

[Time: 2 ½ Hours]

[Marks: 60]

Please check whether you have got the right question paper.

- N.B.:**
- All questions are compulsory.**
 - Figures to the right indicates full marks.**
 - Use of non – programmable scientific calculator is allowed.**

Useful constants

$c = 2.998 \times 10^8 \text{ m.s}^{-1}$

$R = 8.314 \text{ J.K}^{-1}\text{mol}^{-1}$

$= 2.0 \text{ cal.K}^{-1} \text{ mol}^{-1}$

$h = 6.626 \times 10^{-34} \text{ Js}$

$m_e = 9.110 \times 10^{-31} \text{ kg}$

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35.5

$e = 1.602 \times 10^{-19} \text{ C}$

$k = 1.3811 \times 10^{-23} \text{ J.K}^{-1}$

$1 \text{ J} = 6.24 \times 10^{18} \text{ eV}$

$1 \text{ eV} = 8.06 \times 10^3 \text{ cm}^{-1}$

$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$

1. A) Attempt **any two** of the following:

- Define fugacity. How does it vary with temperature and pressure. 4
- Derive Gibbs Duhem Margules equation. 4
- Explain structure of ADP molecule. Explain the hydrolysis of ATP in biological system with the help of thermodynamics. 4
- Derive an equation for Gibb's adsorption isotherm. 4

1. B) Attempt **any one** of the following:

- The partial molar volume of water in a methanol water solution containing 0.61 mole fraction water is $17.2 \text{ cm}^3/\text{mol}$. The density of the solution is 0.92 g/cm^3 . Calculate the partial molal volume of methanol in the solution. $(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$ 4
- Calculate ΔS_{mix} at 298K and 1 atm pressure when 28 g of He (At mass He = 4) is mixed with 100 g of Ne (At mass Ne = 10). 4

2. A) Attempt **any two** of the following:

- Transform Cartesian coordinates (x,y,z) into polar coordinates (r,θ,Φ) and write the expression for Φ. 4
- Explain the need for an approximate solution to a two-electron system. Show how the problem of two electrons can be reduced to the problem of one electron system. 4
- Derive an expression for the most probable distance of an electron from the nucleus in the ground state of a hydrogen atom. 4
- Write the secular determinant for the benzene molecule. Draw the molecular energy level diagram and indicate HOMO, and LUMO from the diagram. 4

2. B) Attempt **any one** of the following:

- What are quantum numbers? Explain the significance of magnetic quantum numbers. 4
- An electron with a mass $9.1 \times 10^{-31} \text{ kg}$ rotates in a circular orbit with a radius of 0.5 \AA . Calculate the energy in eV for $n=2$. 4

3. A) Attempt **any two** of the following:
- Derive the parabolic rate law for the reaction of a gas on the surface of solid particles. 4
 - Explain the kinetics of enzyme inhibition action by uncompetitive inhibition method. 4
 - Derive an expression for the linear free energy relationship of reactions in solutions. 4
 - Discuss the kinetics of regulatory enzymes with the help of Hill's equation. 4
3. B) Attempt **any one** of the following:
- Predict the effect of ionic strength on the rate constant for each of the following reactions. 4
 - $[\text{Pt}(\text{NH}_3)_3\text{Br}]^+ + \text{CN}^- \rightarrow \text{Products}$
 - $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}^+ \rightarrow \text{Products}$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{Hg}^{2+} \rightarrow \text{Products}$
 - $[\text{NO}_2\text{NCO}_2\text{C}_2\text{H}_5]^- + \text{OH}^- \rightarrow \text{Products}$
 - An enzyme hydrolyzed a substrate concentration of $0.03 \text{ mmol dm}^{-3}$, the initial rate was $1.5 \times 10^{-3} \text{ mmol dm}^{-3} \text{ min}^{-1}$ and the maximum rate was $4.5 \times 10^{-3} \text{ mmol dm}^{-3} \text{ min}^{-1}$. Calculate the Michaelis Constant (Km). 4
4. A) Attempt **any two** of the following:
- Derive an expression for Frenkel defects in ionic crystals thermodynamically. 4
 - Draw and discuss the phase diagram of solid-gas system involving formation of amino compounds. 4
 - Draw and discuss the phase diagram of two component systems involving formation of a compound with congruent melting point. 4
 - Draw and discuss the phase diagram of a three-component system consisting of two pairs of partially miscible liquids. 4
4. B) Attempt **any one** of the following:
- If the average energy required to create a vacancy in a metal was 1 eV. Calculate the ratio of vacancies in the metal at 727°C and 227°C . $k_B = 8.625 \times 10^{-5} \text{ eV/K}$. 4
 - Calculate the number of phases, the number of components and the number of degrees of freedom in the following system. 4
 - $\text{CuSO}_4 \cdot \text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4(\text{s}) + \text{H}_2\text{O}(\text{g})$
 - One mole of a pure gas enclosed in a cylinder
5. Attempt **any four** of the following
- Give Kelvin equation. Prove it thermodynamically. 3
 - What do you understand by thermodynamic excess functions? Write an expression for Excess entropy (S^E). 3
 - What are radial probability distribution curves? Sketch radial distribution curves for 1s and 2p orbitals. 3
 - Explain why hydrogen-like atoms represent a two-particle problem. Write the Hamiltonian operator for it. 3
 - Discuss the Lineweaver – Burk plot for an enzyme catalyzed reaction. 3
 - Discuss the factors which affect the reactions in solid state. 3
 - What is line defect? Explain Edge Dislocation. 3
 - Draw phase diagram of a three component system with one pair of partially miscible liquid and explain why tie lines within the binodal curve are neither parallel to each other nor to axis. 3
