Total No. of Printed Pages—8

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(November)

CHEMISTRY

(Major)

(Both New/Old)

Course : 101

(Physical, Inorganic and Organic)

The figures in the margin indicate full marks for the questions

Write the answers to the separate Sections in separate books

Full Marks : 80
Pass Marks : 32/24

Time : 3 hours

SECTION—A

(Physical Chemistry)

(*Marks* : 26)

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

    (a) Potassium crystallizes in b.c.c. unit cell. The number of unit cells present in 1·0 g of potassium is

    (i) $7·7 \times 10^{21}$

    (ii) $1·54 \times 10^{22}$

    (iii) $6·022 \times 10^{23}$

    (iv) $0·0256$

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(b) For one mole of an ideal gas, the kinetic energy is given by

    (i) $E = \dfrac{1}{2}RT$

    (ii) $E = \dfrac{3}{2}RT$

    (iii) $E = \dfrac{5}{2}RT$

    (iv) $E = \dfrac{7}{2}RT$

(c) The rate of evaporation of a liquid depends upon

    (i) surface area

    (ii) temperature

    (iii) nature of liquid

    (iv) All of the above

2. Answer any *three* questions from the following : $2 \times 3 = 6$

(a) Show that the excluded volume is four times the actual volume of a gas molecule.

(b) Frenkel defect is not shown by alkali metal halides but silver halides show this defect. Explain.

(c) Describe any two factors upon which the vapour pressure of a liquid depends.

(d) Explain why we have to define the heat capacities of gases under constant pressure and constant volume conditions.

(e) Determine the interplanar spacing between the (221) planes of a cubic lattice of length 450 pm.

UNIT—I

3. Answer any *two* questions from the following : $3\frac{1}{2} \times 2 = 7$

(a) What is critical phenomenon? Derive the expressions for the critical constants of a gas using van der Waals' equation of states. $1 + 2\frac{1}{2} = 3\frac{1}{2}$

(b) (i) With the help of kinetic gas equation, deduce Charles' law.   2

    (ii) Show that $\dfrac{RT_c}{P_c V_c} = \dfrac{8}{3}$. $1\frac{1}{2}$

(c) (i) What do you mean by mean free path, collision diameter and collision frequency of a gas molecule? Explain the effect of temperature on mean free path. $1\frac{1}{2}+1=2\frac{1}{2}$

(ii) State the law of equipartition of energy. 1

UNIT—II

4. Answer any *one* question from the following : 3

(a) Describe the method for determining the surface tension of a liquid in the laboratory. 3

(b) (i) Write any two differences between nematic and smectic liquid crystals. 2

(ii) Show that surface tension and surface energy have the same dimension. 1

UNIT—III

5. Answer any *two* questions from the following : $3\frac{1}{2}\times2=7$

(a) Define unit cell. What parameters are used to describe a particular system of crystal? Name the seven crystal systems. Which of them is the most symmetrical and which one is the most unsymmetrical?. $\frac{1}{2}+1+1+1=3\frac{1}{2}$

(b) (i) With the help of band theory, explain the difference between a conductor and an insulator. 2

(ii) Why does the electrical conductivity of semiconductors increase with increase in temperature? $1\frac{1}{2}$

(c) (i) Classify each of the following as being either a *p*-type or an *n*-type semiconductor : $\frac{1}{2}+\frac{1}{2}=1$
    (1) Si doped with In
    (2) Si doped with P

(ii) Gold (atomic radius = 0·144 nm) crystallizes in a face-centred unit cell. What is the length of the side of the cell? $1\frac{1}{2}$

(iii) LiCl acquires pink colour when heated in Li vapours. Explain. 1

(Inorganic Chemistry)

(*Marks* : 27)

6. Find out the correct answer out of the following :   1×3=3

   (a) Which of the following transitions involves maximum energy?

      (i) $M^-(g) \rightarrow M(g)$ (ii) $M(g) \rightarrow M^+(g)$

      (iii) $M^+(g) \rightarrow M^{2+}(g)$ (iv) $M^{2+}(g) \rightarrow M^{3+}(g)$

   (b) The geometrical shape of ClF_3 molecule is

      (i) trigonal bipyramidal

      (ii) T-shape

      (iii) trigonal planar

      (iv) pyramidal

   (c) Which of the following has largest bond angle?

      (i) NH_3 (ii) SbH_3
      (iii) PH_3 (iv) AsH_3

7. Answer the following questions :   2×3=6

   (a) The first ionization energy of Be is higher than that of B, while the second ionization energy of B is higher than that of Be. Explain giving reason.

   (b) Using VSEPR theory, predict the structure of ClF_3.

   (c) Bond angle decreases from CH_4 (109·5°) to NH_3 (107°) to H_2O (104·5°). Explain with reason.

8. Answer any *two* questions from the following :   3×2=6

   (a) What do you mean by electronegativity of an element? Calculate the electronegativity of fluorine using Allred-Roschow equation. (Covalent radius of fluorine = 0·72 Å)   1+2=3

   (b) Explain what is linear combination of atomic orbital. Show that the bond order of Be_2 is zero.   2+1=3

   (c) Draw the molecular orbital energy-level diagram for CO molecule and calculate the bond order.   2+1=3

4

9. Answer any *three* questions from the following : $4 \times 3 = 12$

(a) (i) With the help of Slater's rule, show that $4s$ orbital is filled earlier than a $3d$ orbital in K atom.

(ii) Calculate the effective nuclear charge at the periphery of Ti^{3+} ion. 4

(b) What is lattice energy of crystals? Draw Born-Haber cycle for the ionic solid M^+X^- and show how the lattice energy can be computed with its help. $1+2+1=4$

(c) Explain the following on the basis of molecular orbital theory : $2+2=4$

(i) B_2 molecule is paramagnetic in nature

(ii) N_2 molecule is more stable than NO molecule

(d) (i) Among halides of calcium, i.e., CaF_2, $CaCl_2$, $CaBr_2$ and CaI_2; CaI_2 is most covalent. Explain with reason. 2

(ii) Find out the number of unpaired electron in O_2^+ and O_2^-. Also find out their bond order. $1+1=2$

SECTION—C

(Organic Chemistry)

(Marks : 27)

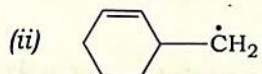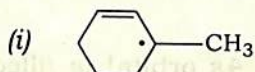**10.** Choose the correct answer of the following : $1 \times 3 = 3$

(a) The IUPAC name of the compound
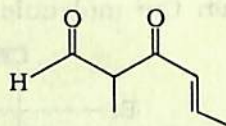
is

(i) 5-formyl hex-2en-3-one
(ii) 5-methyl-4-oxo hex-2en-5al
(iii) 3-keto-2-methyl hex-5-en-al
(iv) 3-keto-2-methyl hex-4-en-al

(b) The most stable radical is

(i)   —CH_3

(ii) —$\dot{C}H_2$

(iii) $CH_2=CH-\dot{C}H_2$

(iv) $CH_2=\dot{C}H$
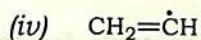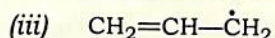
(c) The reaction of methyl trichloroacetate ($Cl_3C-\overset{\overset{\displaystyle O}{||}}{C}-OMe$) with sodium methoxide (NaOMe) gives

(i) carbocation

(ii) carbene

(iii) carbanion

(iv) free radical

11. Answer any *three* questions from the following :   2×3=6

(a) Arrange the following carbocations in order of stability with proper reasoning :

Tropylium cation, benzyl carbocation, allylcarbocation and triphenyl methyl carbocation

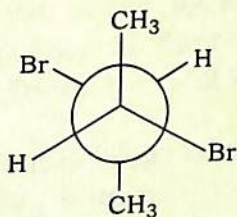*(b)* PhO^- is a weaker base than $CH_3-CH_2-O^-$. Explain on the basis of resonance effect.

(c) Explain any *one* of the following :

(i) The $C-N$ bond length in CH_3CONH_2 is shorter than that in $CH_3-CH_2-NH_2$.

(ii) Dipole moment of acetone is more than formaldehyde.

(d) Butene-2 has greater stability than but-1-ene. Explain.

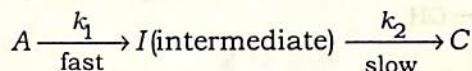*(e)* Write down the relationship between the molecules shown below :

  and
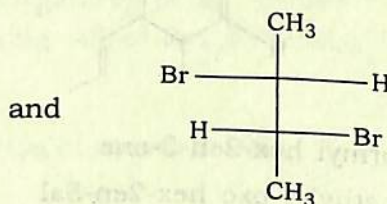
12. Answer any *three* questions from the following : $2\times3=6$

(a) Draw the energy profile for the reaction

$$A \xrightarrow[\text{fast}]{k_1} I(\text{intermediate}) \xrightarrow[\text{slow}]{k_2} C$$
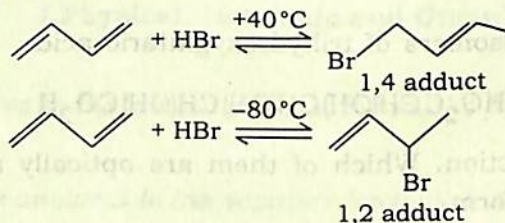
and the reaction is endothermic. 2

(b) Define singlet and triplet carbene showing their structures. 2

(c) Arrange and offer your justification : $1+1=2$
   (i) *p*-Methoxy benzoic acid and benzoic acid (in increasing order of acidity)
   (ii) Me_3C-NH_2 and CH_3-NH_2 in aprotic solvent (in increasing order of basicity)
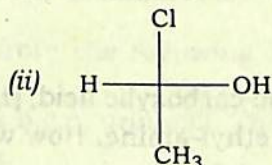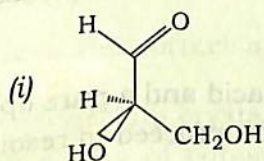
(d) In the reactions given below

which one is kinetic controlled and which is thermodynamic controlled product? Explain with the help of energy profile diagram. 2

(e) What are nitrenes? How are they generated? 2

13. Answer any *six* questions from the following : $2\times6=12$

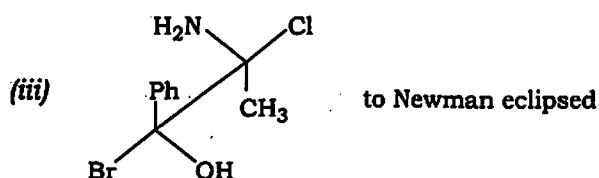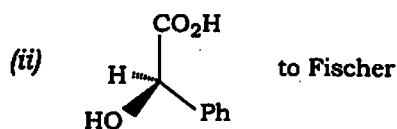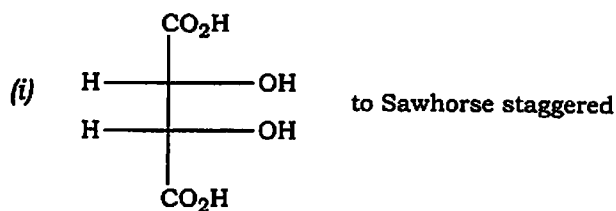(a) Assign R and S to the following compounds : 2

(b) Draw and give stereochemical designation E/Z for the geometrical isomers of 2,4-heptadiene. 2

(c) What are the different simple axes of symmetry present in the benzene molecule? Which is the principal axis in case of benzene? 2

(d) Interconvert the following projection formula as directed (any *two*) : 2

(i)

$$CO_2H$$

H———OH
H———OH

$$CO_2H$$

to Sawhorse staggered

(ii)

$$CO_2H$$

H ‹‹‹‹
HO   Ph

to Fischer

(iii)

H₂N   Cl
  Ph   CH₃
Br   OH

to Newman eclipsed

(e) Draw the stereoisomers of trihydroxyglutaric acid

$$HO_2C\,CH(OH)\,CH(OH)\,CH(OH)\,CO_2H$$

in Fischer projection. Which of them are optically active and which of them are *meso* form? 2

(f) The presence of a chiral centre in an organic compound is neither a necessary nor a sufficient condition to show optical activity. Explain with giving examples. 2

(g) The concentration of an optically active compound dissolved in ethyl alcohol is 3·05 g per 50 ml of solution.

(i) A portion of this solution in a 5 cm sample tube had observed rotation of –1·4°. Calculate the specific rotation of the compound.

(ii) Predict the observed rotation if the same solution was placed in a 10 cm tube. 1+1=2

(h) You are given a racemic carboxylic acid, (±)-lactic acid and a pure optically active base (+)-phenyl ethyl-amine. How would you proceed to resolve the acid? Explain the principle. 2

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