

QP Code : 77303

(2½ Hours)

[ Total Marks : 60

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

Useful constants :

$$c = 2.998 \times 10^8 \text{ms}^{-1}$$

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

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

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

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

$$R = 8.314 \text{JK}^{-1} \text{mol}^{-1}$$

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

$$k = 1.381 \times 10^{-23} \text{Jk}^{-1}$$

$$1 \text{atm} = 1.013 \times 10^5 \text{Nm}^{-2}$$

1. a) Attempt ANY TWO of the following :-
- Using the relation between entropy and probability,  $S = k \ln W$ , derive an expression for residual entropy. 4
  - What are exact differentials? Give their characteristics. 4
  - What is Joule-Thomson coefficient? What are the conclusions drawn when various gases are subjected to Joule-Thomson experiment? 4
  - State the third law of thermodynamics. How is it useful in the determination of absolute entropy of a gas? 4
- b) Attempt ANY ONE of the following :-
- A zinc block of mass 500g at  $100^\circ\text{C}$  is kept in a lake at  $10^\circ\text{C}$ . The total heat capacity at constant pressure of the block is  $150 \text{J/degree}$  at  $100^\circ\text{C}$ . Calculate the entropy change of the universe. 4
  - Calculate Joule-Thomson coefficient for  $\text{N}_2$  gas at  $298 \text{K}$  and  $100$  atmospheric pressure if the van der waal's constants 'a' and 'b' for nitrogen gas are  $1.41 \text{Nm}^3 \text{mol}^{-2}$  and  $3.92 \times 10^{-5} \text{m}^3 \text{mol}^{-1}$  respectively. [Given :  $C_p$  for  $\text{N}_2 = 29.94 \text{JK}^{-1} \text{mol}^{-1}$ ] 4
2. a) Attempt ANY TWO of the following :-
- Define partial molal volume. How is it determined by the method of intercepts? 4
  - Give a brief account of entropy changes in life processes. 4
  - Obtain an expression for free energy change of mixing of gases in terms of mole fraction. 4

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- iv) Explain the significance of fugacity to study thermodynamics of real gases. 4  
How is it evaluated by graphical method?
- b) Attempt ANY ONE of the following :-
- i) Calculate  $\Delta G_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  at  $25^{\circ}\text{C}$  and 1 atmospheric pressure when 10 moles of Helium gas is mixed with 10 moles of Neon gas. 4
- ii) At  $298\text{K}$ , the density of 50 percent by mass of ethanol-water system is  $0.914\text{gcm}^{-3}$ . The partial molal volume of water in ethanol is  $17.4\text{ cm}^3\text{mol}^{-1}$ . Calculate the partial molal volume of ethanol. 4
3. a) Attempt ANY TWO of the following :-
- i) Draw and discuss the graphical representation of a three liquid system involving formation of two pairs of partially miscible liquids. 4
- ii) What do you understand by peritectic reaction? Draw and discuss the phase diagram of a solid-liquid system forming a compound with incongruent melting point. 4
- iii) Derive thermodynamically the Gibbs adsorption isotherm. 4
- iv) Draw and discuss the phase diagram of a ternary system of hydrate not dehydrated by the second salt. 4
- b) Attempt ANY ONE of the following :-
- i) Draw and discuss the phase diagram of solid-gas system involving formation of amino compounds. 4
- ii) Derive thermodynamically the Kelvin equation of the vapour pressure of droplets. 4
4. a) Attempt ANY TWO of the following :-
- i) State the Debye-Huckel's limiting law of mean ionic activity coefficients and explain the terms involved. Discuss the merits of the law. 4
- ii) Explain the relaxation effect for the conductance of strong electrolytes. 4
- iii) Explain the construction and working of the phosphoric acid fuel cell. 4
- iv) Explain the use of enzymes as electrodes. 4

B Attempt ANY ONE of the following :-

i) Calculate the value of the resting membrane potential for the following :-

Ion species	Intra cellular concentration in mM	Extra cellular concentration in mM
K <sup>+</sup>	155	4
Ca <sup>2+</sup>	10 <sup>-4</sup>	1.5

given that  $\frac{2.303RT}{F}$  at 298K = 61.

ii) Calculate the mean activity coefficient of aqueous copper chloride solution containing 40 cm<sup>3</sup> of 0.02m copper chloride and 60 cm<sup>3</sup> of 0.03m sodium sulphate. (A = 0.509 for water at 298K)

5. Attempt ANY FOUR of the following :-

a) Derive the following Maxwell equation

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

b) Show the different stages involved in the conversion of tin from 293K to 573K. Melting point of tin is 505K. Also give  $\Delta S_{\text{Total}}$  with the help of necessary equation.

c) Explain the significance of chemical potential.

d) Give the characteristics of real solutions.

e) Sketch and explain the phase diagram of hydrated double salt not decomposed by water.

f) Adsorption of a certain gas forms a complete monolayer on the surface of silica gel. The volume of the gas adsorbed reduced to STP was found to be 130 cm<sup>3</sup> per gram of adsorbent. Calculate the surface area of the adsorbent if the area occupied by each gas molecule is  $16.2 \times 10^{-20} \text{ m}^2$ .

g) Explain the Debye-Falkenhagen effect.

h) Give the functions of the cell membrane.

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