{conc.H}_2\text{SO}_4$$

$$[D]$$

12. What happens when citric acid is heated with disulphuric acid (oleum) followed by decarboxylation? Show the reaction sequence.

13. Carry out the synthesis of butan-2-one from ethyl acetoacetic ester.

14. Carry out the reaction of ethanoyl chloride with excess of methyl magnesium bromide.

15. (a) Convert cyclohexyl bromide to cyclohexanethiol.

(b) What happens when ethanethiol is treated with an aqueous solution of cupric chloride? 1+1=2
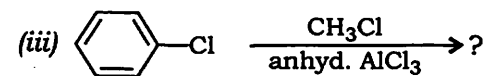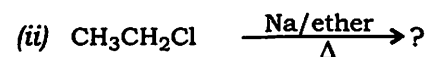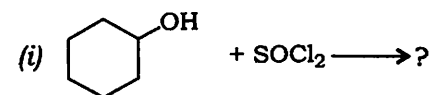
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(5)

SECTION—B

Answer any *five* questions :   6×5=30

16. (a) The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain.   2

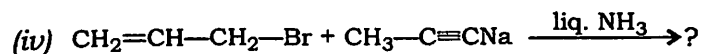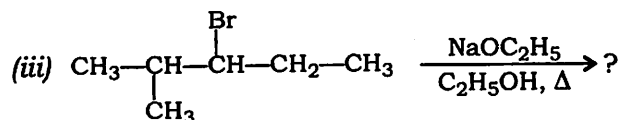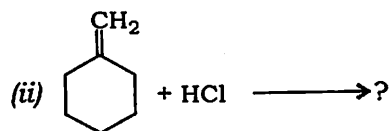(b) Predict the major product in each of the following reactions : $\frac{1}{2} \times 4 = 2$

(i) + $SOCl_2 \longrightarrow$?

(ii) $CH_3CH_2Cl \xrightarrow[\Delta]{\text{Na/ether}}$?

(iii) —Cl $\xrightarrow[\text{anhyd. AlCl}_3]{\text{CH}_3\text{Cl}}$?
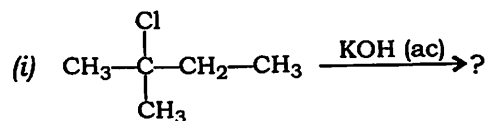
(iv) $CH_3CH_2—Br + NaI \longrightarrow$?

(c) (i) Identify the alkene which will yield 1-chloro-1-methyl cyclohaxane by its reaction with HCl. Write the reactions involved.   1
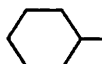
(ii) Which of the following compounds will react faster in S_N1 reaction with $\overset{(-)}{OH}$? Justify your choice.   1

$CH_3—CH_2—Cl$ *or* $C_6H_5—CH_2—Cl$

(Turn Over)
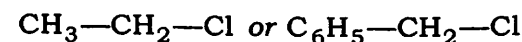
(6)

17. (a) Explain why vinyl chloride is unreactive in nucleophilic substitution reaction. 2

(b) 3-bromocyclohexene is more reactive than 4-bromocyclohexene in hydrolysis with aq. NaOH. Explain why. 2

(c) Predict the major products in the following reactions : ½×4=2

(i) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CH_3 \xrightarrow{KOH\ (ac)} ?$

(ii) + HCl $\longrightarrow$?

(iii) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Br}{|}}{CH}-CH_2-CH_3 \xrightarrow[C_2H_5OH,\ \Delta]{NaOC_2H_5} ?$

(iv) $CH_2=CH-CH_2-Br + CH_3-C\equiv CNa \xrightarrow{liq.\ NH_3} ?$

18. (a) Show how —CH_2OH is prepared by reaction of a suitable Grignard reagent with methanal. 2

(b) Predict the major product and propose a reasonable mechanism of acid catalyzed dehydration of 1-methyl cyclo-hexanol. 2
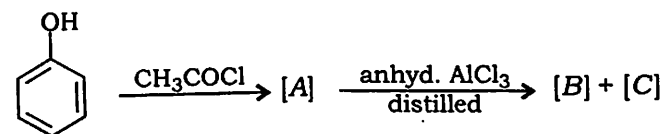
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(7)

(c) Write the reactions of Williamson's synthesis of 2-ethoxy-3-methyl pentane starting from ethanol and 3-methyl pentan-2-ol. 2

19. (a) Identify A, B and C in the following reaction : 1½

 $\xrightarrow{CH_3COCl}$ [A] $\xrightarrow[distilled]{anhyd.\ AlCl_3}$ [B] + [C]

(b) Write the chemical reactions to show the conversions of the following : 2

(i) Phenol to benzophenone

(ii) Aniline to phenol

(c) Sodium phenoxide when heated with CO_2 under pressure at 125 °C yields a product [A] which on acylation produces [B]. Write the reaction sequence to identify [A] and [B]. 1½

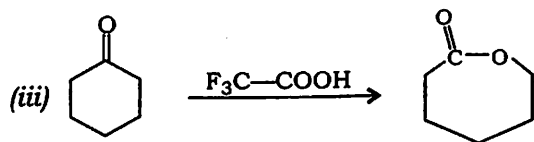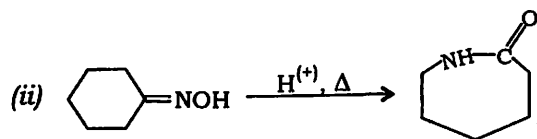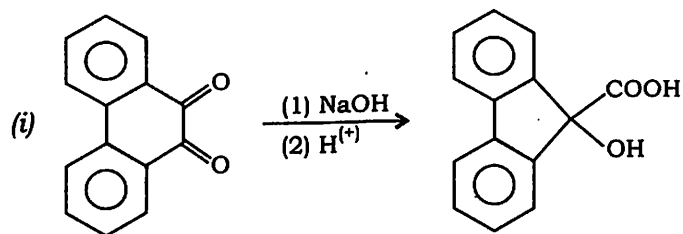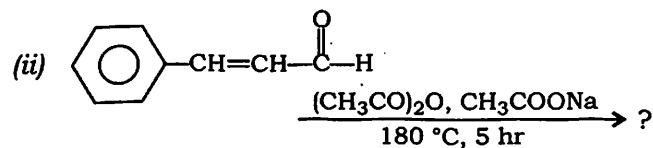(d) Which of the following has the most acidic nature? 1

(i) —OH

Or

(ii)
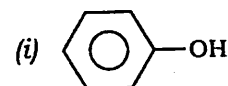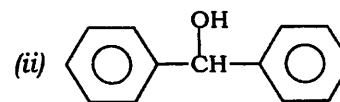
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(8)

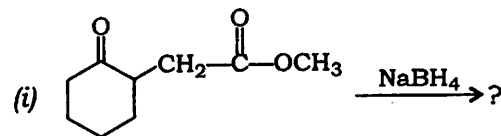**20.** Write the mechanism for the following transformations :   2×3=6

(i)

$$\xrightarrow[\text{(2) } H^{(+)}]{\text{(1) NaOH}}$$

(ii) $\bigcirc\!=\!NOH \xrightarrow{H^{(+)}, \Delta}$

(iii) $\xrightarrow{F_3C\text{—COOH}}$

21. *(a)* Complete and write the mechanism for the following reactions :   2×2=4

   (i)   OHC—CHO $\xrightarrow[\text{(2) } H^{(+)}]{\text{(1) NaOH}}$?

   (ii)

$$\xrightarrow[\text{180 °C, 5 hr}]{(CH_3CO)_2O,\ CH_3COONa}\ ?$$
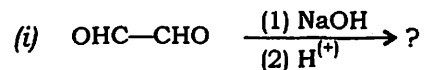
(9)

(b) Write the structure of the product(s) of the following reactions :   1×2=2

(i)

$$\xrightarrow{NaBH_4}\ ?$$

(ii)

$$\xrightarrow{Br_2/NaOH}\ ?$$
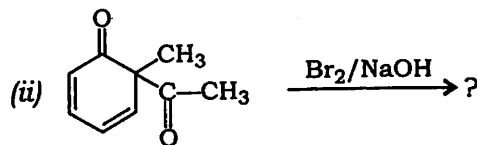
22. *(a)* How would you explain the fact that carboxylic acid is stronger acid than phenol although phenoxide ion has more number of resonating structures than carboxylate ion?   1½

(b) Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes and ketones. Why?   1

(c) What happens when ethanoic acid reacts with red phosphorus and HI?   1

(d) Identify *A*, *B* and *C* in the following reaction :   1½

$$+\ NH_3 \rightleftharpoons [A] \xrightarrow{heat} [B] \xrightarrow[\text{heating}]{\text{strong}} [C]$$
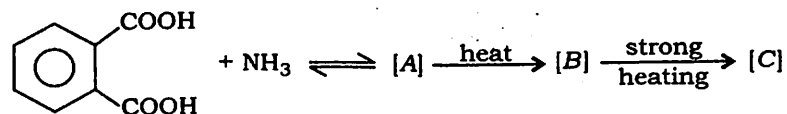
(10)

(e) Write the mechanism for the following reaction : 1

23. (a) Complete the following reactions and write a reasonable mechanism for each :

(i)

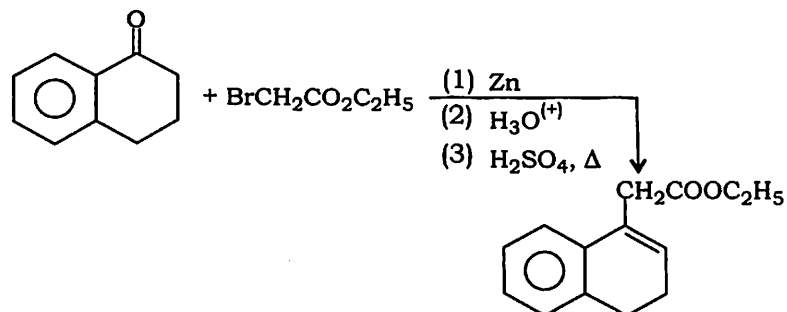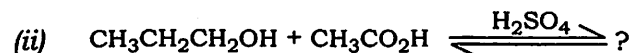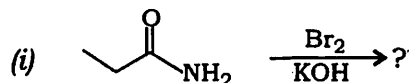(ii) $CH_3CH_2CH_2OH + CH_3CO_2H \underset{}{\overset{H_2SO_4}{\rightleftharpoons}}$?

Why is it necessary to remove the water formed during this reaction as early as possible? 4

(b) What happens when lactic acid is (i) oxidized with nitric acid and (ii) reduced with HI? 2

(11)

24. (a) Using appropriate Grignard reagent, bring out the following conversions :

$1 \times 2 = 2$

(i) Bromomethane to but-2-yne

(ii) Methanol to 2,2-dimethyl propan-1-ol

(b) Show the complete reaction sequence to obtain 2-methyl propanoic acid from diethylmalonate. 2

(c) Obtain ethyl acetoacetate from ethyl acetate and write the mechanism of the reaction. 2

25. (a) Obtain the following : $1\frac{1}{2} \times 2 = 3$

(i) Pentane-2,4-dione from ethyl acetoacetate

(ii) Cyclopentane carboxylic acid and then cyclopentane from diethyl malonate

(b) Explain why organolithium compounds are more reactive than Grignard reagent. 1

(c) Using appropriate organolithium compound, convert pyridine to 2-phenyl pyridine. Write the mechanism of the reaction also. 2

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2021/TDC/CBCS/ODD/
CHMHCC–303T/290

**TDC (CBCS) Odd Semester Exam., 2021
held in March, 2022**

CHEMISTRY

(3rd Semester)

Course No. : CHMHCC–303T

(Phase Equilibria and Chemical Kinetics)

Full Marks : 50
Pass Marks : 20
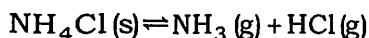
Time : 3 hours

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SECTION—A

Answer any *ten* from the following :   2×10=20

1. What is reduced phase rule? When is it applied?   1+1=2

2. Calculate the number of components and degree of freedom of the following equilibrium :

$$NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$$

(Turn Over)

(2)

3. Explain with the help of Clapeyron-Clausius equation the effect of pressure on the boiling point of water.

4. Derive a statement of Raoult's law with the help of Gibbs-Duhem-Margules equation for ideal binary solution.

5. State and explain lever rule.

6. What are the differences between ideal solution and non-ideal solution?

7. Explain how temperature and use of catalyst affect the reaction rate.   1+1=2

8. A first-order reaction is half complete in half-an-hour. How much will it be complete in one hour?

9. Calculate the activation energy of a reaction whose rate constant is triple by 10° rise in temperature in the vicinity of 27 °C.

10. What is the difference between auto-catalyst and promoters? Give example to each.

22J/720   (Continued)

(3)

11. Why is heterogeneous catalysis preferred over homogeneous catalysis? Explain.

12. What are the properties of enzymes that make them a biocatalyst? Give example of an enzyme catalyzed reaction.   1+1=2

13. What are the factors that affect adsorption of gas on solid surface?

14. Physisorption is reversible while chemisorption is irreversible. Why?

15. What is adsorption isotherm? How are they useful in study of adsorption?

SECTION—B

Answer any *five* from the following :   6×5=30

16. (a) Derive Gibbs' phase rule thermodynamically.   3

    (b) Define incongruent melting point and explain it with the help of Zn-Mg system.   1+2=3

17. (a) Discuss the phase diagram of Pb-Ag system.   3

22J/720   (Turn Over)

(4)

(b) For liquid-vapour equilibrium, show that

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \frac{[T_2 - T_1]}{[T_1 T_2]}$$

Symbols have their usual meanings. 3

18. (a) What are the different types of binary solutions? Derive Gibbs-Duhem-Margules equation for binary liquids.

1+2=3

(b) Explain Raoult's law by using vapour-pressure composition plot of ideal solution. 3

19. (a) Define minimum and maximum boiling azeotropes. Give example of each. 3

(b) Discuss upper critical solution temperature (UCST) with the help of phenol-water system. 3

20. (a) Discuss activated complex theory of bi-molecular reaction. 3

(b) The rate constant of a second-order reaction is 5.70×10^{-5} dm^3 mol^{-1} s^{-1} at 25 °C and 1.64×10^{-4} dm^3 mol^{-1} s^{-1} at 40 °C. Calculate the activation energy and the Arrhenius pre-exponential factor. 3

(5)

21. (a) Discuss the kinetics of reversible reaction. 3

(b) Write short notes on the following :

1½×2=3

(i) Steady-state approximation

(ii) Chain reaction

22. (a) Describe the mechanism of heterogeneous catalyzed reaction at solid surface. 3

(b) Discuss the kinetics of enzyme-catalyzed reaction. 3

23. (a) Enzymes are selective in nature. Explain with an example. 2

(b) What will be the effect of pH and substrate concentration on enzyme catalysis? 1+1=2

(c) Write a short note on acid-base catalysis. 2

24. (a) Explain how surface area and temperature affect the adsorption of gas on solid. 1½+1½=3

(b) State three applications of adsorption process. 3

(**6**)

25. *(a)* Derive an expression for Langmuir adsorption isotherm. 3

(b) Why is Freundlich adsorption isotherm applicable only for low pressure of gas? What will happen if the pressure rises?

$1\frac{1}{2}+1\frac{1}{2}=3$

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