

Total No. of Printed Pages—11

**2 SEM TDC CHM M 1**

**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  $-394 \text{ kJ mol}^{-1}$ . The heat evolved in the combustion of  $6.02 \times 10^{22}$  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,  $\Delta G^\circ$  is
- (i)  $-5.7 \text{ kJ mol}^{-1}$
- (ii)  $5.7 \text{ kJ mol}^{-1}$
- (iii)  $-57 \text{ kJ mol}^{-1}$
- (iv)  $57 \text{ kJ mol}^{-1}$

UNIT—I

Answer any *two* of the following :

$6 \times 2 = 12$

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

2

- (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? 2
4. (a) Derive Kirchoff's equation. 2
- (b) State and explain Hess's law with one suitable example. 2
- (c) The bond enthalpy of  $\text{H}_2(\text{g})$  is  $436 \text{ kJ mol}^{-1}$  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,  $\Delta H_f^\circ(\text{NH}_3) = -46.0 \text{ kJ mol}^{-1}$  2

## 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  $40.8 \text{ kJ mol}^{-1}$  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

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

SECTION—II  
( Inorganic Chemistry )

( Marks : 27 )

8. Choose the correct answer : 1×3=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)  $Cr_2O_3$

## 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  $\text{XeO}_3$  and  $\text{XeF}_4$  prepared? 3
- (d) What are silicones? How can they be prepared? What is silicone rubber? 3
- (e) Give the structures of the following : 3  
 $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_4\text{P}_2\text{O}_7$
10. Write short notes on (any *two*) :  $2 \times 2 = 4$
- (a) Inorganic benzene
- (b) Zeolite
- (c) Hydrazoic acid
- (d) Carboranes

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  $\text{CaO}$ ?
- (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

SECTION—III

( Organic Chemistry )

( Marks : 27 )

13. Choose the correct answer : 1×3=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  $\text{Br}_2$  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  $\text{Br}_2 + \text{anhydrous AlCl}_3$ ?

(i) Benzene

(ii) Nitrobenzene

(iii) Toluene

(iv) Anisole



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)

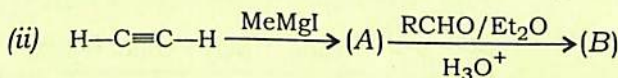
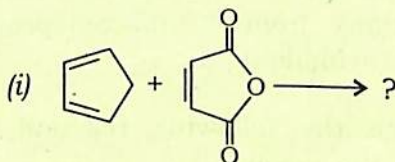
(ii) Alkynes by an  $S_N2$  reaction

(c) Explain, why—

(i)  $R-C \equiv C-R$  gives a ketone on hydration;

(ii) electrophilic addition of  $Br_2$  to an alkene involves bridged bromonium ion. 1+1=2

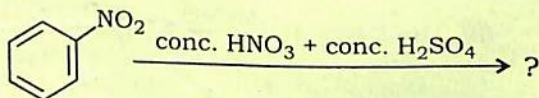
(d) Write down the product(s) obtained in the following reactions : 1+1=2



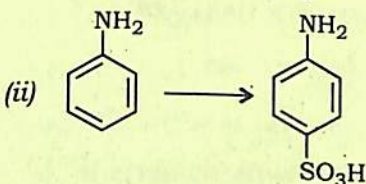
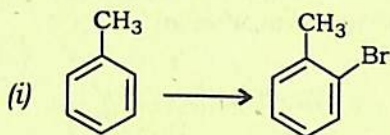
- (e) Explain that hydroboration-oxidation takes place with anti-Markownikoff regioselectivity. 2
- (f) What stereochemical products are obtained when hydroxylation via epoxidation is carried out with *cis*- and *trans*-stilbene? 2
- (g) A hydrocarbon which has the molecular formula  $C_6H_{12}$  was 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



- (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

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