

CHEMISTRY
PAPER - I

Time Allowed : 3 hours

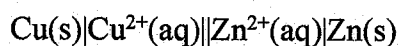
Full Marks : 100

Marks for each question is indicated against it.

Attempt any 5 (five) questions taking not more than 3 (three) questions from each Part.

PART - A

1. (a) Discuss the radius ratio rule for predicting structure of ionic crystals. Elaborate the statement taking examples of NaCl, ZnS and CsCl.
[Ionic radii (Å) : Na⁺ = 1.02; Cs⁺ = 1.67; Zn²⁺ = 0.74; Cl⁻ = 1.81; S²⁻ = 1.84] (6)
- (b) Draw neat diagram of NaCl and CsCl structures and compare the differences between the two structures. (5)
- (c) Draw a labelled phase diagram of a two-component system involving eutectic point and describe the important features. (4)
- (d) How is the Nernst distribution law used in the process of solvent extraction? Derive the expression for the calculation of the amount of a solute left unextracted after a given number of extractions. (2+3=5)
2. (a) Derive expression for the entropy change accompanying variation of temperature and volume. (4)
- (b) Define Gibbs free energy. How does it vary with temperature and pressure? (1+4=5)
- (c) State Nernst Heat Theorem. How does it lead to the enunciation of the third law of thermodynamics? (2+3=5)
- (d) Represent graphically the Maxwell's distribution of molecular velocities of gases and state the important features of the curves. Also discuss the effect of temperature on the distribution of molecular velocities. (3+3=6)
3. (a) Describe the Freundlich adsorption isotherm. (5)
- (b) Calculate the *emf* of the following cell and predict whether the given cell representation is correct or wrong. If not, write the correct cell representation. (5)



$$\text{Given : } E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$$

$$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$$

- (c) What are concentration cells? Derive an expression for *emf* of a concentration cell without transference. (1+4=5)
- (d) Write a brief note on ion selective electrodes and their uses. (5)
4. (a) What are consecutive reaction? Discuss the kinetics of the first order consecutive reactions:
- $$A \xrightarrow{K_1} B \xrightarrow{K_2} C \quad (K_1 \neq K_2)$$
- Depict graphically the variation of concentrations of A, B and C with time. (1+2+3=6)
- (b) Give a detailed account of the transition state theory of reaction rates. In what way is this theory superior to the collision theory? (3+2=5)
- (c) Show that the half-life of a first order reaction is independent of the initial concentration of the reactant. (4)
- (d) Define 'quantum efficiency' or 'quantum yield'. A sample of gaseous HI was irradiated by light of wavelength 253.7nm when 307J of energy was found to decompose 1.30×10^{-3} mole of HI. Calculate the quantum yield for the dissociation of HI. (1+4=5)

PART - B

5. (a) Lithium has the highest ionization potential among alkali metals, yet it is the most powerful reducing agent. Explain. (5)
- (b) Calculate the de Broglie wavelength of a neutron moving with a velocity of $6.0 \times 10^6 \text{ cm s}^{-1}$. The mass of a neutron is equal to $1.675 \times 10^{-24} \text{ g}$. (5)
- (c) Solve Schrodinger wave equation for a particle in a one-dimensional box. (6)
- (d) Write a brief note on nuclear binding energy and correlate it with the nuclear stability. (4)
6. (a) Using the concept of hybridisation and VSEPR theory, predict the shape of (2½+2½=5)
- (i) ClF_3
- (ii) SF_4
- (b) With the help of the molecular orbital theory, explain the stability of O_2 , O_2^- and O_2^{2-} . (5)
- (c) Briefly explain the terms 'essential' and 'trace' elements in biological systems. Mention the biological roles of potassium and calcium ions. (5)
- (d) In the formation of 1 mole of NaCl crystal from 1 mole of sodium and 0.5 mole of chlorine gas, $381.8 \text{ kJ mol}^{-1}$ of energy is released. The enthalpy of sublimation of sodium is $108.5 \text{ kJ mol}^{-1}$, dissociation energy of chlorine is $243.0 \text{ kJ mol}^{-1}$, ionization energy of sodium is $495.2 \text{ kJ mol}^{-1}$, electron affinity of chlorine is $348.3 \text{ kJ mol}^{-1}$. Calculate the lattice energy of NaCl. (use appropriate sign for the energy terms given) (5)

7. (a) "Beryllium compounds are mostly covalent while the rest of group 2 elements form predominantly ionic compounds". Why? (4)
- (b) Explain Why (3+3=6)
- (i) H_2S is a gas while H_2O is a liquid at room temperature.
 - (ii) Zn^{2+} salts are white while Cu^{2+} salts are blue in colour.
- (c) Give an account for the tendency of transition metals to act as catalyst and their unique characteristics to form coordination complex. (3+3=6)
- (d) Discuss the different types of oxides formed by the alkali metals. (4)
8. (a) What is lanthanide contraction? What are the important consequences of lanthanide contraction? (1+4=5)
- (b) "Lanthanide ions typically display weak but sharp absorption spectra". Account for this observation. (5)
- (c) Discuss the oxidizing properties of KMnO_4 in acidic, neutral and alkaline medium. (6)
- (d) How will you obtain linear silicone and cross-linked silicone? (4)

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