2 0 1 9

(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) The extensive property of the system is

      (i) temperature

      (ii) volume

      (iii) refractive index

      (iv) viscosity

(b) For the reaction $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$, the correct statement is

  (i) $\Delta H = \Delta E$

  (ii) $\Delta H > \Delta E$

  (iii) $\Delta H < \Delta E$

  (iv) $\Delta H = 0$

(c) The concentration of sodium acetate solution that should be added to 0·1 M solution of CH_3COOH to produce a solution of pH 5·5 is (pK_a of $CH_3COOH = 4·5$)

  (i)   0·1 M

  (ii)   0·2 M

  (iii) 1·0 M

  (iv)   10·0 M

UNIT—I

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

2. (a) Differentiate between state function and path function with one example of each.   1

   (b) Thermodynamically show that for one mole of an ideal gas $C_P - C_V = R$.   3

   (c) Calculate the difference between the heat of reaction at constant pressure and the heat of reaction at constant volume for the following reaction at a constant temperature

   $$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$ 2
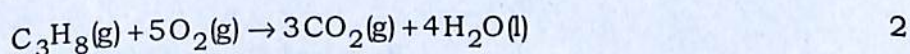
3. (a) Show that for a van der Waals gas, Joule-Thomson coefficient (μ_{JT}) is given by

   $$\mu_{JT} = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$$ 4

   (b) Prove that Joule-Thomson effect is isoenthalpic in nature.   2

4. (a) How are the temperature and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation.   4

   (b) Deduce Kirchhoff's equation.   2

UNIT—II

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

5. (a) For acidic and basic buffers, derive the expressions relating the pH of the buffer solutions with the concentrations of the components.   2+2=4

   (b) Write any three applications of buffer solutions.   1½

6. (a) Define solubility product. Explain why ZnS is precipitated in alkaline medium whereas CuS is precipitated in acidic medium.   1+2½=3½

   (b) Establish the relationship between solubility and solubility product of a sparingly soluble salt.   2

7. (a) Prove that pH + pOH = 14.   1½

   (b) A sulphuric acid solution has pH = 2. Calculate the molarity of the acid solution.   2

   (c) A saturated solution of Ag_2SO_4 has solubility $2.5×10^{-2}$ M. Find its solubility product.   2

SECTION—II

(Inorganic Chemistry)

(*Marks* : 27)

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

   (a) The number of six-membered rings in C_{60} is

      (i)   12

      (ii) 20

      (iii) 16

      (iv) 18

(b) Permutit is

    (i)   a ceramic

    (ii)   a constituent of cement

    (iii) an artificial zeolite

    (iv) a kind of fullerene

(c) Below which temperature CO is a better reducing agent than C?

    (i)   473 K

    (ii)   673 K

    (iii) 373 K

    (iv) 273 K

UNIT—I

9. Answer any *three* questions from the following : $3 \times 3 = 9$

(a) Why are noble gas compounds common in xenon? Explain the structure of XeF_4. $1+2=3$

(b) What are silicones? How can they be prepared? What is silicon rubber?

                $1+1+1=3$

(c) What are phosphazenes? How is $(NPCl_2)_n$ polymer prepared? Draw the structure of $(NPCl_2)_3$. $1+1+1=3$

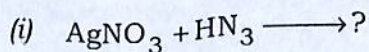*(d)* Classify the following by structural type : $1 \times 3 = 3$

    (i) B_8H_{16}

    (ii) $B_2H_7^{2-}$

    (iii) $C_2B_9H_{12}^-$

(e) Complete the following reactions : $1 \times 3 = 3$

    (i) $AgNO_3 + HN_3 \longrightarrow ?$

    (ii) $CuO + NH_2OH \xrightarrow[\text{medium}]{\text{alkaline}} ?$

    (iii) $AuCl_3 + N_2H_4 \longrightarrow ?$
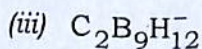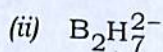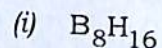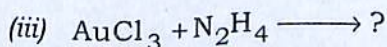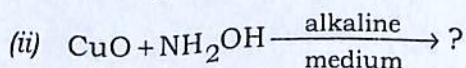
10. Write short notes on the following (any *two*) :   2×2=4

(a) Fullerene (C_{60})

(b) S_4N_4

(c) Carborane

UNIT—II

11. How will you obtain the following (any *two*)?   3×2=6

(a) Manganese from pyrolusite ore

(b) Cobalt from smaltite ore

(c) Vanadium from vanadinite ore

12. Write a short note on the following (any *one*) :   2

(a) Hydrometallurgy

(b) Solvent extraction

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

(a) Sodium cobaltinitrite

(b) Lead chromate

(c) Ammonium molybdate

SECTION—III

(Organic Chemistry)

(*Marks* : 27)

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

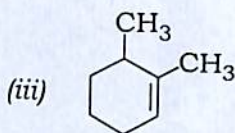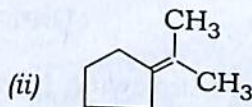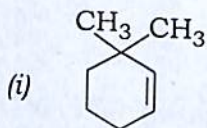(a) The reagents used for the following conversions
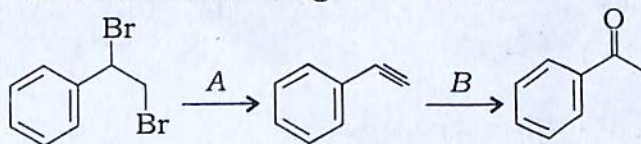
are

(i) alc. KOH and $H_2O/HgSO_4/H_2SO_4$

(ii) alc. KOH and $KMnO_4/H^+$
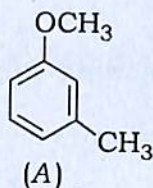
(iii) $NaNH_2$ and $H_2O/HgSO_4/H_2SO_4$

(iv) $NaNH_2$ and $KMnO_4/H^+$

(b) Consider the following reaction

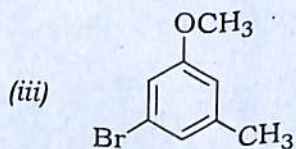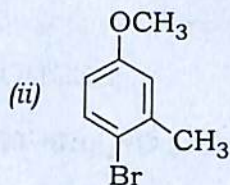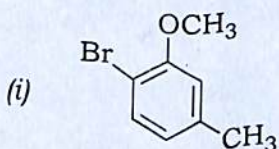$$+ CH_3OH \xrightarrow{E1} ?$$
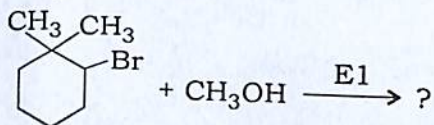
Which of the following is not formed?

(i)

(ii)

(iii)

(iv)
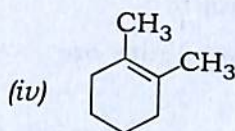
(c) The major product obtained on monobromination $(Br_2/FeBr_3)$ of the following compound (A)

(A)

is

(i)

(ii)

(iii)

(iv)
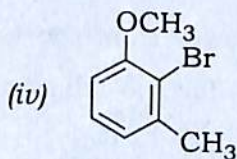
15. Answer any *six* questions from the following :   2×6=12

(a) Give evidences to show that bromination of *cis-* and *trans*-stilbene is stereoselective.   2

(b) What is the role of Hg^{+2} ion in nucleophilic addition reaction of alkynes?   2

(c) What happens, when—

    (i) propyne is treated with B_2H_6 in THF followed by alkaline hydrolysis with H_2O_2/OH^-;

    (ii) cyclopentadiene is treated with methyl acrylate (dienophile) at 80 °C?   1+1=2

(d) Discuss the regioselectivity of the E2 elimination with a suitable example.   2

(e) Using Corey-House synthesis, how can you prepare 2-methylbutane?   2

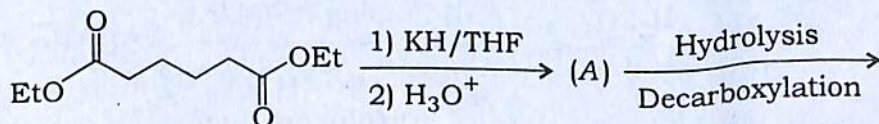(f) Complete the following reaction and discuss the mechanism involved :   2
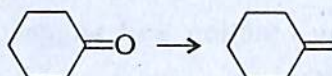
(g) How will you prepare cis-pentene-2 and trans-pentene-2 starting from ethyne?   2

(h) Synthesize styrene from benzaldehyde using Peterson reaction.   2

16. Answer any two questions from the following :   2×2=4

(a) Synthesize a cycloalkane using the following synthetic route :   2

    a cycloalkanone ⟶ a cycloalkane .

(b) Draw perspective and Newman projection for the chair-conformation of cyclohexane.   1+1=2

(c) Explain 1,3-diaxial interaction in the chair-conformation of methyl-cyclohexane.   2

(d) Discuss the conformational analysis of *n*-butane with the help of Newman projection formula.

2

(e) What is Sachse-Mohr theory of strainless rings? Explain with suitable examples.

2

17. Answer any *four* questions from the following :

2×4=8

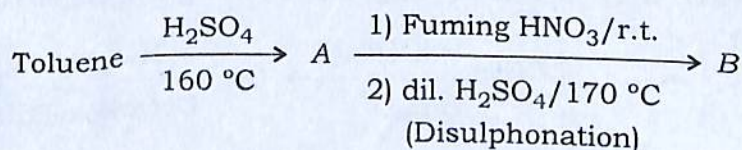(a) Account for the aromatic behaviour of cycloheptatrienyl cation and anthracene.

1+1=2

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

2

 $\xrightarrow{\text{conc. } HNO_3 + \text{conc. } H_2SO_4}$?
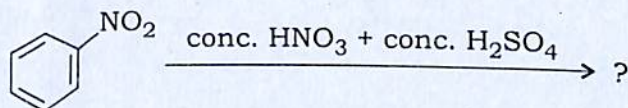
(c) How would you prepare styrene from benzene?

2

(d) Explain why chlorine in chlorobenzene is O/P directing although it has +I effect during electrophilic substitution in benzene.

2

(e) Complete the following reaction :

1+1=2

$$\text{Toluene} \xrightarrow[160 \text{ °C}]{H_2SO_4} A \xrightarrow[\substack{\text{2) dil. } H_2SO_4/170 \text{ °C} \\ \text{(Disulphonation)}}]{\text{1) Fuming } HNO_3/\text{r.t.}} B$$

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 from the following :   1×3=3

(a) The extensive property of the system is

     (i) temperature

     (ii) volume

     (iii) refractive index

     (iv) viscosity

(b) For the reaction $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$, the correct statement is

     (i) $\Delta H = \Delta E$

     (ii) $\Delta H > \Delta E$

     (iii) $\Delta H < \Delta E$

     (iv) $\Delta H = 0$

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

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

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

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

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

UNIT—I

Answer any *two* questions from the following : $6 \times 2 = 12$

2. (a) How are the temperature and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation.   4

   (b) Calculate the work done by the system when 2 moles of an ideal gas expand from 0.01 m^3 to 0.1 m^3 at 300 K isothermally and reversibly.   2

3. (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 quantities.   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 temperature. What will be the heat of formation at constant volume?   2

UNIT—II

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

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

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

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

   (b) Mention two factors upon which the entropy of a system depends.   2

7. *(a)* State and explain Nernst's heat theorem. Write one consequence of the theorem.   2+1=3

(c) Predict whether at 27 °C the following reaction is spontaneous or not :   1½

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(l)$$
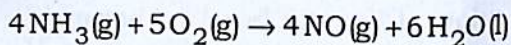
Given, $\Delta H = 10 \cdot 5 \times 10^3\ J\,mol^{-1}$, $\Delta S = 31\ JK^{-1}\,mol^{-1}$

(c) Write the physical significance of Gibbs' free energy.   1

SECTION—II

(Inorganic Chemistry)

(*Marks* : 27)

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

(a) ZSM-5 converts methanol to

     (i) methanal

     (ii) CH_3CHO

     (iii) CO_2

     (iv) gasoline

(b) In XeO_3, xenon is

     (i) sp^3-hybridized

     (ii) dsp^3-hybridized

     (iii) dsp^2-hybridized

     (iv) d^2sp^3-hybridized

(c) In Goldschmidt aluminothermic process, Al-powder acts as

     (i) oxidizing agent

     (ii) reducing agent

     (iii) flux

     (iv) None of the above

9. Answer any *three* questions from the following :

                                                                         $3 \times 3 = 9$

(a) Explain the formation of $3c-2e$ bond in boranes.   3

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

    (i) *Ortho*-silicates

    (ii) Cyclic silicates

(c) How will you prepare XeO_3? Discuss its structure. $1+2=3$

(d) What are zeolites? Mention its uses.   3

(e) Give the method of preparation and structure of phosphazene. $1+2=3$

10. Write short notes on the following (any *two*) : $2 \times 2 = 4$

(a) Hydrazine

(b) Silicones

(c) Fullerene (C_{60})

UNIT—II

11. Describe the extraction of any *two* of the following : $3 \times 2 = 6$

(a) Molybdenum from molybdenite ore

(b) Vanadium from vanadinite ore

(c) Cobalt from smaltite ore

12. Write a short note on the following (any *one*) :   3

(a) Zone refining

(b) Electrorefining metals

13. Complete the following reactions (any *two*) : $1 \times 2 = 2$
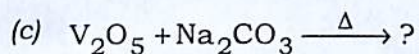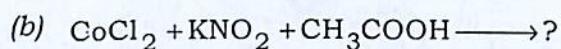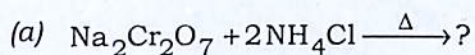
(a) $Na_2Cr_2O_7 + 2NH_4Cl \xrightarrow{\Delta} ?$

(b) $CoCl_2 + KNO_2 + CH_3COOH \longrightarrow ?$

(c) $V_2O_5 + Na_2CO_3 \xrightarrow{\Delta} ?$

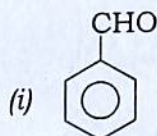<div align="center">

SECTION—III

(**Organic Chemistry**)

(*Marks* : 27)

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

(a) Which compound undergoes reaction with $HNO_3 + H_2SO_4$ at faster rate than benzene?
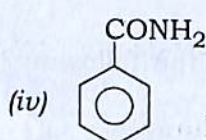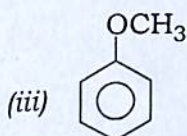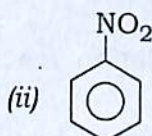
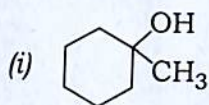(b) In ⌄⌃ $+ Br_2 \longrightarrow X$, product X is

   (i)   (+)-1,2-dibromobutane

   (ii) (±)-1,2-dibromobutane

   (iii) meso-1,2-dibromobutane

   (iv) (–)-1,2-dibromobutane

(c)

 + KOH (alc) $\longrightarrow$ X
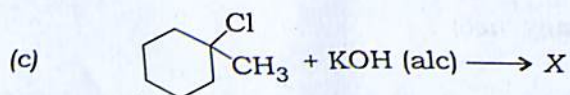
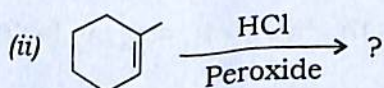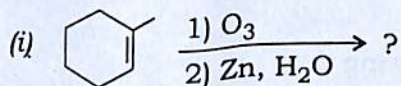The product X in the above reaction is

(i)

(ii)

(iii)

(iv)
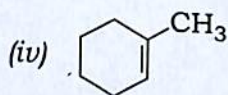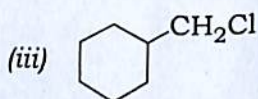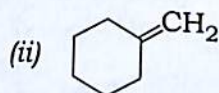
15. Answer any *six* questions from the following :

$2 \times 6 = 12$

(a) Arrange the following compounds in increasing boiling point :
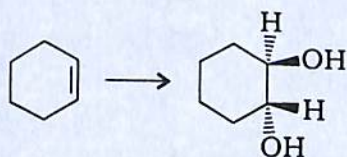
Pentane; 2-methylbutane; 2,2-dimethylbutane; Butane

(b) Complete the following reactions :

(i) $\xrightarrow[\text{2) Zn, H}_2\text{O}]{\text{1) O}_3}$?

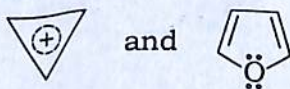(ii) $\xrightarrow[\text{Peroxide}]{\text{HCl}}$?

(c) Using hydroboration-oxidation reaction prepare butanol-1.

(d) Using Corey-House synthesis, prepare an unsymmetrical alkane.

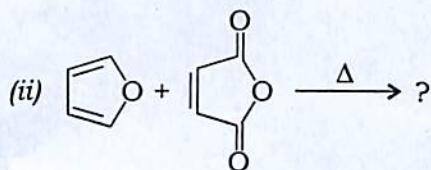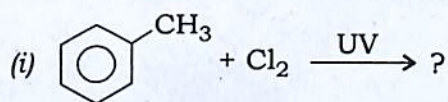(e) How will you convert the following?

(f) Predict aromaticity in the following :

 and

(g) Phenol is more reactive than benzene when reacted with $CH_3Cl + AlCl_3$. Explain.

(h) Complete the following reactions :

(i) + Cl_2 $\xrightarrow{UV}$?

(ii) $\xrightarrow{\Delta}$?

16. Answer any *two* questions from the following : $\qquad$ 3×2=6

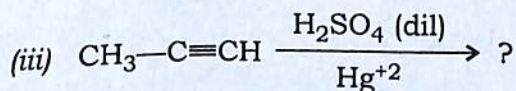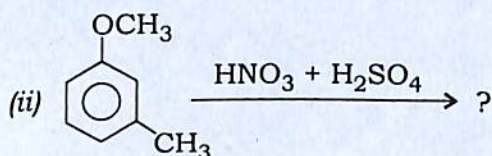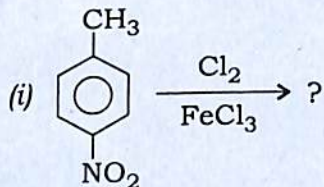*(a)* Discuss the conformation analysis of ethane.

(b) Draw the conformers of bromocyclohexane and explain their stability.

(c) Write a short note on Bayer's strain theory.

17. Answer any *two* questions from the following : $\qquad$ 3×2=6

(a) Identify the products from the following :

(i) $\xrightarrow[FeCl_3]{Cl_2}$?

(ii) $\xrightarrow{HNO_3 + H_2SO_4}$?

(iii) $CH_3 - C \equiv CH$ $\xrightarrow[Hg^{+2}]{H_2SO_4 \text{ (dil)}}$?

(b) Cl is deactivating but *o-p* directing. Explain.

(c) Write a short note on E1cB reaction.

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