

Total No. of Printed Pages—23

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( May )

**CHEMISTRY**

( Major )

Course : 201

( **Physical, Inorganic, Organic** )

( **New Course** )

Full Marks : 80

Pass Marks : 24

Time : 3 hours

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

*Write the answers to the separate Sections  
in separate books*

**SECTION—I**

( **Physical Chemistry** )

( Marks : 26 )

1. Choose the correct answer from the following : 1×3=3

(a) In endothermic reaction

(i)  $H_R > H_P$

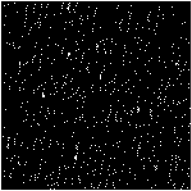
(ii)  $H_R < H_P$

(iii)  $H_R = H_P$

(iv) None of these

P16/650

( Turn Over )



(b) Which of the following pairs has heat of neutralisation equal to  $-57.3$  kJ?

- (i) HCl,  $\text{NH}_4\text{OH}$
- (ii)  $\text{HNO}_3$ , NaOH
- (iii) NaOH,  $\text{CH}_3\text{COOH}$
- (iv)  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{OH}$

(c) The precipitate of calcium fluoride ( $K_{sp} = 1.7 \times 10^{-10}$ ) is obtained when equal volumes of the following are mixed

- (i)  $10^{-4} \text{ M Ca}^{2+} + 10^{-4} \text{ M F}^-$
- (ii)  $10^{-2} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
- (iii)  $10^{-5} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
- (iv)  $10^{-3} \text{ M Ca}^{2+} + 10^{-5} \text{ M F}^-$

UNIT—I

Answer any two from the following :

$6 \times 2 = 12$

2. Calculate the amount of work done when a gas expands—

- (a) isothermally and reversibly from volume  $V_1$  to  $V_2$ ;
- (b) isothermally and irreversibly from volume  $V_1$  to  $V_2$ .

From these, show that the work done in a reversible process is greater than that in an irreversible process.

$2+2+2=6$

3. (a) Establish the relationship between enthalpy change and internal energy change for a gaseous reaction. 2
- (b) For the conversion of one mole of  $\text{SO}_2(\text{g})$  into  $\text{SO}_3(\text{g})$ , the enthalpy of reaction at constant volume is  $-97.027 \text{ kJ}$  at  $298 \text{ K}$ . Calculate the enthalpy of the reaction at constant pressure. 3
- (c) Differentiate between extensive and intensive property with one example. 1
4. (a) Thermodynamically show that for an ideal gas  $C_P - C_V = R$ . 4
- (b) Prove that  $\mu_{JT}$  is zero for an ideal gas. 2

## UNIT—II

5. Answer any two questions from the following :  $5\frac{1}{2} \times 2 = 11$
- (a) Derive the relation  $K_h = K_w / K_a$  for the hydrolysis of a salt of weak acid and a strong base. Explain the acidic or basic nature of aqueous solutions of (i)  $\text{FeCl}_3$  and (ii)  $\text{NH}_4\text{NO}_3$ .  $3\frac{1}{2} + 2 = 5\frac{1}{2}$
- (b) (i) What is buffer solution? Write any two applications of buffer solution. 2
- (ii) Derive an equation for calculating the pH of a basic buffer solution. Calculate the pH of a buffer solution obtained by mixing  $0.2 \text{ mol}$  of  $\text{NH}_4\text{OH}$  and  $0.25 \text{ mol}$  of  $\text{NH}_4\text{Cl}$ . Given  $K_b = 1.8 \times 10^{-5}$ .  $2 + 1\frac{1}{2} = 3\frac{1}{2}$

- (c) (i) Establish the relationship between solubility and solubility product for a sparingly soluble salt. 2
- (ii) Write the difference between ionic product and solubility product. 2
- (iii) The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.  $1\frac{1}{2}$

SECTION—II

( Inorganic Chemistry )

( Marks : 27 )

6. Choose the correct answer from the following:  $1 \times 3 = 3$

(a)  $B_{10}H_{14}$  has styx number 4620. The number of  $BH_2$  group in the compound is

(i) 4

(ii) 6

(iii) 0

(iv) 2

- (b) In sheet silicates, sheet structures are formed when  $\text{SiO}_4$  units have share
- (i) two O atoms
  - (ii) three O atoms
  - (iii) four O atoms
  - (iv) None of the above
- (c) Which of the following metals cannot be extracted by carbon reduction process?
- (i) Pb
  - (ii) Ag
  - (iii) Zn
  - (iv) Al

UNIT—I

7. Answer any *three* of the following :  $3 \times 3 = 9$

- (a) Explain the structure of  $\text{XeF}_2$  and  $\text{XeF}_6$ .  
 $1\frac{1}{2} \times 2 = 3$
- (b) What are zeolites? Give their applications with special reference to softening of hard water.  $1 + 2 = 3$
- (c) How is hydrazine prepared? Discuss its reducing property.  $1 + 2 = 3$
- (d) What are silicones? How can they be prepared? What is silicone rubber? 3
- (e) Give the structures of the following : 3  
 $\text{P}_4\text{O}_{10}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_4\text{P}_2\text{O}_7$

8. Write short notes on (any two) :  $2 \times 2 = 4$

- (a) Metallocarboranes
- (b) Triphenyl phosphine
- (c) Hydrazoic acid
- (d) Buckminsterfullerene

UNIT—II

9. (a) Name one metal that is refined by each of the following processes :  $\frac{1}{2} \times 4 = 2$

- (i) Mond process
- (ii) Electrolysis
- (iii) van Arkel process
- (iv) Zone refining

(b) Describe the extraction of any two of the following :  $3 \times 2 = 6$

- (i) Molybdenum from molybdenite ore
- (ii) Chromium from chromite ore
- (iii) Nickel from pentlandite

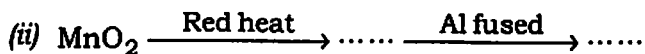
(c) Give the preparation of any two of the following :  $1\frac{1}{2} \times 2 = 3$

- (i) Potassium permanganate
- (ii) Sodium cobaltinitrite
- (iii) Chromyl chloride

( 7 )

Or

Complete the following reactions : 3



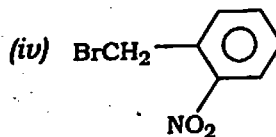
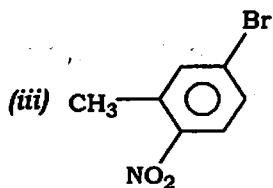
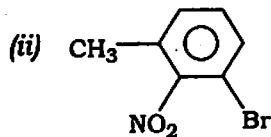
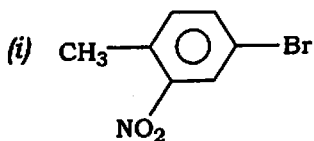
SECTION—III

( Organic Chemistry )

( Marks : 27 )

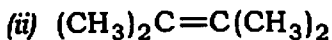
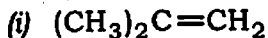
10. Choose the correct answer from the following : 1×3=3

(a) Bromination of o-nitrotoluene gives mainly





(b) Ozonolysis of an alkene gives acetone only as a major product. The alkene is



(iv) None of the above

(c) Hydroboration of propene (reaction with diborane followed by the treatment with alkaline  $\text{H}_2\text{O}_2$ ) forms

(i) propan-1-ol

(ii) propan-2-ol

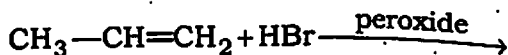
(iii) propane-1,2-diol

(iv) 1,2-diacetoxy mercury propane

11. Answer any six of the following :  $2 \times 6 = 12$

(a) Discuss the mechanism of chlorination of methane.

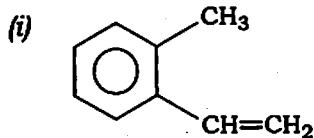
(b) Complete the following reaction and write down the mechanism :



(c) Explain Hofmann's rule of elimination with the help of an example.

(d) Prepare 3-methyl octane with the help of Corey-House synthesis.

- (e) Write the methods of preparation of the following :



from *o*-bromotoluene with the help of Heck reaction.

- (ii) Styrene from benzaldehyde using Wittig reaction.

- (f) Complete the following reaction and suggest the mechanism :



- (g) "The addition of  $Br_2$  in  $CCl_4$  to *trans*-2-butene gives always *meso*-2,3-dibromobutane as a product." Explain.

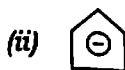
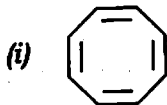
- (h) A hydrocarbon having molecular formula,  $C_6H_{12}$  was subjected to ozonolysis giving equimolar amounts of ethyl methyl ketone and acetaldehyde. Identify the structure of hydrocarbon and give IUPAC name of it. Write down the equations involved.

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

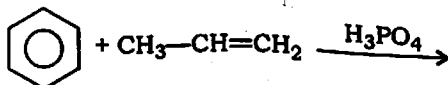
- (a) Discuss the conformational analysis of *n*-butane and draw the potential energy diagram for it.
- (b) Explain 1,3-diaxial interaction in the chair conformation of methyl cyclohexane. "*t*-butylcyclohexane exists 100 percent in the equatorial conformation." Give reasons.
- (c) Synthesize cyclohexane starting from diethyl pimelate using Dieckmann cyclisation.

13. Answer any *four* from the following :  $2 \times 4 = 8$

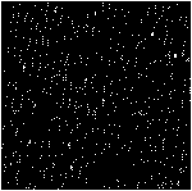
- (a) State Huckel's rule of aromaticity. Identify the following as aromatic or non-aromatic :



- (b) Complete the following reaction and suggest the mechanism :



- (c) "When methyl group is attached to the benzene ring it acts as *ortho-para*-director and activates the benzene ring towards the electrophilic substitution reactions." Explain.
- (d) Aniline in the presence of catalytic amount of anhydrous  $\text{AlCl}_3$  does not undergo F-C alkylation. Explain why.
- (e) A secondary alcohol A,  $\text{C}_3\text{H}_8\text{O}$  on treatment with thionyl chloride to give compound B,  $\text{C}_3\text{H}_7\text{Cl}$ . The compound B reacts with benzene in presence of anhydrous  $\text{AlCl}_3$  to give compound C,  $\text{C}_9\text{H}_{12}$ . Identify A, B, C and write equations for all the reactions.



( 12 )

( Old Course )

Full Marks : 80

Pass Marks : 32

Time : 3 hours

The figures in the margin indicate full marks  
for the questions

Write the answers to the separate Sections  
in separate books

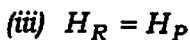
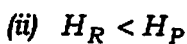
SECTION—I

( Physical Chemistry )

( Marks : 26 )

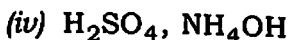
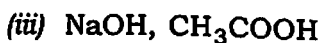
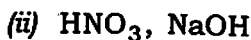
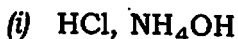
1. Choose the correct answer from the following : 1×3=3

(a) In endothermic reaction



(iv) None of the above

(b) Which of the following pairs has heat of neutralisation equal to  $-57.3$  kJ?



(c) The enthalpy of vaporization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vaporization is  $75 \text{ J K}^{-1} \text{ mol}^{-1}$ . The boiling point of the liquid at one atmosphere is

- (i) 250 K
- (ii) 400 K
- (iii) 450 K
- (iv) 600 K

UNIT—I

Answer any *two* from the following : 6×2=12

2. Calculate the amount of work done when a gas expands—

- (a) isothermally and reversibly from volume  $V_1$  to  $V_2$ ;
- (b) isothermally and irreversibly from volume  $V_1$  to  $V_2$ .

From these, show that the work done in a reversible process is greater than that in an irreversible process. 2+2+2=6

3. (a) Establish the relationship between enthalpy change and internal energy change for a gaseous reaction. 2

- (b) For the conversion of one mole of  $\text{SO}_2(\text{g})$  into  $\text{SO}_3(\text{g})$ , the enthalpy of reaction at constant volume is  $-97.027 \text{ kJ}$  at  $298 \text{ K}$ . Calculate the enthalpy of the reaction at constant pressure. 3
- (c) Differentiate between extensive and intensive property with one example. 1
4. (a) Thermodynamically show that for an ideal gas  $C_P - C_V = R$ . 4
- (b) Prove that  $\mu_{\text{JT}}$  is zero for an ideal gas. 2

UNIT—II

5. Answer any *two* questions from the following :  $5\frac{1}{2} \times 2 = 11$
- (a) Deduce an expression for entropy changes associated with the changes in volume and temperature of an ideal gas. 4
- (b) Calculate the change in entropy when  $28 \text{ g}$  of  $\text{H}_2$  gas expands reversibly from  $2 \text{ lit}$  to  $20 \text{ lit}$  at  $27^\circ \text{C}$ .  $1\frac{1}{2}$



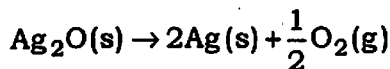
6. (a) State and explain Nernst heat theorem. 2

(b) Explain how the third law of thermodynamics can be used for the evaluation of absolute entropy of a substance. 3½

7. (a) Distinguish between Helmholtz free energy and Gibbs' free energy. 2

(b) Discuss the criteria of spontaneity in terms of Gibbs' free energy. 1½

(c) For the reaction



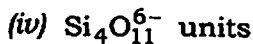
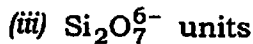
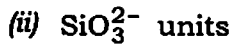
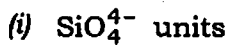
calculate the temperature at which free energy change is equal to zero.  $\Delta H$  for the reaction is  $+30.50 \text{ kJ mol}^{-1}$  and  $\Delta S$  is  $0.066 \text{ kJ mol}^{-1}$  at 1 atm pressure. Predict the nature of the reaction below this temperature. 2

SECTION—II  
( Inorganic Chemistry )

( Marks : 27 )

8. Choose the correct answer from the following : 1×3=3

(a) Pyrosilicate contains



(b)  $\text{B}_{10}\text{C}_2\text{H}_{12}$  is isostructural and isoelectronic with



(c) Electrolytic reduction method is used in extraction of

(i) metalloid

(ii) transition metals

(iii) highly electronegative elements

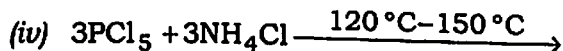
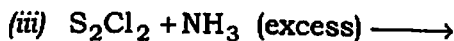
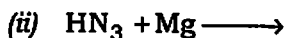
(iv) highly electropositive elements

UNIT—I

9. Answer any *three* of the following :  $3 \times 3 = 9$
- (a) Discuss the formation of B—H—B bond in  $B_2H_6$  molecule.  $BH_3$  does not exist but  $BF_3$  is a stable molecule. Explain.  $2+1=3$
- (b) How will you prepare  $XeO_3$ ? Discuss its structure.  $1+2=3$
- (c) What are zeolites? Mention its uses.  $1+2=3$
- (d) Why borazine is called 'inorganic benzene'? How many isotopic disubstituted borazene molecules  $B_3N_3H_4X_2$  are possible without changing the fundamental ring structure?  $2+1=3$
- (e) How is hydrazine prepared by Raschig's method? Discuss its reducing properties.  $1+2=3$
10. Write short notes on (any *two*) :  $2 \times 2 = 4$
- (a) Fullerene ( $C_{60}$ )
- (b) Carboranes
- (c) Silicone polymers

Or

Complete the following reactions : 1×4=4



UNIT—II

11. (a) Give the changes taking place during roasting of sulphide ores. 2

(b) Write a note on van Arkel process for purification of metals. 2

12. (a) Describe a method (giving necessary chemical equation) for the extraction of the following (any two) : 3×2=6

(i) Nickel metal from bessemerised matte

(ii) Chromium trioxide from chromite ore

(iii) Molybdenum from molybdenite ore

(b) What happens when the following is done (Write any one)? 1

(i) Hydrogen sulphide gas is passed through an acidified aqueous solution of potassium permanganate

(ii) Sodium cobaltinitrite solution is added to potassium chloride solution

SECTION—III

( Organic Chemistry )

( 'Marks : 27 )

13. Choose the correct answer from the following :  $1 \times 3 = 3$

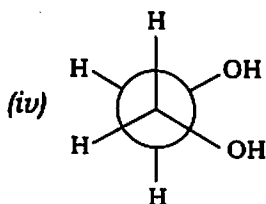
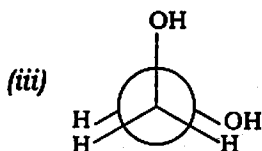
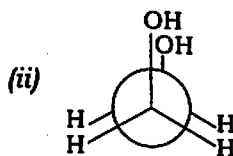
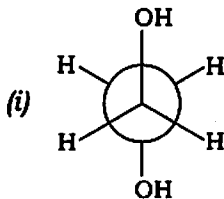
(a) On mixing certain alkane with  $\text{Cl}_2$  and irradiating with UV light, it forms only one monochloro alkane. The alkane is

- (i) propane
- (ii) pentane
- (iii) isopentane
- (iv) neopentane

(b) Which of the following is used for the conversion of 2-hexyne into *trans*-hexene-2?

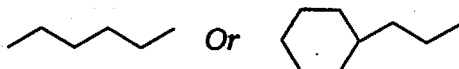
- (i)  $\text{H}_2/\text{Pd}/\text{BaSO}_4$
- (ii)  $\text{NaBH}_4/\text{CH}_3\text{OH}$
- (iii) Li or Na/liq.  $\text{NH}_3$
- (iv)  $\text{LiAlH}_4$

- (c) Which of the following conformers for ethylene glycol is most stable?



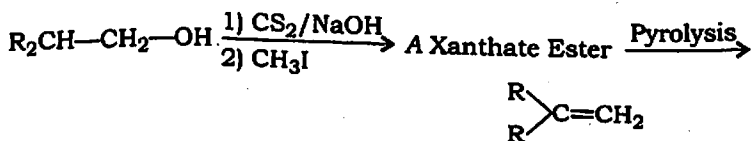
14. Answer any six of the following :  $2 \times 6 = 12$

- (a) Synthesize the following by using Corey-House synthesis :

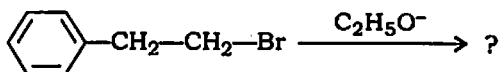


- (b) Addition of HCl to 3,3-dimethyl but-1-ene gives two isomeric alkyl halides. Explain.

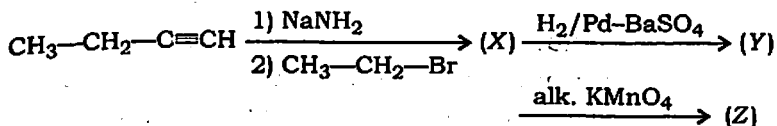
- (c) How will you convert the following?



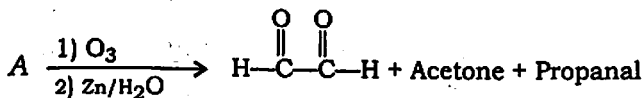
- (d) Give evidences to show that bromination of *cis*- and *trans*-butene-2 is stereoselective.
- (e) Explain the mechanism involved in the following reaction and give the product obtained :



- (f) Identify (X), (Y) and (Z) in the following synthetic scheme :



- (g) How would you synthesize styrene by using Wittig reaction?
- (h) An unsaturated hydrocarbon A adds two equivalents of  $\text{H}_2$  and on reductive ozonolysis gives the following products :



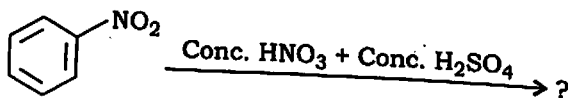
What is the structure of A?

15. Answer any *three* of the following :  $2 \times 3 = 6$

- (a) How would you synthesize methyl cyclopentane from diethyl malonate and a suitable dibromoalkane?
- (b) What are the conformational enantiomers and conformational diastereomers of *n*-Butane? Represent them in Newman projections.
- (c) Draw the energy profile for the conformations of cyclohexane. Why is the chair conformation free of strain?
- (d) Diethyl adipate on treatment with sodium ethoxide undergoes intramolecular condensation to give a cyclic ketone. Complete the reaction.
- (e) Draw the perspective representation and Newman projection of axial and equatorial methyl cyclohexanes.

16. Answer any *three* of the following :  $2 \times 3 = 6$

- (a) Complete the following reaction and suggest the mechanism :





- (b) What is aromaticity? Account for the aromatic behaviour of cyclopentadienyl anion and pyridine.
- (c) *n*-propyl benzene is best prepared by acylation followed by reduction of the carbonyl group with Zn/Hg+HCl rather than by direct alkylation of benzene with *n*-propyl chloride. Explain.
- (d) How would you prepare styrene from benzene and mesitylene from acetone?

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