

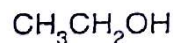
- N.B. (1) All the questions are compulsory.  
 (2) Figures to the right indicate full marks.  
 (3) Use of non-programmable scientific calculator is allowed.

## Useful constants :

$c = 2.998 \times 10^8 \text{ ms}^{-1}$	$k = 1.3811 \times 10^{-23} \text{ JK}^{-1}$
$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$	$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$
$h = 6.625 \times 10^{-34} \text{ Js}$	$1 \text{ atmosphere} = 1.01325 \times 10^5 \text{ Nm}^{-2}$
$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$	$M_e = 9.110 \times 10^{-31} \text{ kg}$
$e = 1.602 \times 10^{-19} \text{ C}$	$O = 16$
$N = 14$	

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

- Explain the term exact differential. If  $T = f(P, V)$ . Show that  $dT$  is an exact differential. 4
- What is Joule-Thomson effect ? Prove that the enthalpy of the system remains constant in an adiabatic expansion. 4
- Give the expression for Gibbs free energy change and explain how it can be used to predict the possibility of a chemical reaction. 4
- State the characteristics of entropy. Giving reason, say which molecule of the pair given below has greater molar entropy under the same conditions. 4



(b) Attempt any one of the following :—

- The enthalpy of reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  at  $27^\circ\text{C}$  is  $-91940 \text{ J}$ . What will be its value at  $50^\circ\text{C}$  ? The molar heat capacities at constant pressure and  $27^\circ\text{C}$  for nitrogen, hydrogen and ammonia are  $28.45$ ,  $28.32$  and  $37.07 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. 4
- Calculate the entropy change when one mole of ice at  $273 \text{ K}$  is converted to water at  $373 \text{ K}$  at one atmosphere. The molar heat of fusion of ice is  $6002 \text{ J mol}^{-1}$ . Molar heat capacity in the given range of temperatures is  $75.22 \text{ JK}^{-1} \text{ mol}^{-1}$ . 4

2. (a) Attempt any two of the following :—

- Define enthalpy. Show that the enthalpy of mixing of ideal gas at constant temperature and pressure is zero. 4
- Explain the significance of fugacity to study thermodynamics of real gases. How is it evaluated by graphical method ? 4
- What is partial molal volume ? How is it determined by intercept method ? 4
- Explain with reference to free energy change, the role of ATP in biological system. 4

(b) Attempt any one of the following :—

- (i) At 25°C, the density of 50 percent by mass ethanol-water system is  $0.914 \text{ g cm}^{-3}$ . The partial molal volume of water in solution is  $17.4 \text{ cm}^3 \text{ mol}^{-1}$ . Calculate the partial molal volume of ethanol. 4
- (ii) One mole of nitrogen gas is mixed with three moles of oxygen gas at 298 K to form a mixture at the final pressure of one atmosphere, the initial pressure of each being also one atmosphere. Calculate the molar entropy of mixing. 4

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

- (i) Explain the phase diagram for two component system of solid-gas involving hydrates of copper sulphate. 4
- (ii) Explain phase diagram for two component system involving formation of a compound with congruent melting point. 4
- (iii) Derive the kelvin equation of vapour pressure of the liquid droplets. 4
- (iv) Draw and explain phase diagram for three component system involving formation of two pairs of partially miscible liquids. 4

(b) Attempt any one of the following :—

- (i) Explain the phase diagram of ternary system of hydrated salt not de hydrated by second salt. 4
- (ii) Explain the phase diagram of ternary system of double salt decomposed by water. 4

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

- (i) Prove the validity of Debye-Hyckel limiting equation. 4
- (ii) State and explain Debye-Huckel-Onsager equation. 4
- (iii) Why fuel cells are an emerging technology ? How can they become competitive with other power generating technologies ? 4
- (iv) Explain the process of adsorption of proteins onto metal surface from solution. 4

(b) Attempt any one of the following :—

- (i) Calculate the activity coefficient of  $\text{Zn}^{2+}$  and  $\text{Cl}^-$  in an aqueous solution of  $2 \times 10^{-3} \text{ m ZnCl}_2$ . ( $A = 0.509$  at 298 K.) 4
- (ii) Calculate the value of resting membrane potential for the following at 298 K. 4

	$[\text{ion}]_{\text{in}}$	$[\text{ion}]_{\text{out}}$
$\text{Na}^+$	15 mM	145 mM
$\text{Cl}^-$	4 mM	115 mM

$$\text{At 298 K } \frac{2 \cdot 303 RT}{F} = 60 \cdot 0.$$



5. Attempt any four of the following :—

- (a) State the Third Law of Thermodynamics. Why is it not applicable to supercooled liquids ?
  - (b) Show the different stages involved in the conversion of tin from 293 K to 573 K. Melting point of tin is 505 K. Also give  $\Delta S_{\text{total}}$  with the help of necessary expression.
  - (c) Explain one physical significance of chemical potential.
  - (d) 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. Find  $\Delta G_{\text{mixing}}$ .
  - (e) Write the mathematical expression of B. E. T. equation. How is it used to determine the surface area of solid adsorbent ?
  - (f) Sketch qualitatively the labelled phase diagram for ternary system of hydrated double salt decomposed by water.
  - (g) Draw the alkaline fuel cell and write the reactions occurring at anode and cathode.
  - (h) Explain the behaviour of conductance of strong electrolyte under high alternating current frequencies.
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