QP Code : 13136

(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 :

$c = 2{\cdot}998 \times 10^{8}\ ms^{-1}$
$R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$
$h = 6{\cdot}625 \times 10^{-34}\ Js$
$N_A = 6{\cdot}023 \times 10^{23}\ mol^{-1}$
$e = 1{\cdot}602 \times 10^{-19}\ C$
$k = 1{\cdot}3811 \times 10^{-23}\ JK^{-1}$
$1J = 6{\cdot}24 \times 10^{18}\ eV$
$1eV = 8{\cdot}06 \times 10^{3}\ cm^{-1}$
$1\ atmosphere = 1{\cdot}01325 \times 10^{5}\ Nm^{-2}$
$M_e = 9{\cdot}110 \times 10^{-31}\ kg$
$O = 16$
$H = 1$

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

(i) Derive Kirchhoff equation. Explain how it can be used to determine heat of reaction at a given temperature provided the value at the other temperature is known. 4

(ii) Derive Maxwell relation $\left(\frac{dT}{dV}\right)_s = -\left(\frac{dP}{dS}\right)_v$; starting from definition of entropy. 4

(iii) Define and discuss Joule-Thomson coefficient. What happens when various gases are subjected to Joule-Thomson experiment ? 4

(iv) "Residual entropy is exception to third law of thermodynamics." Explain with the help of suitable example. 4

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

(i) Calculate the entropy change in transforming 24 g of ice into water at 0°C, molar heat of fusion = 6·009 kJ mol^{-1} , and also for transition of one mole of liquid water to steam at 373 K, if enthalpy change for the transition is 40·8 kJ mol^{-1}. 4

(ii) At constant pressure of one atmosphere, the enthalpy of fusion of water at 273 K is 6·0 kJ mol^{-1}. Calculate the value for the same at 263 K. 4
Cp for H_2O (l) = 74·46 J mol^{-1} K^{-1}
Cp for H_2O (s) = 37·2 J mol^{-1} K^{-1}.

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

(i) Derive Duhem - Margules equation. 4

(ii) Define fugacity. How it is determined from the equation of state ? 4

(iii) Give a brief account of entropy and free energy changes of any biochemical reaction. 4

(iv) Obtain an expression for free energy change of mixing of ideal gases in terms of mole fraction. 4

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

(i) Calculate ΔG_{mix}, ΔH_{mix} and ΔS_{mix} at 298 K and one atmosphere pressure when 10 moles of He are mixed with 10 moles of Ne. 4

(ii) The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0·3713 are 188·2 $cm^3\ mol^{-3}$ and 176·14 $cm^3\ mol^{-1}$ respectively. The molar masses of A and B are 241·4 g mol^{-1} and 198·2 g mol^{-1}. What is the volume of a solution of mass 1·000 kg ? 4

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

(i) Explain the phase diagram of two component system involving formation of a compound with congruent melting point. 4

(ii) Explain the phase diagram for three component system involving formation of two pairs of partially miscible liquids. 4

(iii) Derive mathematical expression of the Laplace which relates pressure across a surface to the curvature of the surface. 4

(iv) Sketch qualitatively and explain the phase diagram for ternary system of hydrated salt dehydrated by second salt. 4

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

(i) Describe two component system of solid-gas with the formation of amino compound. 4

(ii) Write the basic postulates of B. E. T. equation. Give its expression and identify the terms involved in it. 4

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

(i) What are the factors which affect the mobility of ions in conductance of strong electrolyte ? Explain them. 4

(ii) Explain how Debye-Huckel limiting equation is modified for concentrated solutions. 4

(iii) Explain the structure and functions of cell membrane. 4

(iv) With the help of suitable diagram, explain the working of alkaline fuel cell. 4

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

(i) Calculate the mean activity coefficient for 1×10^{-3} m aqueous solution of $K_3[Fe(CN)_6]$. For aqueous solution at 298 K, A = 0·509. 4

(ii) Calculate the resting potential for each of the following at 298 K. 4

	$[ion]_{in}$	$[ion]_{out}$
K^+	10 mM	100 mM
Cl^-	4 mM	40 mM

At 298 K, $\frac{2 \cdot 303\ RT}{F} = 61\ 0$.

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

(a) "Standard molar entropies depend on the mass of the substance". Explain with suitable example.

(b) Explain why $S_{steam} > S_{water} > S_{ice}$.

(c) Explain hydrolysis of ATP.

(d) Give the chracteristics of real solutions.

(e) Explain why, in general, the plait point lies either to the left or to the right of the maximum of the binodal curve. Under what condition will the plait point coincide with the maximum point.

(f) Explain the phase diagram of ternary system of double salt not decomposed by water.

(g) Explain the behaviour of strong electrolyte under high potential gradient.

(h) Explain why fuel cells are an emerging technology.
