Total No. of Printed Pages—12

2 SEM TDC CHM M 1

2014

(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 system absorbs 10 kJ of heat and does 4 kJ of work. The internal energy of the system

(i) decreases by 6 kJ

(ii) increases by 6 kJ

(iii) decreases by 14 kJ

(iv) increases by 14 kJ

(b) The bond energies of $N \equiv N$, H—H and N—H bonds are 945, 436 and 391 kJ mol^{-1} respectively. The enthalpy of the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is

(i) – 93 kJ

(ii) 102 kJ

(iii) 90 kJ

(iv) 105 kJ

(c) The favourable conditions for a spontaneous reaction are

(i) $T\Delta S > \Delta H$, ΔH = +ve, ΔS = +ve

(ii) $T\Delta S > \Delta H$, ΔH = +ve, ΔS = –ve

(iii) $T\Delta S = \Delta H$, ΔH = –ve, ΔS = –ve

(iv) $T\Delta S = \Delta H$, ΔH = +ve, ΔS = +ve

UNIT—I

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

2. (a) Show that the Joule-Thomson coefficient (μ_{JT}) for a van der Waals gas is given by

$$\mu_{JT} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

3

(b) Show that the value of μ_{JT} is zero for an ideal gas. 3

3. Calculate the 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

4. (a) Establish the relationship between enthalpy change and internal energy change for a gaseous reaction. 2

(b) The enthalpy of fusion of water at 273 K is 6·0 kJ mol^{-1} at constant pressure of 1 atmosphere. Calculate its value at 263 K.

Given $\overline{C}_{p\,H_2O\,(l)} = 74 \cdot 46$ J mol^{-1} K^{-1}

$\overline{C}_{p\,H_2O\,(s)} = 37 \cdot 2$ J mol^{-1} K^{-1} 2

(c) Show that the slope of *P-V* curve of an adiabatic change is greater than the slope of *P-V* curve for an isothermal change. 2

UNIT—II

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

5. *(a)* Deduce an expression for entropy-changes associated with the changes in volume and temperature of an ideal gas. 4

(b) Helium, weighing 4 g, is expanded reversibly from 1 atm to one-fifth of the original pressure at 30 °C. Calculate the change in its entropy assuming it to be an ideal gas. 1½

6. *(a)* Write the physical significance of Helmholtz free energy and Gibbs' free energy. 2

(b) Deduce an expression showing the variation of Helmholtz free energy with volume at constant temperature for an ideal gas. 2

(c) For the reaction

$$Ag_2O\,(s) \rightarrow 2Ag\,(s) + \frac{1}{2}O_2\,(g)$$

calculate the temperature at which the reaction will be at equilibrium. ΔH and ΔS for the reaction is $+30 \cdot 50$ kJ mol^{-1} and $0 \cdot 066$ kJK^{-1} mol^{-1} respectively at 1 atm pressure. 1½

7. *(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

SECTION—II

(Inorganic Chemistry)

(*Marks* : 27)

8. Choose the correct answer : 1×3=3

(a) Organophosphorus compounds are generally used as

(i) herbicides

(ii) fungicides

(iii) insecticides

(iv) rodenticides

(b) In XeF_6, xenon is

(i) dsp^2 hybridized

(ii) d^2sp^3 hybridized

(iii) dsp^3 hybridized

(iv) d^3sp^3 hybridized

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

(i) roasting

(ii) calcination

(iii) smelting

(iv) carbon reduction

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

(a) What are closo-, nido- and arachno-boranes? Give one example of each. 3

(b) How will you prepare XeO_3? Discuss the structure of XeF_2. 1+2=3

(c) Give the structure of the following : 1+2=3

(i) Orthosilicates

(ii) Cyclic silicates

(d) How is hydrazine prepared by Raschig's method? Discuss its reducing properties. 1+2=3

(e) What are zeolites? Mention its uses. 1+2=3

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

(a) Wade's rule

(b) Silicones

(c) Buckminsterfullerene

11. (a) Discuss giving suitable examples the use of the following processes in metallurgy (any *two*) : 2×2=4

(i) Zone refining

(ii) Solvent extraction

(iii) Electrolytic reduction

(b) Why are magnesium and aluminium frequently used for the extraction of metals like Mn, Co and Cr from their ores? 3

Or

Discuss the role of carbon in the extraction of metal with two examples.

(c) Describe the extraction of any *one* of the following : 4

(i) Pure nickel from pentlandite

(ii) Chromium from chromite ore

SECTION—III

(Organic Chemistry)

(*Marks* : 27)

12. Choose the correct answer : 1×3=3

(a) $(CH_3)_2CHBr \xrightarrow[2)\ CuI \\ 3)\ (CH_3)_2CH—CH_2—Br]{1)\ Li} (A)$

This is Corey-House method of synthesis of *A*, which is

(i) $(CH_3)_2CH—CH_2—CH_2—CH_2—CH_3$

(ii) $(CH_3)_2CH—CH_2—CH(CH_3)_2$

(iii) $(CH_3)_2CH—CH_2—CH_2—CH_3$

(iv) None of the above

(b) Identify a reagent from the following which can easily distinguish between but-1-yne and but-2-yne :

(i) Bromine, CCl_4

(ii) H_2, Lindlar catalyst

(iii) Dilute H_2SO_4, $HgSO_4$

(iv) Ammoniacal Cu_2Cl_2 solution

(c) Amongst the following, the compound that can be most readily sulphonated is

(i) toluene

(ii) benzene

(iii) chlorobenzene

(iv) nitrobenzene

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

(a) How would you synthesize an alkene by using Chugaev reaction? Explain with a suitable example that the reaction follows *E*1 reaction pathway. 2

(b) Give an explanation for the following statement : 2

"In the E_2 reaction a threo form gives *trans*-olefin while an erythro form gives a *cis*-olefin."

(c) Discuss the stereospecific nature of the following reactions by showing the structures of *A* and *B* : 2

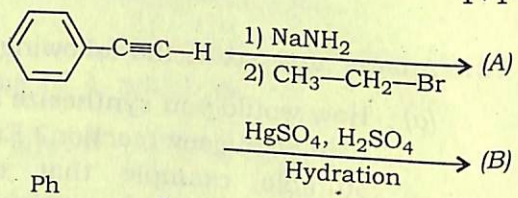
cis- and *trans*-stilbene $\xrightarrow{C_6H_5COOH}$ *(A)*

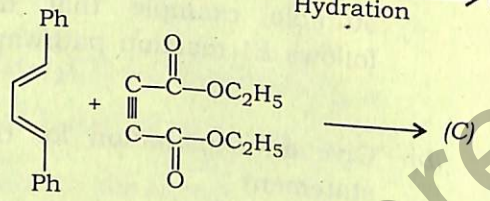
$\xrightarrow{H_3O^{\oplus} \text{ or } OH^{\ominus}}$ *(B)*

(d) Why conjugated dienes undergo 1,4-addition? Explain with a suitable example. 2

(e) How would you synthesize styrene by using Wurtz reaction? Discuss the mechanism of the reaction. 2

(f) Write down the products obtained in the following reactions : 1+1=2

(i) 

(ii) 

(g) Addition of HBr to propene yields 2-bromopropane while in presence of benzoyl peroxide the same reaction yields 1 bromopropane. Explain and give mechanism. 2

(h) An unsaturated hydrocarbon *(A)* adds two equivalents of H_2 and on reductive ozonolysis gives butane 1,4-dial, ethanal and propanone. Give the structure of *(A)*, write its IUPAC name and explain the reaction involved. 2

(Continued)

14. Answer any *two* questions : 2×2=4

(a) Draw the conformations of cyclohexane and account for the stability of the chair form. 2

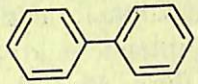
(b) Discuss the conformational analysis of *n*-butane and draw the potential energy curve diagram of it. 2

(c) What is meant by inversion of chair conformation of cyclohexane? Discuss 1,3-diaxial interaction in the chair conformation of methyl cyclohexane. 2

(d) Starting from a diester of a dicarboxylic acid, how will you obtain cyclopentane? Discuss the mechanism of the reaction. 2

15. Answer any *four* of the following : 2×4=8

(a) Define Hückel's rule of aromaticity. Mention whether the following are aromatic or not : 2

(i) 

(ii) 

(b) Giving reasons, write down the directing nature of the following groups for electrophilic substitution on benzene : 2

(i) —CN

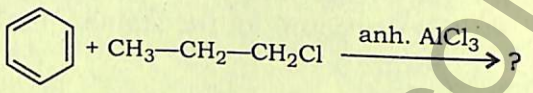
(ii) $—NH_2$

(iii) —COOR

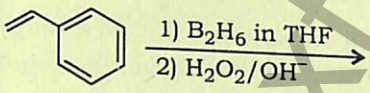
(iv) —OCOR

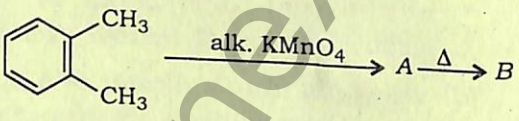
(Turn Over)

(c) Complete the following reaction and write its mechanism : 2



(d) Complete the following reactions : 1+1=2

(i) 

(ii) 

(e) Chlorine is *ortho-para* director towards aromatic electrophilic substitution reaction but ring deactivator. Explain. 2

(f) An aromatic hydrocarbon of the molecular formula C_9H_{12} upon oxidation gives a dibasic acid $C_8H_6O_4$. Nitration of this dibasic acid yields only one mononitro derivative. Suggest the structure of the arene. 2

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