

(2½ Hours)

[Total Marks : 60]

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

Useful constants :—

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

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

$$h = 6.625 \times 10^{-34} \text{ Js}$$

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

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

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

$$k = 1.3811 \times 10^{-23} \text{ JK}^{-1}$$

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

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

$$1 \text{ atmosphere} = 1.01325 \times 10^5 \text{ Nm}^{-2}$$

$$H = 1$$

$$O = 16$$

1. (a) Attempt any **two** of the following :—
- What are exact differentials ? If V is a function of T and P . Show that for ideal gas dV is exact differential. 4
 - “In Joule-Thomson experiment enthalpy of the system remains constant.” Prove. 4
 - Explain the concept of residual entropy. 4
 - State the ‘Third law of Thermo dynamics’ and show how it can be used to determine the absolute entropies of liquid. 4
- (b) Attempt any **one** of the following :—
- Calculate the entropy change for conversion of one mole of steam at 373K to one mole of ice at 273K. 4
 $C_p(\text{water}) = 75.6 \text{ JK}^{-1} \text{ mol}^{-1}$
 Molar enthalpy of vapourisation = 40.645 KJ mol⁻¹
 Molar enthalpy of fusion = 6.003 KJ mol⁻¹

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- (ii) The heat of formation of one mole of HI (g) from hydrogen and iodine vapours at 25°C is 33.6 kJ. Find the heat of formation at 10°C. The heat capacities ($\text{JK}^{-1} \text{mol}^{-1}$) are as follows :—

$$\text{H}_2 (\text{g}) : C_p = 27.3 + 0.0071 T$$

$$\text{I}_2 (\text{v}) : C_p = 27.3 + 0.0160 T$$

$$\text{HI} (\text{g}) : C_p = 27.3 + 0.0067 T$$

2. (a) Attempt any two of the following :—
- (i) What is fugacity ? Explain graphical method for its determination. 4
 - (ii) Obtain an expression for free energy change of mixing of ideal gases in terms of mole-fraction. 4
 - (iii) Derive Gibbs-Duhem-Margules equation. 4
 - (iv) How are entropy changes related to life processes ? Whether these processes violate second law of thermodynamics ? Justify your answer. 4
- (b) Attempt any one of the following :—
- (i) Calculate entropy change of mixing at NTP for 32 g of oxygen and 2g of hydrogen gas assuming no chemical reaction occurs and mixture behaves ideally. 4
 - (ii) The partial molal volume of methanol in a methanol-water solution containing 0.39 mole-fraction of methanol is $39.2 \text{ cm}^3 \text{mol}^{-1}$. The density of solution is 0.91 gcm^{-3} . Calculate the partial molal volume of water in the solution. 4
3. (a) Attempt any two of the following :—
- (i) What do you understand by peritectic reaction ? Draw a phase diagram of a system exhibiting incongruent compound formation. 4
 - (ii) Derive thermodynamically the Gibbs adsorption isotherm. 4
 - (iii) Explain the phase diagram of ternary system of double salt decomposed by water. 4
 - (iv) Explain the phase diagram of two component system of solid-gas involving hydrates of copper sulphate. 4
- (b) Attempt any one of the following :—
- (i) Derive mathematical expression of Laplace equation relating pressure difference across curved surface. 4
 - (ii) Explain the phase diagram of ternary system of hydrate not dehydrated by second salt. 4
4. (a) Attempt any two of the following :—
- (i) Discuss the modified form of Debye-Huckel limiting law applicable to electrolytic solution at appreciable concentration. 4
 - (ii) Discuss the validity of Debye-Huckel-Onsagar equation for aqueous solutions. 4

- (iii) Give an account of enzymes as electrode. 4
 (iv) What are the merits of fuel cells ? Write the electrode actions taking place in alkaline fuel cell, also name the primary fuel, electrolyte and charge carrier. Give one major application for the same. 4

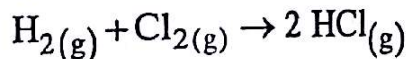
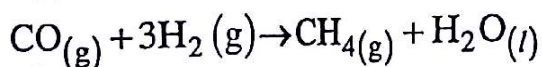
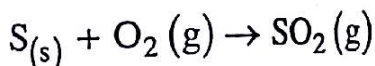
(b) Attempt any **one** of the following :—

- (i) Calculate the activity coefficient of copper and nitrate ions and mean activity coefficient for 0.02 m solution of $\text{Cu}(\text{NO}_3)_2$ at 298K ($A = 0.509$ at 298K). 4
 (ii) The concentration ratio of a divalent cation is 0.001. Find the resting membrane potential $\left(\frac{2 \cdot 303RT}{F} \text{ at } 298\text{K} = 61\right)$. What does the concentration ratio indicate ? 4

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

- (a) Arrange the following reactions according to increasing values of standard enthalpy changes.



Answer by inspection and state reason.

- (b) Derive the following Maxwell's equation.

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

- (c) What are exoergonic and endoergonic reactions ?
 (d) Explain hydrolysis of A.T.P.
 (e) Explain why in general various tie lines within the binodal curve are parallel neither to the side of the triangle nor to each other. Under what conditions will the various tie lines be parallel to each other ?
 (f) Sketch qualitatively the labelled phase diagram of ternary system of hydrated double salt decomposed by water.
 (g) What are fuel cells ? Give the advantages of Phosphoric acid fuel cell.
 (h) Explain relaxation effect of conductance of strong electrolytes.
