

Total No. of Printed Pages—12

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(May)

CHEMISTRY

(Major)

Course : 201

(**Physical, Inorganic, Organic**)

(Both New/Old Course)

Full Marks : 80

Pass Marks : 32/24.

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) Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litres at 300 K. The enthalpy change (in kJ) for the process is

(i) 11.4

(ii) -11.4

(iii) 0

(iv) 4.8

(b) Enthalpy of neutralization of HCl with NaOH is x . The heat evolved when 500 ml of 2 N HCl are mixed with 250 ml of 4 N, NaOH will be

(i) $500x$

(ii) $100x$

(iii) x

(iv) $10x$

(c) According to second law of thermodynamics, a process is spontaneous if during the process

(i) $\Delta S_{\text{universe}} > 0$

(ii) $\Delta S_{\text{universe}} = 0$

(iii) $\Delta H_{\text{system}} > 0$

(iv) $\Delta S_{\text{universe}} = \Delta S_{\text{system}}$

Or

To make a solution of pH=12, the amount of NaOH dissolved in one litre of the solution should be

(i) 0.1 g

(ii) 0.2 g

(iii) 0.4 g

(iv) 1.2 g

UNIT—I

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

2. (a) What is Joule-Thomson effect? Show that this effect is isoenthalpic in nature. 1+3=4

(b) Derive a relationship between Joule-Thomson coefficient and thermodynamic quantity. 2

3. (a) How are the temperature and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation. 4

(b) One mole of an ideal gas ($\bar{C}_v = 12.55 \text{ JK}^{-1} \text{ mol}^{-1}$) at 300 K is compressed adiabatically and reversibly to one-fourth of its original volume. Calculate the final temperature of the gas. 2

4. (a) Deduce Kirchhoff's equation. 2

(b) State and explain Hess's law with one suitable example. 2

(c) The heat of formation of methane at 27 °C is -19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume? 2

UNIT—II

Question No. 5 for New Course and
Question No. 6 for Old Course

5. Answer any *two* questions from the following :
- $5\frac{1}{2} \times 2 = 11$
- (a) (i) Derive an expression for the pH of an aqueous solution of a salt of strong base and weak acid. 3
- (ii) The hydrogen ion concentration of 0.02 M sodium acetate is found to be 3.0×10^{-9} M at 25 °C. Calculate the hydrolysis constant of this salt ($K_w = 1.0 \times 10^{-14}$). 2½
- (b) (i) Derive an expression relating the pH of a buffer solution with the concentration of its components. 3
- (ii) Calculate the pH of a solution obtained by mixing 0.083 mole of acetic acid and 0.091 mole of sodium acetate and making the volume 500 ml. K_a for acetic acid is 1.75×10^{-5} . 2½
- (c) (i) Write the definition of solubility product. Explain why ZnS is precipitated in alkaline medium whereas CuS is precipitated in acidic medium. $1 + 2\frac{1}{2} = 3\frac{1}{2}$
- (ii) The solubility product of silver chromate is 2.0×10^{-12} at 25 °C. Calculate the solubility at this temperature. 2

6. Answer any two questions from the following : 5½×2=11

(a) (i) Deduce an expression for efficiency of a Carnot engine working between two temperatures T_1 and T_2 . 4

(ii) An engine operates between 100 °C and 0 °C. Find the efficiency of the engine. 1½

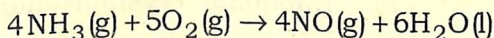
(b) (i) Derive an expression for entropy increase during isothermal mixing of two ideal gases. 3½

(ii) Deduce the following relation : 2

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

(c) (i) State and explain the third law of thermodynamics. How can it be verified experimentally? 2+2=4

(ii) Predict whether at 27 °C, the following reaction is spontaneous or not : 1½



Given, $\Delta H = +9080 \text{ J mol}^{-1}$ and

$$\Delta S = +35.7 \text{ JK}^{-1} \text{ mol}^{-1}.$$

SECTION—II

(Inorganic Chemistry)

(Marks : 27)

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

(a) ZSM-5 is used as catalyst in the synthesis of

(i) *o*-xylene

(ii) *m*-xylene

(iii) *p*-xylene

(iv) toluene

(b) The hybridization used by carbon in fullerene (C_{60}) is

(i) sp

(ii) sp^2

(iii) sp^3

(iv) dsp^2

(c) The purification of metals by zone-refining is based on the principle of

(i) fractional crystallization

(ii) fractional distillation

(iii) vacuum distillation

(iv) distillation under reduced pressure

UNIT—I

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

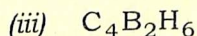
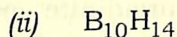
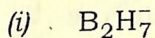
(a) Discuss the structure and bonding of diborane. Show with reaction that bridging hydrogen is different from terminal hydrogen. $2+1=3$

(b) Why are noble gas compounds common in xenon? Explain the structure of XeOF_4 . $1+2=3$

(c) How are silicates classified? Draw the structure of primary units in chain and cyclic silicates. $1+2=3$

(d) What is phosphazene? How is $(\text{NPCl}_2)_3$ prepared? Draw the structure of $(\text{NPCl}_2)_3$. 3

(e) Classify the following by structural type : $1 \times 3 = 3$



9. Write short notes on any *two* of the following : $2 \times 2 = 4$

(a) Hydroxylamine

(b) S_4N_4

(c) Silicone rubber

UNIT—II

10. (a) Give the preparation of any *two* of the following : 1½×2=3
- (i) Potassium dichromate
 - (ii) Sodium cobaltinitrite
 - (iii) Ni-DMG

Or

The oxides of the metals such as Zn, Cu, Pb, etc., are reduced by carbon at high temperature whereas those of Al, Mg, Ca, etc., are not. Explain giving reasons. 3

- (b) Describe the extraction of any *two* of the following : 3×2=6
- (i) Manganese from pyrolusite
 - (ii) Cobalt from smaltite ore
 - (iii) Vanadium from vanadinite ore
- (c) Write a note on hydrometallurgy. 2

SECTION—III

(Organic Chemistry)

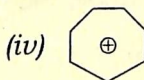
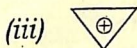
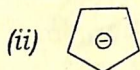
(Marks : 27)

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

(a) Arrange the following alkanes in the order of increasing boiling point :

- (i) *n*-hexane
- (ii) 3-methyl pentane
- (iii) 2,2-dimethyl butane
- (iv) *n*-heptane

(b) Which of the following is not aromatic?



(c) When 1-butyne is treated with dilute H_2SO_4 in presence of HgSO_4 , the major product is

- (i) $\text{CH}_3\text{CH}_2\text{COCH}_3$
- (ii) $\text{CH}_3\text{CH}_2\text{CHO} + \text{HCHO}$
- (iii) $\text{CH}_3\text{CH}_2\text{CHO}$
- (iv) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$

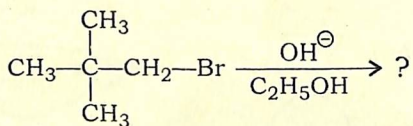
12. Answer any six of the following : $2 \times 6 = 12$

(a) Outline all the steps involved in the preparation of *n*-butane starting from bromoethane using Corey-House synthesis.

(b) How do you prepare an alkene by pyrolysis of an ester? Write necessary chemical equations.

(c) Addition of bromine in CCl_4 to *cis*-2-butene gives (\pm)-2,3-dibromobutane, while that for *trans*-2-butene gives *meso*-2,3-dibromobutane. Explain this with mechanism.

(d) Complete the following reaction and write the plausible mechanism :

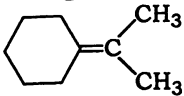


(e) Discuss the mechanism of addition of hypohalous acid to an unsymmetrical alkene with an example.

(f) What is the decreasing order of acidity of ethane, ethylene and acetylene? Also give proper explanation to that order.

(g) Write the methods of preparation of the following :

(i) Styrene from ethanol by using Chugaev reaction

(ii)  from cyclohexanone

by using Wittig reaction

(h) Discuss ozonolysis reaction to an alkyne with an example.

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

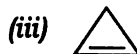
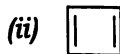
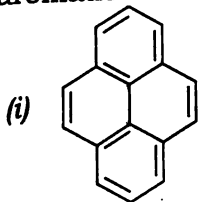
(a) What do you mean by conformational analysis? Draw the most stable conformation of cyclohexane showing axial and equatorial hydrogens.

(b) How do you obtain cyclopentane starting from diethyladipate? Write all necessary equations.

(c) What do you mean by angle strain? Calculate the angle strain for cyclopropane ring.

14. Answer any *four* of the following : $2 \times 4 = 8$

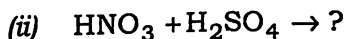
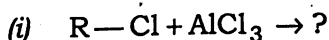
(a) What is aromaticity? Identify the following compounds as aromatic, anti-aromatic or non-aromatic :



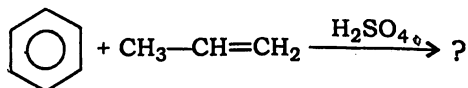
(b) The —NH_2 group attached to a benzene ring is *ortho*- and *para*-directing while —NO_2 group is *meta*-directing. Explain why.

(c) Why is nitrobenzene a suitable solvent for Friedel-Crafts alkylation of phenyl bromide while benzene is not?

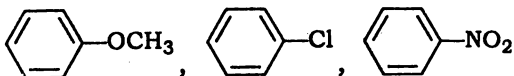
(d) Show the formation of electrophiles in the following reactions :



(e) Complete the following reaction and write the mechanism of the reaction :



(f) Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile. Give reasons :



Total No. of Printed Pages—23

2 SEM TDC CHM M 1 (N/O)

2 0 1 6

(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

- (b) Which of the following pairs has heat of neutralisation equal to -57.3 kJ?
- (i) HCl, NH_4OH
 - (ii) HNO_3 , NaOH
 - (iii) NaOH, CH_3COOH
 - (iv) H_2SO_4 , NH_4OH
- (c) The precipitate of calcium fluoride ($K_{\text{sp}} = 1.7 \times 10^{-10}$) 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.

$2+2=6$

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 kJ at 298 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 μ_{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) FeCl_3 and (ii) NH_4NO_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 mol of NH_4OH and 0.25 mol of NH_4Cl . Given $K_b = 1.8 \times 10^{-5}$. $2 + 1\frac{1}{2} = 3\frac{1}{2}$

(4)

- (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 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 XeF_2 and 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
 P_4O_{10} , H_3PO_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

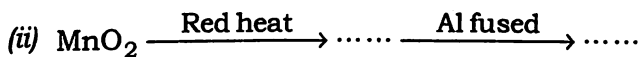
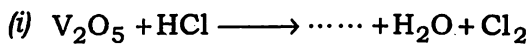
(c) Give the preparation of any two of the following : $1\frac{1}{2} \times 2 = 3$

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

(7)

Or

Complete the following reactions : 3



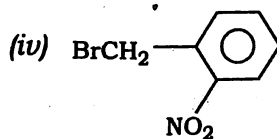
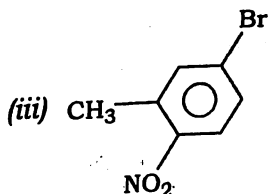
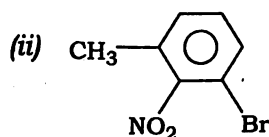
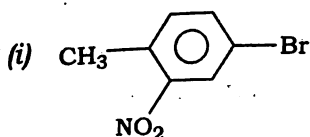
SECTION—III

(Organic Chemistry)

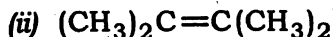
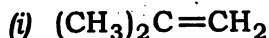
(Marks : 27)

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 H_2O_2) forms

(i) propan-1-ol

(ii) propan-2-ol

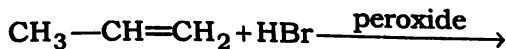
(iii) propane-1,2-diol

(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.

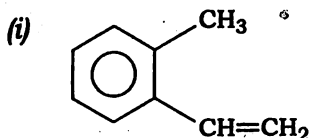
(b) Complete the following reaction and write down the mechanism :



(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.

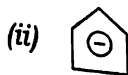
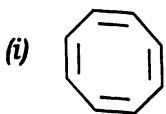
- (h) A hydrocarbon having molecular formula, C_6H_{12} was subjected to ozonolysis giving equimolar amounts of ethyl methyl ketone and acetaldehyde. Identify the structure of hydrocarbon and give IUPAC name of it. Write down the equations involved.

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

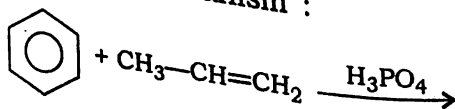
- (a) Discuss the conformational analysis of *n*-butane and draw the potential energy diagram for it.
- (b) Explain 1,3-diaxial interaction in the chair conformation of methyl cyclohexane. "*t*-butylcyclohexane exists 100 percent in the equatorial conformation." Give reasons.
- (c) Synthesize cyclohexane 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 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 AlCl_3 to give compound C, C_9H_{12} . Identify A, B, C and write equations for all the reactions.

- (i) $H_R < H_P$
- (ii) $H_R > H_P$
- (iii) $H_R = H_P$

(iv) None of the above

(b) Which of the following

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

(12)

(Old Course)

Full Marks : 80

Pass Marks : 32

Time : 3 hours

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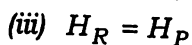
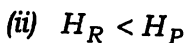
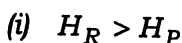
SECTION—I

(Physical Chemistry)

(Marks : 26)

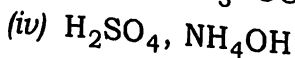
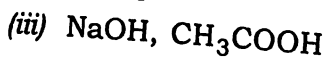
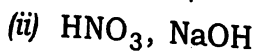
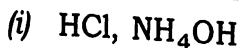
1. Choose the correct answer from the
following : 1×3=3

(a) In endothermic reaction



(iv) None of the above

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



P16/650

(Continued)

(c) The enthalpy of vaporization of a liquid is 30 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

(Turn Over)

- (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 kJ at 298 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 μ_{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 g of H_2 gas expands reversibly from 2 lit to 20 lit at 27°C . $1\frac{1}{2}$

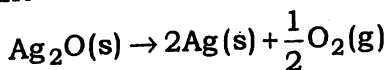
6. (a) State and explain Nernst heat theorem. 2

(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



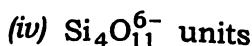
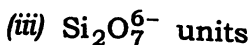
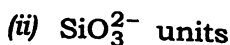
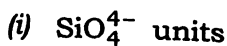
calculate the temperature at which free energy change is equal to zero. ΔH for the reaction is $+30.50 \text{ kJ mol}^{-1}$ and ΔS is $0.066 \text{ kJ mol}^{-1}$ at 1 atm pressure. Predict the nature of the reaction below this temperature. 2

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

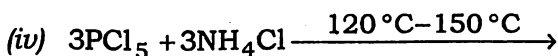
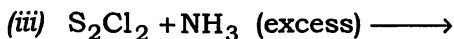
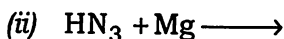
(iv) highly electropositive elements

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 : 1×3=3

(a) On mixing certain alkane with 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?

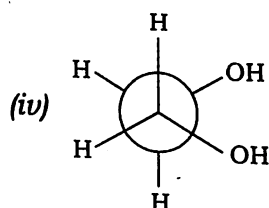
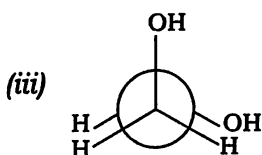
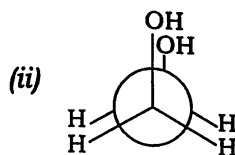
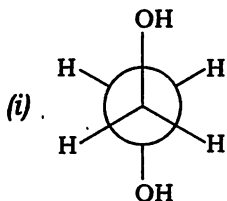
(i) $\text{H}_2/\text{Pd}/\text{BaSO}_4$

(ii) $\text{NaBH}_4/\text{CH}_3\text{OH}$

(iii) Li or Na/liq. NH_3

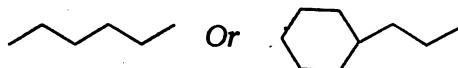
(iv) LiAlH_4

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



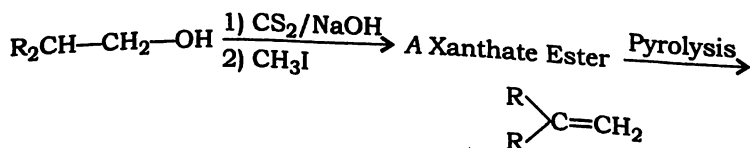
14. Answer any six of the following : 2×6=12

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



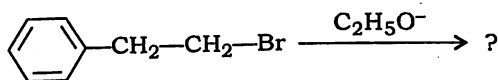
- (b) Addition of HCl to 3,3-dimethyl but-1-ene gives two isomeric alkyl halides. Explain.

- (c) How will you convert the following?

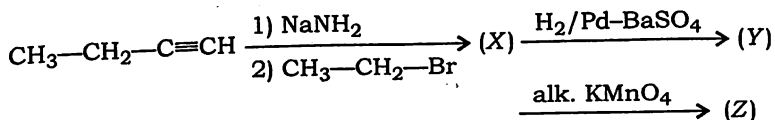


(d) Give evidences to show that bromination of *cis*- and *trans*-butene-2 is stereoselective.

(e) Explain the mechanism involved in the following reaction and give the product obtained :

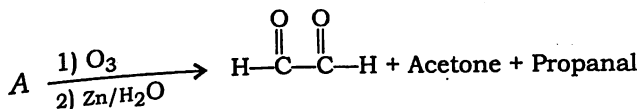


(f) Identify (X), (Y) and (Z) in the following synthetic scheme :



(g) How would you synthesize styrene by using Wittig reaction?

(h) An unsaturated hydrocarbon A adds two equivalents of H_2 and on reductive ozonolysis gives the following products :



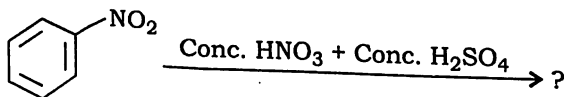
What is the structure of A?

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?

2017

(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) Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is

(i) 11.4

(ii) -11.4

(iii) 0

(iv) 4.8

(b) If one mole of ammonia gas and one mole of hydrogen chloride gas are mixed in a closed container to form ammonium chloride vapour, then

(i) $\Delta H < \Delta E$

(ii) There is no relationship

(iii) $\Delta H > \Delta E$

(iv) $\Delta H = \Delta E$

(c) The solubility product (K_{sp}) of ferric hydroxide in aqueous solution is 3.8×10^{-38} at 298 K. The solubility of Fe^{3+} ions will increase, when

(i) pH is increased

(ii) pH is 7

(iii) pH is decreased

(iv) saturated solution is exposed to atmosphere

UNIT-I

Answer any two of the following :

6×2=12

2. (a) How are the temperature and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation.

4

(b) An ideal gas ($\bar{C}_P = 29.1 \text{ JK}^{-1} \text{ mol}^{-1}$) is expanded reversibly and adiabatically from a volume of 1.43 dm^3 at a pressure of 303975 Pa and temperature 298 K until the volume is 2.86 dm^3 . Calculate the final temperature of the gas.

2

3. (a) What is Joule-Thomson effect? Prove that this effect is isenthalpic in nature.

1+2=3

(b) Thermodynamically show that for an ideal gas, $C_P - C_V = R$.

3

4. (a) Deduce Kirchoff's equation. 2

(b) Explain, giving reasons, the following (any two) : 2×2=4

- (i) For reactions involving condensed phases, $\Delta H = \Delta E$.
- (ii) Enthalpy of neutralization of a strong monobasic acid by a strong base is always equal to $-57.32 \text{ kJ mol}^{-1}$.
- (iii) The Hess' law of constant heat summation is a direct consequence of the first law of thermodynamics.

UNIT—II

5. Answer any two of the following : 5½×2=11

(a) (i) Derive an expression for the pH of an aqueous solution of a salt of strong base and weak acid. 3

(ii) Calculate the pH of 0.1 M aqueous solution of sodium acetate. (pK_a of acetic acid is 4.8) 1½

(iii) Explain why the ionic product of water increases with increase of temperature. 1

(b) (i) Derive the expressions relating the pH of buffer solutions (for both acidic and basic buffers) with the concentration of the components. 2+2=4

(ii) 40 ml of 0.1 M ammonia solution is mixed with 20 ml of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution = 4.74) 1½

(c) (i) What is solubility product? Explain why CoS is precipitated in alkaline medium whereas CdS is precipitated in acidic medium. 1+2=3

(ii) Define ionic product of water. Show that $pK_w = \text{pH} + \text{pOH}$. 1+1½=2½

SECTION—II

(Inorganic Chemistry)

(Marks : 27)

6. Find out the correct answer from the following :

1×3=3

(a) Hybridization involved in the formation of XeOF_4 molecule is sp^3d^2 . The shape of the molecule is

(i) octahedral

(ii) square pyramidal

(iii) trigonal bipyramidal

(iv) pentagonal bipyramidal

(b) The zeolite ZSM-5 is used as catalyst in the manufacture of

(i) toluene

(ii) o-xylene

(iii) p-xylene

(iv) m-xylene

(c) The electrolytic reduction method is used in extraction of

(i) metalloid

(ii) transition metals

(iii) highly electronegative elements

(iv) highly electropositive elements

UNIT—I

7. Answer any three of the following :

3×3=9

(a) How are silicates classified? Give one example of each class.

(b) What are closo-, nido- and arachno-boranes? Give example of each.

(c) How will you prepare hydrazoic acid? What are azides? Mention two uses of it.

(d) Explain the preparation and structure of Borazine.

(e) Describe the preparation and uses of tetrasulphur tetranitride (S_4N_4).

8. Write short notes on (any two) :

2×2=4

(a) Fullerenes

(b) Hydroxylamine

(c) Silicones

UNIT—II

9. Write short note on (any one) :

2

(a) Solvent extraction

(b) Hydrometallurgy

10. Give the preparations of the following (any two) :

1½×2=3

(a) Cobalt nitrate

(b) Ammonium molybdate

(c) Potassium dichromate

11. How will you obtain the following (any two)?

3×2=6

(a) Manganese from pyrolusite ore

(b) Cobalt from smaltite ore

(c) Vanadium from vanadinite ore

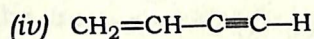
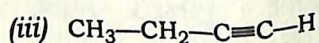
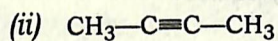
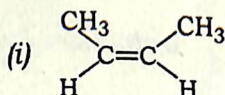
(Organic Chemistry)

(Marks : 27)

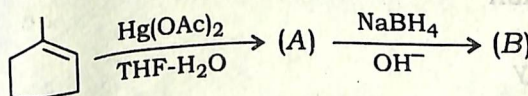
12. Choose the correct answer from the following :

1×3=3

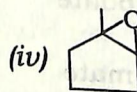
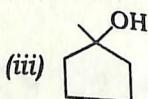
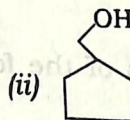
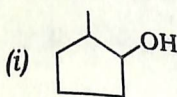
(a) Which of the following hydrocarbons has the lowest dipole moment?



(b) The final product (B) formed in the sequence of the reactions



is

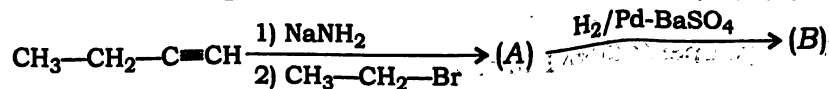
(c) The compound with molecular formula C_8H_{10} , which will give only two isomers on electrophilic substitution with $\text{Cl}_2/\text{FeCl}_3$ or $\text{HNO}_3/\text{H}_2\text{SO}_4$, is(i) *p*-xylene(ii) *m*-xylene(iii) *o*-xylene

(iv) ethyl benzene

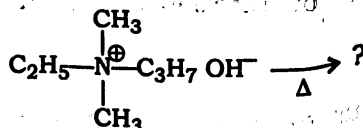
13. Answer any six of the following : 2×6=12

- (a) An alkane (A) C_7H_{16} is produced by the reaction of lithium di(3-pentyl) cuprate with ethylbromide. What is the structure of (A)?
- (b) Synthesize 2-methylpropene from 2-methyl-propanol-1 by using Chugaev reaction.
- (c) What is the best stereospecific conformation for E2 elimination? Explain with a suitable example.
- (d) Give the evidences to show that bromination of *trans*-2 butene and *cis*-2 butene is stereoselective.

(e) Complete the following reactions :



(f) Predict the most stable alkene formed in the following Hofmann elimination :



- (g) Explain that hydroboration reaction is regioselective.
- (h) What product do you expect from the reaction between phenylacetylene and dil H_2SO_4 in the presence of Hg^{+2} ion?

14. Answer any two of the following :

2×2=4

- (a) Synthesize cyclopentane from a suitable dinitrile using Thorpe-Ziegler reaction.
- (b) Discuss the conformational analysis of *n*-butane and draw the energy profile diagram.

(c) Why is the chair conformation free of angle strain?

(d) Draw the Newmann projection formula for axial and equatorial methyl cyclohexane.

15. Answer any four of the following :

2×4=8

(a) Arrange the following compounds in order of increasing tendency to undergo electrophilic aromatic substitution reaction with proper explanation :

Nitrobenzene, Benzene and Toluene

(b) Define Hückel's rule of aromaticity. Mention whether the following are aromatic or not :

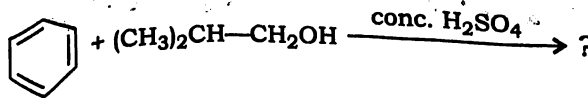
(i) Cyclopentadienyl anion

(ii) Phenanthrene

(c) Give the mechanism of nitration of toluene.

(d) How will you explain the directive influence of $-\text{CH}=\text{CH}_2$ group, when attached to the benzene ring?

(e) Predict the major product in the following reaction :



(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) Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is

(i) 11.4

(ii) -11.4

(iii) 0

(iv) 4.8

(b) If one mole of ammonia gas and one mole of hydrogen chloride gas are mixed in a closed container to form ammonium chloride vapour, then

(i) $\Delta H < \Delta E$

(ii) There is no relationship

(iii) $\Delta H > \Delta E$

(iv) $\Delta H = \Delta E$

(c) The enthalpy and entropy changes for a chemical reaction are -2.5×10^3 cal and 7.4 cal deg^{-1} respectively. The reaction at 298 K is

(i) spontaneous

(ii) reversible

(iii) irreversible

(iv) non-spontaneous

UNIT—I

Answer any two of the following :

6×2=12

2. (a) How are the temperature and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation.

4

- (b) An ideal gas ($\bar{C}_P = 29.1 \text{ JK}^{-1} \text{ mol}^{-1}$) is expanded reversibly and adiabatically from a volume of 1.43 dm^3 at a pressure of 303975 Pa and temperature 298 K until the volume is 2.86 dm^3 . Calculate the final temperature of the gas. 2
3. (a) What is Joule-Thomson effect? Prove that this effect is isoenthalpic in nature. 1+2=3
- (b) Thermodynamically show that for an ideal gas $C_P - C_V = R$. 3
4. (a) Deduce Kirchhoff's equation. 2
- (b) Explain, giving reasons, the following (any two) : 2×2=4
- (i) For reactions involving condensed phases, $\Delta H = \Delta E$.
- (ii) Enthalpy of neutralization of a strong monobasic acid by a strong base is always equal to $-57.32 \text{ kJ mol}^{-1}$.
- (iii) The Hess' law of constant heat summation is a direct consequence of the first law of thermodynamics.

UNIT—II

5. Answer any two of the following : 5½×2=11
- (a) (i) Deduce an expression for entropy changes associated with the changes in temperature and pressure of an ideal gas. 4
- (ii) Calculate the entropy change involved in the isothermal reversible expansion of 5 moles of an ideal gas from a volume of 10 dm^3 to 100 dm^3 at 300 K . 1½
- (b) (i) Deduce an expression for efficiency of a Carnot engine working between two temperatures T_1 and T_2 . 4
- (ii) Liquid helium boils at 4 K and liquid hydrogen boils at 20 K . What is the efficiency of a reversible engine operating between heat reservoirs at these temperatures? 1½

- (c) (i) State and explain the third law of thermodynamics. How can it be verified experimentally? 2+2=4
- (ii) Write the physical significance of Gibbs' free energy. 1½

SECTION—II
(Inorganic Chemistry)
(Marks : 27)

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

(a) Permutit is

- | | |
|-----------------------------|------------------------------|
| (i) a ceramic | (ii) a constituent of cement |
| (iii) an artificial zeolite | (iv) a kind of fullerene |

(b) In XeF_2 , xenon is

- | | |
|----------------------------|---------------------------|
| (i) sp^3d hybridized | (ii) sp^3d^2 hybridized |
| (iii) sp^3d^3 hybridized | (iv) dsp^2 hybridized |

(c) The first step in the extraction of metals from the carbonate ore is

- | | |
|----------------|-----------------------|
| (i) roasting | (ii) calcination |
| (iii) smelting | (iv) carbon reduction |

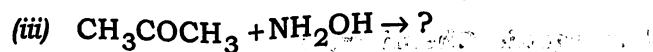
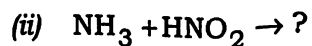
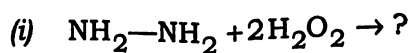
UNIT—I

7. Answer any three of the following : 3×3=9

- (a) What are *closo*-, *nido*- and *arachno*-boranes? Give example of each. 3
- (b) Discuss the structure of XeF_4 . What happens when it is hydrolyzed at low temperature (-80°C)? 2+1=3
- (c) How are silicates classified? Draw the structures of primary units in pyrosilicates and chain silicates. 1+2=3

(d) What are silicones? How can they be prepared? What is silicone rubber? 3

(e) Complete the following reactions : 1×3=3



8. Write short notes on (any two) : 2×2=4

(a) Inorganic benzene

(b) Zeolite

(c) Hydroxylamine

UNIT—II

9. (a) How will you obtain the following (any two)? 3×2=6

(i) Manganese from pyrolusite

(ii) Cobalt from smaltite ore

(iii) Vanadium from vanadinite ore

(b) Write short notes on (any two) : 2×2=4

(i) Zone refining

(ii) Solvent extraction

(iii) Electrolytic reduction

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

(i) Chromic oxide is heated with aluminium powder

(ii) Carbon monoxide gas is passed over nickel powder at 50 °C

SECTION—III

(Organic Chemistry)

(Marks : 27)

10. Choose the correct answer from the following :

1×3=3

(a) Out of the following, the alkene that exhibits optical isomerism is

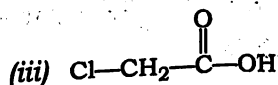
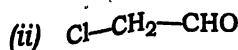
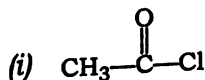
(i) 3-methyl-2-pentene

(ii) 2-methyl-1-pentene

(iii) 3-methyl-1-pentene

(iv) 2-methyl-2-pentene

(b) What is the product formed when acetylene reacts with hypochlorous acid?



(c) Presence of a nitro group in a benzene ring

(i) renders the ring basic

(ii) deactivates the ring towards nucleophilic substitution

(iii) deactivates the ring towards electrophilic substitution

(iv) activates the ring towards electrophilic substitution

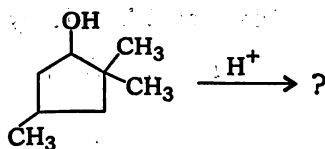
11. Answer any six of the following :

2×6=12

(a) How do you account for acidic nature of alkynes as compared to alkenes? Give two reactions in which acetylene behaves as an acid.

(b) Synthesize propene from acetaldehyde using Peterson reaction.

- (c) Rearrangement is very common in E1 as in S_N1. Predict the product obtained in the following elimination reaction :



- (d) What stereochemical products are obtained when hydroxylation via epoxidation is carried out with *cis*- and *trans*-stilbene?
- (e) An unsaturated hydrocarbon (A) adds two molecules of H₂ and on reductive ozonolysis gives butane-1,4 dial, ethanal and propanone. Give the structure (A) and explain the reactions involved.
- (f) Explain why—
- R—C≡C—R gives a ketone on hydrolysis;
 - electrophilic addition of Br₂ to an alkene involves bridged bromonium ion.
- (g) How would you prepare a phosphorous ylide from Ph₃P? Synthesize styrene from a suitable aldehyde by using the ylide.
- (h) What is Wittig reagent? Synthesize styrene from a suitable aldehyde by using Wittig reagent.

12. Answer any three of the following :

2×3=6

- Explain Baeyer strain theory. Why is it not applicable to cyclohexane?
- Synthesize cyclohexane from esters of pimelic acid (Dieckmann reaction).
- Draw the Newmann projection of chair- and boat-conformation of cyclohexane.
- Draw different conformations of methyl cyclohexane. Assign their stabilities in an energy profile.
- Convert cyclohexanone into cyclopentanone.

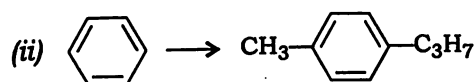
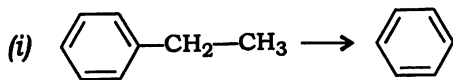
13. Answer any *three* of the following :

2×3=6

(a) What is aromaticity? Account for the aromatic behaviour of—

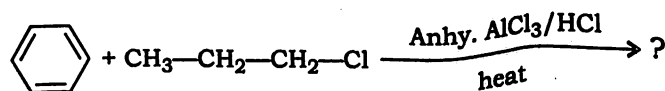
- (i) cyclopropenyl cation;
- (ii) 1,3-cyclopentadienyl anion.

(b) Suggest methods for the following conversions :



(c) The —NH_2 group attached to a benzene ring is *o-/p*-directing, while —NO_2 group is *meta*-directing. Explain, why.

(d) Complete the following reaction and write its mechanism :



(e) Complete the following reactions :

