(2½ Hours) [Total Marks : 60

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

Useful constants :—

$c = 2{\cdot}998 \times 10^{8}\ ms^{-1}$

$R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$

$h = 6{\cdot}625 \times 10^{-34}\ Js$

$m_e = 9{\cdot}110 \times 10^{-31}\ kg$

$N_A = 6{\cdot}023 \times 10^{23}\ mol^{-1}$

$e = 1{\cdot}602 \times 10^{-19}\ C$

$k = 1{\cdot}3811 \times 10^{-23}\ JK^{-1}$

$1J = 6{\cdot}24 \times 10^{18}\ eV$

$1eV = 8{\cdot}06 \times 10^{3}\ cm^{-1}$

1 atomosphere $= 1{\cdot}01325 \times 10^{5}\ Nm^{-2}$

H = 1

C = 16

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

(i) Derive the expressions to show how entropy varies with temperature at constant volume and at constant pressure. 4

(ii) Starting with vander Waals equation, Show that— 4

$$\mu_{JT} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$ where terms have usual meaning.

(iii) State the third law of thermodynamics and show how it can be used to calculate the absolute entropies of solid. 4

(iv) "Entropies of substances like CO and N_2O are not zero at 0K." Explain. 4

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(b) Attempt any **one** of the following :— 4

(i) Write the chemical equation for formation of one mole of ammonia. Using the following data calculate the standard entropy change for formation of ammonia.

Standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 190·6, 130·7 and 192·5$JK^{-1}mol^{-1}$ respectively.

(ii) Calculate the enthalpy of fusion ΔH_f of ice at −10°C from the following data. 4

ΔH_f at 0° C is 6·02kJ mol^{-1},

$C_{p(ice)} = 37 \cdot 66\ JK^{-1}mol^{-1}$,

$C_{p(water)} = 75 \cdot 31 JK^{-1}mol^{-1}$

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

(i) What is fugacity ? How it can be evaluated from vander Waal equation of state ? 4

(ii) Obtain an expression for entropy change of mixing of ideal gases in terms of mole-fraction. 4

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

(iv) What is ATP ? Explain its structure. Give any one biochemical reaction involving ATP with reference to changes in free energy. 4

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

(i) Calculate entropy change when 5·6dm^3 of oxygen were mixed with 16·8dm^3 of hydrogen at NTP assuming no chemical reaction occurs and the mixture behaves ideally. 4

(ii) The partial molal volume of water in a methanol-water solution containing 0·61 mole-fraction of water is 17·2cm^3mol^{-1}. The density of solution is 0·92gcm^{-3}. Calculate the partial molal volume of methanol in the solution. 4

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

(i) Explain the phase diagram of two component system of solid-gas equilibria of formation of amino compound. 4

(ii) What is incongruent melting point ? Explain phase diagram of a suitable system consisting of incongruent melting point. 4

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

(iv) Explain labelled phase diagram of three component system consisting of formation of two pairs of partially miscible liquids. 4

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

(i) Derive thermodyamically the Kelvin equation of the Vapour pressure of droplets. 4

(ii) Explain the phase diagram of ternary system of hydrate dehydrated by second salt. 4

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

(i) Explain the relaxation effect. Write the expression for Debye–Huckel–Onsagar equation and explain the meaning of the terms. 4

(ii) Give the theory behind membrane potential and the method of measurement of the same. 4

(iii) Discuss the working of high temperature fuel cells. 4

(iv) Explain the Debye–Huckel theory of activity coefficient. 4

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

(i) Calculate the activity coefficient of sodium and sulphate ions and the mean activity coefficient of a 0·05m solution of sodium sulphate at 298K (A = 0·509 at 298K) 4

(ii) Calculate the sign and value of resting membrane potential for :— 4

	$[\text{ion}]_{in}$ mM	$[\text{ion}]_{out}$ mM
Na^+	15	145
K^+	140	4

$\left(\frac{2 \cdot 303RT}{F} \text{ at } 298K = 61 \cdot 0\right)$

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

(a) "Standard molar entropies depend upon structure of the substance." Give reason.

(b) Derive the following Maxwell's equation :

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

(c) Explain chemical potential for non-ideal solutions.

(d) Show that enthalpy of ideal mixing of gases is zero.

(e) Explain the phase diagram of ternary system of double salt decomposed by water

(f) Sketch qualitatively the labelled phase diagram of ternary system of hydrated double salt not decomposed by water.

(g) Give advantages of fuel cell over the conventional cells.

(h) Explain 'Wien effect.'
