1 SEM TDC CHM M 1

2021

(March)

CHEMISTRY

(Major)

Course : 101

(Physical, Inorganic and Organic)

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—A

(Physical Chemistry)

(*Marks* : 26)

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

(a) Amorphous solids do not have

(i) sharp melting point

(ii) characteristic geometrical shapes

(iii) regularity of the structure

(iv) All of the above

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

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

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

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

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

(c) With the increase in temperature, the viscosity of a liquid

(i) decreases

(ii) increases

(iii) remains unchanged

(iv) first increases then decreases

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

(a) From kinetic gas equation, derive Charles' law.

(b) Write the effect of temperature on the viscosity of a liquid.

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

(d) By X-ray diffraction it is found that nickel crystals are face-centred cubic. The edge of the unit cell is 3·52 Å. The atomic mass of nickel is 58·7 and its density is 8·94 g cm^{-3}. Calculate Avogadro's number from the data.

(e) Calculate the number of atoms present in a body-centred unit cell.

UNIT—I

3. Answer any *two* questions from the following : 3½×2=7

(a) What is critical phenomenon? Derive the expressions for the critical constants of a gas using van der Waals' equation of states. 1+2½=3½

(b) (i) Define mean free path, collision diameter and collision frequency of gas molecules. What is the effect of temperature on mean free path? 1½+1=2½

(ii) What is Boyle's temperature? 1

(c) Derive reduced equation of states. What do you mean by continuity of states? 2½+1=3½

UNIT—II

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

(a) Describe the method of determining the viscosity of a liquid in the laboratory. 3

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

(ii) Describe any one factor upon which the vapour pressure of a liquid depends. 1

UNIT—III

5. Answer any *two* questions from the following : 3½×2=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? ½+1+1+1=3½

(b) *(i)* What are extrinsic and intrinsic semiconductors? Give examples. 1+1=2

(ii) Conductivity of semiconductor increases with increasing temperature. Explain. 1½

(c) *(i)* Classify each of the following as being either a *p*-type or an *n*-type semiconductor : ½+½=1

(1) Si doped with In

(2) Si doped with P

(ii) LiCl acquires pink colour when heated in Li vapour. Explain. 1

(iii) Calculate the packing efficiency of simple cubic crystal. 1½

SECTION—B

(Inorganic Chemistry)

(*Marks* : 27)

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

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

(i) $M^{+}(g) \rightarrow M^{2+}(g)$

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

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

(iv) $M^{-}(g) \rightarrow M(g)$

(b) The oxygen species which possesses the maximum bond strength is

(i) O_2^+

(ii) O_2

(iii) O_2^-

(iv) O_2^{2-}

(c) The geometrical shape of ClF_3 molecule is

(i) trigonal bipyramidal

(ii) T-shape

(iii) trigonal planar

(iv) see-saw

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

(a) Explain two factors on which ionization energy of an element depends.

(b) Explain why 4*s*-orbital is filled earlier than 3*d*-orbital.

(c) NO and NO^- are both paramagnetic. Explain on the basis of MOT.

(d) Why is there a decrease in bond angle from NH_3 to H_2O? Explain on the basis of VSEPR theory.

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

(a) Define electron affinity. Write its SI unit. Explain giving reason—zinc and cadmium have negative values of electron affinity. 1+½+1½=3

(b) State and explain with examples the Slater's rules for calculating effective nuclear charge. 3

(c) What is Allred-Rochow scale of measuring the electronegativity of an atom? How does partial ionic character depend on electronegativity difference? 2+1=3

9. Answer any *three* questions from the following : 4×3=12

(a) Using VSEPR theory, predict the structure of SO_2, PCl_3, SF_4 and BeF_2. 1×4=4

(b) What is lattice energy of an ionic crystal? 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) Arrange the following in order of increasing bond order and bond length :

$$O_2, O_2^-, O_2^+, O_2^{2+}$$

Find out the number of unpaired electron in each case. 2+2=4

(d) Compare bond length and magnetic properties of CN and CN^- species with the help of molecular orbital theory. 2+2=4

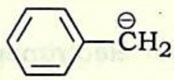
SECTION—C

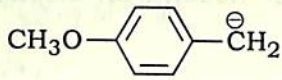
(Organic Chemistry)

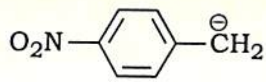
(*Marks* : 27)

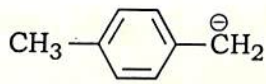
10. Choose the correct answer from the following : 1×3=3

(a) Which is stable carbanion?

(i) 

(ii) 

(iii) 

(iv) 

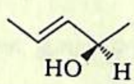
(b) In which of the following, resonance of $-NH_2$ group is possible?

(i) 1-Aminobutane

(ii) Ethylamine

(iii) Benzylamine

(iv) *p*-Toluidine

(c)  is named as

(i) (2*S*, 3*E*) pent-3 en-2ol

(ii) (2*R*, 3*E*) pent-3 en-2ol

(iii) (2*E*, 3*R*) pent-2 en-3ol

(iv) (2*E*, 3*s*) pent-2 en-3ol

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

(a) With proper justification, arrange the following in order of increasing stability :

$$CH_3-\overset{\ominus}{C}H_2,\ CH\equiv\overset{\ominus}{C},\ CH_2=\overset{\ominus}{C}H$$

(b) PhO^- is a weaker base than $CH_3-CH_2O^-$. Explain on the basis of resonance effect.

(c) Sketch the Newman projection of mesotartaric acid.

(d) Dichloroacetic acid is stronger acid than acetic acid. Justify it.

(e) Explain the stability of the following carbocations with the concept of hyperconjugation :

$$Me_3\overset{\oplus}{C} \text{ and } Me_2\overset{\oplus}{C}H$$

UNIT—I

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

(a) Write a short note on nonclassical carbonium ion or ambidient nucleophile. 2

(b) Draw the energy profile diagram for the two-step reaction :

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I\,(\text{intermediate}) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B$$

Given $k_{-1} > k_1 > k_2 > k_{-2}$ and the reaction is exothermic. 2

(c) Define singlet and triplet carbenes showing their structures. 2

(d) Give reason for the following : 1+1=2

(i) SO_3 acts as an electrophile.

(ii) HS^- is a better nucleophile than $\bar{O}H$ but HO^- is a better base than HS^-.

(e) Arrange the following : 1+1=2

(i) $C_6H_5-\dot{C}H-CH_3$, $C_6H_5-\dot{C}H-CH=CH_2$, $C_6H_5-CH_2-\dot{C}H_2$, $C_6H_5-\dot{C}(CH_3)_2$ [in order of increasing stability]

(ii) $C_6H_5-\overset{\oplus}{C}H_2$, $CH_3-\overset{\oplus}{C}H_2$, $(CH_3)_3\overset{\oplus}{C}$, $CH_2=CH-\overset{\oplus}{C}H_2$ [in order of decreasing stability]

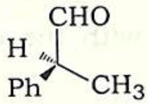
UNIT—II

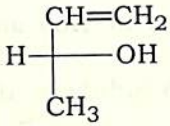
13. Answer any *six* questions from the following : 2×6=12

(a) Define plane of symmetry and centre of symmetry giving one example for each. 2

(b) Draw the stereochemical designation E/Z for the geometrical isomers of but-2ene-1,4-dioic acid. 2

(c) Assign R/s designation to the following compounds (any *two*) : 1×2=2

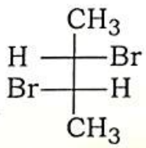
(i) 

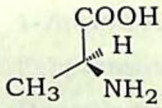
(ii) 

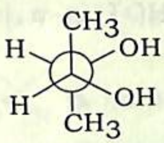
(iii) *L*-glyceraldehyde

(d) Sketch the flying wedge and Newman projection for *trans*-stilbene (C_6H_5—CH=CH—C_6H_5). 2

(e) Interconvert the following projection formulae as directed (any *two*) : 1×2=2

(i)  to Newman projection

(ii)  to Fischer projection

(iii)  to Fischer projection

(f) Write a short note on geometrical isomerism due to >C=N— bond with example. 2

(g) Draw the three stereoisomers of tartaric acid in Fischer projections. Which of them are enantiomers and which is meso? 2

(h) The presence of chiral centre in organic compounds is neither a necessary nor sufficient condition for showing enantiomerism. Explain. 2

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