Total No. of Printed Pages—23

2 SEM TDC CHM M 1 (N/O)

2016

(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) In endothermic reaction

(i) $H_R > H_P$ *(ii)* $H_R < H_P$

(iii) $H_R = H_P$ *(iv)* None of these

(b) Which of the following pairs has heat of neutralisation equal to –57·3 kJ?

(i) HCl, NH_4OH

(ii) HNO_3, NaOH

(iii) NaOH, CH_3COOH

(iv) H_2SO_4, NH_4OH

(c) The precipitate of calcium fluoride ($K_{sp} = 1 \cdot 7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed

(i) 10^{-4} *M* Ca^{2+} + 10^{-4} *M* F^-

(ii) 10^{-2} *M* Ca^{2+} + 10^{-3} *M* F^-

(iii) 10^{-5} *M* Ca^{2+} + 10^{-3} *M* F^-

(iv) 10^{-3} *M* Ca^{2+} + 10^{-5} *M* F^-

UNIT—I

Answer any *two* from the following : 6×2=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 work done in a reversible process is greater than that in an irreversible process. 2+2+2=6

(Continued)

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

(b) For the conversion of one mole of $SO_2(g)$ into $SO_3(g)$, the enthalpy of reaction at constant volume is –97·027 kJ at 298 K. Calculate the enthalpy of the reaction at constant pressure. 3

(c) Differentiate between extensive and intensive property with one example. 1

4. (a) Thermodynamically show that for an ideal gas $C_P - C_V = R$. 4

(b) Prove that μ_{JT} is zero for an ideal gas. 2

UNIT—II

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

(a) Derive the relation $K_h = K_w / K_a$ for the hydrolysis of a salt of weak acid and a strong base. Explain the acidic or basic nature of aqueous solutions of (i) $FeCl_3$ and (ii) NH_4NO_3. 3½+2=5½

(b) (i) What is buffer solution? Write any two applications of buffer solution. 2

(ii) Derive an equation for calculating the pH of a basic buffer solution. Calculate the pH of a buffer solution obtained by mixing 0·2 mol of NH_4OH and 0·25 mol of NH_4Cl. Given $K_b = 1 \cdot 8 \times 10^{-5}$. 2+1½=3½

(Turn Over)

(c) (i) Establish the relationship between solubility and solubility product for a sparingly soluble salt. 2

(ii) Write the difference between ionic product and solubility product. 2

(iii) The pH of a sample of vinegar is 3·76. Calculate the concentration of hydrogen ion in it. 1½

SECTION—II

(Inorganic Chemistry)

(*Marks* : 27)

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

(a) $B_{10}H_{14}$ has styx number 4620. The number of BH_2 group in the compound is

(i) 4

(ii) 6

(iii) 0

(iv) 2

(Continued)

(b) In sheet silicates, sheet structures are formed when SiO_4 units have share

(i) two O atoms

(ii) three O atoms

(iii) four O atoms

(iv) None of the above

(c) Which of the following metals cannot be extracted by carbon reduction process?

(i) Pb

(ii) Ag

(iii) Zn

(iv) Al

UNIT—I

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

(a) Explain the structure of XeF_2 and XeF_6. 1½×2=3

(b) What are zeolites? Give their applications with special reference to softening of hard water. 1+2=3

(c) How is hydrazine prepared? Discuss its reducing property. 1+2=3

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

(e) Give the structures of the following : 3

P_4O_{10}, H_3PO_4, $H_4P_2O_7$

(Turn Over)

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

(a) Metallocarboranes

(b) Triphenyl phosphine

(c) Hydrazoic acid

(d) Buckminsterfullerene

UNIT—II

9. *(a)* Name one metal that is refined by each of the following processes : ½×4=2

(i) Mond process

(ii) Electrolysis

(iii) van Arkel process

(iv) Zone refining

(b) Describe the extraction of any *two* of the following : 3×2=6

(i) Molybdenum from molybdenite ore

(ii) Chromium from chromite ore

(iii) Nickel from pentlandite

(c) Give the preparation of any *two* of the following : 1½×2=3

(i) Potassium permanganate

(ii) Sodium cobaltinitrite

(iii) Chromyl chloride

(Continued)

10

Or

Complete the following reactions : 3

(i) $V_2O_5 + HCl \longrightarrow \cdots\cdots + H_2O + Cl_2$

(ii) $MnO_2 \xrightarrow{\text{Red heat}} \cdots\cdots \xrightarrow{\text{Al fused}} \cdots\cdots$

(iii) $CoCl_2 + KNO_2 + CH_3COOH \longrightarrow \cdots\cdots$

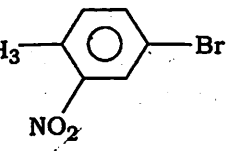
SECTION—III

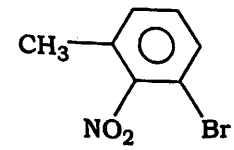
(Organic Chemistry)

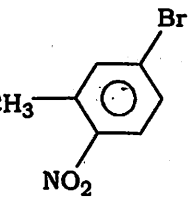
(*Marks* : 27)

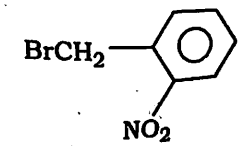
10. Choose the correct answer from the following : 1×3=3

(a) Bromination of *o*-nitrotoluene gives mainly

(i) 

(ii) 

(iii) 

(iv) 

(Turn Over)

(b) Ozonolysis of an alkene gives acetone only as a major product. The alkene is

(i) $(CH_3)_2C=CH_2$

(ii) $(CH_3)_2C=C(CH_3)_2$

(iii) $CH_3CH=CHCH_3$

(iv) None of the above

(c) Hydroboration of propene (reaction with diborane followed by the treatment with alkaline H_2O_2) forms

(i) propan-1-ol

(ii) propan-2-ol

(iii) propane-1,2-diol

(iv) 1,2-diacetoxy mercury propane

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

(a) Discuss the mechanism of chlorination of methane.

(b) Complete the following reaction and write down the mechanism :

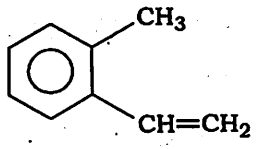
$$CH_3—CH=CH_2+HBr \xrightarrow{\text{peroxide}}$$

(c) Explain Hofmann's rule of elimination with the help of an example.

(d) Prepare 3-methyl octane with the help of Corey-House synthesis.

(Continued)

(e) Write the methods of preparation of the following :

(i) 

from *o*-bromotoluene with the help of Heck reaction.

(ii) Styrene from benzaldehyde using Wittig reaction.

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

$$R_3C—CH=CH_2+HCl \longrightarrow$$

(g) "The addition of Br_2 in CCl_4 to *trans*-2-butene gives always *meso*-2,3-dibromobutane as a product." Explain.

(h) A hydrocarbon having molecular formula, C_6H_{12} was subjected to ozonolysis giving equimolar amounts of ethyl methyl ketone and acetaldehyde. Identify the structure of hydrocarbon and give IUPAC name of it. Write down the equations involved.

(Turn Over)

12. Answer any *two* of the following : 2×2=4

(a) Discuss the conformational analysis of *n*-butane and draw the potential energy diagram for it.

(b) Explain 1,3-diaxial interaction in the chair conformation of methyl cyclohexane. "*t*-butylcyclohexane exists 100 percent in the equatorial conformation." Give reasons.

(c) Synthesize cyclohexane starting from diethyl pimelate using Dieckmann cyclisation.

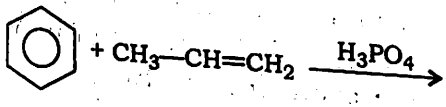
13. Answer any *four* from the following : 2×4=8

(a) State Huckel's rule of aromaticity. Identify the following as aromatic or non-aromatic :

(i) 

(ii) 

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



(Continued)

(c) "When methyl group is attached to the benzene ring it acts as *ortho-para*-director and activates the benzene ring towards the electrophilic substitution reactions." Explain.

(d) Aniline in the presence of catalytic amount of anhydrous $AlCl_3$ does not undergo F-C alkylation. Explain why.

(e) A secondary alcohol *A*, C_3H_8O on treatment with thionyl chloride to give compound *B*, C_3H_7Cl. The compound *B* reacts with benzene in presence of anhydrous $AlCl_3$ to give compound *C*, C_9H_{12}. Identify *A*, *B*, *C* and write equations for all the reactions.

(Turn Over)