

Total No. of Printed Pages—12

2 SEM TDC CHM M 1 (N/O)

2015

(May)

CHEMISTRY

(Major)

Course : 201

(Physical, Inorganic, Organic)

(Both New/Old Course)

Full Marks : 80

Pass Marks : 32/24

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) Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litres at 300 K. The enthalpy change (in kJ) for the process is

(i) 11.4

(ii) -11.4

(iii) 0

(iv) 4.8

(2)

(b) Enthalpy of neutralization of HCl with NaOH is x . The heat evolved when 500 ml of 2 N HCl are mixed with 250 ml of 4 N, NaOH will be

(i) $500x$

(ii) $100x$

(iii) x

(iv) $10x$

(c) According to second law of thermodynamics, a process is spontaneous if during the process

(i) $\Delta S_{\text{universe}} > 0$

(ii) $\Delta S_{\text{universe}} = 0$

(iii) $\Delta H_{\text{system}} > 0$

(iv) $\Delta S_{\text{universe}} = \Delta S_{\text{system}}$

Or

To make a solution of pH=12, the amount of NaOH dissolved in one litre of the solution should be

(i) 0.1 g

(ii) 0.2 g

(iii) 0.4 g

(iv) 1.2 g

(3)

UNIT—I

Answer any two from the following : 6×2=12

2. (a) What is Joule-Thomson effect? Show that this effect is isoenthalpic in nature.

1+3=4

(b) Derive a relationship between Joule-Thomson coefficient and thermodynamic quantity.

2

3. (a) How are the temperature and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation.

4

(b) One mole of an ideal gas ($\bar{C}_v = 12.55 \text{ JK}^{-1} \text{ mol}^{-1}$) at 300 K is compressed adiabatically and reversibly to one-fourth of its original volume. Calculate the final temperature of the gas.

2

4. (a) Deduce Kirchhoff's equation.

2

(b) State and explain Hess's law with one suitable example.

2

(c) The heat of formation of methane at 27 °C is -19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume?

2

(4)

UNIT—II

Question No. 5 for New Course and
Question No. 6 for Old Course

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

(a) (i) Derive an expression for the pH of an aqueous solution of a salt of strong base and weak acid. 3

(ii) The hydrogen ion concentration of 0.02 M sodium acetate is found to be 3.0×10^{-9} M at 25 °C. Calculate the hydrolysis constant of this salt ($K_w = 1.0 \times 10^{-14}$). $2\frac{1}{2}$

(b) (i) Derive an expression relating the pH of a buffer solution with the concentration of its components. 3

(ii) Calculate the pH of a solution obtained by mixing 0.083 mole of acetic acid and 0.091 mole of sodium acetate and making the volume 500 ml. K_a for acetic acid is 1.75×10^{-5} . $2\frac{1}{2}$

(c) (i) Write the definition of solubility product. Explain why ZnS is precipitated in alkaline medium whereas CuS is precipitated in acidic medium. $1 + 2\frac{1}{2} = 3\frac{1}{2}$

(ii) The solubility product of silver chromate is 2.0×10^{-12} at 25 °C. Calculate the solubility at this temperature. 2

P15—2500/530

(Continued)

(5)

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

(a) (i) Deduce an expression for efficiency of a Carnot engine working between two temperatures T_1 and T_2 . 4

(ii) An engine operates between 100 °C and 0 °C. Find the efficiency of the engine. $1\frac{1}{2}$

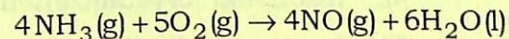
(b) (i) Derive an expression for entropy increase during isothermal mixing of two ideal gases. $3\frac{1}{2}$

(ii) Deduce the following relation : 2

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

(c) (i) State and explain the third law of thermodynamics. How can it be verified experimentally? $2 + 2 = 4$

(ii) Predict whether at 27 °C, the following reaction is spontaneous or not : $1\frac{1}{2}$



Given, $\Delta H = +9080 \text{ J mol}^{-1}$ and

$$\Delta S = +35.7 \text{ JK}^{-1} \text{ mol}^{-1}.$$

P15—2500/530

(Turn Over)

(6)

SECTION—II

(Inorganic Chemistry)

(Marks : 27)

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

(a) ZSM-5 is used as catalyst in the synthesis of

(i) *o*-xylene

(ii) *m*-xylene

(iii) *p*-xylene

(iv) toluene

(b) The hybridization used by carbon in fullerene (C_{60}) is

(i) sp

(ii) sp^2

(iii) sp^3

(iv) dsp^2

(c) The purification of metals by zone-refining is based on the principle of

(i) fractional crystallization

(ii) fractional distillation

(iii) vacuum distillation

(iv) distillation under reduced pressure

P15—2500/530

(Continued)

(7)

UNIT—I

8. Answer any *three* of the following : $3 \times 3 = 9$

(a) Discuss the structure and bonding of diborane. Show with reaction that bridging hydrogen is different from terminal hydrogen. $2 + 1 = 3$

(b) Why are noble gas compounds common in xenon? Explain the structure of $XeOF_4$. $1 + 2 = 3$

(c) How are silicates classified? Draw the structure of primary units in chain and cyclic silicates. $1 + 2 = 3$

(d) What is phosphazene? How is $(NPCl_2)_3$ prepared? Draw the structure of $(NPCl_2)_3$. 3

(e) Classify the following by structural type : $1 \times 3 = 3$

(i) $B_2H_7^-$

(ii) $B_{10}H_{14}$

(iii) $C_4B_2H_6$

9. Write short notes on any *two* of the following : $2 \times 2 = 4$

(a) Hydroxylamine

(b) S_4N_4

(c) Silicone rubber

P15—2500/530

(Turn Over)

(8)

UNIT—II

10. (a) Give the preparation of any *two* of the following : $1\frac{1}{2}\times 2=3$

- (i) Potassium dichromate
- (ii) Sodium cobaltinitrite
- (iii) Ni-DMG

Or

The oxides of the metals such as Zn, Cu, Pb, etc., are reduced by carbon at high temperature whereas those of Al, Mg, Ca, etc., are not. Explain giving reasons. 3

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

- (i) Manganese from pyrolusite
- (ii) Cobalt from smaltite ore
- (iii) Vanadium from vanadinite ore

(c) Write a note on hydrometallurgy. 2

(9)

SECTION—III

(Organic Chemistry)

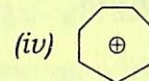
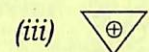
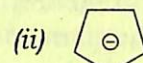
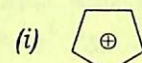
(Marks : 27)

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

(a) Arrange the following alkanes in the order of increasing boiling point :

- (i) *n*-hexane
- (ii) 3-methyl pentane
- (iii) 2,2-dimethyl butane
- (iv) *n*-heptane

(b) Which of the following is not aromatic?



(c) When 1-butyne is treated with dilute H_2SO_4 in presence of HgSO_4 , the major product is

- (i) $\text{CH}_3\text{CH}_2\text{COCH}_3$
- (ii) $\text{CH}_3\text{CH}_2\text{CHO} + \text{HCHO}$
- (iii) $\text{CH}_3\text{CH}_2\text{CHO}$
- (iv) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$

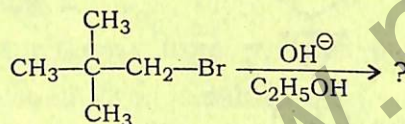
12. Answer any six of the following : $2 \times 6 = 12$

(a) Outline all the steps involved in the preparation of *n*-butane starting from bromoethane using Corey-House synthesis.

(b) How do you prepare an alkene by pyrolysis of an ester? Write necessary chemical equations.

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

(d) Complete the following reaction and write the plausible mechanism :

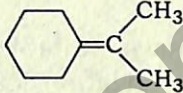


(e) Discuss the mechanism of addition of hypohalous acid to an unsymmetrical alkene with an example.

(f) What is the decreasing order of acidity of ethane, ethylene and acetylene? Also give proper explanation to that order.

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

(i) Styrene from ethanol by using Chugaev reaction

(ii)  from cyclohexanone by using Wittig reaction

(h) Discuss ozonolysis reaction to an alkyne with an example.

13. Answer any two of the following : $2 \times 2 = 4$

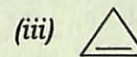
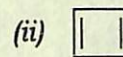
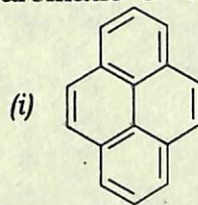
(a) What do you mean by conformational analysis? Draw the most stable conformation of cyclohexane showing axial and equatorial hydrogens.

(b) How do you obtain cyclopentane starting from diethyladipate? Write all necessary equations.

(c) What do you mean by angle strain? Calculate the angle strain for cyclopropane ring.

14. Answer any four of the following : $2 \times 4 = 8$

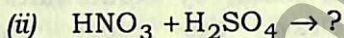
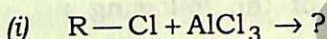
(a) What is aromaticity? Identify the following compounds as aromatic, anti-aromatic or non-aromatic :



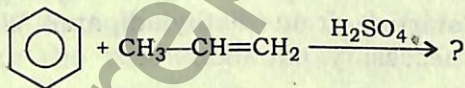
(b) The $-\text{NH}_2$ group attached to a benzene ring is *ortho*- and *para*-directing while $-\text{NO}_2$ group is *meta*-directing. Explain why.

(c) Why is nitrobenzene a suitable solvent for Friedel-Crafts alkylation of phenyl bromide while benzene is not?

(d) Show the formation of electrophiles in the following reactions :



(e) Complete the following reaction and write the mechanism of the reaction :



(f) Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile. Give reasons :

