Q.P. Code : 35767

[2½ Hours] **[Marks: 60]**

Please check whether you have received the correct question paper.

N.B:
1. All questions are compulsory.
2. Figures to the right indicate full marks.
3. Use of non-programmable scientific calculator is allowed.

Useful constants

$c = 2{\cdot}998 \times 10^{8}$ ms^{-1}	$R = 8{\cdot}314$ JK^{-1} mol^{-1}
$h = 6{\cdot}626 \times 10^{-34}$ Js	$N_A = 6{\cdot}022 \times 10^{23}$ mol^{-1}
$e = 1{\cdot}602 \times 10^{-19}$ C	$k = 1{\cdot}381 \times 10^{-23}$ JK^{-1}
$1J = 6{\cdot}24 \times 10^{18}$eV	1 atm = $1{\cdot}013 \times 10^{5}$ Nm^{-2}
$1eV = 8{\cdot}06 \times 10^{3}$ cm^{-1}	

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

i) What are spherical harmonics? Write the expression for 'theta' equation 'phi' equation and 'R' equation obtained by the method of separation of variables of Schrodinger wave equation in terms of spherical coordinates. **4**

ii) Name the four quantum numbers and describe any one of them. **4**

iii) What do you mean by the term 'atomic unit'? Write the value of the following quantities in terms of atomic units **4**
   a) Charge of an electron
   b) Angular momentum
   c) Energy of an electron in the first orbit

iv) Write the secular determinant for benzene molecule. Draw the molecular energy level diagram for benzene and indicate HOMO, LUMO from the diagram. **4**

(B) Attempt **any one** of the following :

i) What is the probability of an electron being found at a distance of $r = 0, \frac{1}{2},\ 1\ and\ \frac{3}{2}$ a.u. from the nucleus of hydrogen atom in 1s state? **4**

ii) Consider CO molecule as rigid rotor, the internuclear distance is $1{\cdot}131 \times 10^{-10}$m. Calculate the rotational energy for J = 2 and J = 3. **4**

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

i) Two ideal gases 1 and 2 are initially at the same temperature but at different pressures P_1 and P_2 respectively. If n_1 moles of gas 1 and n_2 moles of gas 2 are mixed isothermally, then show that **4**

$$\Delta G_{mix} = RT\,[n_1 \ln (p/P_1) + n_2 \ln (p/P_2)]$$

ii) Derive thermodynamically the Gibbs adsorption isotherm equation. **4**

iii) Define fugacity. How does it vary with pressure and temperature? **4**

iv) What do you mean by thermodynamic excess functions? Obtain an expression for **4**
   (a) Excess entropy (S^E) (b) Excess enthalpy (H^E)

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(B) Attempt **any one** of the following :

i) The volume of an aqueous solution of sodium chloride at 298K is given by $\frac{V}{cm^3} = 1003 + 16{\cdot}2m + 1{\cdot}77m^{3/2} + 0{\cdot}12m^2$ where m = molality of solute (moles of solute) n_2 per kg of solvent. **4**
Calculate the partial molal volume of the components for m = 0·1 mol kg^{-1} (The mass of water is kept constant as 1000g)

ii) Calculate ΔG_{mix} and ΔS_{mix} at 298K and 1 atm pressure when 28g of He (At mass He = 4) is mixed with 100g of Ne (At mass Ne = 20) **4**

3. (A) Attempt **any two** of the following :

i) Derive the kinetic expression for the contracting sphere rate law of reactions in solid state. **4**

ii) Derive an expression to show the effect of ionic strength on the rate constant of the reaction. **4**

iii) Discuss the Lineweaver-Burk's plot which is used for the analysis of the rate data of :- 1) Competitive inhibition and 2) non-competitive inhibition enzyme catalysed reaction. **4**

iv) Discuss the kinetics of regulatory enzymes. **4**

(B) Attempt **any one** of the following :

i) Calculate the concentration of a non-competitive inhibitor ($K_I = 2{\cdot}5 \times 10^{-4}$ mol dm^{-3}) needed to yield 60% inhibition of an enzyme catalysed reaction. **4**

ii) Predict the effect of ionic strength on the rate constant for each of the following reactions :- **4**

1. $[Cr(urea)_6]^{3+} + H_2O \rightarrow$ Products
2. $CH_3COOC_2H_5 + OH^- \rightarrow$ Products
3. $CH_2BrCOO^- + S_2O_3^{2-} \rightarrow$ Products
4. $Fe^{2+} + [Co(C_2O_4)_3]^{3-} \rightarrow$ Products

4. (A) Attempt **any two** of the following :

i) Derive an equation for vacancy defects in elemental solids. **4**

ii) Describe two component system of gas-solid with the formation of amino compound. **4**

iii) Explain the phase diagram of a two component system involving formation of a compound with congruent melting point. **4**

iv) Draw and discuss the phase diagram of a three component system consisting of two pairs of partially miscible liquids. **4**

(B) Attempt **any one** of the following :

i) Determine the number of phases, the number of components and degree of freedom of the following systems : **4**
1. $CuSO_4{\cdot}5H_2O_{(s)} \rightleftarrows CuSO_4{\cdot}3H_2O_{(s)} + 2H_2O_{(g)}$
2. Solid carbon in equilibrium with gaseous CO, CO_2 and O_2 at 100ºC

ii) The interionic distance between a certain alkali halide (mol.wt 74·46) and NaCl structure is 0·32nm. Calculate the density of the salt for 0·1% Frenkel defects. ($N = 6{\cdot}022 \times 10^{23}$). **4**

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5. Attempt **any four** of the following : **12**

(a) Give the characteristics of real solutions.

(b) Write the BET equation and explain the terms involved in it.

(c) Transform cartesian coordinates (x, y, z) into polar coordinates (r, θ ϕ). Identify r, θ, ϕ.

(d) Write the expression for radial wave functions of 2p and 3d orbitals.

(e) Derive Hammet's equation of linear free energy relationship.

(f) Discuss the effect of pH on enzyme catalysed reactions.

(g) Explain the terms :-

i) Plait point

ii) Binodal curve

(h) What are line defects. Explain Screw dislocation.