FYUG Odd Semester Exam., 2025

CHEMISTRY

(3rd Semester)

Course No. : CHMDSM–201T

(Fundamentals of Chemistry—II)

Full Marks : 70

Pass Marks : 28

Time : 3 hours

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

UNIT—I

1. Answer any *two* of the following questions :

$2 \times 2 = 4$

(a) Graphite is a conductor of electricity but diamond is not. Explain with proper reasoning.

(b) Predict the products of the following chemical reactions and draw the structure of the products : $1+1=2$

(i) $B_2H_6 \xrightarrow{H_2O} ?$

(ii) $B_2H_6 \xrightarrow[\text{High temperature}]{NH_3 \text{ (Excess)}} ?$

(Turn Over)
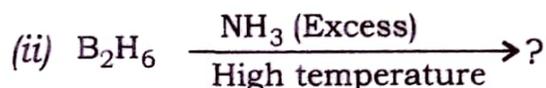
(c) What is meant by the catenation property of carbon? Why does carbon exhibit a stronger tendency for catenation compared to other elements of group-14? 1+1=2

2. Answer any *one* of the following questions : 10

   (a) (i) Write one method of preparation of B_2H_6. Discuss the structure and bonding in B_2H_6. Why are the B—H—B bond angles smaller than the normal tetrahedral angle?

                                       1+3+1=5

      (ii) Discuss the chemistry of borax bead test taking copper salt as an example. 3

      (iii) Predict the products of the following reactions : 1+1=2

        (1) $B(OH)_3 + C_2H_5OH$ (excess) $\xrightarrow{\text{conc. } H_2SO_4}$?

        (2) $2Al \text{ (s)} + 2NaOH \text{ (aq)} \xrightarrow{6H_2O}$?

   (b) (i) What are silicones? How will you synthesize silicone from methyl chloride? Give two uses of silicones.

                                       1+2+1=4

(ii) What are zeolites? Discuss the use of zeolites as catalysts.   1+2=3

(iii) What is inorganic benzene? Boron fluoride exists as BF_3 but boron hydride does not exist as BH_3. Justify the statement with appropriate reasons.   1+2=3

UNIT—II

3. Answer any *two* of the following questions :

2×2=4

(a) Give the mathematical formulation of first law of thermodynamics and explain the terms involved in it.

(b) Explain the terms enthalpy of formation and standard enthalpy of formation.   1+1=2

(c) Prove that in a reversible process, net entropy change for the system and surroundings is zero.

4. Answer any *one* of the following questions :   10

(a) (i) Define heat capacity at constant pressure (C_P) and heat capacity at constant volume (C_V). Deduce the relation between C_P and C_V for n moles of an ideal gas.   2+3=5

(4)

(ii) What are integral and differential enthalpies of solution? Explain. 2

(iii) Is enthalpy of formation an intensive or extensive property? The heat evolved on dissolving $CuSO_4(s)$ in water is $86·6$ kJ mol^{-1}. Calculate the standard enthalpy of formation (ΔH_f°) of $CuSO_4(s)$.

$$[\ \Delta H_f^\circ \ (Cu^{2+}) = 64·4 \ kJ \ mol^{-1},$$

$$\Delta H_f^\circ \ (SO_4^{2-}) = -747·8 \ kJ \ mol^{-1}]$$

$$1+2=3$$

(b) (i) What is meant by bond energy? How does bond energy help to determine the enthalpy of a reaction? How does the enthalpy of a reaction vary with temperature? Discuss in detail. $1+1+3=5$

(ii) Calculate the enthalpy change for the following reaction :

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$
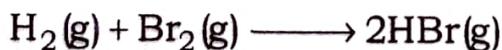
The bond energies of H—H, Br—Br and H—Br are 435 kJ mol^{-1}, 192 kJ mol^{-1} and 364 kJ mol^{-1} respectively. 2

(iii) What is resonance energy? The enthalpy of hydrogenation of benzene is -209 kJ mol^{-1} and the enthalpy of hydrogenation of typical alkene is -120 kJ mol^{-1}. Calculate the resonance stabilization energy of benzene in kJ mol^{-1}.   1+2=3

UNIT—III

5. Answer any *two* of the following questions :

                                             2×2=4

(a) What do you mean by phase diagram? Explain the term 'triple point' with an example.   1+1=2

(b) Write the difference between ideal and non-ideal solutions with appropriate examples.

(c) Write the mathematical expression of Gibbs' phase rule and explain the various terms involved in it.

6. Answer any *one* of the following questions :   10

(a)   (i) State Raoult's law for a solution of volatile liquids. Prove that the relative lowering of vapour pressure of a solution containing non-volatile solute is equal to the mole fraction of the solute in the solution.   1+2=3

(*Turn Over*)

(ii) Liquid A (molecular mass 46 g mol^{-1}) and liquid B (molecular mass 18 g mol^{-1}) form an ideal solution. At 293 K, the vapour pressures of pure A and pure B are 44·5 and 17·5 mm of Hg, respectively. Calculate—

(1) the vapour pressure of a solution of A in B (mole fraction of A is 0·2);

(2) the composition of the vapour phase.   2+1=3

(iii) Draw the labelled phase diagram of sulphur system and discuss the significance of various areas, curves and points.   4

(b) (i) Draw and explain the vapour pressure composition curves for non-ideal solutions showing positive and negative deviations from Raoult's law.   2½+2½=5

(ii) What are azeotropes? Define maximum boiling azeotropes and minimum boiling azeotropes with one example of each.   1+2=3

(Continued)

(iii) Answer the following questions using Gibbs' phase rule :   1+1=2

(1) Water can exist in three phases : solid, liquid and vapour. Calculate the number of degrees of freedom at the triple point in the water system.

(2) Can a one-component system exist in four phases in equilibrium? Justify.

UNIT—IV

7. Answer any *two* of the following questions :

$$2\times2=4$$

(a) How can you prepare the following?   1+1=2
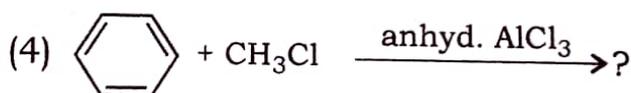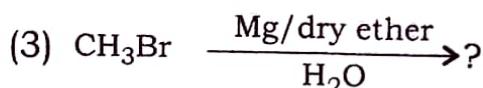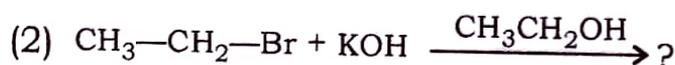
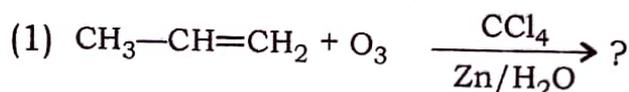(i) Ethane from sodium propionate

(ii) Benzene from ethyne

(b) What happens when (write equation only)

(i) two molecules of ethylbromide is treated with metallic sodium in dry ether;

(ii) 2-methylpropene is treated with H—Br in the presence of H_2O_2?

(8)

(c) Show the mechanism of addition of bromine to but-2-yne. Comment on the stereochemistry of the product.

8. Answer any *one* of the following questions : 10

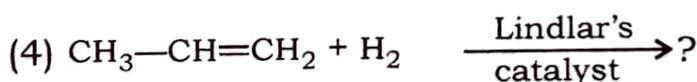(a) (i) Predict the products of the following reactions : $1\times4=4$

(1) $CH_3—CH=CH_2 + O_3 \xrightarrow[Zn/H_2O]{CCl_4} ?$

(2) $CH_3—CH_2—Br + KOH \xrightarrow{CH_3CH_2OH} ?$

(3) $CH_3Br \xrightarrow[H_2O]{Mg/dry\ ether} ?$

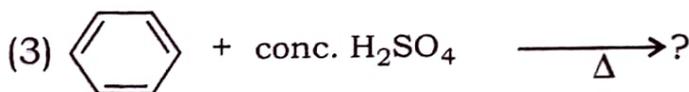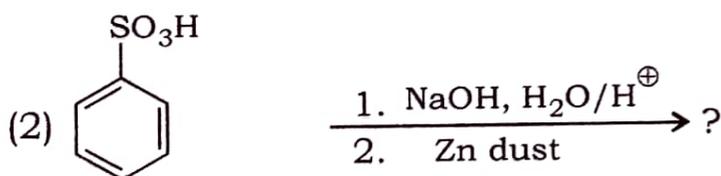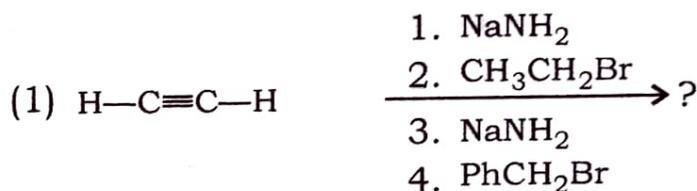(4) $+ CH_3Cl \xrightarrow{anhyd.\ AlCl_3} ?$

(ii) Discuss with appropriate mechanism—

(1) nitration reaction of benzene;

(2) Friedel-Crafts acylation reaction of benzene. $3+3=6$

(b) (i) Why does the pink colour of Baeyer's reagent disappear when added to any alkene? Discuss with appropriate chemical reaction. 2

(ii) Predict the products of the following chemical reactions : $1 \times 5 = 5$

(1) $H—C \equiv C—H$ $\xrightarrow{\begin{array}{l}1.\ NaNH_2 \\ 2.\ CH_3CH_2Br \\ 3.\ NaNH_2 \\ 4.\ PhCH_2Br\end{array}}$?

(2) [benzene ring with SO_3H substituent] $\xrightarrow{\begin{array}{l}1.\ NaOH,\ H_2O/H^{\oplus} \\ 2.\ \ \ Zn\ dust\end{array}}$?

(3) [cyclohexadiene ring] $+$ conc. H_2SO_4 $\xrightarrow{\Delta}$?

(4) $CH_3—CH=CH_2 + H_2$ $\xrightarrow[\text{catalyst}]{\text{Lindlar's}}$?

(5) [benzene ring]$—COOH$ $\xrightarrow[\Delta]{NaOH/CaO}$?

(iii) State and justify Markwonikoff's rule taking a suitable reaction as example. 3

UNIT—V

9. Answer any *two* of the following questions :
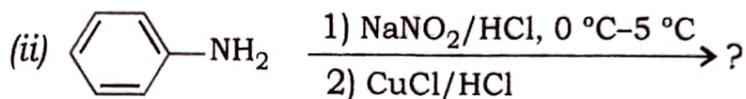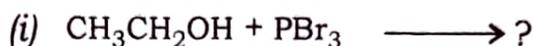
$2 \times 2 = 4$

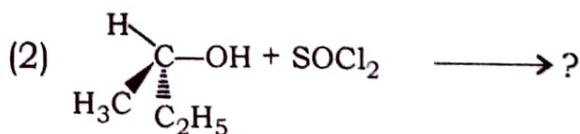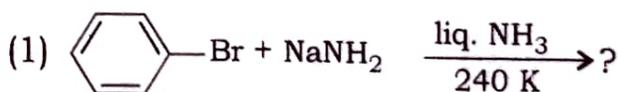(a) What happens when ethylbromide is treated with (i) AgCN and (ii) KCN? Give the chemical reactions. $1+1=2$

(*Turn Over*)

(b) Predict the products of the following chemical reactions : $1 \times 2 = 2$

(i) $CH_3CH_2OH + PBr_3 \longrightarrow ?$

(ii) [benzene ring]$-NH_2$ $\xrightarrow[\text{2) CuCl/HCl}]{\text{1) NaNO}_2\text{/HCl, 0 °C–5 °C}}$?

(c) How can anisole be synthesized from methyl iodide using the Williamson ether synthesis reaction? Give the chemical reactions.
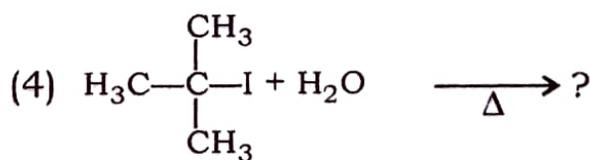
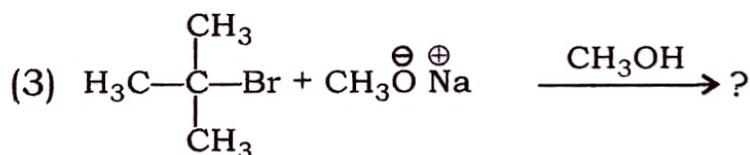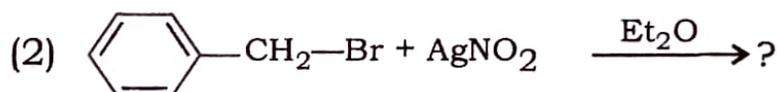10. Answer any *one* of the following questions : 10

(a) (i) Complete the following chemical reactions with appropriate mechanisms : $3 \times 2 = 6$

(1) [benzene ring]$-Br + NaNH_2$ $\xrightarrow[\text{240 K}]{\text{liq. NH}_3}$?

(2) $\underset{H_3C}{\overset{H}{>}}\underset{C_2H_5}{\overset{}{C}}-OH + SOCl_2 \longrightarrow ?$

(ii) Chlorine in chlorobenzene, unlike chloroalkanes, shows very less reactivity towards nucleophilic substitution reaction of halogen by reagents such as NaOH, NH_3, KCN, etc. Justify. 2

(Continued)

(iii) How will you synthesize aryl halides using the Gattermann reaction? Give the chemical equations.   2

(b)   (i) Predict the products of the following chemical reactions : $1×4=4$

(1) $\langle\!\!\!\!\bigcirc\!\!\!\!\rangle$—OH $\xrightarrow[\text{2. Cl}_2/\text{FeCl}_3]{\text{1. Zn dust}}$?

(2) $\langle\!\!\!\!\bigcirc\!\!\!\!\rangle$—$CH_2$—Br + $AgNO_2$ $\xrightarrow{Et_2O}$?

(3) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + CH_3\overset{\oplus}{O}\ \overset{\ominus}{Na}$ $\xrightarrow{CH_3OH}$?

(4) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-I + H_2O$ $\xrightarrow{\Delta}$?
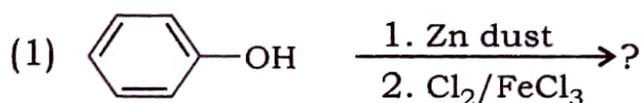
(ii) Predict the product of the following reaction with appropriate mechanism :   3
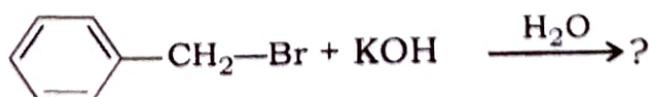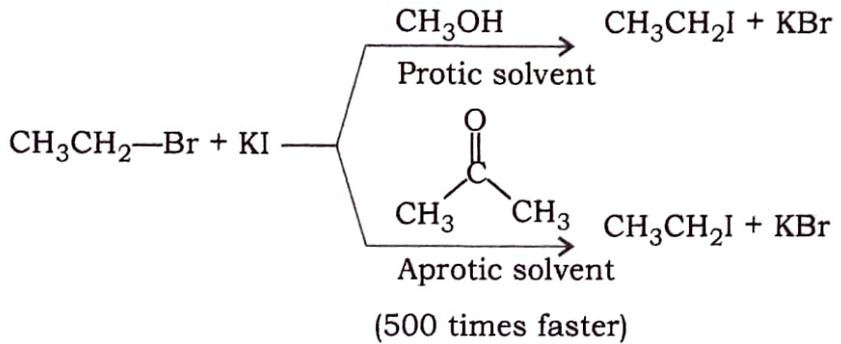
$\langle\!\!\!\!\bigcirc\!\!\!\!\rangle$—$CH_2$—Br + KOH $\xrightarrow{H_2O}$?

(iii) Explain the following observation with suitable reasons : 2

$$CH_3CH_2-Br + KI$$

Protic solvent $\xrightarrow{CH_3OH}$ $CH_3CH_2I + KBr$

Aprotic solvent $\xrightarrow{\underset{CH_3 \quad CH_3}{\overset{O}{\overset{\|}{C}}}}$ $CH_3CH_2I + KBr$

(500 times faster)

(iv) How would you prepare vicinal ethylene dibromide from ethene? Give the chemical equation. 1

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