CHEMICAL ENGINEERING THERMODYNAMICS

SET -1

PART-A

a.	(iii)	work
b.	(ii)	1
c.	(iii)	$x_1 + x_2 = 1$
d.	(i)	Partial pressure
e.	(iii)	Fugacity coefficient
f.	(i)	$H^E = H - H^{id}$
g.	(i)	one
h.	(iv)	1.0
i.	(iv)	Negative
j.	(ii)	$\Delta G^0 = -RTlnK$

PART -B

a.	**Theorem of law of corresponding state**
	The law says that all gases under the same reduced condition of temperature and pressure have the same compressibility factor. The compressibility factor Z is a function of reduced temperature and reduced pressure only. $Z = f(P_r\ ,T_r)$
b.	**Define point function. Give examples.**
	Properties of a substance describes its present state and do not give a record of its previous history. Point function, do not depend upon path followed to reach a given state. Examples temperature, pressure, volume. It is represented by a point on the graph.
c.	**Define Non-ideal solutions**.
	According to Raoults law, the total pressure of an ideal solution varies linearly with its, molar composition. Another important criterion of an ideal liquid mixture is that when a component of the mixture is brought into contact with other components, mixing does not cause any change in the average intermolecular force. Consequently there is no change in internal energy or volume due to mixing. Therefore , there would be no absorption or evaluation of heat . But incase of a non ideal solution, there is change in internal energy on mixing of components and there will be either evaluation or absorption of heat
d.	**What is the modified equation of Raoults Law?**
	P= $x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}$ Where x_1 and x_2 are the mole fraction of component 1 and 2; $\gamma_1$and γ_2 are the activity coefficient of component 1 and 2; P_1^{sat}, P_2^{sat} are the vapor pressure of component 1 and 2.
e.	**Define partial molar property**
	The increase in extensive property (M) of a system on account of addition of one mole of its respective constituents, at constant temperature, pressure and moles of other constituents remaining unaltered to such a large amount of system that this addition has a negligible effect on the composition of the system $\overline{M} = \left(\frac{\partial M}{\partial n_i}\right)_{T,P,n_j} \quad j \neq i$
f.	**Lewis Randall Rule**
	Defined as that the fugacity of each species in as ideal solution is proportional to its mole fraction; the proportionality constant is the fugacity of pure species “i" in

	the same physical state as the solution and the same temperature and pressure.
g.	**Application of G-D equation**
	1. Thermodynamic consistency of experimental data can be tested using G-D equation. 2. If experimental data are available for the activity coefficient of one components in binary solution over certain concentration range, the activity coefficient of the other component over the same composition range can be estimated using G-D equations.
h.	**What are the criteria for chemical Equilibrium?**
	The criterion for a chemical reaction to occur at equilibrium is that the free energy change is zero. Similar to criteria for phase equilibria, the temperature and pressure of all the components be identical when two or more chemical species are in equilibrium. Thus the criteria for chemical equilibria may be stated as $\Delta G = 0$ at constant temperature and pressure.
i.	**Differentiate homogenous and heterogeneous reaction?**
	Homogenous, the reaction in which all the reactants and the products are found to be in a single phase, and which takes place in one phase alone. Heterogeneous the reaction in which two phase involved for the reaction to proceed. Example, ammonia synthesis reaction in which solid catalyst present fall under the heterogeneous reaction.
j.	**Write the effect of temperature on the equilibrium constant.**
	For endothermic reaction, increase in temperature, the equilibrium constant will increase. For an exothermic reaction, increase in temperature, the equilibrium constant will decrease.

PART-C

3a	**Calculate the volume occupied by one mole of oxygen at 300 K and 100 bar using** **(a) The ideal gas law** **(b) The van der Waals equation.** **Take *a* = 0.1378 N m^4/mol^2 and *b* = 3.18 × 10^{-5} m^3/mol.**
	Solution **Ideal gas law** **(4Marks)** $V = \frac{RT}{P}$ $V = \frac{8.314\frac{J}{mol\,K} \times 300K}{100 \times 10^5 \frac{N}{m^2}} = 2.4942 \times 10^{-4} m^3$ **The van der Waals equation** **(6 Marks)** $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ *a* = 0.1378 N m^4/mol^2 and *b* = 3.18 × 10^{-5} m^3/mol $\left(100 \times 10^5 + \frac{0.1378}{V^2}\right)(V - 3.18 \times 10^{-5}) = 8.314 \times 300$ By trial and error method the volume is $2.3 \times 10^{-4} m^3$
3b	**Derive the Q,W,ΔU, and ΔU relation for the following Process** a) **Constant volume process**

b) **Constant pressure process**

c) **Constant temperature process**

Solution

$$\Delta U = Q - W$$

a. Constant volume process

$$W = \int PdV$$

$$W = 0$$

$$\Delta U = Q = C_V dT$$

$$\Delta H = C_P dT$$

b. Constant pressure process

$$\Delta H = C_P dT$$

$$dU = dQ - dW$$

$$dW = PdV$$

$$dU = C_V dT$$

c. Isotherm Process

$$\Delta U = C_V dT$$

$$\Delta U = 0 \ (Consatant\ Temperature)$$

$$\Delta H = C_P dT$$

$$\Delta H = 0\ (Contant\ Temperature)$$

$$Q = W = \int PdV$$

$$Q = W = RTln\frac{V_2}{V_1}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Constant temperature

$$P_1V_1 = P_2V_2$$

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$Q = W = RTln\frac{P_1}{P_2}$$

4a **Assuming Raoults law to be valid for the system benzene (1)-ethyl benzene (2) and the vapor pressures given by Antoine equations**

$$\boldsymbol{lnP_1^{sat} = 13.8858 - \frac{2788.51}{T - 52.41}}$$

$$\boldsymbol{lnP_2^{sat} = 14.0045 - \frac{3279.47}{T - 60.00}}$$

Where P is in kPa and Tis in K.

Calculate P-x-y data at 373 k. nad Tabulate for various mole fraction.

Solution

$$lnP_1^{sat} = 13.8858 - \frac{2788.51}{373 - 52.41} = 5.1877$$

$$P_1^{sat} = 179.064kPa$$

$$lnP_2^{sat} = 14.0045 - \frac{3279.47}{373 - 60.00} = 3.5270$$

$$P_2^{sat} = 34.0204kPa$$

Ideal solution the raouls law

$$P = P_1^{sat}x_1 + P_2^{sat}x_2$$

$$y_1 = \frac{P_1^{sat}x_1}{P}$$

Take x1=0.2

$$P = P_1^{sat}x_1 + P_2^{sat}x_2$$

$$P = 179.064 \times 0.2 + 34.0204 \times 0.8 = 63.03kPa$$

$$y_1 = \frac{P_1^{sat}x_1}{P}$$

$$y_1 = \frac{179.064 \times 0.2}{63.03} = 0.568$$

Similar for

x1	0.2	0.4	0.6	0.8	1.0
y1	0.568	0.778	0.888	0.955	1.0
Pressure kPa	62.03	92.04	121.04	150.05	179.06

4b

For a binary system draw the graphical diagram and explain the following

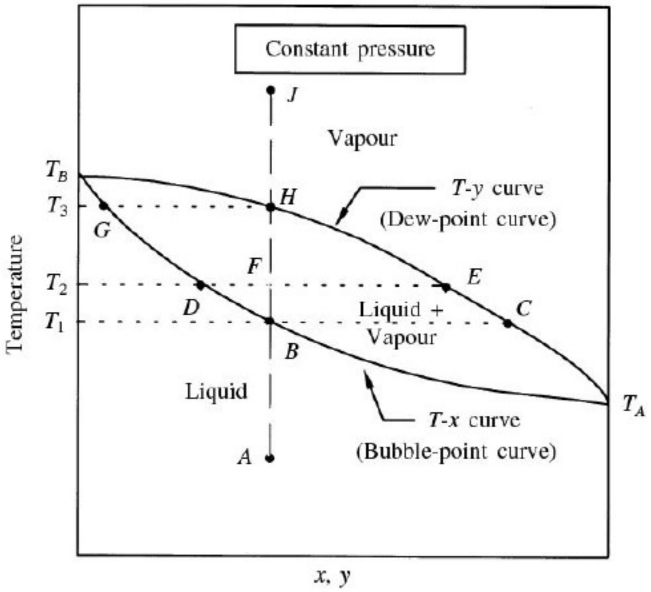
(a) T-xy diagram

(b)P-xy diagram

(c) xy diagram

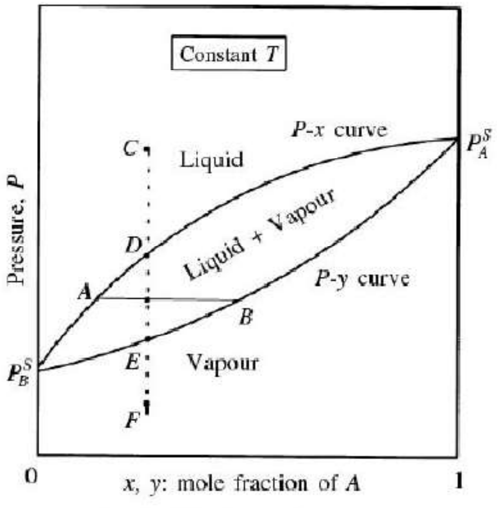
T-x-y Boiling point diagram

The boiling point diagrams are plots of temperature as ordinate against composition of liquid and vapour as abscissa . The composition of liquid is usually indicated by the mole fraction of more volatile component in the liquid, *x*, and the composition of the vapour is indicated by the mole fraction of the more volatile component in the vapour, *y*. Therefore, the boiling point diagrams are also called *T-x-y* diagrams. The upper curve in Fig. gives the temperature versus vapour composition (*y*), and is known as the **'dew-point curve'**. The lower curve in the figure is temperature versus liquid composition (*x*), also called the '**bubble-point curve'**. Below the bubble-point curve the mixture is subcooled liquid and above the dew-point curve the mixture is superheated vapour. Between the bubble-point and dew-point curves the mixture cannot exist as a single phase, it spontaneously separates into saturated liquid and vapour phases that are in equilibrium.



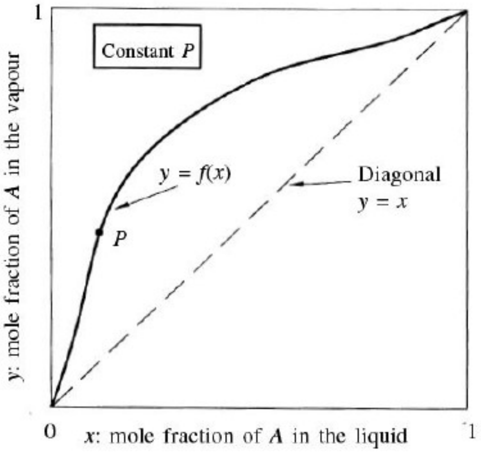
P-x-y Diagram

Vapour–liquid equilibrium data at constant temperature are represented by means of *P-x-y* diagrams; Fig. shows a typical *P-x-y* diagram. The pressure at $x = 0$ is the vapour pressure of pure *B*(P_B^S) and the pressure at $x =1$ is the vapour pressure of pure *A*(P_A^S). Since component *A* is assumed to be more volatile, and therefore, the *P-x-y* diagram slopes upwards as shown in the figure. The *P-y* curve lies below the *P-x* curve so that for any given pressure, $y > x$. A solution lying above the *P-x* curve is in the liquid region and that lying below the *P-y* curve is in the vapour region. In between *P-x* and *P-y* curves the solution is a mixture of saturated liquid and vapour. A horizontal line such as *AB* connects the liquid and vapour phases in equilibrium and is therefore, a tie line.



x-y Equilibrium diagram.

The vapour–liquid equilibrium data at constant pressure can be represented on a x versus y plot or an equilibrium distribution diagram. If the vapour composition is taken as the ordinate and the liquid composition is taken as the abscissa, a tie line such as line BC on the boiling point diagram gives rise to a point such as point P on the distribution diagram (Fig.) Since the vapour is richer in the more volatile component, the curve lies above the diagonal on which $x = y$ A liquid–vapour equilibrium curve very close to the diagonal means that the composition of the vapour is not much different from the composition of the liquid with which it is in equilibrium; when the curve coincides with the diagonal, x and y are equal



5a

At 300 K and 1 bar the volumetric data for a liquid mixture of benzene and cyclohexane are represented by $\boldsymbol{V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.264 \times 10^{-6} x_1^2}$, where x1 is the mole fraction of benezene and V has the units of m3/mol. Find expression for the partial molar volumes of benzene and cyclohxane.

Solution

$$V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.264 \times 10^{-6} x_1^2$$

$$\overline{V_1} = V - x_2 \frac{\partial V}{\partial x_2}$$

$$\overline{V_1} = V + (1 - x_1) \frac{\partial V}{\partial x_1}$$

$$V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.64 \times 10^{-6} x_1^2$$

Differentiate the above

$$\frac{\partial V}{\partial x_1} = 0 - 6.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1$$

$$\overline{V_1} = V + (1 - x_1) \frac{\partial V}{\partial x_1}$$

$$\overline{V_1} = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.64 \times 10^{-6} x_1^2 + (1 - x_1)(-6.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1)$$

$$\overline{V_1} = 92.6 \times 10^{-6} - 5.28 \times 10^{-6} x_1 + 2.64 \times 10^{-6} x_1^2$$

$$\overline{V_2} = V - x_1 \frac{\partial V}{\partial x_1}$$

$\overline{V_2} = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.64 \times 10^{-6} x_1^2 - x_1(-6.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1)$-

$$\overline{V_2} = 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2$$

Partial molar volume of benzene

$$\overline{V_1} = 92.6 \times 10^{-6} - 5.28 \times 10^{-6} x_1 + 2.64 \times 10^{-6} x_1^2$$

Partial molar volume of benzene

$$\overline{V_2} = 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2$$

5b	**Do the following equation satisfy Gibbs- Duhem equations?** $\boldsymbol{ln\gamma_1 = Ax_2^2 + Bx_2^2(3x_1 - x_2)}$ $\boldsymbol{ln\gamma_2 = Ax_1^2 + Bx_1^2(x_1 - 3x_2)}$
	Solution **(10 Marks)** $ln\gamma_1 = Ax_2^2 + Bx_2^2(3x_1 - x_2)$ $Ax_2^2 + Bx_2^2(3x_1 - x_2) = A(1 - x_1^2) + B(3x_2^2x_1 - x_2^2x_2)$ $\frac{\partial\gamma_1}{\partial x_1} = 2.A.(1 - x_1)(-1) + B(3.x_2^2.(1) + 3.x_1.2(1-x_1)(-1) - 3.(1 - x_1^2)(-1))$ $= -2.A.x_2 + B(3.x_2^2 - 6.x_1.x_2 + 3.x_2^2$ $= -2.A.x_2 - B6.x_1.x_2 + B6\,x_2^2$ $x_1\frac{\partial\gamma_1}{\partial x_1} = x_1x_2[-2A - 6B(x_1 - x_2)]$ A $ln\gamma_2 = Ax_1^2 + Bx_1^2(x_1 - 3x_2)$ $A(1 - x_2^2) + B(x_1^3 - 3x_2x_1^2)$ $\frac{\partial\gamma_2}{\partial x_2} = 2.A.(1 - x_2)(-1) + B(3.(1 - x_2^2).(-1) - 3.x_2.2(1-x_2)(-1) - 3.x_1^2)(1)$ $= -2.A.x_1 - B6.(x_1^2).+B.6.x_1x_2$ $x_2\frac{\partial\gamma_2}{\partial x_2} = x_1x_2[-2A - 6B(x_1 - x_2)]$ B Comparing the equation (A) and (B) $x_1\frac{dln\gamma_1}{dx_1} = x_2\frac{dln\gamma_2}{dx_2}$ Thus the equation satisfies G-D equations.
6a	**A gas mixture containing 12mol% SO_2, 8mol%O_2 and 80mol% N_2 is fed to a catalyst chamber containing 1 atm 610°C for conversion in to SO3. What is equilibrium conversion of SO_2 to SO_3. The reaction is** $\boldsymbol{SO_2 + \frac{1}{2}O_2 \rightarrow SO_3}$

Solution

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

Let ε be the equilibrium conversion

Component	feed	Equilibrium
SO_2	12	12-ε
O_2	8	8-0.5 ε
N_2	80	80
SO_3	-	ε
Total Moles		100-0.5 ε

$$K_P = K_y P^{1-1-0.5}$$

$$8.5 = K_y(1)^{1-1-0.5}$$

$$8.5 = K_y$$

$$8.5 = \frac{y_{so_3}}{y_{so_2} y_{O_2}^{0.5}}$$

$$8.5 = \frac{\frac{\varepsilon}{100-0.5\varepsilon}}{\frac{12-\varepsilon}{100-0.5\varepsilon} \times \left(\frac{8-0.5\varepsilon}{100-0.5\varepsilon}\right)^{0.5}}$$

$$8.5 = \frac{\varepsilon(100-0.5\varepsilon)^{0.5}}{(2-\varepsilon)(8-0.5\varepsilon)^{0.5}}$$

By trial and error method $\varepsilon = 7.67$

Percentage conversion SO_2 to SO_3

$$\frac{7.67 \times 100}{12} = 64\%$$

6b

Acetic acid is esterified in the liquid phase with ethanol at 100°C and atmospheric pressure to produce ethyl acetate and water according to the reaction.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

If initially there is one mole each of acetic acid and ethanol, estimate the mole fraction of ethyl acetate in the reacting mixture at equilibrium.

Component	$\Delta \boldsymbol{H}_{\mathbf{298}}^{\mathbf{0}}$	$\Delta \boldsymbol{G}_{\mathbf{298}}^{\mathbf{0}}$
Acetic acid	**-484,500J**	**-389,900J**
Ethanol	**-277,690J**	**-174,780J**
Ethyl acetate	**-463250J**	**-318,280J**
Water	**-285,830J**	**-237,130J**

Solution

$\sum \Delta H\ Prouduct\ - \sum \Delta H\ Reactant$ (5 Marks)

ΔH_{298}^{0} for the reaction = -463250-285,830-(-484,500-277,690)=13110J

$\sum \Delta G\ Product - \sum \Delta G\ Reactant$

ΔG_{298}^{0} for the reaction = -318,280-237,130-(-389,900-174,780)=9270J

$$\Delta G^0 = -RTlnK$$

$$lnK = -\frac{\Delta G^0}{RT} = \frac{-9270\ J}{\frac{8.314J}{mol\ K} \times 298} = -3.740 = K_{298} = 0.0238$$

$$ln\frac{K_{373K}}{K_{298K}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$ln\frac{K_{700K}}{0.0238} = \frac{13110J}{8.314J/molK}\left(\frac{1}{298} - \frac{1}{373}\right)$$

$$K_{373K} = 0.0689$$

Initially one mole is present (5 Marks)

Total number of moles=$(1-\varepsilon) + (1-\varepsilon) + \varepsilon + \varepsilon = 2$

	Number of moles of acetic acid $=(1-\varepsilon)$; mole fraction$=\frac{(1-\varepsilon)}{2}$ Number of moles of ethanol$=(1-\varepsilon)$; mole fraction$=\frac{(1-\varepsilon)}{2}$ Number of moles of ethyl acetate $=\varepsilon$; mole fraction $=\frac{\varepsilon}{2}$ Number of moles of water$=\varepsilon$; mole fraction $=\frac{\varepsilon}{2}$ Equilibrium constant $K=\frac{x_{ethylacetate}\times x_{water}}{x_{acetic\ acid}\times x_{ethanol}}$ $0.0689=\frac{\frac{\varepsilon}{2}\times\frac{\varepsilon}{2}}{\frac{(1-\varepsilon)}{2}\times\frac{(1-\varepsilon)}{2}}$ $\boldsymbol{\varepsilon=0.208}$ Mole fraction of ethyl acetate =(0.208/2)=**0.104 Answer**