

CHEMISTRY

FIRST PAPER

Full Marks : 200

Time : 3 hours

The figures in the margin indicate full marks
for the questions

1. (a) What is de Broglie's hypothesis? Derive the expression for the wavelength of matter waves. An electron is accelerated through a potential difference of 100 volts. What is the de Broglie wavelength associated with it? 1+3+3=7
- (b) Name those effects which can be explained by assuming the wave nature of electromagnetic radiation and the particle nature of electromagnetic radiation. 2
- (c) Write the electronic configurations of the following atom or ions and give the number of unpaired electrons present : 2×3=6
- Fe^{3+} , Cu^+ and P

(2)

- (d) What do you understand by quantum numbers? Give a brief account of all the four quantum numbers to describe atomic structure. 1+4=5
2. (a) How can you justify that—
- (i) common salt is an ionic compound but sugar is a covalent compound;
 - (ii) BF_3 is planar but NH_3 is pyramidal? 2×2=4
- (b) State Fajans rule of polarization and then explain the following : 4+2=6
- (i) AgCl is covalent but KCl is ionic;
 - (ii) LiCl is not soluble in water but NaCl is soluble.
- (c) Draw the molecular orbital diagram for superoxide anion (O_2^-). Whether the bond length in O_2^- is longer or shorter than that in O_2 ? 4+1=5
- (d) Using the concept of hybridization, explain the structure and bonding in acetylene molecule. 5
3. (a) Mention the conditions at which real gases deviate from ideal behaviour. What are the causes of such deviations? Explain how ideal gas equation is modified to give van der Waals equation of real gases. 2+2+4=8

(3)

- (b) What do you understand by mean free path of gas molecules? Show the dependence of mean free path of gas molecules with pressure at a particular temperature. 2+2=4
- (c) Three gm-moles of a real gas occupy 10 litres at 15 atmosphere pressure. Find out its temperature. Given $a = 3.59$ and $b = 0.043$ in the usual litre-atmosphere units. 5
- (d) Calculate the ratio of root mean square velocity (c_{rms}), average velocity (c_{av}) and most probable velocity (c_{mp}) of a gas at a particular temperature. 3
4. (a) Depending upon the interactions with the surroundings, what are the different types of system dealt in thermodynamics? Define these systems with examples. 2+3=5
- (b) What is state function? Explain what you understand by state variables. 2+2=4
- (c) Establish the relation $dH = T dS + V dP$. All the terms have their usual meanings. 5

(4)

(d) (i) 8 g of He gas at 300 K expands reversibly and isothermally from $2 \times 10^{-2} \text{ m}^3$ to $4 \times 10^{-2} \text{ m}^3$. Calculate the entropy change for the gas. 3

(ii) A reversible heat engine working between 273 K and 373 K absorbs 746 J of heat from the source. Calculate (1) the work done, (2) the heat given to the sink and (3) the efficiency of the engine. 3

5. (a) (i) State first law of thermodynamics and explain with example that it is incapable to predict the direction of a process. 1+2=3

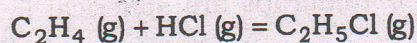
(ii) Find the expression of energy change in a cyclic process. 2

(b) Derive the relation

$$C_P - C_V = \left[\left(\frac{dU}{dV} \right)_T + P \right] \left(\frac{dV}{dT} \right)_P$$

where symbols have their usual meanings. 5

- (c) Define enthalpy. Calculate the enthalpy change of the reaction



Given that enthalpy of formations of $\text{C}_2\text{H}_5\text{Cl} (\text{g})$, $\text{HCl} (\text{g})$ and $\text{C}_2\text{H}_4 (\text{g})$ are -112 kJ mol^{-1} , $-92.35 \text{ kJ mol}^{-1}$ and $52.30 \text{ kJ mol}^{-1}$ respectively. 1+4=5

- (d) (i) State the thermodynamic conditions which are required to establish the feasibility of a process. 3

- (ii) Calculate the amount of work done by 2 moles of an ideal gas at 298 K in a reversible isothermal expansion from 20 litres to 40 litres. 2

6. (a) Define the term coefficient of viscosity and give the mathematical relation to characterize it. What is the unit of coefficient of viscosity in CGS and SI systems and how are they related?

2+2+2+2=8

- (b) Explain why—

- (i) the meniscus of water layer in capillary glass tube is curve in shape;

(6)

(ii) clothes dry more rapidly on a dry day than on a humid day;

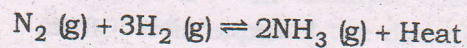
(iii) raindrops are spherical in shape.

2×3=6

(c) Out of water and ethanol one is more viscous than the other. Which one you think to be more viscous and why? 3

(d) Calculate the ratio of the coefficient of thermal expansion (α) and the coefficient of compressibility (k) for an ideal gas. 3

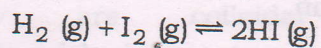
7. (a) Discuss the effect of pressure and temperature for the progress of the following reversible reaction : 5



(b) Deduce van't Hoff's equation to establish the effect of temperature on chemical equilibrium. 5

(c) Derive Gibbs-Duhem equation which relates the change in chemical potential with the composition of the system. What is the significance of this equation? 5+1=6

- (d) Find an expression for the equilibrium constant K_c for the following reaction : 4



8. (a) Explain the terms osmosis, osmotic pressure and isotonic solution. Why is the measurement of molecular weight of solute by osmotic pressure method advantageous over the molecular weight by other colligative properties? 3+2=5
- (b) What do you mean by boiling point of a liquid? When sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is added to water, the boiling point of solution increases. How would you explain this phenomenon? 2+3=5
- (c) State the laws of osmotic pressure. A solution of 0.5 g of a polymer in 1.2 dm^3 of an aqueous solution has an osmotic pressure of 3.84 torr at 300 K. Calculate the molecular weight of the polymer. 2+3=5
- (d) Define the terms molarity, molality and mole fraction. Find an expression of the mole fraction of a two-component system. 3+2=5

9. (a) Derive the integrated rate equation for a first-order chemical reaction. Mention the characteristics of the first-order reaction. 3+2=5

(b) Define half-life of a chemical reaction and find an expression of it. Describe briefly the half-life method of determination of order of a chemical reaction. The half-life of a chemical reaction changes from 50 minutes to 25 minutes when the concentration is reduced to half of the initial concentration. Calculate the order of the reaction. 1+1+2+2=6

(c) Write briefly about the Michaelis-Menten mechanism of enzyme-catalyzed reaction. 5

(d) Write short notes on the following : 2+2=4
(i) Unimolecular reaction
(ii) Activation energy and its determination

10. (a) Define the terms surface energy and surface tension. What is the SI unit of surface tension? How does surface tension vary with temperature? 4

- (b) Discuss the applications of adsorption in industry and everyday life. 5
- (c) How are colloidal solutions distinguished from true solutions and suspensions? How are they classified? Why are lyophilic colloids more stable than lyophobic colloid? $2+3+2=7$
- (d) Explain giving reasons of the following : $2+2=4$
- (i) The clear sky looks blue.
 - (ii) Alum is used in the town water supply.
