2 0 1 7

(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 ($\overline{C}_P = 29.1 \ JK^{-1} \ mol^{-1}$) 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

2

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 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 = pH + pOH. 1+1½=2½

(Inorganic Chemistry)

(*Marks* : 27)

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

(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 : $3 \times 3 = 9$

(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

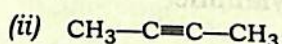(b) Cobalt from smaltite ore
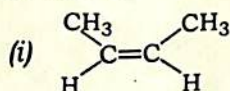
(c) Vanadium from vanadinite ore
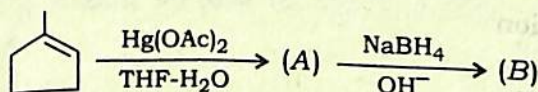
(**Organic Chemistry**)

(*Marks* : 27)

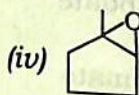12. Choose the correct answer from the following :   1×3=3

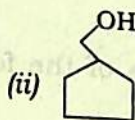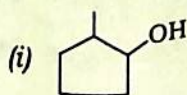(a) Which of the following hydrocarbons has the lowest dipole moment?

(i) CH_3 CH_3
    $\underset{H}{\overset{}{C}}=\underset{H}{\overset{}{C}}$

(ii) $CH_3-C\equiv C-CH_3$

(iii) $CH_3-CH_2-C\equiv C-H$

(iv) $CH_2=CH-C\equiv C-H$
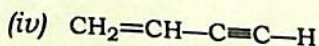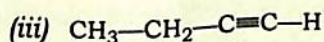
(b) The final product (B) formed in the sequence of the reactions

$$\triangle \xrightarrow[\text{THF-H}_2\text{O}]{\text{Hg(OAc)}_2} (A) \xrightarrow[\text{OH}^-]{\text{NaBH}_4} (B)$$

is

(i) [structure with OH]

(ii) [structure with OH]

(iii) [structure with OH]

(iv) [epoxide structure]
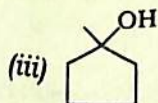
(c) The compound with molecular formula C_8H_{10}, which will give only two isomers on electrophilic substitution with $Cl_2/FeCl_3$ or HNO_3/H_2SO_4, is

(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 :

$$CH_3-CH_2-C\equiv CH \xrightarrow[\text{2) } CH_3-CH_2-Br]{\text{1) } NaNH_2} (A) \xrightarrow{H_2/Pd\text{-}BaSO_4} (B)$$
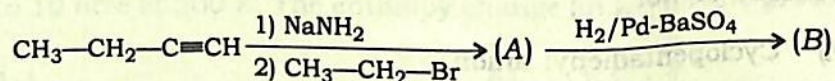
(f) Predict the most stable alkene formed in the following Hofmann elimination :

$$C_2H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}-C_3H_7 \ OH^- \xrightarrow{\Delta} ?$$
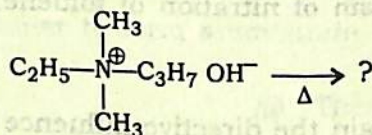
(g) Explain that hydroboration reaction is regioselective.

(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 : $2 \times 4 = 8$

(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 :
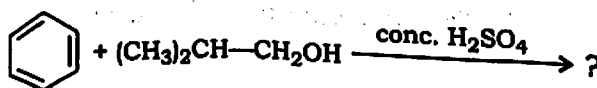
(i) Cyclopentadienyl anion

(ii) Phenanthrene

(c) Give the mechanism of nitration of toluene.

(d) How will you explain the directive influence of $—CH=CH_2$ group, when attached to the benzene ring?

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

$$\bigcirc + (CH_3)_2CH—CH_2OH \xrightarrow{\text{conc. } H_2SO_4} ?$$

Full Marks : 80

Pass Marks : 32

Time : 3 hours

The figures in the margin indicate full marks for the questions

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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 $-2·5 \times 10^3$ 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 $(\bar{C}_P = 29 \cdot 1 \ \text{JK}^{-1} \ \text{mol}^{-1})$ is expanded reversibly and adiabatically from a volume of $1 \cdot 43 \ \text{dm}^3$ at a pressure of 303975 Pa and temperature 298 K until the volume is $2 \cdot 86 \ \text{dm}^3$. 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 $-57 \cdot 32 \ \text{kJ mol}^{-1}$.

(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 $10 \ \text{dm}^3$ to $100 \ \text{dm}^3$ 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

11

P7/573 [P.T.O.

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

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

    (i) $NH_2—NH_2 + 2H_2O_2 \rightarrow ?$

    (ii) $NH_3 + HNO_2 \rightarrow ?$

    (iii) $CH_3COCH_3 + NH_2OH \rightarrow ?$
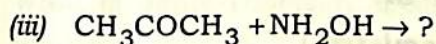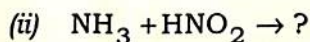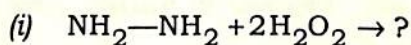
8. Write short notes on (any *two*) :   2×2=4

    (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

12

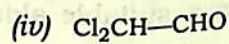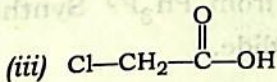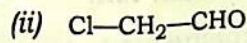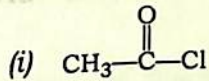## SECTION—III

(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?

(i) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-Cl$ (ii) $Cl-CH_2-CHO$

(iii) $Cl-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH$ (iv) $Cl_2CH-CHO$

(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.

[P.T.O.

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

$$\text{(structure: cyclopentane ring with OH, two } CH_3 \text{ groups and one } CH_3) \xrightarrow{H^+} ?$$
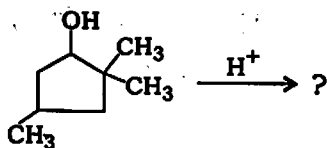
(d) What stereochemical products are obtained when hydroxylation via epoxidation is carried out with *cis*- and *trans*-stilbene?

(e) An unsaturated hydrocarbon (A) adds two molecules of H_2 and on reductive ozonolysis gives butane-1,4 dial, ethanal and propanone. Give the structure (A) and explain the reactions involved.

(f) Explain why—

   (i) $R—C\equiv C—R$ gives a ketone on hydrolysis;

   (ii) electrophilic addition of Br_2 to an alkene involves bridged bromonium ion.

(g) How would you prepare a phosphorous ylide from Ph_3P? 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

   (a) Explain Baeyer strain theory. Why is it not applicable to cyclohexane?

   (b) Synthesize cyclohexane from esters of pimelic acid (Dieckmann reaction).

   (c) Draw the Newmann projection of chair- and boat-conformation of cyclohexane.

   (d) Draw different conformations of methyl cyclohexane. Assign their stabilities in an energy profile.
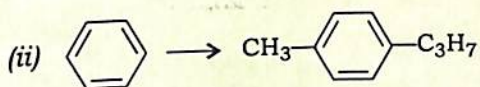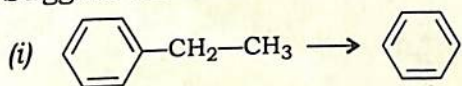
   (e) Convert cyclohexanone into cyclopentanone.

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

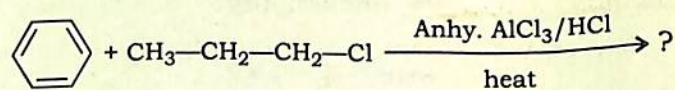(a) What is aromaticity? Account for the aromatic behaviour of—

   (i)   cyclopropenyl cation;

   (ii) 1,3-cyclopentadienyl anion.

(b). Suggest methods for the following conversions :

   (i)   —CH$_2$—CH$_3$ ⟶

   (ii)   ⟶ CH$_3$— —C$_3$H$_7$

(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 :

    + CH$_3$—CH$_2$—CH$_2$—Cl $\xrightarrow[\text{heat}]{\text{Anhy. AlCl}_3/\text{HCl}}$?

(e) Complete the following reactions :

   (i) $\xrightarrow{\text{alk. KMnO}_4}$ (A) $\xrightarrow{\Delta}$ (B)

   (ii) $\xrightarrow[\text{2) H}_2\text{O}_2/\text{OH}^-]{\text{1) B}_2\text{H}_6 \text{ in THF}}$?

★ ★ ★