

2 0 1 3

(May)

CHEMISTRY

(Major)

Course : 201

(Physical, Inorganic, Organic)

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 :

1×3=3

(a) A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(2)

- (iii) used to determine pressure-volume work
(iv) whose value depends on temperature only
- (b) The enthalpy of combustion of carbon is -394 kJ mol^{-1} . The heat evolved in the combustion of 6.02×10^{22} atoms of carbon is
- (i) 3940 kJ
(ii) 394 kJ
(iii) 39.4 kJ
(iv) 0.394 kJ
- (c) The equilibrium constant for a reaction is 10. The value of standard free energy, ΔG° is
- (i) -5.7 kJ mol^{-1}
(ii) 5.7 kJ mol^{-1}
(iii) -57 kJ mol^{-1}
(iv) 57 kJ mol^{-1}

UNIT—I

Answer any two of the following :

6×2=12

2. (a) Explain why we have to define the heat capacity of gases under constant pressure and constant volume condition.

2

P13—2000/1098

(Continued)

(3)

- (b) Thermodynamically show that for an ideal gas $C_P - C_V = R$. 3
- (c) Differentiate between extensive and intensive property with one example. 1
3. (a) What is Joule-Thomson effect? Prove that this effect is isoenthalpic. 2
- (b) Deduce a relation between temperature and volume for an adiabatic expansion of an ideal gas. 2
- (c) One mole of an ideal gas ($\bar{C}_V = 12.55 \text{ J K}^{-1} \text{ mol}^{-1}$) at 300 K is compressed adiabatically and reversibly to one-fourth of its original volume. What is the final temperature of the gas?
4. (a) Derive Kirchhoff's equation.
- (b) State and explain Hess's law with one suitable example.
- (c) The bond enthalpy of $\text{H}_2(\text{g})$ is 436 kJ mol^{-1} and that of $\text{N}_2(\text{g})$ is $941.3 \text{ kJ mol}^{-1}$. Calculate the average bond enthalpy of an N—H bond in ammonia.
Given, $\Delta H_f^\circ(\text{NH}_3) = -46.0 \text{ kJ mol}^{-1}$

P13—2000/1098

(Turn O

(4)

UNIT—II

Answer any two of the following :

$5\frac{1}{2} \times 2 = 11$

5. (a) Deduce an expression for the entropy changes associated with the changes in temperature and pressure of an ideal gas. 4
- (b) The enthalpy of vaporization of water is 40.8 kJ mol^{-1} at 373 K. Calculate the change in entropy of the transition of water to steam at 373 K. $1\frac{1}{2}$
6. (a) Derive an expression for entropy increase during isothermal mixing of two ideal gases. 3
- (b) Discuss the criteria of spontaneity in terms of Gibbs' free energy. 1
- (c) For a reaction, $\Delta H = 10.5 \times 10^3 \text{ J mol}^{-1}$ and $\Delta S = 31 \text{ JK}^{-1} \text{ mol}^{-1}$ at 298 K. Decide whether the reaction is spontaneous or not at this temperature. $1\frac{1}{2}$
7. (a) State and explain the third law of thermodynamics. How can it be verified experimentally? $2+2=4$
- (b) Prove that

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad 1\frac{1}{2}$$

P13—2000/1098

(Continued)

(5)

SECTION—II

(Inorganic Chemistry)

(Marks : 27)

8. Choose the correct answer :

$1 \times 3 = 3$

- (a) B_nH_{n+6} belongs to
- (i) closo
 - (ii) nido
 - (iii) arachno
 - (iv) hypo
- (b) The number of five-membered faces present in fullerene is
- (i) 12
 - (ii) 20
 - (iii) 25
 - (iv) 36
- (c) The metal oxide which cannot be reduced by carbon is
- (i) ZnO
 - (ii) PbO
 - (iii) Fe_2O_3
 - (iv) Cr_2O_3

P13—2000/1098

(T

(6)

UNIT—I

9. Answer any *three* of the following : $3 \times 3 = 9$
- (a) Explain the formation of $3c-2e$ bond in boranes. 3
 - (b) What are phosphazenes? How is $(\text{NPCl}_2)_x$ polymer prepared? $1+2=3$
 - (c) Why are noble gas compounds common in xenon? How are XeO_3 and XeF_4 prepared? 3
 - (d) What are silicones? How can they be prepared? What is silicone rubber? 3
 - (e) Give the structures of the following : 3
 H_3PO_2 , H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$

10. Write short notes on (any *two*) : $2 \times 2 = 4$
- (a) Inorganic benzene
 - (b) Zeolite
 - (c) Hydrazoic acid
 - (d) Carboranes

P13—2000/1098

(Continued)

(7)

UNIT—II

11. Answer any *three* of the following : $2 \times 3 = 6$
- (a) Describe the changes taking place during roasting of a sulphide ore.
 - (b) Why calcium cannot be obtained by carbon reduction of CaO ?
 - (c) Explain the role of solvent extraction in metallurgical process.
 - (d) What is hydrometallurgy? Where is it generally used? Give one example of hydrometallurgical process.
 - (e) Reducing capabilities of elements generally decrease with increase in temperature but that of carbon increases. Why?

12. Describe the extraction of any *two* of the following : $2\frac{1}{2} \times 2 = 5$
- (a) Molybdenum from wolfeite ore
 - (b) Cobalt from smaltite ore
 - (c) Vanadium from vanadinite ore

P13—2000/1098

(Turn Over)

(8)

SECTION—III
(Organic Chemistry)
(Marks : 27)

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

(a) Which of the following groups activates the benzene ring toward electrophilic substitution reaction?

- (i) $-\text{NO}_2$
- (ii) $-\text{SO}_3\text{H}$
- (iii) $-\text{OCH}_3$
- (iv) $-\text{CHO}$

(b) The addition of Br_2 to *cis*-butene gives

- (i) (+) 2,3-dibromobutane only
- (ii) (-) 2,3-dibromobutane only
- (iii) racemic-2,3-dibromobutane
- (iv) meso-2,3-dibromobutane

(c) Which of the following reacts fastest with Br_2 + anhydrous AlCl_3 ?

- (i) Benzene
- (ii) Nitrobenzene
- (iii) Toluene
- (iv) Anisole

-2000/1098

(Continued)

(9)

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

(a) Give the mechanism of elimination of second-order on alkyl halide. 2

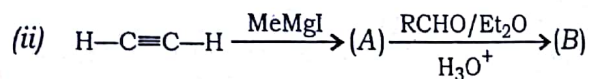
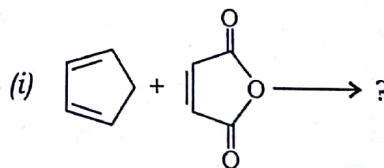
(b) Write the method of preparation of the following (any one) : 2

- (i) 2-Methyl propene by using chloromethyl trimethyl silane (Peterson reaction)
- (ii) Alkynes by an $\text{S}_{\text{N}}2$ reaction

(c) Explain, why—

- (i) $\text{R}-\text{C}\equiv\text{C}-\text{R}$ gives a ketone on hydration;
- (ii) electrophilic addition of Br_2 to an alkene involves bridged bromonium ion. 1+1=2

(d) Write down the product(s) obtained in the following reactions : 1+1=2



P13—2000/1098

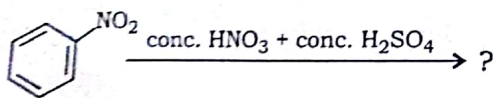
(Turn Over)

(10)

- (e) Explain that hydroboration-oxidation takes place with anti-Markownikoff regioselectivity. 2
- (f) What stereochemical products are obtained when hydroxylation via epoxidation is carried out with *cis*- and *trans*-stilbene? 2
- (g) A hydrocarbon which has the molecular formula C_6H_{12} was subjected to ozonolysis and it gives equimolecular quantities of ethyl methyl ketone and acetaldehyde. Assign the structure and give IUPAC name to the hydrocarbon. 2
- (h) How would you synthesise isoprene from acetylene? 2

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

- (a) Discuss the Dieckman cyclisation reaction with mechanism. 2
- (b) Show how you will prepare 1-methylcyclobutane from 1,3-dibromopropane and diethylmalonate. 2
- (c) Complete the following reaction and suggest the mechanism : 2

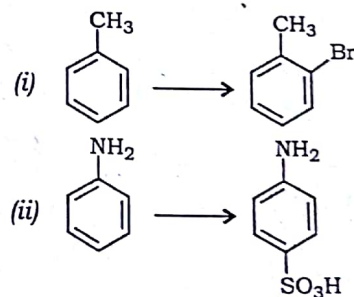


13-2000/1098

(Continued)

(11)

- (d) Compare the torsional strain in the gauche conformation of *n*-butane with that in the anticonformation. Draw the Newman projection of both and indicate the values of the dihedral angles between the methyl groups. 2
- (e) Represent axial and equatorial substituted methylcyclohexane in perspective and Newman projection. Why is equatorial substituted conformation more stable than the axial conformation? 2
- (f) What is aromaticity? Account for the aromatic behaviour of cyclopropenyl cation and 1,3-cyclopentadienyl anion. 2
- (g) Suggest reagents for the following conversions : 1+1=2



- (h) How would you prepare styrene from benzene and mesitylene from acetone? 1+1=2

P13-2000/1098

2 SEM TDC CHM M 1