

Q2. Expression for chemical potential of an ideal solution:

The chemical potential of a component  $i$  in a solution can be defined as

$$\mu_i = \bar{G}_i = \left( \frac{dG^t}{dn_i} \right)_{T, P, n_j} \quad \text{--- (1)}$$

The total free energy  $G^t$  of a solution is a function of pressure, temperature and number of moles of various components.

$$G^t = f(P, T, n_1, n_2, \dots, n_i, \dots) \quad \text{--- (2)}$$

The total differential  $dG^t$  is

$$dG^t = \left( \frac{dG^t}{dP} \right)_{T, N} dP + \left( \frac{dG^t}{dT} \right)_{P, N} dT + \sum \left( \frac{dG^t}{dn_i} \right)_{P, T, n_j \neq i} dn_i \quad \text{--- (3)}$$

Using equation (1),

$$\text{(3)} \Rightarrow dG^t = \left( \frac{dG^t}{dP} \right)_{T, N} dP + \left( \frac{dG^t}{dT} \right)_{P, N} dT + \sum \mu_i dn_i \quad \text{--- (4)}$$

For a closed system, when there is no change in the amount of various constituents,

$$dG = V dP - S dT \quad \text{--- (5)}$$

Considering the total properties of the system

$$dG^t = V^t dP - S^t dT$$

from which, it follows that

$$\left( \frac{dG^t}{dT} \right)_{P, N} = -S^t ; \quad \left( \frac{dG^t}{dP} \right)_{T, N} = V^t \quad \text{--- (6)}$$

Equation (4) can be written as

$$dG^t = V^t dP - S^t dT + \sum \mu_i dn_i \quad \text{--- (7)}$$

This is the fundamental relationship for changes in the free energy of a solution. At constant temperature and pressure, the change in the free energy is due entirely to the changes in the number of moles and is given by

$$dG_{T,P}^t = \sum \mu_i dn_i \quad \text{--- (3)}$$

### 23. Effect of Temperature and Pressure on Chemical Potential:

Effect of Temperature:

$$\mu_i = \bar{G}_i = \left( \frac{dG^t}{dn_i} \right)_{T,P,n_j} \quad \text{--- (1)}$$

$$\left( \frac{d\mu_i}{dT} \right)_{P,N} = \frac{d^2 G^t}{dT dn_i} \quad \text{--- (2)}$$

w.k.t,  $\left( \frac{dG^t}{dT} \right)_{P,N} = -S^t \quad \text{--- (3)}$

Differentiating equation (3) w.r.t  $n_i$   
 $-\left( \frac{dS^t}{dn_i} \right)_{P,T,n_j} = \frac{d^2 G^t}{dn_i dT} \quad \text{--- (4)}$

Evaluating eqns (2) and (4)  
 $\left( \frac{d\mu_i}{dT} \right)_{P,N} = -\left( \frac{dS^t}{dn_i} \right)_{P,T,n_j} = -\bar{S}_i \quad \text{--- (5)}$

where  $\bar{S}_i$  is the partial molar entropy of the component  $i$  in the solution. This result, though gives the variation of chemical potential with temperature, can be put in a more useful form as follows:

Since  $G = H - TS$ ;  $\bar{G}_i = \bar{H}_i - T\bar{S}_i$ ;  $\mu_i = \bar{H}_i - T\bar{S}_i$

$$-\bar{S}_i = \frac{\mu_i - \bar{H}_i}{T} \quad \text{--- (6)}$$

WKT

$$\left( \frac{\partial(\mu_i/T)}{\partial T} \right)_{P,N} = \frac{T(\partial\mu_i/\partial T) - \mu_i}{T^2}$$

Substituting equations (5) & (6) in the above equation

$$\left[ \frac{\partial(\mu_i/T)}{\partial T} \right]_{P,N} = -\frac{\bar{H}_i}{T^2} \quad \text{--- (7)}$$

Equation (7) predicts the effect of temperature on chemical potential.

Effect of pressure:

$$\mu_i = \bar{G}_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} \quad \text{--- (1)}$$

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T,N} = \frac{\partial^2 G^t}{\partial P \partial n_i} \quad \text{--- (2)}$$

WKT,

$$\left( \frac{\partial G^t}{\partial P} \right)_{T,N} = V^t \quad \text{--- (3)}$$

$$\frac{\partial^2 G^t}{\partial n_i \partial P} = \left( \frac{\partial V^t}{\partial n_i} \right)_{P,T,n_j} = \bar{V}_i \quad \text{--- (4)}$$

Evaluating equations (2) and (4)

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T,N} = \bar{V}_i \quad \text{--- (5)}$$

The rate of change of chemical potential with pressure is thus equal to the partial molar volume of the constituent.

Q4. P.T the chemical potential  $\mu_i = \left(\frac{dU}{dn_i}\right)_{S, V, n_j}$

The internal energy of a system may be expressed as a function of thermodynamic state and moles of the components like the Gibb's free energy.

$$U^t = f(S^t, V^t, n_1, n_2, \dots, n_i, \dots)$$

which gives

$$dU^t = \left(\frac{dU^t}{dS^t}\right)_{V, N} dS^t + \left(\frac{dU^t}{dV^t}\right)_{S, N} dV^t + \sum \left(\frac{dU^t}{dn_i}\right)_{S, V, n_j \neq i} dn_i \quad \text{--- (1)}$$

Since  $dU = Tds - PdV$  for a closed system

$$\left(\frac{dU^t}{dS^t}\right)_{V, N} = T ; \quad \left(\frac{dU^t}{dV^t}\right)_{S, N} = -P \quad \text{--- (2)}$$

Combining these with eqn (1)

$$dU^t = TdS^t - PdV^t + \sum \left(\frac{dU^t}{dn_i}\right)_{S, V, n_j \neq i} dn_i \quad \text{--- (3)}$$

WKT,  $G = H - TS = U + PV - TS$

$$dG = dU + PdV + VdP - TdS - SdT$$

The change in the total free energy at constant temperature and pressure is therefore,

$$dG_{T, P}^t = dU^t + PdV^t - TdS^t \quad \text{--- (4)}$$

Combining equations (3) and (4)

$$dG_{T, P}^t = \sum \left(\frac{dU^t}{dn_i}\right)_{S, V, n_j \neq i} dn_i \quad \text{--- (5)}$$

WKT,  $dG_{T, P}^t = \sum \mu_i dn_i \quad \text{--- (6)}$

Comparing equation (5) and (6)

$$\sum \mu_i dn_i = \sum \left(\frac{dU^t}{dn_i}\right)_{S, V, n_j \neq i} dn_i$$

$$\mu_i = \left(\frac{dU^t}{dn_i}\right)_{S, V, n_j \neq i} \quad \text{--- (7)}$$

25. Gibbs-Duhem equation:

In a mixture, the partial molar properties of the components are related to one another by one of the most useful equations in thermodynamics, the Gibbs-Duhem equation. It tells us how the partial molar properties change with compositions at constant temperature and pressure.

At constant temperature and pressure, the property  $M^t$  of the solution is the sum of the partial molar properties of the constituents, each weighted according to the number of moles of the respective constituents.

$$M^t = \sum n_i \bar{M}_i \quad \text{--- (1)}$$

The total derivative  $dM^t$  gives the change in the property of the solution at constant  $T$  and  $P$ .

$$dM^t = \sum n_i d\bar{M}_i + \sum \bar{M}_i dn_i \quad \text{--- (2)}$$

where  $M$  is the molar value of the property of the solution  $M^t$ . But, since  $M^t = f(T, P, n_1, n_2, \dots)$ , at constant  $T$  and  $P$ , which gives

$$dM^t = \sum \bar{M}_i dn_i \quad \text{--- (3)}$$

Evaluating eqns (2) and (3) gives

$$\boxed{\sum n_i d\bar{M}_i = 0} \quad \text{--- (4)}$$

This result is the general form of the Gibbs-Duhem equation. If the property under consideration is the Gibbs free energy of the solution, then the above equation becomes

$$\sum n_i d\mu_i = 0 \quad \text{--- (5)}$$

Dividing throughout by  $n$ , the <sup>(45)</sup> total number of moles in the solution

$$\sum x_i d\mu_i = 0 \quad \text{--- (5)}$$

Here  $x_i$  is the mole fraction of component  $i$  in the solution and  $\mu_i$  is the chemical potential of the component.

Other forms of Gibbs-Duhem Equation:

Consider a binary solution made up of components 1 and 2 whose mole fractions in the solution are  $x_1$  and  $x_2$  respectively. Equation (5) can be written as

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad \text{--- (7)}$$

where  $\mu_1$  and  $\mu_2$  are the chemical potentials of component 1 and 2 respectively. This can be rearranged as

$$x_1 d\mu_1 = -x_2 d\mu_2$$

Dividing by  $dx_1$  and noting that  $dx_1 = -dx_2$  in binary mixtures, the above result gives

$$x_1 \frac{d\mu_1}{dx_1} = x_2 \frac{d\mu_2}{dx_2} \quad \text{--- (8)}$$

Introducing the relationship between chemical potential and the fugacity  $d\mu_i = RT d(\ln \bar{f}_i)$  into the above equation (8)

$$x_1 \frac{d \ln \bar{f}_1}{dx_1} = x_2 \frac{d \ln \bar{f}_2}{dx_2} \quad \text{--- (9)}$$

(4b)

Since activity  $a_i = \bar{f}_i / f_i^0$ , fugacities in eqn (9) may be replaced in terms of activity as

$$x_1 \frac{d \ln(a_1 f_1^0)}{dx_1} = x_2 \frac{d \ln(a_2 f_2^0)}{dx_2}$$

Since  $f_i^0$ , the fugacity in the standard state, is independent of the composition of the solution,

$$\frac{d \ln(f_i^0)}{dx_1} = 0$$

Thus the Gibbs-Duhem equation in terms of activity is

$$\boxed{x_1 \frac{d \ln a_1}{dx_1} = x_2 \frac{d \ln a_2}{dx_2}} \quad \text{--- (10)}$$

By definition,  $a_i = \gamma_i x_i$ . Substitute this into eqn (10) and thus the most important and widely used form of the Gibbs-Duhem equation, that involving the activity coefficients, is obtained.

$$x_1 \frac{d \ln \gamma_1 x_1}{dx_1} = x_2 \frac{d \ln \gamma_2 x_2}{dx_2}$$

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_1 \frac{d \ln x_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2} + x_2 \frac{d \ln x_2}{dx_2}$$

The second terms on both sides of the above equation vanish, as they are equal to unity. Therefore

$$\boxed{x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2}} \quad \text{--- (11)}$$

26. Let the initial molar free energies of gas 1 be  $\mu_1^*$  and of gas 2 be  $\mu_2^*$ , and the final molar energies (after mixing) be  $\mu_1$  and  $\mu_2$  respectively.

Before mixing:

$$G_{\text{initial}} = n_1 \mu_1^* + n_2 \mu_2^* \quad \text{--- (1)}$$

After mixing:

$$G_{\text{final}} = n_1 \mu_1 + n_2 \mu_2 \quad \text{--- (2)}$$

WRT, for a pure ideal gas, the chemical potential of the  $i^{\text{th}}$  component at constant temperature under a pressure  $P^*$  is given by

$$\mu_i^* = \mu_i^0 + RT \ln P^* \quad \text{--- (3)}$$

On substitution of eqn (3) into (1), it yields

$$G_{\text{initial}} = n_1 (\mu_1^0 + RT \ln P_1^*) + n_2 (\mu_2^0 + RT \ln P_2^*) \quad \text{--- (4)}$$

Again, on mixing of the gases under pressure  $P$ , the chemical potential at partial pressure  $P_i$  will be

$$\mu_i = \mu_i^0 + RT \ln P_i \quad \text{--- (5)}$$

Hence, equation (2) can be expressed as

$$G_{\text{final}} = n_1 (\mu_1^0 + RT \ln P_1) + n_2 (\mu_2^0 + RT \ln P_2) \quad \text{--- (6)}$$

Therefore, the free energy change of mixing is

$$\begin{aligned} \Delta G_{\text{mixing}} &= G_{\text{final}} - G_{\text{initial}} \\ &= (n_1 \mu_1^0 + n_1 RT \ln P_1 + n_2 \mu_2^0 + n_2 RT \ln P_2) - (n_1 \mu_1^0 + n_1 RT \ln P_1^* + n_2 \mu_2^0 + n_2 RT \ln P_2^*) \\ &= RT (n_1 \ln P_1 + n_2 \ln P_2) - RT (n_1 \ln P_1^* + n_2 \ln P_2^*) \\ \Delta G_{\text{mixing}} &= RT n_1 \ln \frac{P_1}{P_1^*} + n_2 \ln \frac{P_2}{P_2^*} \quad \text{--- (7)} \end{aligned}$$

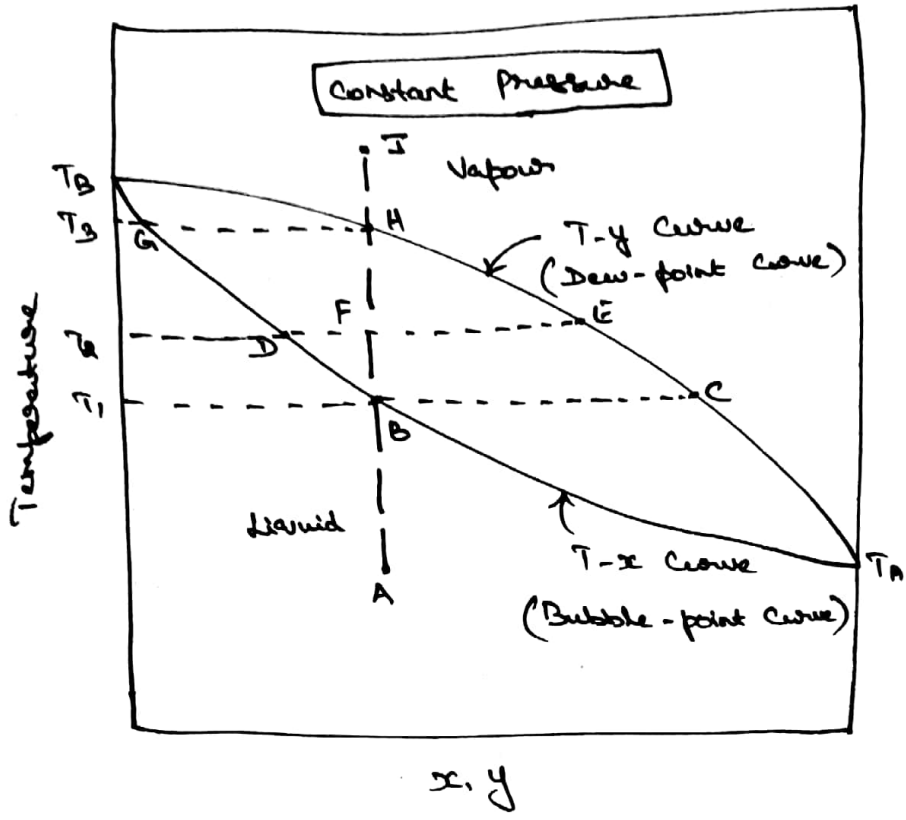


## 27. T-x-y Diagram & Boiling Point Diagram: (48)

Consider a binary system made up of components A and B. Component A is assumed to be more volatile than B, i.e. the vapour pressure of A is greater than that of B at any given temperature. For a binary liquid mixture in equilibrium with its vapour, according to the Gibbs phase rule, the number of degrees of freedom is two. When the pressure is fixed, say liquid phase composition, can be changed independently and other properties such as the temperature and the vapour phase compositions get uniquely determined. Vapour-liquid equilibrium data at constant pressure are usually represented by means of either the temperature composition diagrams (the T-x-y diagrams or the boiling point diagrams) or the distribution diagrams (x-y diagrams & equilibrium curves).

### 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 components in the liquid,  $x$ , and the composition of the vapour is indicated by the mole fraction of the more volatile components in the vapour,  $y$ . Therefore, the boiling point diagrams are called T-x-y diagrams.



The upper curve in figure 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.

To make these points clearer, consider a mixture whose temperature and composition ( $x_1$ ) are such that it is represented by point A in figure. Since the point A lies below the bubble-point curve,

the solution is entirely liquid. The mixture is taken in a closed container and the pressure over the system is maintained at a constant value by a piston. The mixture is heated slowly so that its temperature increases along the vertical line passing through point A till point B on the bubble-point curve is reached. The temperature  $T_1$  corresponding to point B, is the bubble point of the original mixture. The first bubble of the vapour is produced at this temperature and it will have the composition ( $y_1$ ) represented by point C on the upper curve. The vapour is richer in the more volatile component. Therefore  $y_1 > x_1$ , and the dew-point curve lies above the bubble-point curve. The mixtures at point B and C are the liquid and vapour at equilibrium at the system pressure and temperature  $T_1$ . Since both are at the same temperature, they can be joined by a horizontal line BC, known as a 'tie line'. Further heating will result in the vaporisation of more liquid, and at temperature  $T_2$  the system will consist of saturated liquid represented by point D and saturated vapour represented by point E, which are in equilibrium. Since the vapour formed is not removed from the system, the overall composition of the combined mixture of liquid and vapour will be same as  $x_1$ , the composition of the original mixture. However, the relative amounts of the liquid and vapour change as the temperature is changed.

(51)

These relative amounts are given by the ratio in which the point representing the combined mixture (in this case, point F) divides the tie line DE. By material balance consideration, it can be easily verified that

$$\frac{\text{Amount of liquid}}{\text{Amount of vapour}} = \frac{\text{Line EF}}{\text{Line DF}}$$

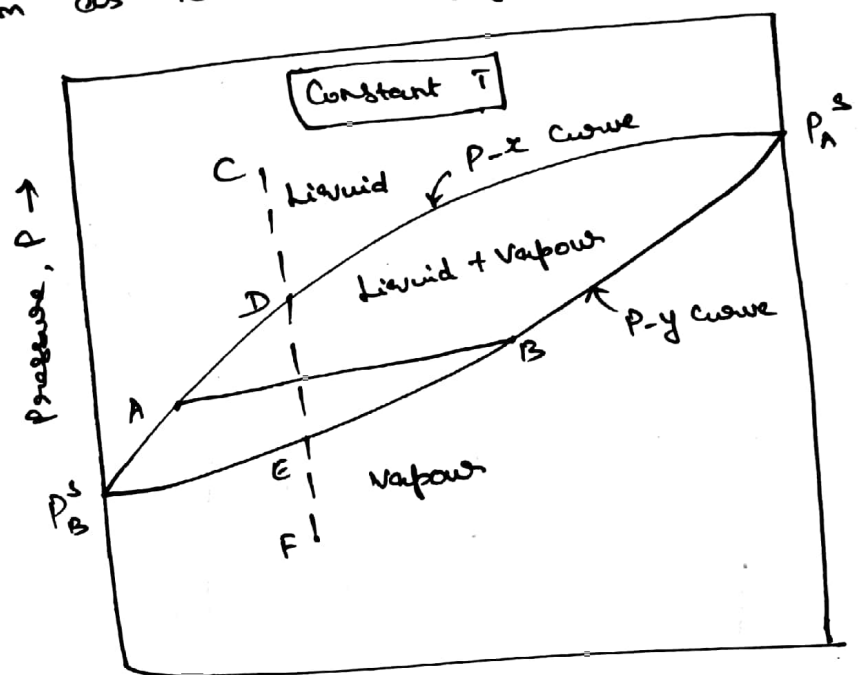
If heating is continued, eventually a temperature  $T_3$  is reached when almost all liquid is vaporized.

The last drop of liquid getting vaporized at this temperature has a composition denoted by point G and the equilibrium vapour has the composition at H same as the original mixture. Temperature  $T_3$  is the dew point of the original mixture. The mixture temperature increases along the vertical line HI on further heating. On cooling the super-heated mixture at point J, the first drop of condensate appears when the temperature drops to  $T_3$ , the dew point of the mixture and the composition of the liquid is given by point G.

It has been seen that the mixture at point A has vaporized over a temperature range from  $T_1$  (the bubble point) to  $T_3$  (the dew point), unlike a pure substance, which vaporizes at a single temperature known as the boiling point of the substance. For a solution, the term 'boiling point' has no meaning because at a given pressure the temperature during vaporization of a solution varies from the bubble point to the dew point.

### P-x-y Diagram:

Vapour-liquid equilibrium data at constant temperature are represented by means of P-x-y diagram as shown in figure (a)



Fig(a) - x, y: mole fraction of A

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. Assume that a liquid mixture whose conditions may be represented by the point C in figure, is taken in a closed container. When the pressure over this system is reduced at constant temperature, the first bubble of vapour forms at point D, and the vaporization

goes to completion at point E. Further reduction in pressure leads to the production of superheated vapour represented by point F. The effect of temperature on P-x-y diagram is shown in figure (b). When the temperature is less than the critical temperature of both components, the looped curve such as the one shown at the bottom of fig (b) results. The other two curves refer to temperatures greater than the critical temperature of A.

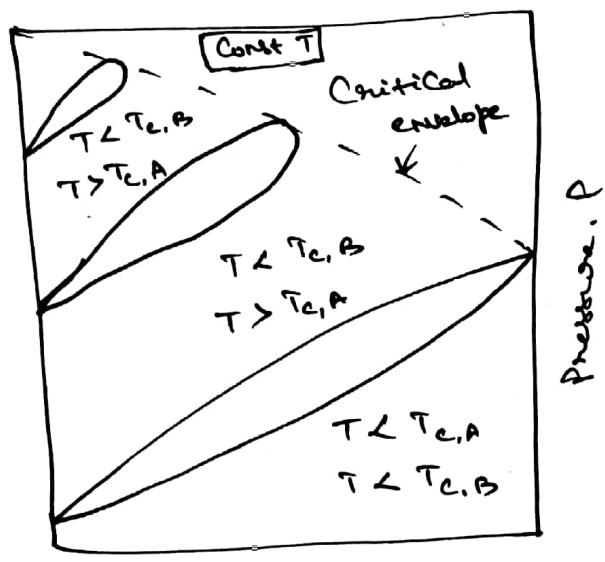


Fig (b) x, y: mole fraction of A

Q8. Solution:

From Raoult's law,

$$\bar{p}_i = x_i P_i^s$$

For a binary solution,

$$\bar{p}_1 = x_1 P_1^s ; \bar{p}_2 = x_2 P_2^s \quad \text{--- (1)}$$

The total pressure P is the sum of the partial pressures

$$P = x_1 P_1^s + x_2 P_2^s = x_1 P_1^s + (1-x_1) P_2^s$$

$$P = P_2^s + (P_1^s - P_2^s) x_1 \quad \text{--- (2)}$$

By Dalton's Law

(54)

$$\bar{P}_1 = y_1 P \quad ; \quad \bar{P}_2 = y_2 P \quad \text{--- (2)}$$

Combining equations (1) and (3)

$$y_1 P = x_1 P_1^s$$

$$\boxed{y_1 = x_1 \frac{P_1^s}{P}} \quad \text{--- (4)}$$

Put  $x_1 = 0.5$  in equation (2)

∴ Equimolar mixture  
 $x_1 = x_2 = 0.5$

$$P_1^s = 135.4 \text{ kPa} \quad \& \quad P_2^s = 54 \text{ kPa}$$

$$P = 54 + (135.4 - 54) \cdot 0.5$$

$$\boxed{P = 94.7 \text{ kPa}}$$

This is the pressure at the beginning of vaporization.

$$(2) \Rightarrow x_1 = \frac{P - P_2^s}{P_1^s - P_2^s}$$

Substitute this in eqn (4)

$$y = \frac{P - P_2^s}{P_1^s - P_2^s} \times \frac{P_1^s}{P}$$

On rearranging this equation

$$P = \frac{P_1^s P_2^s}{P_1^s - y_1 (P_1^s - P_2^s)}$$

Put  $y_1 = 0.5$

$$P = \frac{135.4 \times 54}{135.4 - 0.5 (135.4 - 54)}$$

$$P = 77.2 \text{ kPa}$$

This is the pressure at the end of vaporization.