

1 SEM TDC CHM M 1 (Both N/O)

2017

(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 :

1×3=3

(a) The root mean square velocity of an ideal gas at constant pressure varies with the density d as

(i) d^2

(ii) d

(iii) \sqrt{d}

(iv) $1/\sqrt{d}$

- (b) The vapour pressure of non-polar liquids is
- (i) fairly high as compared to polar liquids
 - (ii) fairly low as compared to polar liquids
 - (iii) the same as that of polar liquids
 - (iv) None of the above
- (c) In *p*-type semiconductors, the conductivity is due to
- (i) negative holes
 - (ii) positive holes
 - (iii) mobile electrons
 - (iv) valence electrons

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

2×3=6

- (a) Out of NH_3 and N_2 , NH_3 has higher values of van der Waals' constant *a*. Explain giving reason.
- (b) Calculate the critical pressure of oxygen if the values of van der Waals' constants *a* and *b* are $1.32 \text{ dm}^6 \text{ bar mol}^{-2}$ and $0.0312 \text{ dm}^3 \text{ mol}^{-1}$ respectively.
- (c) Viscosity of a liquid decreases with increase in temperature. Explain.
- (d) Calculate the packing fraction of a body-centred cubic unit cell.
- (e) Define radius ratio. How does it affect the coordination numbers of ions in the lattice?

UNIT—I

3. Answer any *two* questions from the following :

$3\frac{1}{2} \times 2 = 7$

- (a) (i) Find the relation among 'root mean square velocity', 'most probable velocity' and 'average velocity' of a gas. 2
- (ii) Calculate the most probable velocity of nitrogen molecules at 15°C . $1\frac{1}{2}$

- (b) What do you mean by equipartition of energy? In the light of it, calculate C_v and C_p of a diatomic molecule of a gas and hence find C_p / C_v .
 $1+2+\frac{1}{2}=3\frac{1}{2}$
- (c) (i) Write van der Waals' equation for n moles of a gas. Explain physical significance of van der Waals' constants a and b . $1+1=2$
- (ii) Explain critical phenomenon. $1\frac{1}{2}$

UNIT—II

4. Answer any *one* question from the following : 3
- (a) Describe the method for determining the viscosity of a liquid in the laboratory. 3
- (b) (i) What is vapour pressure of a liquid? Explain the effect of temperature on it. $1+1=2$
- (ii) Write two applications of non-Newtonian liquids. 1

UNIT—III

5. Answer any *two* questions from the following : $3\frac{1}{2} \times 2 = 7$
- (a) (i) Derive an expression showing the relation between the spacings of the lattice planes and the wavelength of the X-rays used to study the crystal structure. $2\frac{1}{2}$
- (ii) Mention two differences between crystalline and amorphous solids. 1
- (b) Discuss how you would use the systematic absence of reflection in the diffraction pattern to distinguish between the three types of cubic Bravais lattices. $3\frac{1}{2}$
- (c) Sodium crystallizes in b.c.c. structure with edge length 4.24 Å. Calculate (i) its density and (ii) radius of Na atom. $2\frac{1}{2}+1=3\frac{1}{2}$

SECTION—B
(Inorganic Chemistry)

(Marks : 27)

6. Find out the correct answer out of the following :

1×3=3

(a) The effective nuclear charge (Z^*) for 3p electron of iron is

- (i) 6.1
- (ii) 9.75
- (iii) 10.9
- (iv) 14.75

(b) Which of the following is diamagnetic?

- (i) O_2^+
- (ii) O_2^-
- (iii) O_2^{2-}
- (iv) None of the above

(c) Which of the following has highest lattice energy?

- (i) CaF_2
- (ii) MgO
- (iii) $NaCl$
- (iv) LiF

7. Answer the following questions :

2×3=6

(a) Define ionization energy. How does it vary along the period of a periodic table?

$\frac{1}{2} + 1\frac{1}{2} = 2$

(b) Write a note on partial ionic character in covalent bonds.

2

(c) Discuss the conditions necessary for the formation of an electrovalent bond.

2

8. Answer any two questions :

3×2=6

(a) Define effective nuclear charge. A 4s orbital is filled earlier than a 3d orbital. Explain with example on the basis of Slater's rule.

1+2=3

(b) (i) The formation of $F^{-}(g)$ from $F(g)$ is exothermic while that of $O^{2-}(g)$ from $O(g)$ is endothermic. Explain giving reasons. 1½

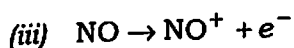
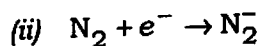
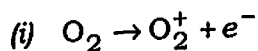
(ii) First ionization energy of carbon atom is greater than that of boron whereas the reverse is true for the second ionization energy. Explain. 1½

(c) Define ionic radii. Calculate the ionic radii of Na^{+} and F^{-} ions in NaF crystals (Interionic distance of Na^{+} and $F^{-} = 2.31 \text{ \AA}$). 1+2=3

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

(a) What are the conditions for the combination of atomic orbitals? Draw the molecular orbital energy-level diagram for NO molecule and determine its bond order. 2+2=4

(b) What are bond order and bond length? What are the expected changes in bond order and bond length that accompany the following ionization processes? 1+3=4



(c) (i) Bond angles of H_2O , H_2S and H_2Se are 104.5° , 92.5° and 91.0° respectively. How would you account for this? 2

(ii) Account for the following decreasing trend of repulsive interactions : 2
 $lp-lp > lp-bp > bp-bp$ (lp = lone pair and bp = bond pair)

(d) (i) Calculate the enthalpy of formation of magnesium fluoride from the following data : 2

Sublimation enthalpy of Mg = $146.4 \text{ kJ mol}^{-1}$

Dissociation enthalpy of fluorine = $158.8 \text{ kJ mol}^{-1}$

Ionisation enthalpy of Mg = $2186.0 \text{ kJ mol}^{-1}$

Electron gain enthalpy of fluorine = $-332.6 \text{ kJ mol}^{-1}$

Lattice energy of $MgF_2 = -2922.5 \text{ kJ mol}^{-1}$

(ii) Write a note on covalent ionic resonance. 2

SECTION—C
(Organic Chemistry)
(Marks : 27)

10. Choose the correct answer of the following :


1×3=3

(a) Which is stable carbanion?

- (i) $\text{C}_6\text{H}_5\overset{\ominus}{\text{C}}\text{H}_2$
- (ii) $\text{PCH}_3\text{O}-\text{C}_6\text{H}_4\overset{\ominus}{\text{C}}\text{H}_2$
- (iii) $\text{P}-\text{NO}_2\text{C}_6\text{H}_4\overset{\ominus}{\text{C}}\text{H}_2$
- (iv) $\text{P}-\text{CH}_3-\text{C}_6\text{H}_4\overset{\ominus}{\text{C}}\text{H}_2$

(b) Which of the following species is not electrophilic in nature?

- (i) Cl^{\oplus}
- (ii) BH_3
- (iii) NO_2^{\oplus}
- (iv) H_3O^+

(c)  is named as

- (i) (2*S*, 3*E*) Pent-3 en-2 ol
- (ii) (2*R*, 3*E*) Pent-3 en-2 ol
- (iii) (2*E*, 3*R*) Pent-2 en-3 ol
- (iv) (2*E*, 3*S*) Pent-2 en-3 ol

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

2×3=6

(a) Draw the orbital picture of the following compounds (any one) :

2

- (i) $\text{CH}_2=\text{C}=\text{CH}_2$
- (ii) $\text{CH}_2=\text{C}=\text{O}$

(b) What are carbanions? If the following groups are present in the α -position of the carbanion, what will be the relative order of their stability?

$-\text{C}\equiv\text{N}$, $-\text{NO}_2$, halogens (X) and alkyl group

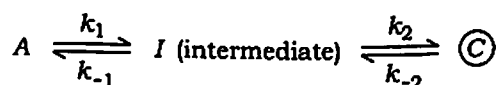
1+1=2

- (c) Compare the acidity of *p*-nitrobenzoic acid and *p*-methoxybenzoic acid on the basis of resonance effect. 2
- (d) Select soft and hard acids and bases from the following AC to HSAB principle.
 $\bar{\text{CN}}$, Ag^+ , SO_3 , RNH_2 2
- (e) Represent *threo* and *erythro* forms of tartaric acid in 3D Newman projections. 2

UNIT—I

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

- (a) What is hyperconjugation? In ethane, the C—C bond length is 1.54 Å, but in propene, C—C bond length is 1.50 Å. Explain. 2
- (b) Write a note on either non-classical carbonium ion or ambident nucleophile. 2
- (c) Draw the energy profile diagram for the two-steps reaction 2



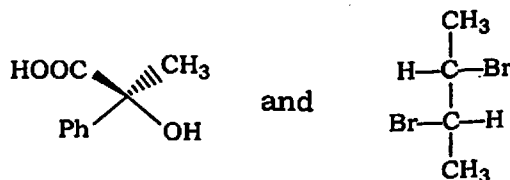
Given $k_{-1} > k_1 > k_2 > k_{-2}$ and the reaction is exothermic.

- (d) Arrange the following in the order of decreasing basicity and offer explanation to support your answer. 2
- $\text{P}-\text{CH}_3\text{O}-\text{C}_6\text{H}_4\text{NH}_2$, $\text{P}-\text{HO}-\text{CH}_2-\text{C}_6\text{H}_4\text{NH}_2$,
 $\text{P}-\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{NH}_2$ and $\text{C}_6\text{H}_5-\text{CH}_2\text{NH}_2$
- (e) The addition of singlet carbene to a multiple bond is a stereoselective and a stereospecific reaction, but the addition of triplet carbene is non-stereoselective. Explain with suitable examples. 2

UNIT—II

13. Answer any *four* questions from the following : 3×4=12

- (a) (i) Draw the structure of (2*E*, 4*Z*) 2,4 Hexadien-oic acid. 1
- (ii) Assign *R* or *S* to the following : 1+1=2



- (b) What is meant by the term racemization? Active 2-benzoyl propanoic acid undergoes racemization when treated with NaOC_2H_5 in ethanol. Offer an explanation. 1+2=3
- (c) Both mesotartaric acid and racemic tartaric acid are optically inactive. State the reason for the optical inactivity in each case. How can you distinguish them? 1+2=3
- (d) Define plane of symmetry and centre of symmetry giving one example for each. $1\frac{1}{2} \times 2 = 3$
- (e) How would you determine the configurations of diastereomers of butenedioic acid by using chemical methods? 3
- (f) Write a note on asymmetric synthesis giving two suitable examples. 3
