2 0 1 8

(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 : $1 \times 3 = 3$

(a) The enthalpy of combustion of carbon is -394 kJ mol^{-1}. The heat evolved in the combustion of $6 \cdot 02 \times 10^{22}$ atoms of carbon is

(i) 3940 kJ

(ii) 394 kJ

(iii) 39·4 kJ

(iv) 0·394 kJ

(b) Enthalpy change of a reaction does not depend upon the

   (i) conditions of a reaction

   (ii) initial and final states of the system

   (iii) physical states of reactants and products

   (iv) number of steps in the reaction

(c) Degree of hydrolysis of a salt of weak acid and weak base

   (i) increases with concentration

   (ii) decreases with concentration

   (iii) is independent of concentration

   (iv) None of the above

UNIT—I

Answer any *two* of 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 amount of 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) Enthalpy of formation of ethane at constant pressure is $-110 \cdot 46$ kJ mol^{-1} at 298 K. Find its value at constant volume.   2

(c) Differentiate between bond dissociation energy and bond energy giving one example.   2

4. *(a)* Derive the relationship between Joule-Thomson coefficient and thermodynamic properties.   3

(b) Prove that Joule-Thomson coefficient is zero for an ideal gas.   3

UNIT—II

Answer any *two* questions from the following : $5\frac{1}{2} \times 2 = 11$

5. *(a)* Derive an expression for the pH of an aqueous solution of a salt of strong acid and weak base. $3\frac{1}{2}$

(b) Explain the acidic or basic nature of aqueous solutions of *(i)* CH_3COONa and *(ii)* $(NH_4)_2SO_4$.   2

6. *(a)* Equimolar solution of NH_4OH and NH_4Cl forms a buffer solution. Derive an expression relating the pH of this buffer solution with the concentration of its components. $2\frac{1}{2}$

(b) Define buffer capacity.   1

(c) In an aqueous solution, molar concentration of NH_4OH is $0 \cdot 2$ M and that of $(NH_4)_2SO_4$ is $0 \cdot 1$ M. Calculate the pH of buffer solution. $K_b = 1 \cdot 0 \times 10^{-5}$.   2

7. *(a)* Distinguish solubility product from ionic product. $1\frac{1}{2}$

(b) A dilute solution of HCl contains Cu^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+} ions. On passing H_2S gas in this solution, which metal ions will be precipitated as metal sulphides and why?   2

(c) The solubility products of Ag_2CrO_4 and $AgBr$ are 32×10^{-12} (mole $L^{-1})^3$ and 4×10^{-14} (mole $L^{-1})^2$ respectively. Calculate the ratio of molarities of their saturated solutions.   2

SECTION—II

(Inorganic Chemistry)

(*Marks* : 27)

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

(a) The number of five-membered faces present in C_{60} is

     (i) 12

     (ii) 20

     (iii) 24

     (iv) 36

(b) Pyrosilicate contains

     (i) SiO_4^{4-} units

     (ii) SiO_3^{2-} units

     (iii) $Si_2O_7^{6-}$ units

     (iv) $Si_4O_{11}^{6-}$ units

(c) The metal oxide which cannot be reduced by carbon is

     (i) ZnO

     (ii) PbO

     (iii) Fe_2O_3

     (iv) Cr_2O_3

UNIT—I

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

(a) Explain the formation of 3C—2e bond in diborane (B_2H_6).   3

(b) Explain the structure of the following compounds :   1½×2=3

     (i) XeO_3

     (ii) XeF_4

(c) Classify the following by structural type :   1+1+1=3

     (i) $B_{10}H_{18}$

     (ii) $B_{11}H_{13}^{2-}$

     (iii) $C_2B_7H_{12}^{-}$

(d) Explain why (any *two*) :   1½×2=3

     (i) Borazine is called inorganic benzene.

     (ii) Hydrazine is used as rocket fuel.

     (iii) XeF_6 cannot be stored in glass vessel.

(e) How is triphenyl phosphine prepared? Mention its two uses.   1+2=3

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

(a) Zeolite

(b) Hydrazoic acid

(c) Wade's rule

UNIT—II

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

(a) Nickel from pentlandite

(b) Chromic oxide from its ore

(c) Molybdenum from molybdenite ore

12. Give the preparations of the following (any *two*) :   1½×2=3

(a) Chromyl chloride

(b) Ni-DMG

(c) $KMnO_4$

13. Write a short note on (any *one*) :   2
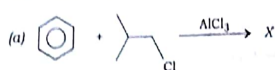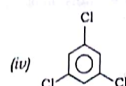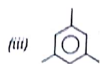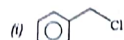
(a) van Arkel process

(b) Zone refining

(Organic Chemistry)

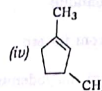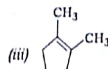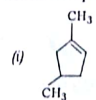(Marks : 27)

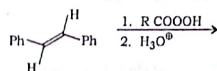14. Choose the correct answer from the following : 1×3=3

(a)

In the above reaction, compound X is

(i)

(ii)

(iii)

(iv)

(b) Which compound would give 5-keto-2-methylhexanal on ozonolysis?

(i)

(ii)

(iii)

(iv)

(c) The product of the reaction

is

(i) (+)-1,2-diphenylethane-1,2-diol

(ii) (–)-1,2-diphenylethane-1,2-diol

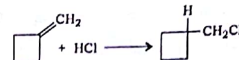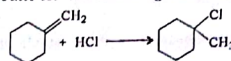(iii) (±)-1,2-diphenylethane-1,2-diol

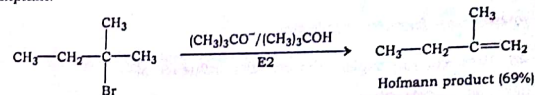(iv) meso-1,2-diphenylethane-1,2-diol
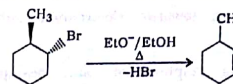
15. Answer any six of the following : 2×6=12

(a) Account for the following observations :

(b) 2-Bromo-2-methylbutane undergoes E2 elimination of HBr in the presence of t-BuO$^-$ to give an excess of less-substituted alkene (the Hofmann product), even though the leaving group is a neutral one. Explain.
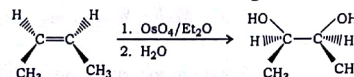
(c) Write the mechanism of the following reaction :

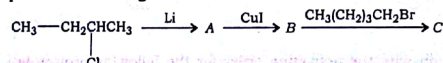(d) Write two synthetic importances of Wittig reaction giving suitable example.

(e) Write a short note on Heck reaction.

(f) Write the mechanism of the following reaction :

(g) Complete the following reaction :

$$CH_3—CH_2CHCH_3 \xrightarrow{Li} A \xrightarrow{CuI} B \xrightarrow{CH_3(CH_2)_3CH_2Br} C$$

(with Cl on the CH carbon)

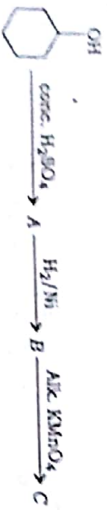(h) Give examples of regioselective and stereoselective reactions.

16. Answer any two of the following : $2\times2=4$

(a) Why is boat conformation of cyclohexane less stable than that of chair conformation?

(b) Explain why equatorial methylcyclohexane is more stable than axial methylcyclohexane.

(c) Complete the following reaction :

$$\xrightarrow{conc.\ H_2SO_4} A \xrightarrow{H_2/Ni} B \xrightarrow{Alk.\ KMnO_4} C$$

(d) Synthesize cyclopentane from a calcium salt of adipic acid.

17. Answer any four of the following : $2\times4=8$

(a) How will you explain the directive influence of—

   (i) —CH=CH$_2$;

   (ii) —CCl$_3$ group;

   when attached to benzene ring towards electrophilic substitution reaction?

(b) Synthesize o-nitroaniline using sulphonation and desulphonation processes.

(c) How would you prepare o-acyltoluene from toluene, though the o-position is a less-effective position?

(d) Classify the following compounds as aromatic, anti-aromatic and non-aromatic :

   (i)

   (ii)

   (iii)

   (iv)
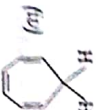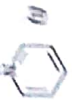
(e) Explain why the activating order for the following groups is

$$O^- > —OH > —OCOR$$

(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 : 25)

1. Choose the correct answer from the following : $1\times3=3$

(a) The enthalpy of combustion of carbon is −394 kJ mol^{-1}. The heat evolved in the combustion of $6\cdot02\times10^{22}$ atoms of carbon is

   (i) 3940 kJ

   (ii) 394 kJ

   (iii) 39·4 kJ

   (iv) 0·394 kJ

(b) Enthalpy change of a reaction does not depend upon the

   (i) conditions of a reaction

   (ii) initial and final states of the system

   (iii) physical states of reactants and products

   (iv) number of steps in the reaction

(c) At equilibrium, Gibbs free energy (ΔG)

   (i) is > 0

   (ii) is < 0

   (iii) is zero

   (iv) depends upon reaction

UNIT—I

6×2=12

Answer any *two* of the following :

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 amount of 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) Enthalpy of formation of ethane at constant pressure is -110.46 kJ mol^{-1} at 298 K. Find its value at constant volume. 2

   (c) Differentiate between bond dissociation energy and bond energy giving one example. 2

4. (a) Derive the relationship between Joule-Thomson coefficient and thermodynamic quantities. 3

   (b) Prove that Joule-Thomson coefficient is zero for an ideal gas. 3

UNIT—II

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

5. (a) Deduce an expression for entropy increase during the isothermal mixing of two ideal gases. 3½

   (b) Enthalpy of fusion of ice is 6.025 kJ mol^{-1}. Calculate the entropy change when 9 g ice melts into water at 273 K. 2

6. (a) Deduce the following relation : 2

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

   (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. Discuss the criteria of spontaneity in terms of Gibbs free energy. 2+1½=3½

   (b) For the reaction $2A + B \rightarrow C$ at 298 K, $\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range? 2

SECTION—II

(Inorganic Chemistry)

(*Marks* : 27)

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

   (a) The shape of XeF_4 molecule is

   (i) tetrahedral

   (ii) octahedral

   (iii) square plannar

   (iv) trigonal

   (b) In $Ni(CO)_4$, the oxidation state of nickel is

   (i) +4

   (ii) +3

   (iii) +2

   (iv) 0

   (c) The metal which cannot be extracted by carbon reduction process is

   (i) Al

   (ii) Zn

   (iii) Pb

   (iv) Ag

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

   (a) Give the method of preparation and explain the structure of borazine. 1+2=3

   (b) Explain the bonding structure of diborane (B_2H_6). 3
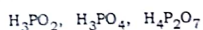
(c) Discuss the structure of—

   (i) XeF_4;

   (ii) $XeOF_4$. $1\frac{1}{2} \times 2 = 3$

(d) Give the structures of the following : $1 + 1 + 1 = 3$

   H_3PO_2, H_3PO_4, $H_4P_2O_7$

(e) Give one method of preparation, chemical property and use of hydrazoic acid. $1 + 1 + 1 = 3$

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

  (a) Fullerene (C_{60})

  (b) Tetrasulphur tetranitride (S_4N_4)

  (c) Wade's rule

UNIT—II

11. (a) How will you obtain the following (any *two*)? $3 \times 2 = 6$

   (i) Chromic oxide from its ore

   (ii) Nickel from pentlandite

   (iii) Manganese from pyrolusite

  (b) Write short notes on (any *two*) : $2 \times 2 = 4$

   (i) van Arkel process

   (ii) Hydrometallurgy

   (iii) Carbon reduction

  (c) Complete the following reaction :   1

   $Mn_3O_4 + Al \longrightarrow \underline{\ ?\ } + \underline{\ ?\ }$

SECTION—III

(Organic Chemistry)

(Marks : 27)

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

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

   (i) H_2 / Pd / $BaSO_4$

   (ii) Li or Na / Liq. NH_3

   (iii) $NaBH_4$ / CH_3OH
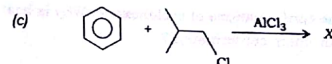
   (iv) $LiAlH_4$

  (b) Hydroboration of propene forms
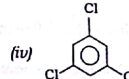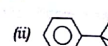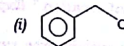
   (i) propan-1-ol

   (ii) propane-1,2-diol

   (iii) propan-2-ol

   (iv) 1,2-diacetoxy mercury propane

  (c)

   In the above reaction, compound X is

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

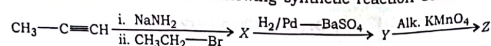 (a) Addition of HBr to 3,3-dimethyl-but-1-ene gives isomeric alkyl halides. Explain.

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

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

$$CH_3-C\equiv CH \xrightarrow[\text{ii. } CH_3CH_2-Br]{\text{i. } NaNH_2} X \xrightarrow{H_2/Pd-BaSO_4} Y \xrightarrow{\text{Alk. } KMnO_4} Z$$
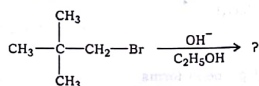
(d) Write two synthetic importances of Wittig reaction giving suitable example.

(e) Prepare n-pentane with the help of Corey-House synthesis.

(f) X is an alkene and on ozonolysis, it gives a mixture of acetaldehyde and acetone as a product. Identify X and write down the reactions.

(g) Complete the following reaction and suggest the mechanism :

$$CH_3-\underset{\underset{CH_3}{\overset{CH_3}{|}}}{\overset{|}{C}}-CH_2-Br \xrightarrow[C_2H_5OH]{OH^-} \text{ ?}$$

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

14. Answer any *three* questions from the following : 2×3=6

(a) Draw the energy profile for the conformations of cyclohexane. Why is boat conformation less stable than chair conformation?

(b) Synthesize cyclopentane starting from diethyladipate.

(c) "t-butyl cyclohexane exists 100% in equatorial conformation." Explain.
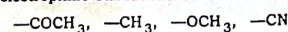
(d) Define angle strain. Calculate the angle strain for cyclobutane ring.

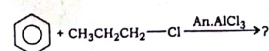15. Answer any *three* from the following : 2×3=6

(a) Classify the following compounds as aromatic, anti-aromatic or non-aromatic :

(i)

(ii)

(iii)

(iv)

(b) Which of the following groups are o-/p- and m-directing towards aromatic electrophilic substitution?

$$-COCH_3, \quad -CH_3, \quad -OCH_3, \quad -CN$$

(c) Complete the following reaction and suggest the mechanism :

$$\text{(benzene)} + CH_3CH_2CH_2-Cl \xrightarrow{\text{An.AlCl}_3} \text{?}$$

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

★ ★ ★