

LECTURE

7

CHE 415

Chemical Engineering Thermodynamics II

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Phase Diagrams for Binary Systems



Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:
 - Describe phase diagram for binary system.
 - Application of fundamental equations to solving 2-phase equilibrium problems.



QUALITATIVE METHODS FOR PHASE EQUILIBRIUM CONDITIONS

- ❑ Let us introduce this section by showing how the phase behavior of binary systems are represented by diagrams.
- ❑ For a non-reacting PVT system, the phase rule $F = 2 - \pi + N$ is used to estimate the maximum number of independent intensive variables required to specify the thermodynamic state of the system.
- ❑ For a single phase equilibrium (i.e. $\pi = 1$), containing two chemical species ($N = 2$), F , the degree of freedom becomes 3.
- ❑ This implies that 3 independent intensive variables can be chosen to specify the equilibrium condition of such a system.
- ❑ The 3-dimensional diagram such produced is called a Phase or space diagram. Typical example are the P-T-x diagrams similar to the surface diagram.
- ❑ Within this space, the state of pairs of phases ($\pi = 2$), coexisting at equilibrium ($F = 2$), define surfaces;
- ❑ similarly the states of three phases ($\pi = 3$) coexisting in equilibrium ($F = 1$) are represented as space curves.



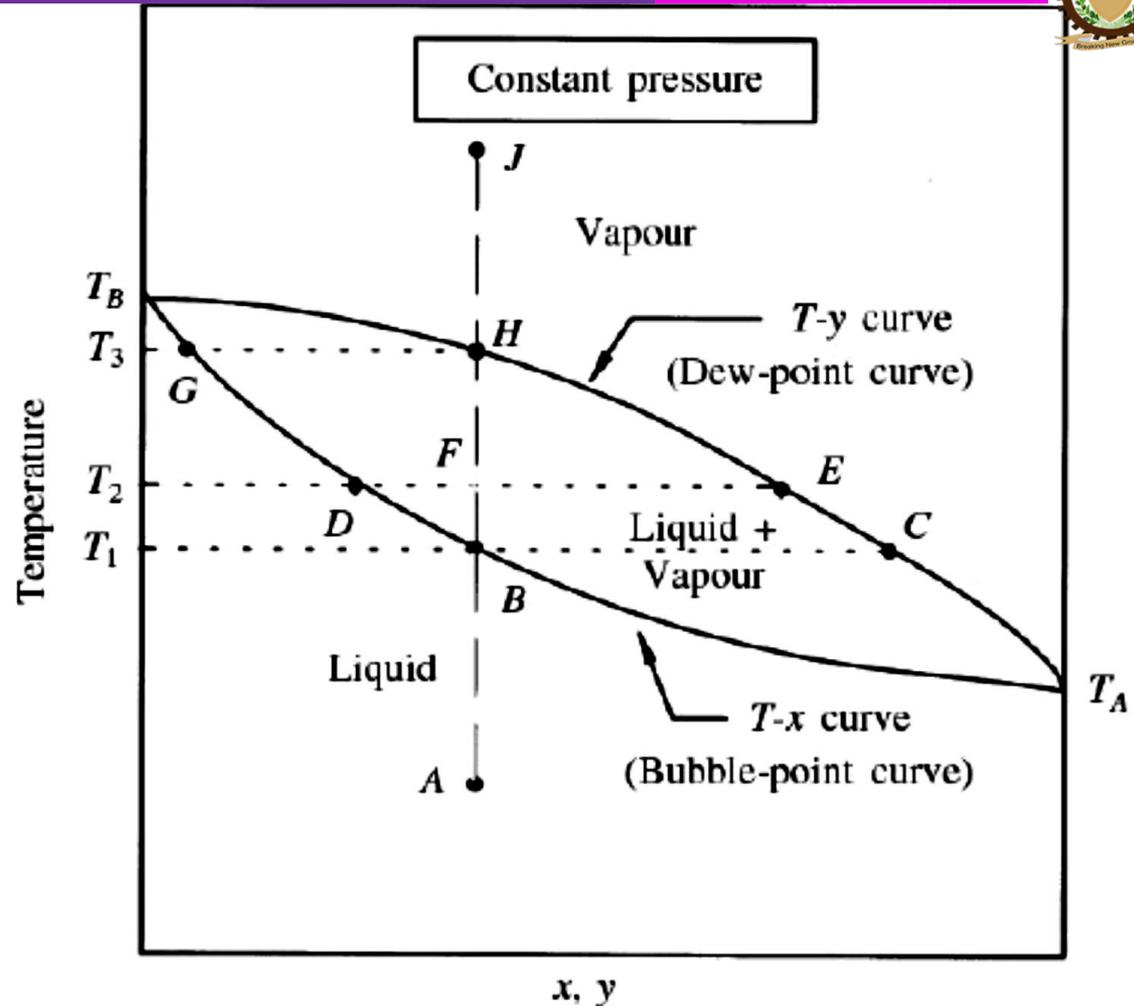
TWO-DIMENSIONAL PHASE EQUILIBRIUM DIAGRAMS

- ❑ These diagrams are obtained from intersections of the three-dimensional surfaces and curves with planes of constant pressures or constant temperatures. They include:
- ❑ VLE 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 or equilibrium curves).

□ Boiling-point diagram.

The boiling point diagrams are plots of T as ordinate vs composition of liquid (x) and vapour (y) 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 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'.



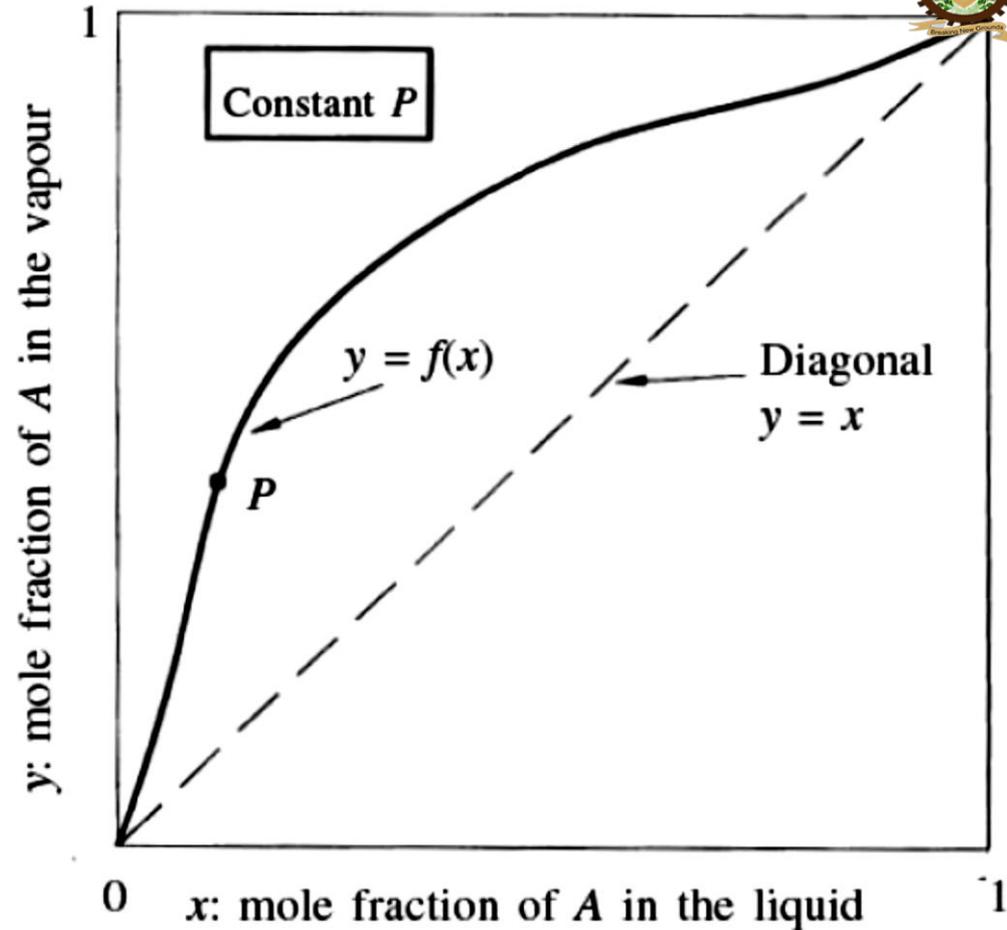
QUALITATIVE METHODS FOR PHASE EQUILIBRIUM CONDITIONS

- ❑ 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.



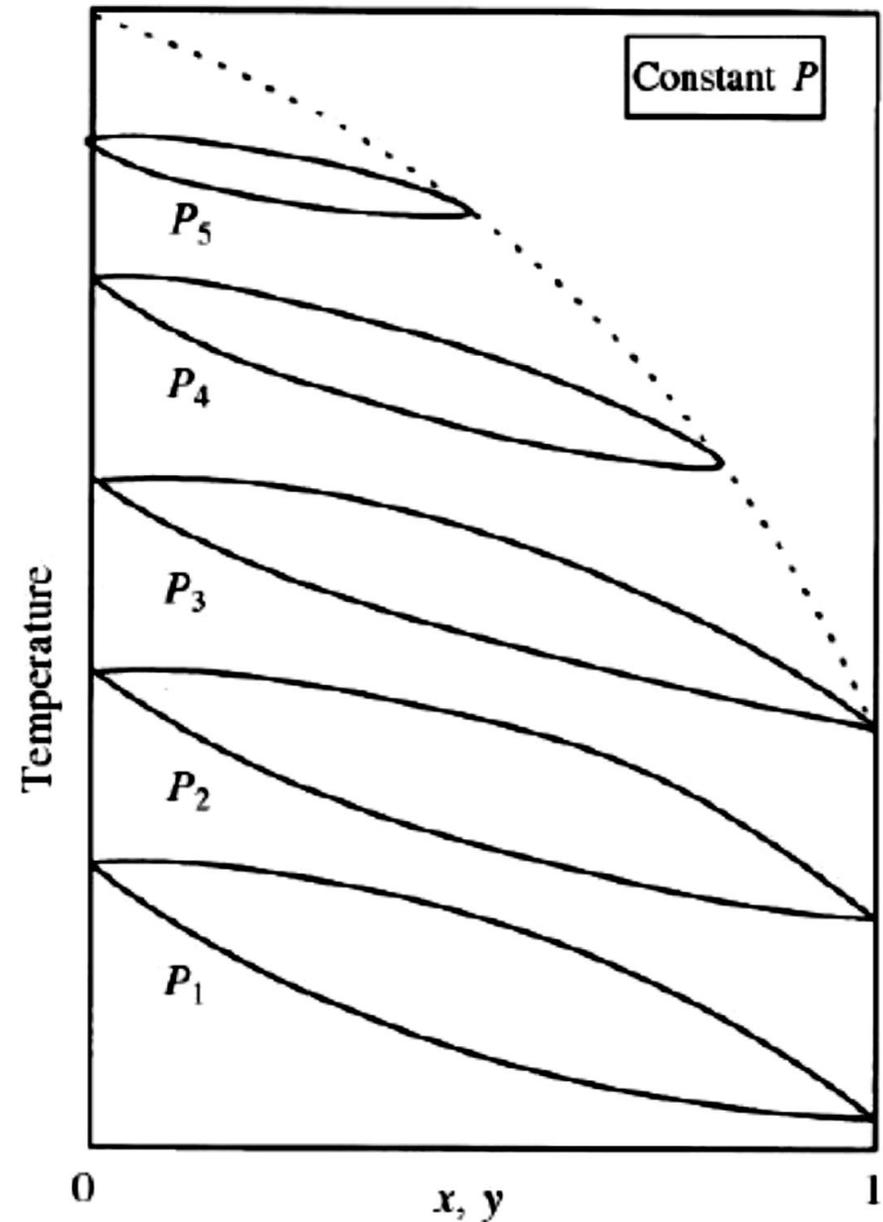
□ **Equilibrium diagram.**

- The VLE data at constant pressure can also be represented on a x vs 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.
- Since the vapour is richer in the more volatile component, the curve lies above the diagonal on which $x = y$.
- VLE 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.

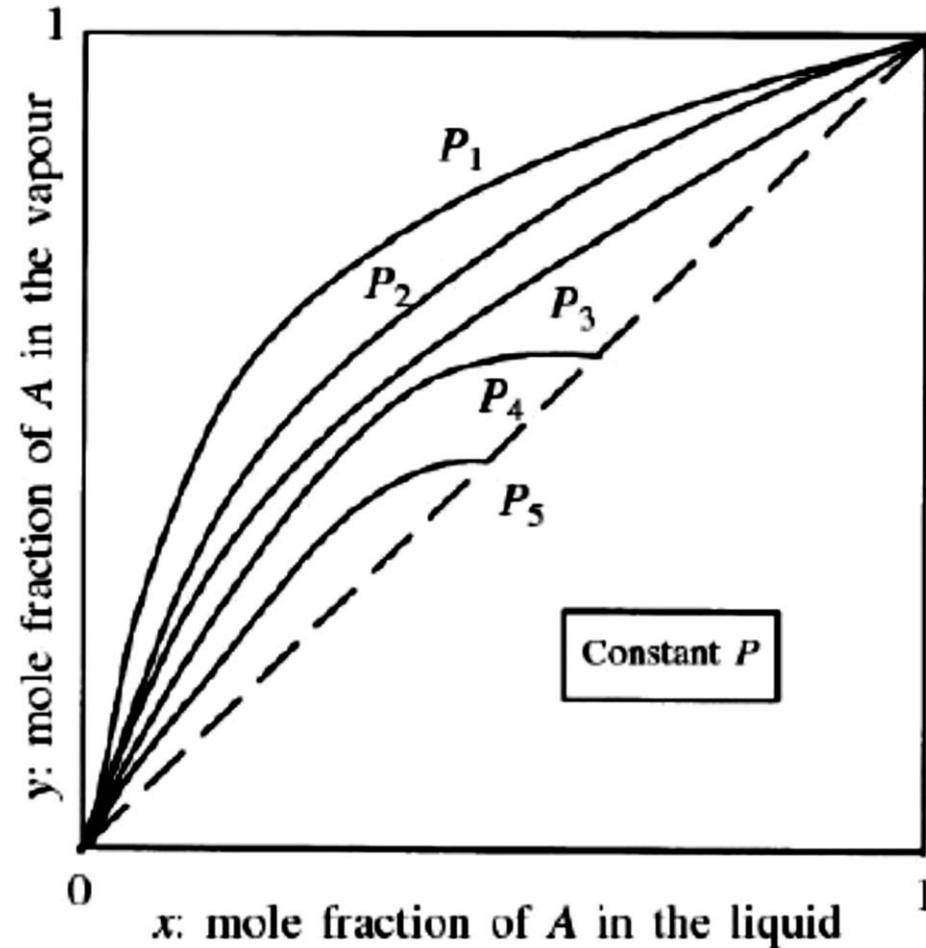


Effect of pressure on VLE.

- ❑ On the boiling point diagram the temperatures corresponding to $x = 0$ and $x = 1$ are the boiling points of pure substances B and A respectively.
- ❑ The boiling points of pure substances increase with pressure.
- ❑ Consequently the boiling point diagrams at higher pressures will be above the boiling point diagrams at lower pressures as shown in the fig.7-3.
- ❑ Since the relative volatility decreases as pressure is increased, the closed loop formed by the dew-point and bubble-point curves become narrow at high pressures.



- ❑ Figure 7.4 indicates the effect of pressure on the distribution diagram.
- ❑ In Fig. 7-3, P_3 is the *critical pressure* for component A and above this pressure, the looped curves are shorter.



Constant-temperature Equilibria

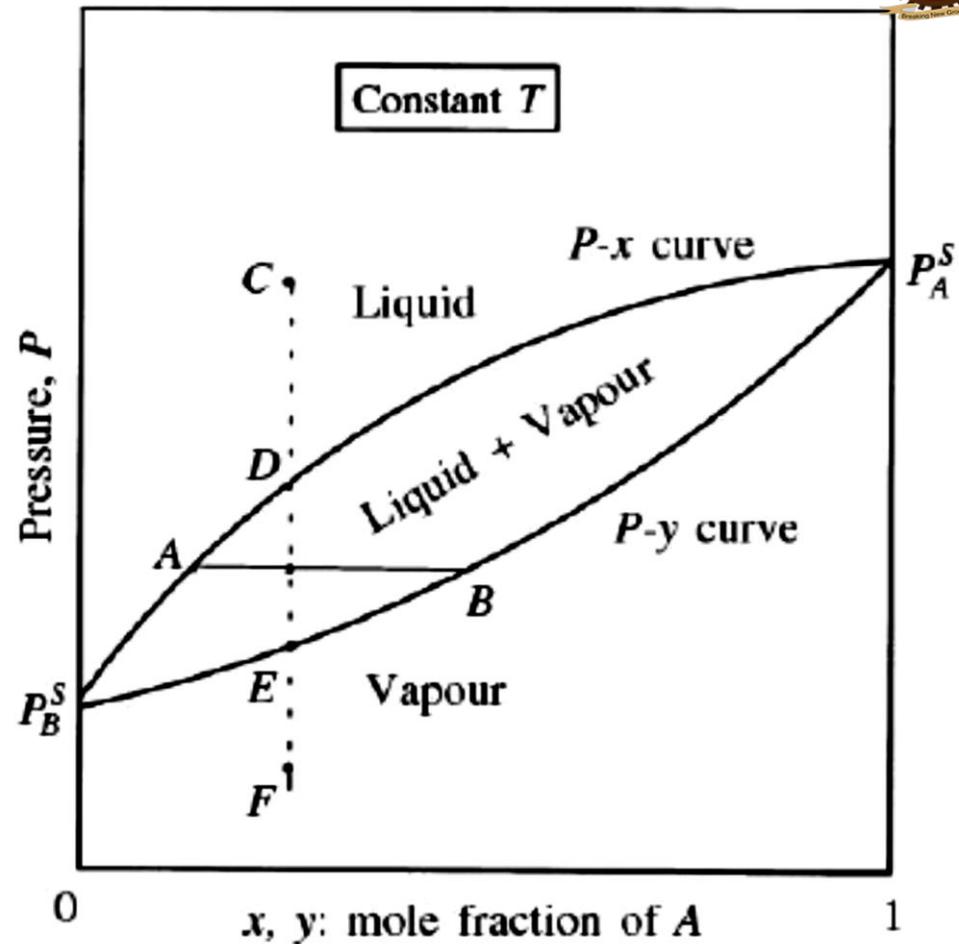
□ VLE data at constant temperature are represented by means of P - x - y diagrams; Fig. 7.5 shows a typical P - x - y diagram.

□ The pressure at $x = 0$ is the vapour pressure of pure B and the pressure at $x = 1$ is the vapour pressure of pure A .

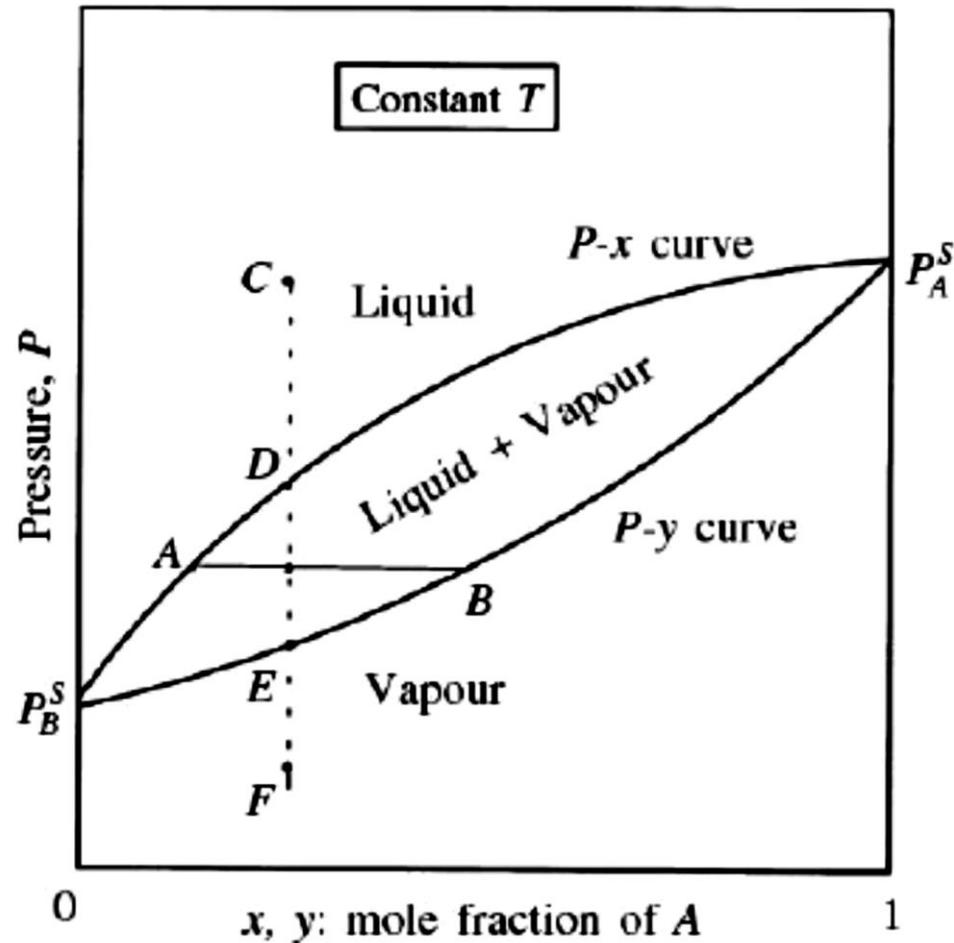
□ Since component A is assumed to be more volatile, and therefore, the P - x - y diagram slopes upwards as shown in the figure.

□ The P - y curve lies below the P - x curve so that for any given pressure, $y > x$.

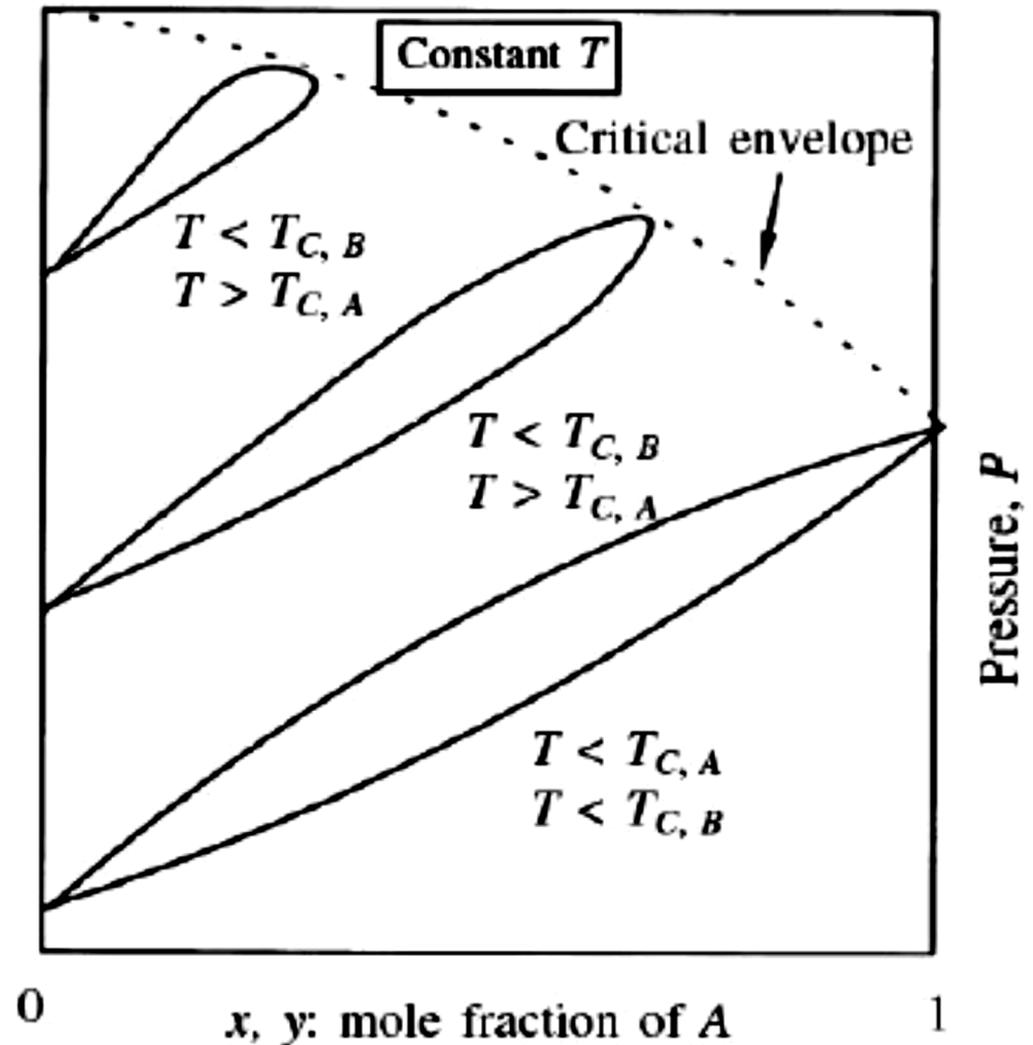
□ A solution lying above the P - x curve is in the liquid region and that lying below the P - y curve is in the vapour region. In between P - x and P - y curves the solution is a mixture of saturated liquid and vapour.



- ❑ A horizontal line such as AB connects the liquid and vapour phases in equilibrium and is therefore, a tie line.
- ❑ Assume that a liquid mixture whose conditions may be represented by the point C in Fig.7-5, 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 vaporisation 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 Fig. 7.6.
- ❑ 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. 7.6 results.
- ❑ The other two curves refer to temperatures greater than the critical temperature of A.





VAPOUR-LIQUID EQUILIBRIUM CALCULATIONS

- Recall that one of the criterion for chemical equilibrium in terms of fugacity is expressed as

$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \dots = \hat{f}_i^\pi \quad (i = 1, 2, \dots, N) \quad 7-1$$
- This asserts that the fugacity \hat{f}_i of each component i in an N -component system must be the same in all phases at equilibrium.
- According to phase rule, there are **2 - π + N** degrees of freedom in an N -component, π -phase system. The degree of freedom implies the number of independent intensive variables that must be specify to render the system determinate.
- For equilibrium between a single vapour phase and a single liquid phase, Eqn.7-1 becomes
- $$\hat{f}_i^v = \hat{f}_i^l \quad (i = 1, 2, \dots, N) \quad 7-2$$
- For a vapour mixture, $\hat{f}_i^v = y_i \hat{\phi}_i P$, and for component i in the liquid phase $\hat{f}_i^l = x_i \gamma_i f_i^0$.

 - where γ_i is the activity coefficient for liquid and f_i^0 is the standard state fugacity
- Substituting for \hat{f}_i^v and \hat{f}_i^l in Eqn.7-2 gives,
- $$y_i \hat{\phi}_i P = x_i \gamma_i f_i^0 \quad (i = 1, 2, \dots, N) \quad 7-3$$



VAPOUR-LIQUID EQUILIBRIUM CALCULATIONS

- ❑ For an ideal solution and the vapour phase is a mixture of ideal gases,
- ❑ $\hat{\phi}_i = 1$
- ❑ For the liquid phase being an ideal solution, $\gamma_i = 1$,
- ❑ and $f_i^0 = f_i(P) = P_i^{sat}$
- ❑ Substitution in Eqn.7-3 yields
- ❑
$$y_i P = x_i P_i^{sat} \quad (i = 1, 2, \dots, N) \quad 7-4$$
- ❑ Eqn.7-4 is the statement of Raoult's law. It represents the simplest possible vapour-liquid equilibrium behavior. It is often used to construct the P-x,y; T-x,y and the equilibrium diagram.

- ❑ **To construct the P-x,y diagram.**
- ❑ NB: This is done at a constant temperature
- ❑ Considering a binary system of components (1) and (2)
- ❑ Applying the Raoult's law to each component gives,
- ❑
$$y_1 P = x_1 P_1^{sat} \quad 7-5$$
- ❑
$$y_2 P = x_2 P_2^{sat} \quad 7-6$$
- ❑ By adding Eqns. 7-5 and 7-6 yields



VAPOUR-LIQUID EQUILIBRIUM CALCULATIONS

$$\square \quad (y_1 + y_2)P = x_1 P_1^{sat} + x_2 P_2^{sat} \quad 7-7$$

$$\square \text{ But } \quad \sum y_i = 1 \text{ and } x_2 = 1 - x_1$$

$$\square \text{ Hence, } \quad P = P_2^{sat} + x_1(P_1^{sat} - P_2^{sat}) \quad 7-8$$

\square Substitution of 7-8 in Q7-5 and solution for y_1 yields

$$\square \quad y_1 = \frac{x_1 P_1^{sat}}{P_2^{sat} + x_1(P_1^{sat} - P_2^{sat})} \quad 7-9$$

\square Eqns.7-8 and 7-9 are equations for the bubble-point and dew-point curves respectively needed for the construction of the P-x,y diagram.

\square So at a suggested value of x_1 values of P and y_1 are calculated for the plot of the P-x,y diagram.

\square **To construct the T-x,y diagram.**

\square At the given total pressure, the bubble-point curve is constructed by solving Eqn.7-8 for the bubble-point composition x_1 at representative values of T between the saturation temperatures of the pure components:

$$\square \quad x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}} \quad 7-10$$



VAPOUR-LIQUID EQUILIBRIUM CALCULATIONS

- The corresponding equilibrium composition on the dew-point curve are obtained by substitution of Eqn.7-10 in 7-5 and solution for y_1

$$\square \quad y_1 = \left(\frac{P_1^{sat}}{P} \right) \left(\frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}} \right) \quad 7-11$$

- Example 1.
- VLE in the benzene-toluene system is well represented by Raoult's law at low and moderate pressures. Construct the P-x,y diagram at 900C and the T-x,y diagram at 101.3 kPa total pressure for this system. Vapour pressure data for benzene(1) and toluene(2) are given in the table:

T/°C	P_1^{sat} /kPa	P_2^{sat} /kPa	T/°C	P_1^{sat} /kPa	P_2^{sat} /kPa
80.1	101.3	38.9	98	170.5	69.8
84	114.1	44.5	100	180.1	74.2
88	128.5	50.8	104	200.4	83.6
90	136.1	54.2	108	222.5	94.0
94	152.6	61.6	110.6	237.8	101.3



ASSIGNMENT

Binary system acetonitrile(1)/nitromethane(2) conforms closely to Raoult's law. Vapour pressures for the pure species are given by the following Antoine equations:

$$\bullet \ln P_1^{sat} = 14.2724 - \frac{2,945.47}{t + 224.00}$$

$$\bullet \ln P_2^{sat} = 14.2043 - \frac{2,972.64}{t + 209.00} \quad (\text{for } P_1^{sat} \text{ and } P_2^{sat} \text{ in kPa and } t \text{ in } ^\circ\text{C})$$

(a) Prepare a graph showing P vs x_1 and P vs x_2 for a temperature of 75°C

(b) Prepare a graph showing t vs x_1 and t vs x_2 for a pressure of 70 kPa.



**THANK YOU
FOR
YOUR
ATTENTION!
ANY QUESTIONS?**