[Time: 2 ½ Hours] **[Marks : 60]**

Please check whether you have got the right question paper.

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

Useful constants

$c = 2.998 \times 10^{8}\ m.s^{-1}$
$e = 1.602 \times 10^{-19}\ C$
$R = 8.314\ J.K^{-1}mol^{-1}$
$= 2.0\ cal.K^{-1}\ mol^{-1}$
$k = 1.3811 \times 10^{-23}\ J.K^{-1}$
$h = 6.626 \times 10^{-34} Js$
$1J = 6.24 \times 10^{18}\ eV$
$m_e = 9.110 \times 10^{-31}\ kg$
$1eV = 8.06 \times 10^{3} cm^{-1}$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$
$1\ amu = 1.66 \times 10^{-27}\ kg$

Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35.5, Br = 80

1. A) Attempt ***any two*** of the following:
   i) Derive thermodynamically the Kelvin equation of vapour pressure of droplets. 4
   ii) What is partial molal volume? How will you evaluate it by intercept method? 4
   iii) Explain structure of ATP molecule with diagram. Giving one example of biochemical reaction involving ATP. 4
   iv) How will you evaluate fugacity from the Vander Waal's equation of state? 4

1. B) Attempt **any one** of the following:
   i) For solution of 1×10^{-4} M butanoic acid the rate of change of surface tension with respect to concentration is $-0.080\ Nm^{-1}\ mol^{-1}$. Using Gibbs adsorption isotherm, calculate the surface excess of butanoic acid ($R = 8.314\ J.K^{-1}mol^{-1}$) 4
   ii) Calculate the entropy change when 5.2 dm^3 of Oxygen is mixed with 16.8 dm^3 of hydrogen at NTP combines assuming no chemical change takes place and mixture behaves ideally. 4

2. A) Attempt ***any two*** of the following:
   i) Express Schrodinger's wave equation for a hydrogen atom in terms of polar coordinates and split it into three equations by separating the variables. 4
   ii) Write the expression for total wave function for 1s, 2s, and 2p orbital of a hydrogen atom. 4
   iii) Discuss any two methods of obtaining the approximate solution of the Schrödinger wave 4
   iv) Write the secular determinant for 1,3- butadiene molecule. Draw the molecular energy level diagram and indicate HOMO, and LUMO from the diagram. 4

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

i) Consider HBr as a rigid rotor with an inter-nuclear region of 147.1 pm. Calculate rotational energy for J = 2. (m_H = 1.00 amu; m_{Br} = 80 amu) 4

ii) What are quantum numbers? Explain the significance of magnetic quantum numbers. 4

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

i) Derive an expression for the first-order rate law of kinetics of reactions in solid state. 4

ii) Explain the kinetics of inhibition of enzyme action by competitive method. 4

iii) Describe Lineweaver-Burk and Eadie Analysis of the rate data of enzyme catalyzed reaction. 4

iv) Derive an expression for the linear free energy relationship of reactions in solutions. 4

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

i) Urease enzyme hydrolyzed urea at [S] = 0.04mmol dm^{-3} with a Michaelis Constant (Km) value of around 0.08 mmol dm^{-3}. The initial rate observed was $2.5x10^{-3}$ mmol $dm^{-3}.min^{-1}$. Calculate the maximum rate of the enzyme catalyzed reaction. 4

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

(a) $Pb^{2+} + [Co(C_2O_4)_3]^{2-} \rightarrow$ Products
(b) $CH_3COOCH_3 + OH^- \rightarrow$ Products
(c) $[Co(NH_3)_5Cl]^{2+} + Fe^{2+} \rightarrow$ Products
(d) $S_2O_8^{2-} + I^- \rightarrow$ Products

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

i) Derive an expression to find the concentration of vacancy defects in elemental solids. 4

ii) Explain the phase diagram of a two components system of solid-gas involving formation of hydrates of copper sulphate. 4

iii) Draw and discuss the phase diagram of two component systems involving formation of a compound with congruent melting point. 4

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

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

i) The density of Schottky defects in a certain sample of sodium chloride is 5 x 10^{11} m^{-3} at 25°C. If the observed interionic (Na^+Cl^-) distance is 2.82 A^o. What is the average energy required to create one Schottky defect? (K_B = 8.625 x 10^{-5} eV/K) 4

ii) Calculate the number of phases, the number of components and the number of degrees of freedom in the following system. 4

(a) $2\ KClO_{3(s)} \rightleftharpoons 2KCl_{(s)} + 3\ O_{2(g)}$
(b) Solid iodine in equilibrium with iodine vapour

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

a) What are the characteristics of real gases? Show that μ=$[\frac{\partial E}{\partial n1}]\ s, v, n2$ 3

b) State BET equation and explain the terms involved in it. 3

c) Calculate the most probable distance of an electron from the nucleus in the ground state of a hydrogen atom. 3

d) State and explain the variation principle. 3

e) Discuss the factors which affect the reactions in solid state. 3

f) Write a short note on enzyme activation by metal ions. 3

g) What is meant by line defect? Explain Screw dislocation. 3

h) Define the following terms – 3

i) Number of Components ii) Peritectic reaction iii) Plait point

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