

(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 scientific calculator is allowed.

Useful constants :-

$$c = 2.998 \times 10^8 \text{ ms}^{-1}; \quad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1};$$

$$h = 6.626 \times 10^{-34} \text{ Js}; \quad N_A = 6.023 \times 10^{23} \text{ mol}^{-1};$$

$$e = 1.602 \times 10^{-19} \text{ C}; \quad k = 1.381 \times 10^{-23} \text{ JK}^{-1};$$

$$1 \text{ J} = 6.24 \times 10^{18} \text{ eV}; \quad 1 \text{ eV} = 8.06 \times 10^3 \text{ cm}^{-1};$$

$$m_e = 9.11 \times 10^{-31} \text{ kg}; \quad 1 \text{ atmosphere} = 1.01325 \times 10^5 \text{ Nm}^{-2};$$

$$O = 16, N = 14, \quad C = 12$$

$$H = 1, S = 32 \quad Cl = 35.5$$

1. (a) Attempt any two of the following :-

(i) What is Joule - Thomson effect ? Explain the consequences of this effect on real and 4
ideal gases.

(ii) Derive the following Maxwell's relation : 4

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

(iii) Explain the term residual entropy with suitable example. 4

(iv) Explain the term coupled reaction with the help of suitable example. 4

(b) Attempt any one of the following :-

(i) Calculate the entropy changes for fusion and vapourisation of one mole of water at its 4
normal freezing point and boiling point. The molar enthalpy of fusion and
vapourisations are 6.01 kJ mol^{-1} and $40.80 \text{ kJ mol}^{-1}$ respectively. Also calculate
the entropy change when 1 mole of steam is condensed at 373 K and the water is
cooled to 273 K to get ice. The c_p for the process is $75.6 \text{ JK}^{-1} \text{ mol}^{-1}$ (ii) Calculate the Joule -Thomson's coefficient (μ_{JT}) for $\text{CO}_{2(g)}$ at 273 K . 4The van der Waal's constants a and b for $\text{CO}_{2(g)}$ are $0.36 \text{ Nm}^4 \text{ mol}^{-2}$ and
 $4.3 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ respectively [Given $c_p = 38.50 \text{ JK}^{-1} \text{ mol}^{-1}$]

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2. (a) Answer any two of the following :-

(i) What is fugacity of real gases ? How is it determined by graphical method ? 4

(ii) Derive Gibbs-Duhem -Margules equation. 4

(iii) Give a brief account of entropy changes in life processes. 4

(iv) Explain the physical significance of chemical potential. 4

(b) Answer any one of the following :-

(i) Calculate the change in chemical potential when 2 moles of oxygen gas is expanded from pressure of 10 atmosphere to pressure of 2 atmosphere at 300K ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$). 4

(ii) Calculate the entropy of mixing when 128g of SO_2 , 96g of oxygen and 80g of SO_3 are mixed at constant temperature, assuming no chemical reaction is occurring. 4

3. (a) Attempt any two of the following :-

(i) Discuss the application of the phase rule to solid gas equilibria taking into consideration the formation of various hydrates of copper sulphate. 4

(ii) Draw phase diagram of two component system in which the two components form a stable compound with incongruent melting point. 4

(iii) Derive thermodynamically the Kelvin equation of vapour pressure of liquid droplets. 4

(iv) Discuss briefly B.E.T. theory of multilayer adsorption. 4

(b) Attempt any one of the following :-

(i) Draw and discuss the phase diagram for ternary system of hydrate not dehydrated by second salt. 4

(ii) Discuss the graphical representation of three liquid system involving formation of two pairs of partially miscible liquids. 4

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4. (a) Attempt any two of the following :-

- (i) Explain the theory of membrane potential. 4
- (ii) Draw a labelled diagram of alkaline fuel cell. Explain how is it better than conventional cells. 4
Give the reactions taking place at anode and cathode.
- (iii) Discuss the factors which affect the mobility of ions in strong electrolyte 4
- (iv) Explain the Debye - Falkenhagen effect for conductance of strong electrolytes. 4

(b) Attempt any one of the following :-

(i) Calculate the resting membrane potential for 4

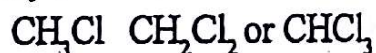
Ion species	Intracellular concentration (mM)	Extracellular concentration (mM)
Cl ⁻	4	120
Na ⁺	150	5

$$\left(\text{Given: } \frac{2.303RT}{F} = 60 \right)$$

(ii) Calculate the activity coefficient of barium and chloride ions and mean activity coefficient of 0.01m solution of barium chloride at 298 K (A = 0.509 for water at 298K) 4

5. (a) Attempt any four of the following :- 12

(i) Define entropy. Explain which of the following will have higher value for standard molar entropy and why?



(ii) Explain the determination of absolute entropy with the help of heat capacity concept.

(iii) Explain the term i) partial molal volume

ii) partial molal enthalpy

(iv) Obtain the relation $\Delta G = nRT \sum x_i \ln x_i$

(v) Sketch qualitatively and explain the ternary system of hydrated double salt not decomposed by water.

(vi) For a 1×10^{-4} M aqueous solution of n-propanoic acid, $\frac{dr}{dc} = -0.080 \text{ Nm}^2 \text{ mol}^{-1}$ at 25°C

using Gibbs adsorption equation, determine the surface excess of n-propanoic acid

(vii) What is membrane? What are the components and physical properties of a cell membrane?

(viii) State Debye-Huckel - Onsager equation and identify the terms involved.