

# CH2351 Chemical Engineering Thermodynamics II

Unit – I, II

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## Phase Equilibria

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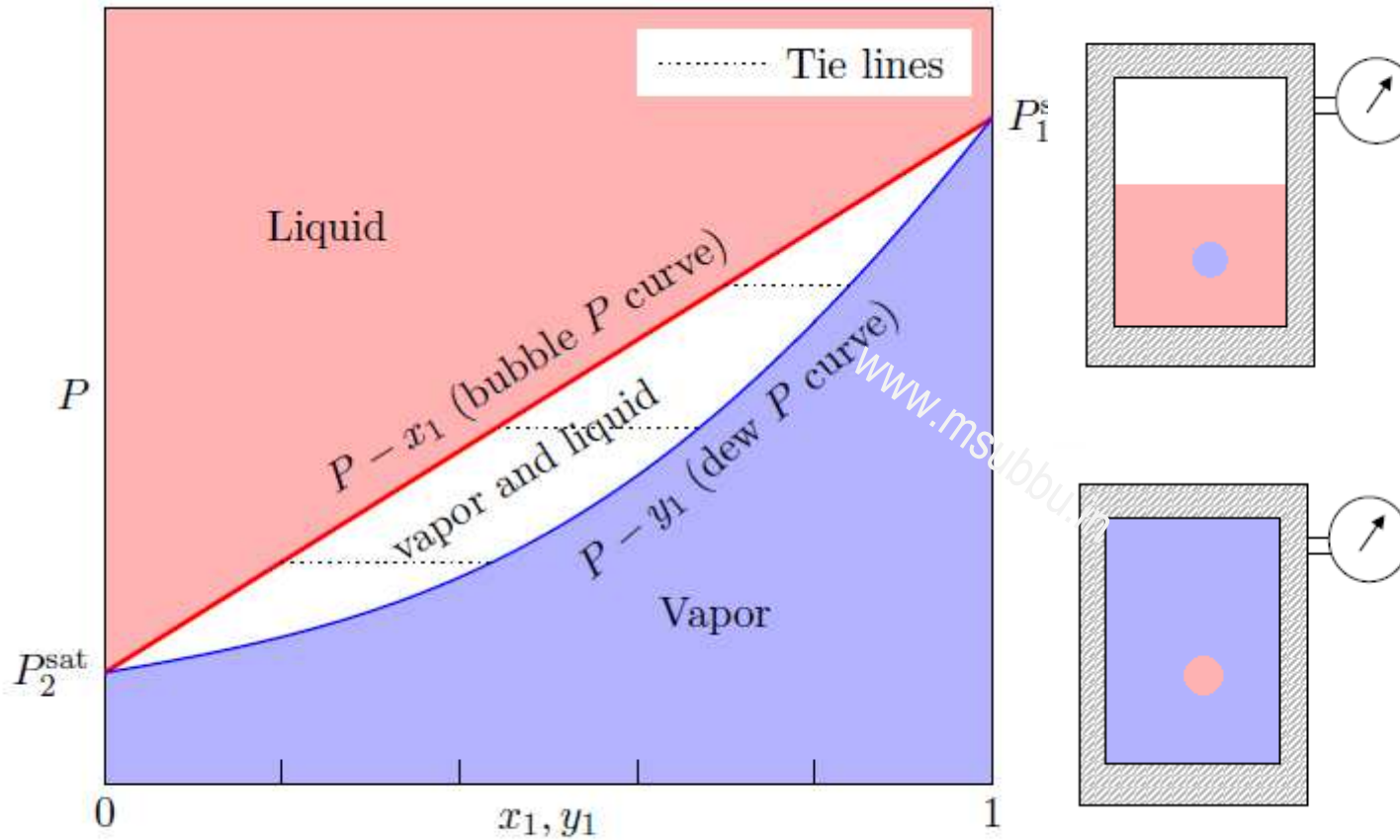
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# Contents

Criteria for vapor-liquid equilibrium between phases in multi component non-reacting systems in terms of chemical potential and fugacity, estimation of fugacity of liquid, Raoult's law, constant temperature and constant pressure VLE ( $P_{xy}$ ,  $T_{xy}$  diagrams), effect of temperature and pressure on VLE, P-T diagram, deviations from ideality – positive and negative deviations, models for activity coefficient, azeotropes – minimum and maximum boiling azeotropes

# Ideal Solution



Note: The composition of the bubble is different from the liquid and is richer in the more volatile component.

Note: The composition of the "dew" is different from the vapor and is richer in the less volatile component.

Figure 9.1:  $Pxy$  diagram of ideal solution

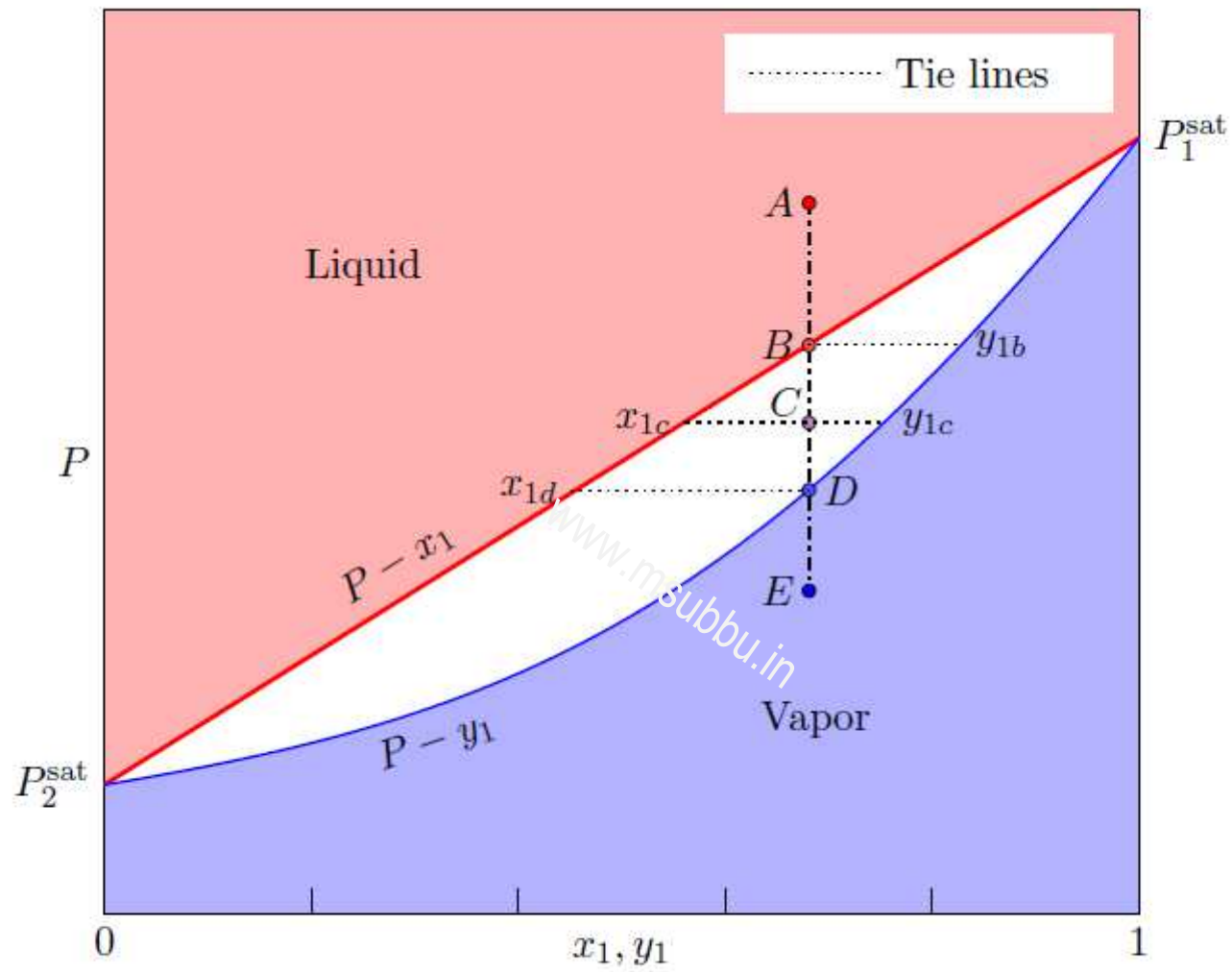


Figure 9.2: Vaporization process of ideal solution ( $Pxy$  diagram)

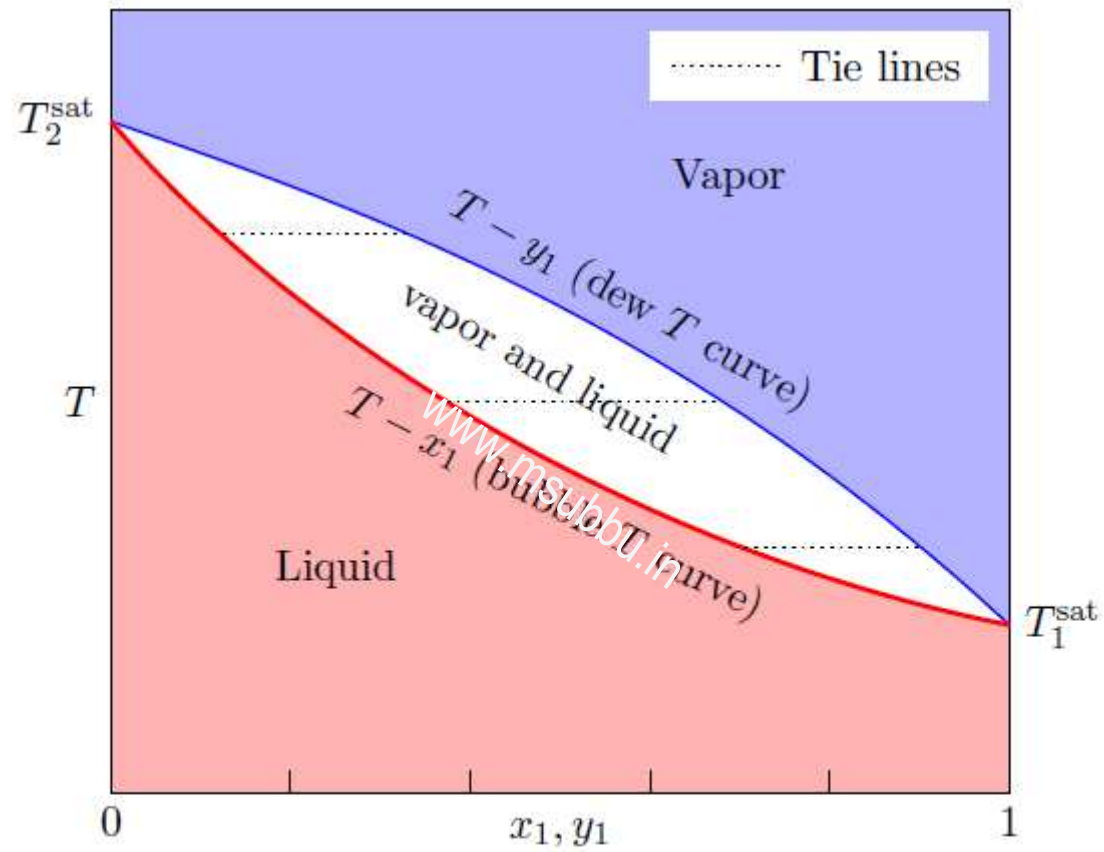
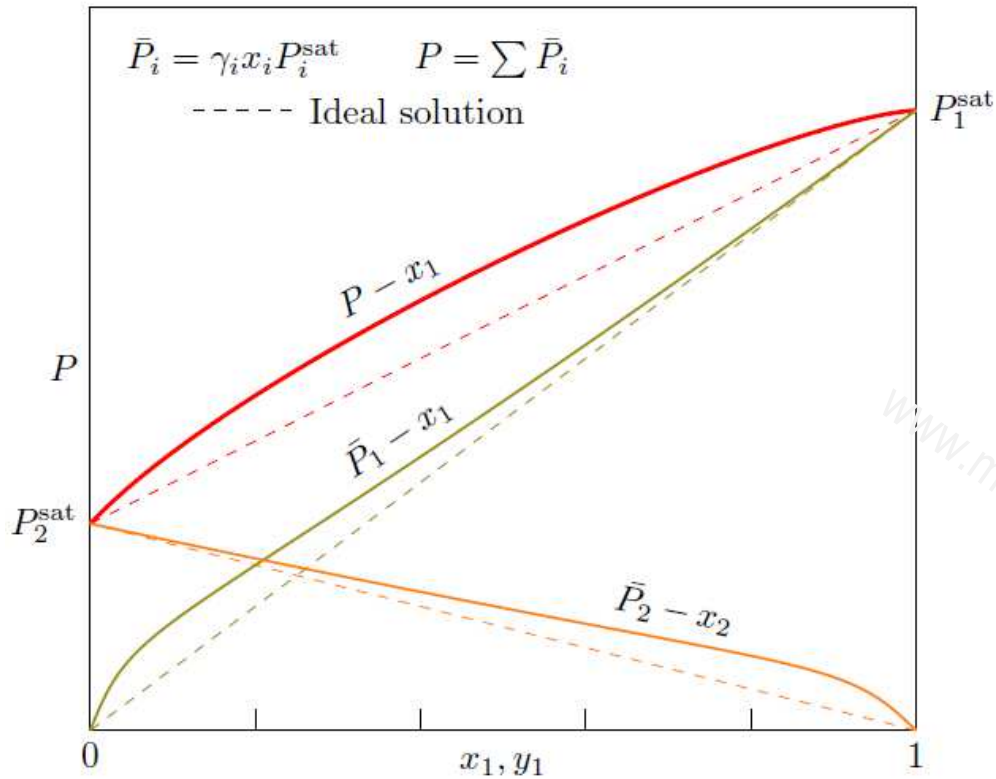
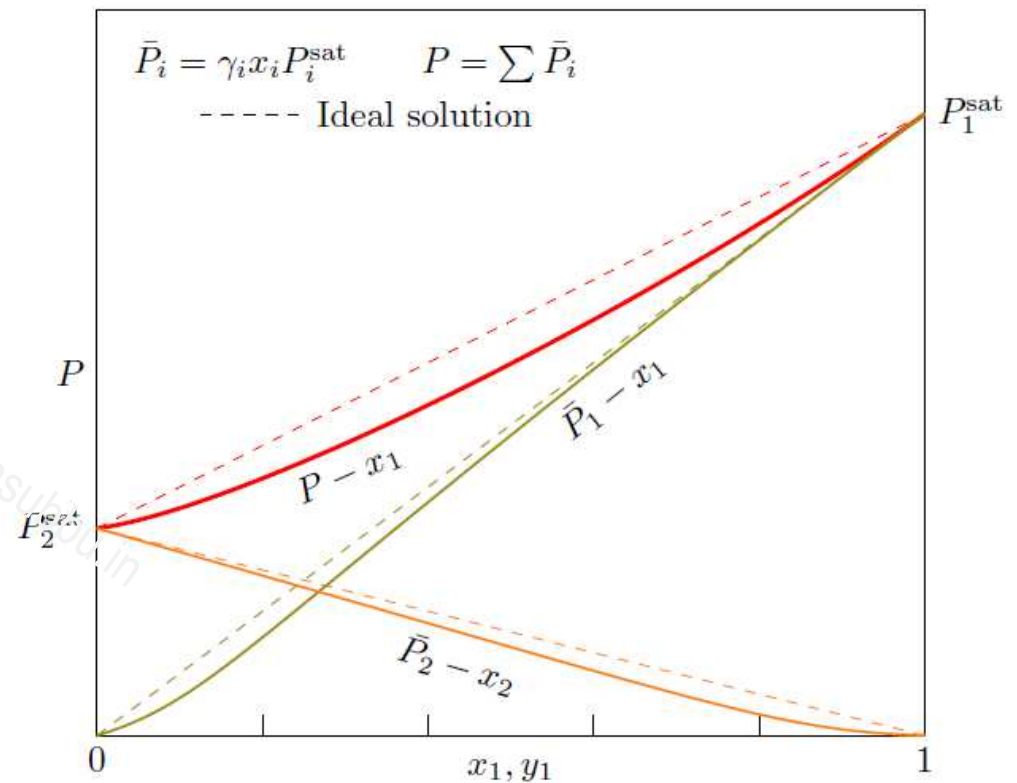


Figure 9.3:  $Txy$  diagram of ideal solution

# Deviations from Ideal Solution

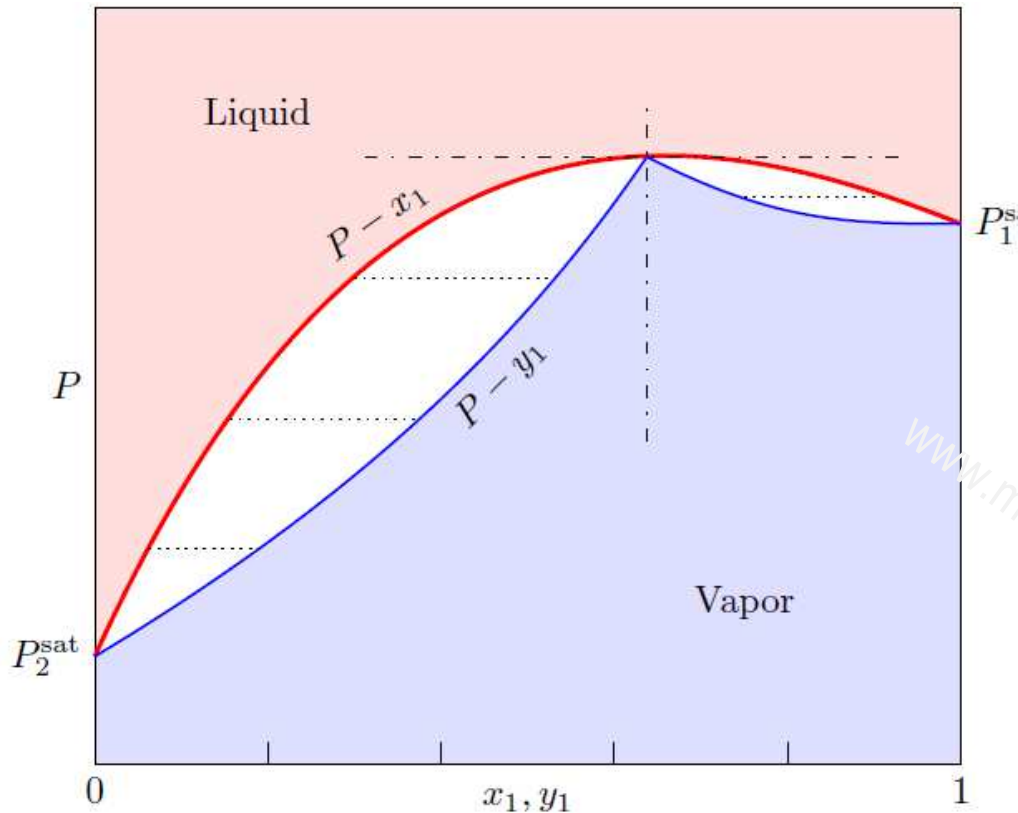


Constant Temperature Equilibria ( $Px$  diagram)  
 Non-Ideal solution  
 (positive deviation from ideality;  $\gamma_i > 1$ )

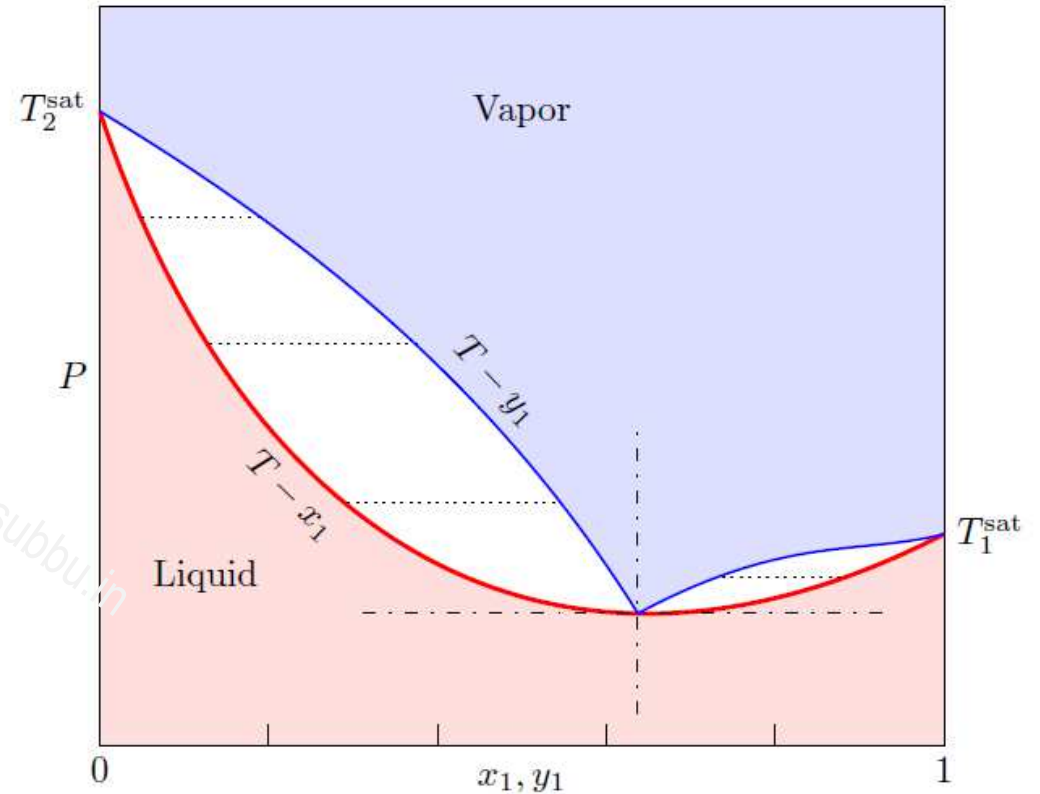


Constant Temperature Equilibria ( $Px$  diagram)  
 Non-Ideal solution  
 (negative deviation from ideality;  $\gamma_i < 1$ )

# Minimum Boiling Azeotrope



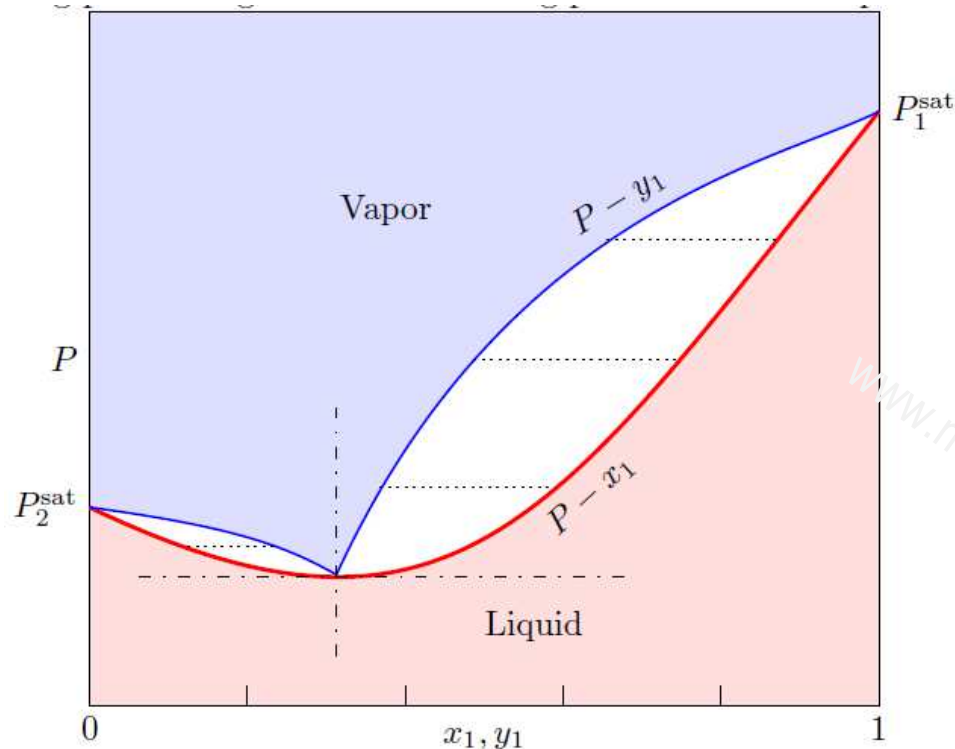
Constant Temperature Equilibria ( $Pxy$  diagram)  
Minimum boiling azeotrope



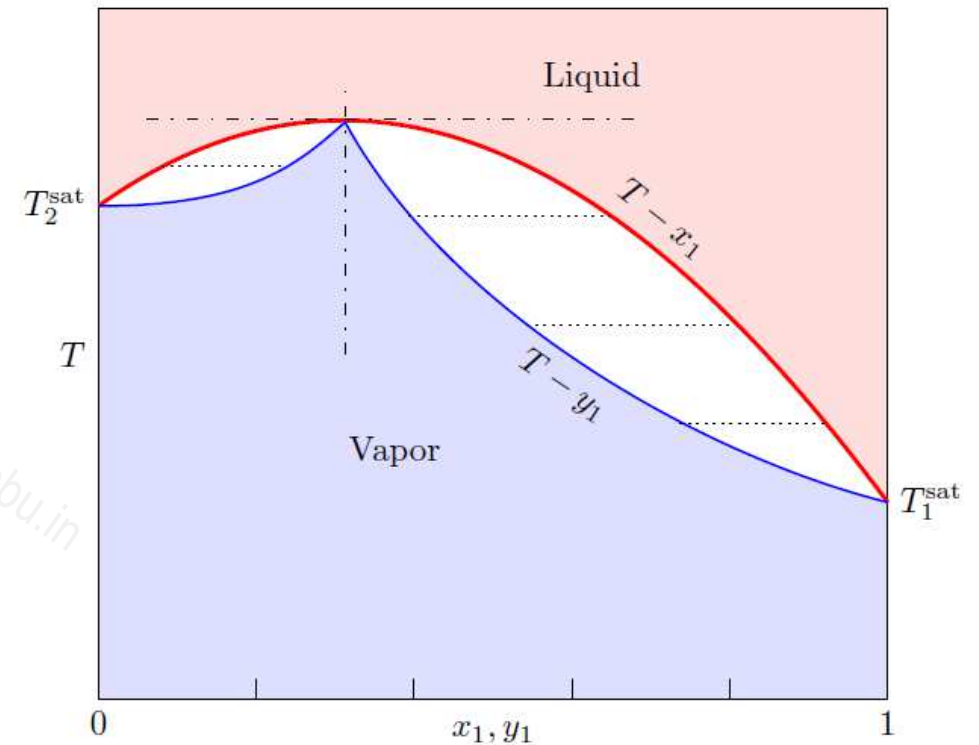
Constant Pressure Equilibria ( $Txy$  diagram)  
Minimum boiling azeotrope

Ex: Ethanol - water system.

# Maximum Boiling Azeotrope



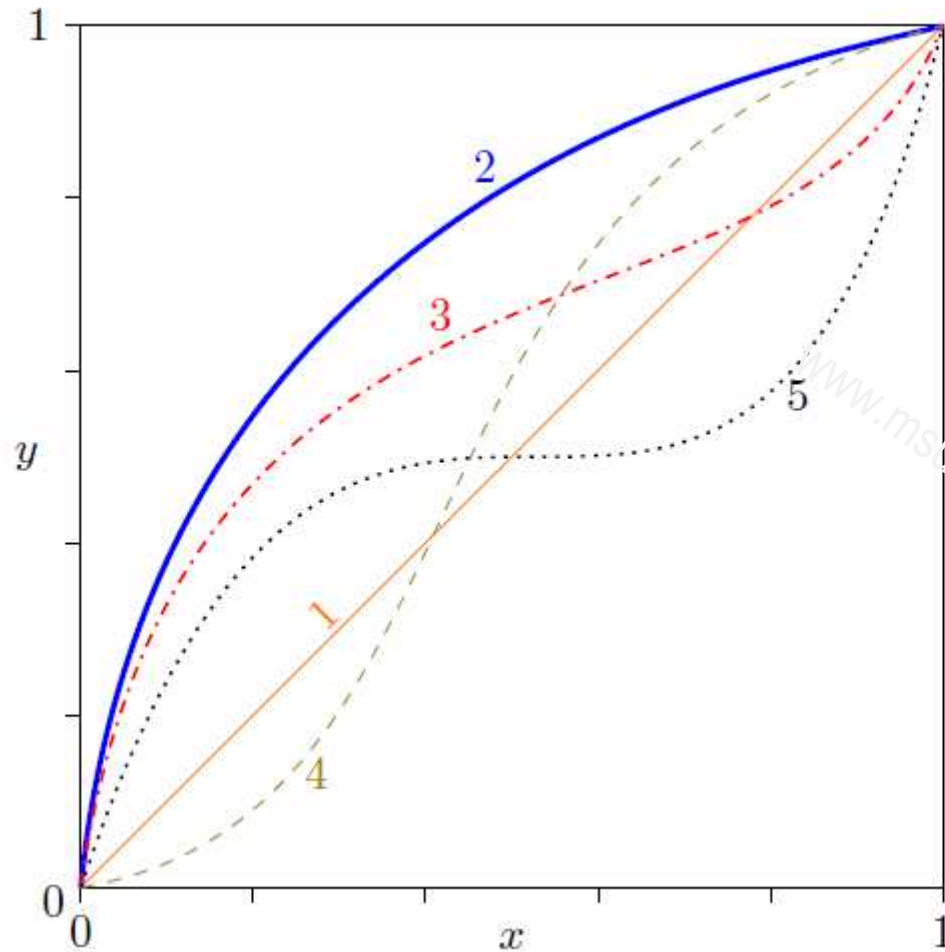
Constant Temperature Equilibria ( $Pxy$  diagram)  
Maximum boiling azeotrope



Constant Pressure Equilibria ( $Txy$  diagram)  
Maximum boiling azeotrope



# $x$ - $y$ Diagrams

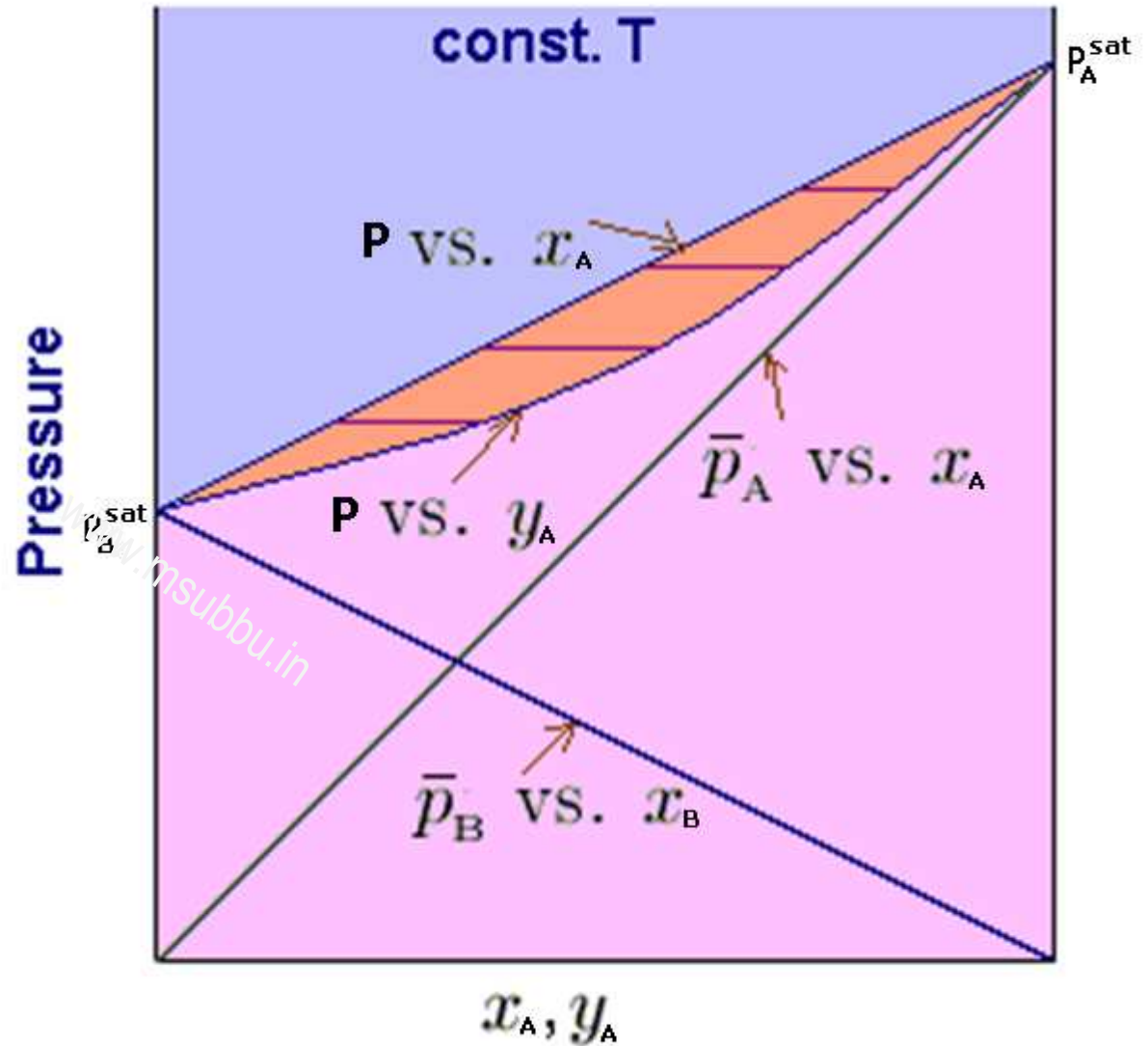


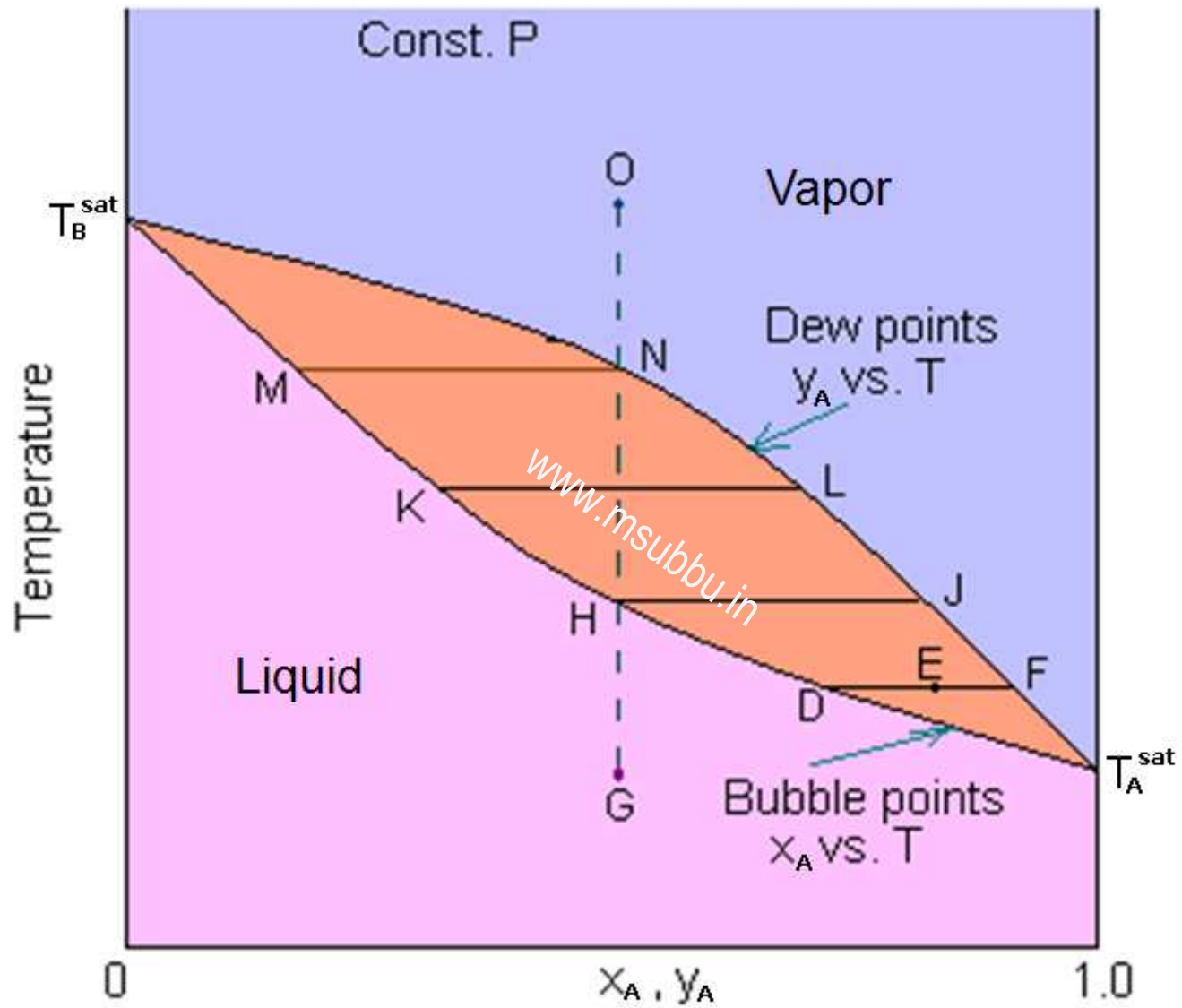
- 1. Stereoisomers,  $\alpha = 1$
- 2. Ideal solutions
- - - 3. Minimum boiling azeotropes
- - - 4. Maximum boiling azeotropes
- ..... 5. Heteroazeotropes

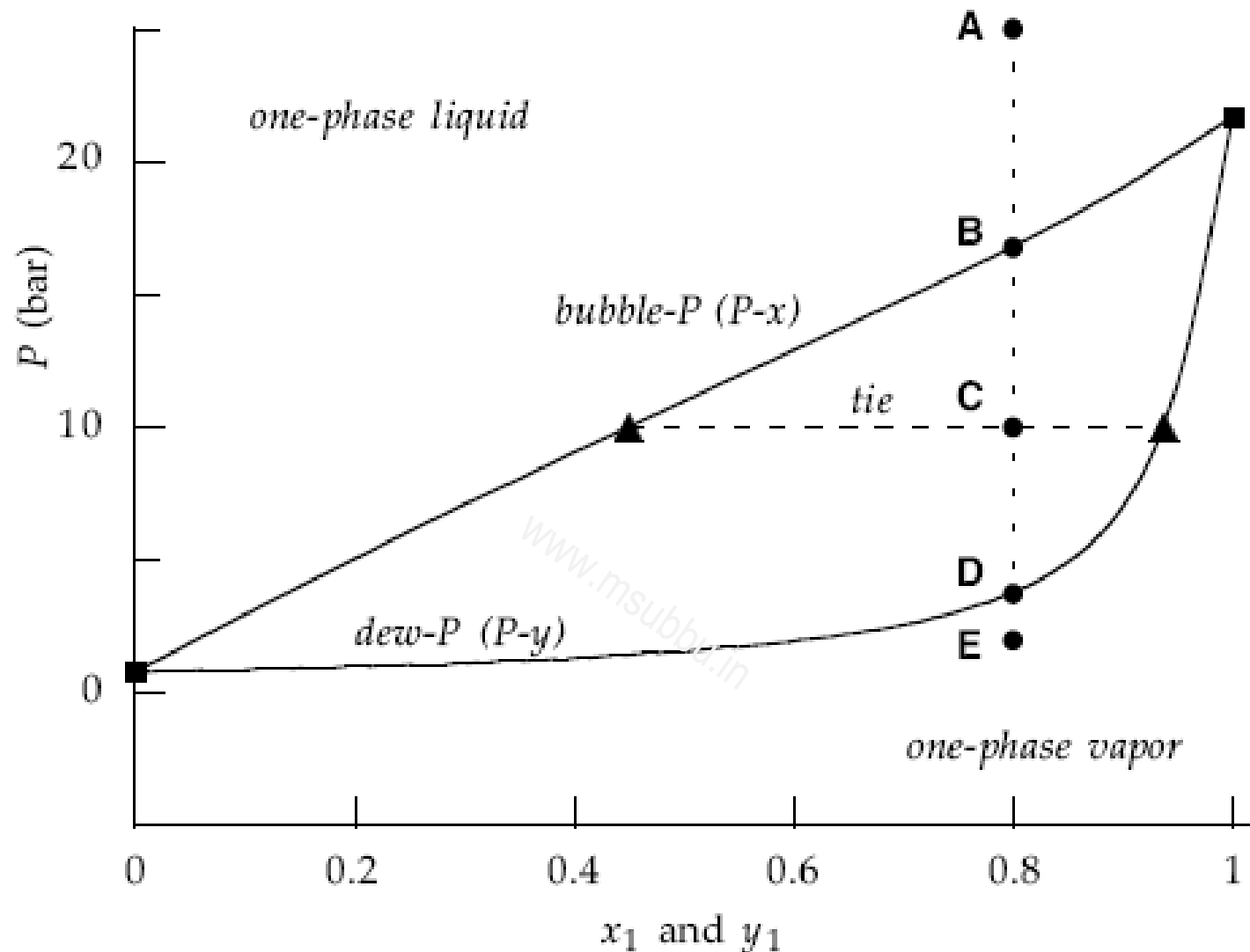
# Raoult's Law

$$P = x_A P_A^{\text{sat}} + x_B P_B^{\text{sat}}$$

$$y_A = x_A P_A^{\text{sat}} / P$$







**Figure 9.4** Isothermal  $Pxy$  diagram at 330 K computed from the Redlich-Kwong equation of state. Component 1 is an alkane; 2 is an aromatic. Broken vertical line represents a reversible isothermal expansion from one-phase liquid at A to one-phase vapor at E. Broken horizontal line is the vapor-liquid tie line at 10 bar. Filled squares mark pure-component vapor pressures at 330 K. Note that component 1 is more volatile than component 2.

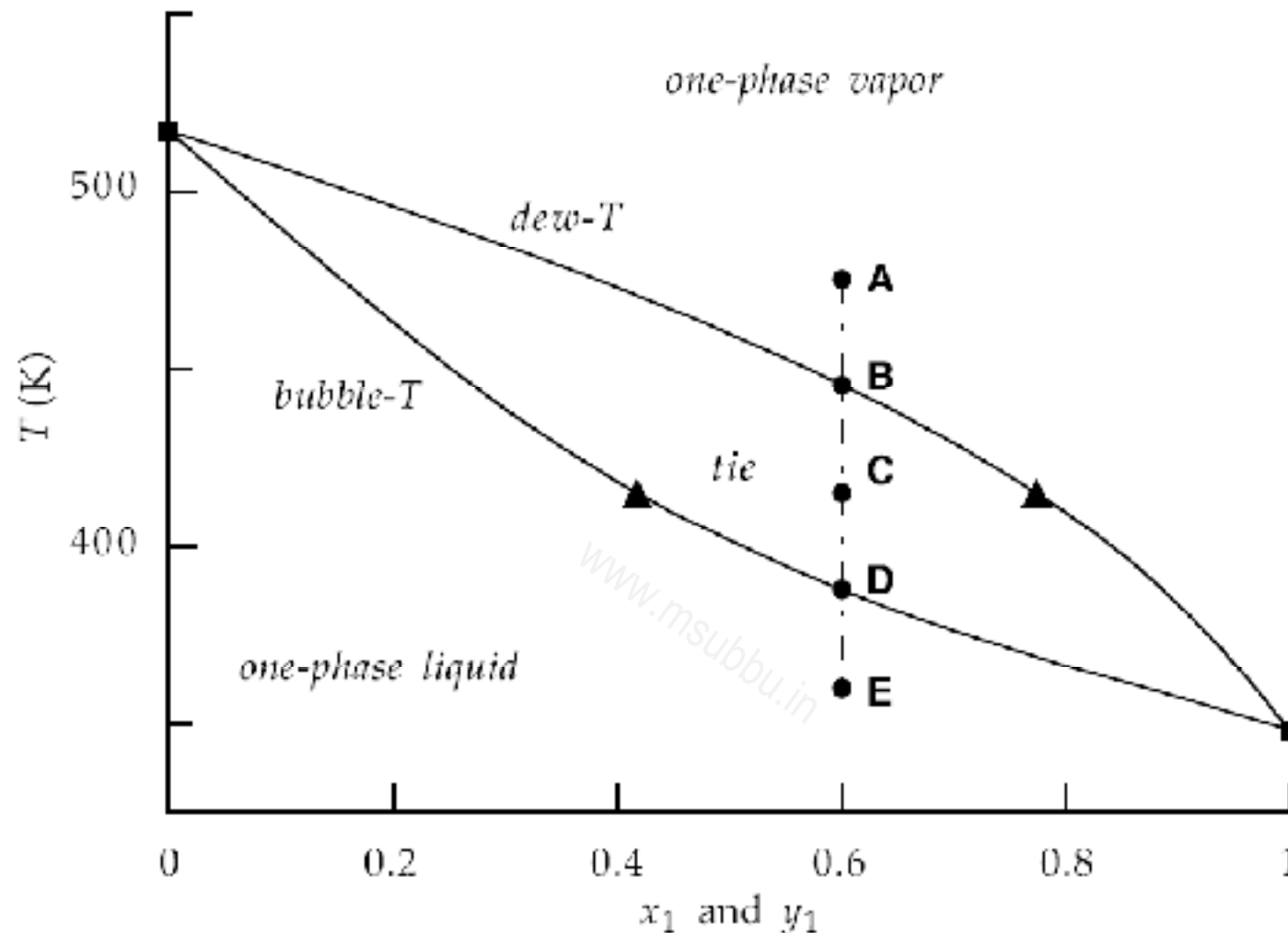


Figure 9.6 Isobaric  $Txy$  diagram at 30 bar for the same alkane(1)-aromatic(2) mixture shown in Figure 9.4. The broken vertical line represents a reversible isobaric cooling from one-phase vapor at A to one-phase liquid at E. The broken horizontal line is the vapor-liquid tie line at 415 K. Filled squares are pure-component boiling points at 30 bar.

# Effect of Temperature

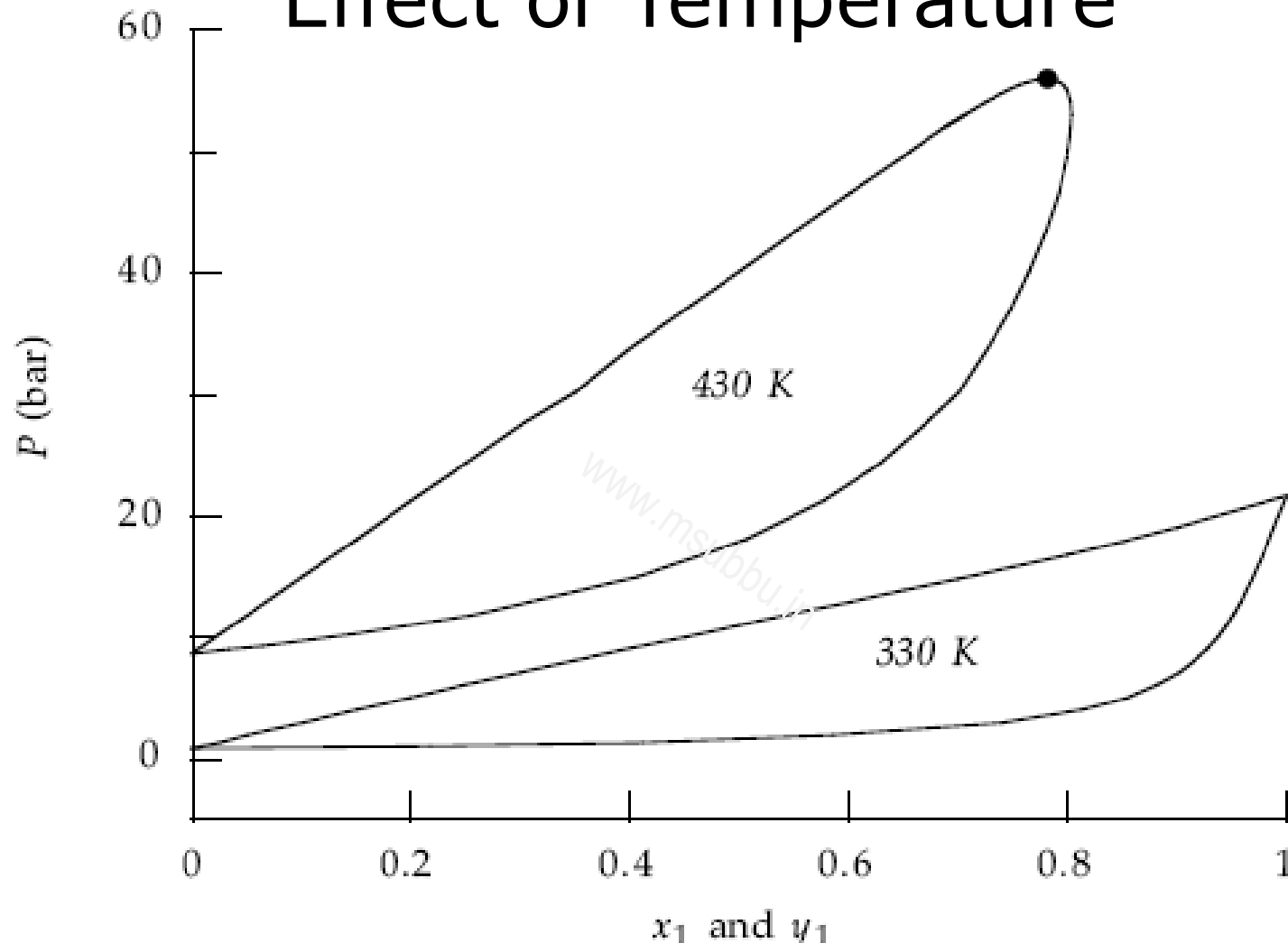


Figure 9.5 Effect of temperature on the  $Pxy$  diagram for the alkane(1)-aromatic(2) mixture of Figure 9.4. The 330 K-isotherm is subcritical, but the 430 K-isotherm has a critical point (dot) at 56.1 bar and  $z_1 = 0.781$ . Computed from Redlich-Kwong equation.

# Effect of Pressure

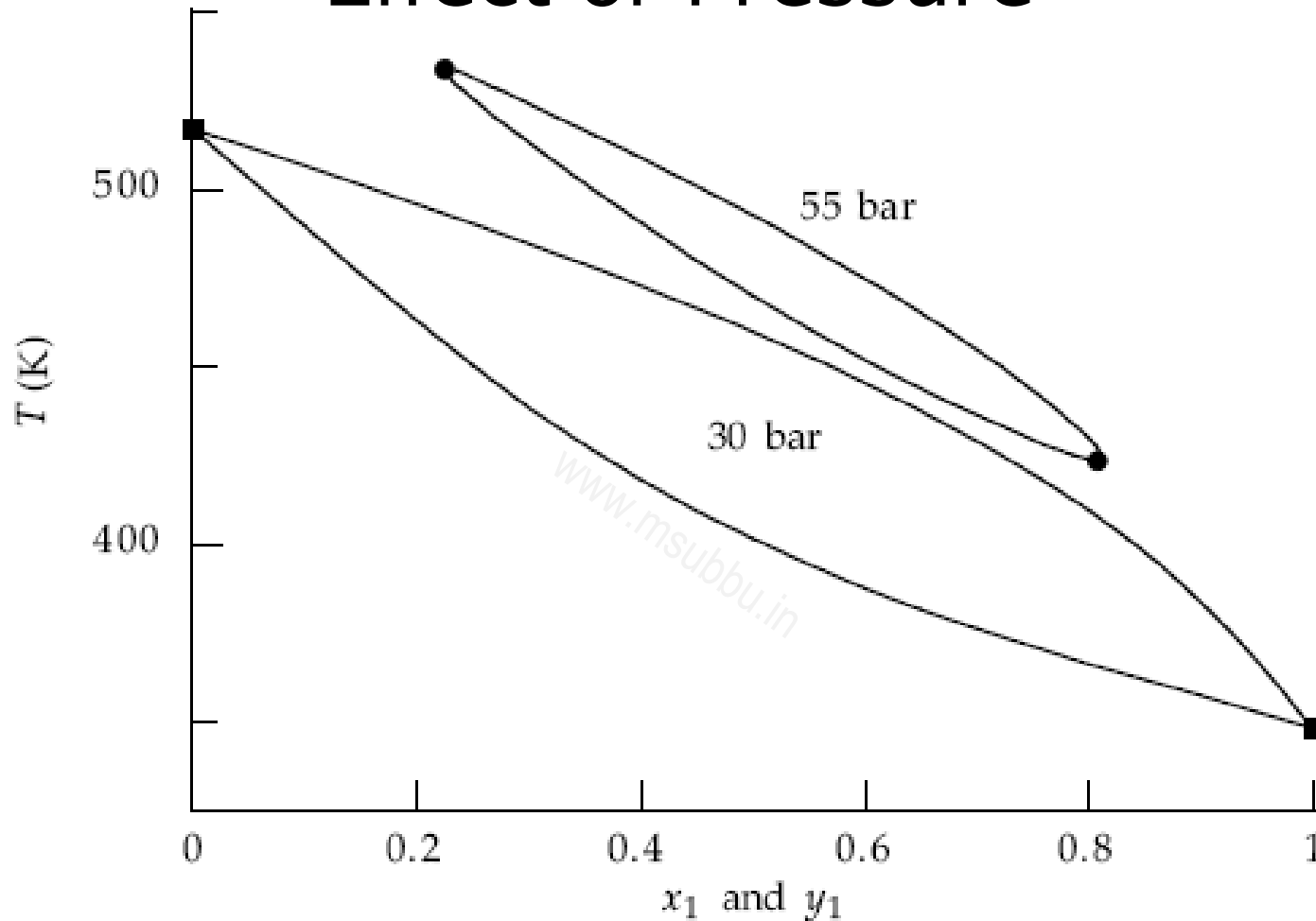


Figure 9.7 Effect of pressure on the  $Txy$  diagram for the alkane(1)-aromatic(2) mixture of Figure 9.6. At 30 bar all these mixtures are subcritical, but at 55 bar two critical points occur (dots): one at 423.55 K with  $z_1 = 0.8075$  and another at 533.60 K with  $z_1 = 0.2255$ . Filled squares mark pure-component boiling points at 30 bar.

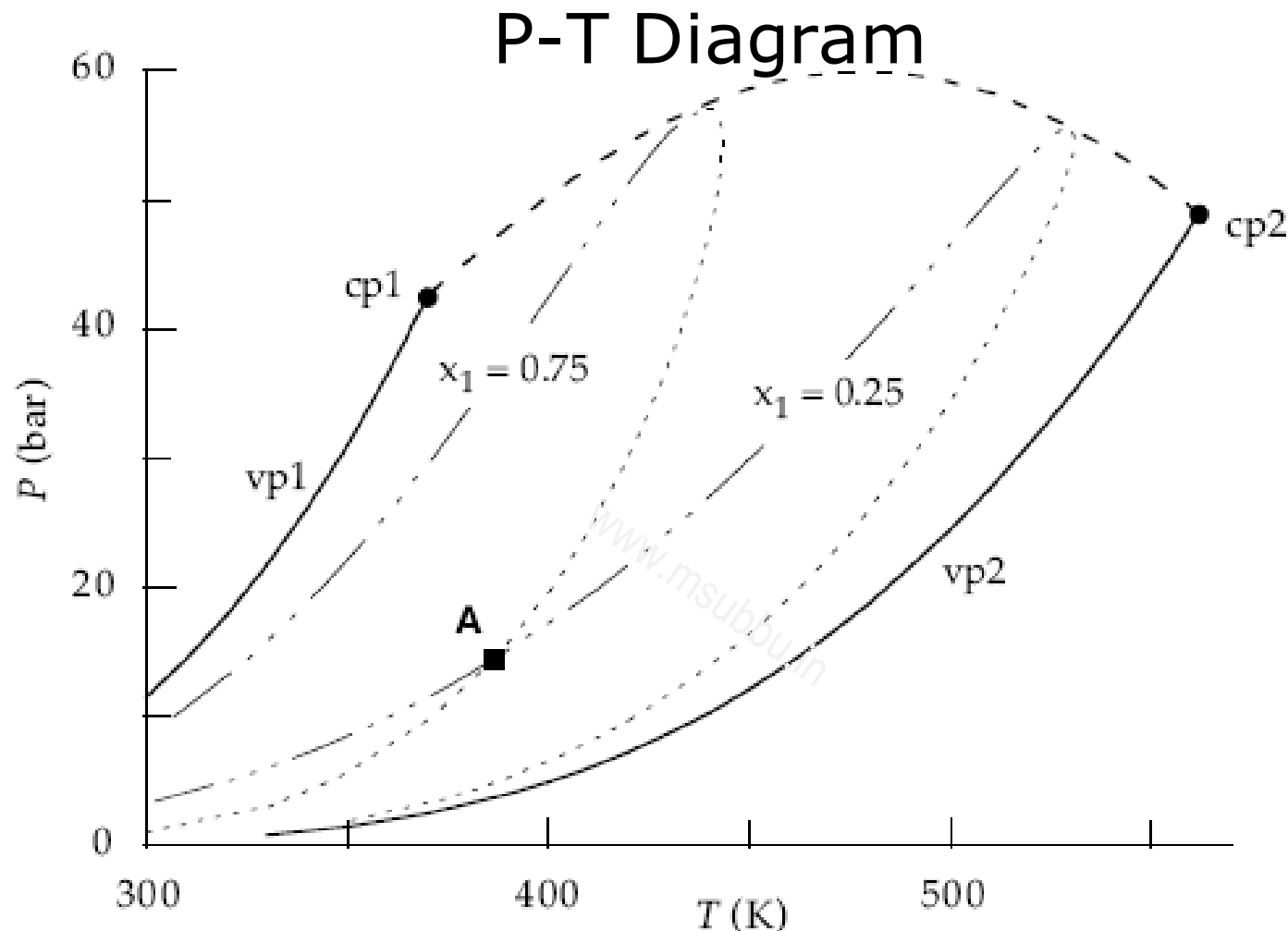


Figure 9.8 Pressure-temperature diagram for the alkane(1)-aromatic(2) mixture in Figures 9.4-9.7. Solid lines are pure vapor-pressure curves, ending at pure critical points (filled circles). Dashed line is the mixture critical line. Dash-dot lines are liquid constant-composition lines; small dashed lines are vapor constant-composition lines. Filled square at A is a vapor-liquid equilibrium point; it occurs at 14.5 bar, 386.7 K,  $x_1 = 0.25$ ,  $y_1 = 0.75$ .



# Deviation from Ideal Solution

- The activity coefficients express the departure from ideality and thus define the excess Gibbs energy of the solution.
- Deviation from ideality is said to be positive when  $\gamma > 1$  ( $\ln \gamma$  is positive) and negative when  $\gamma < 1$  ( $\ln \gamma$  is negative).

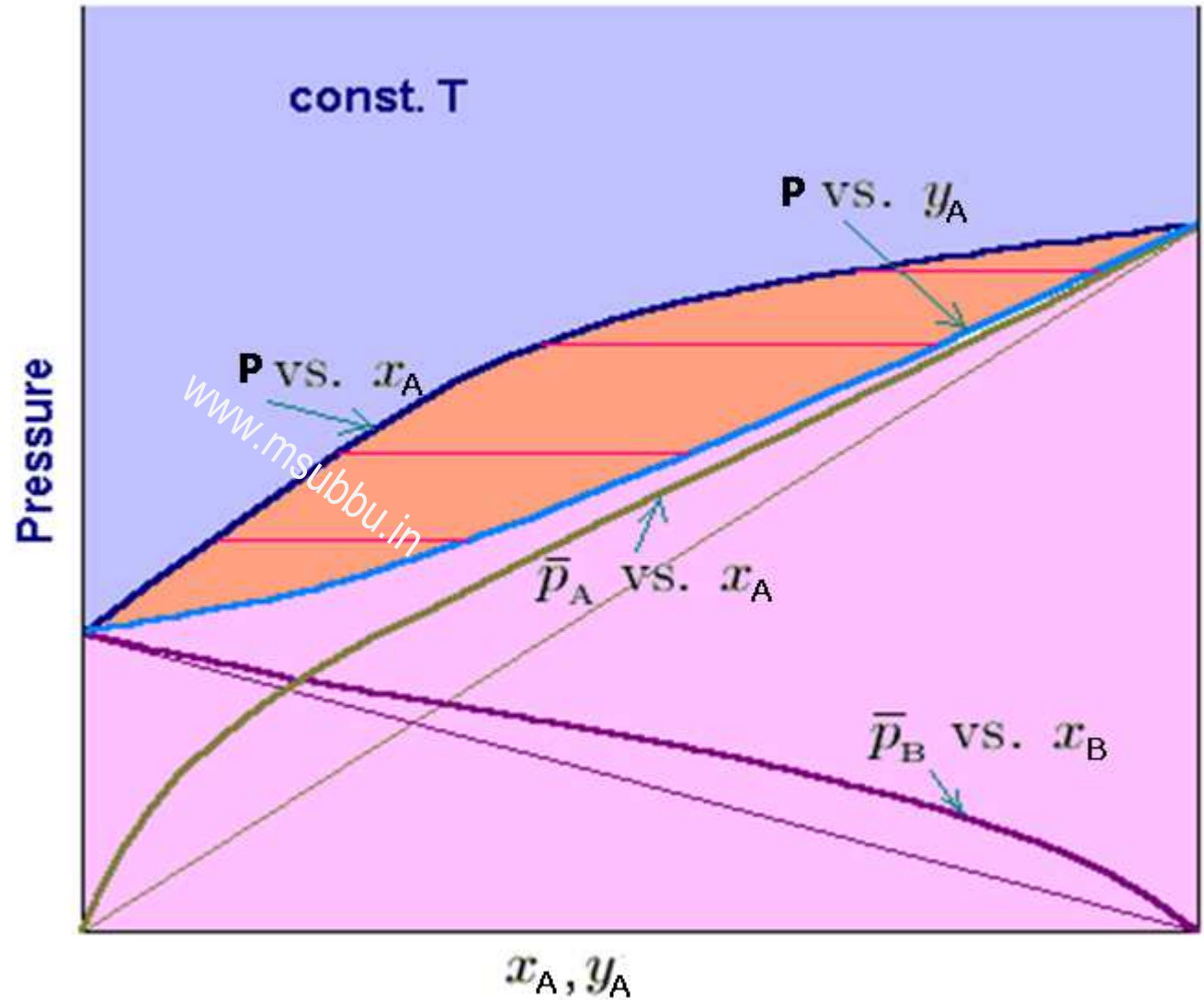
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# Positive Deviation from Raoult's Law

$$P = \gamma_A x_A p_A^{\text{sat}} + \gamma_B x_B p_B^{\text{sat}}$$

$\gamma_i$  greater than 1

$\ln \gamma_i$  positive

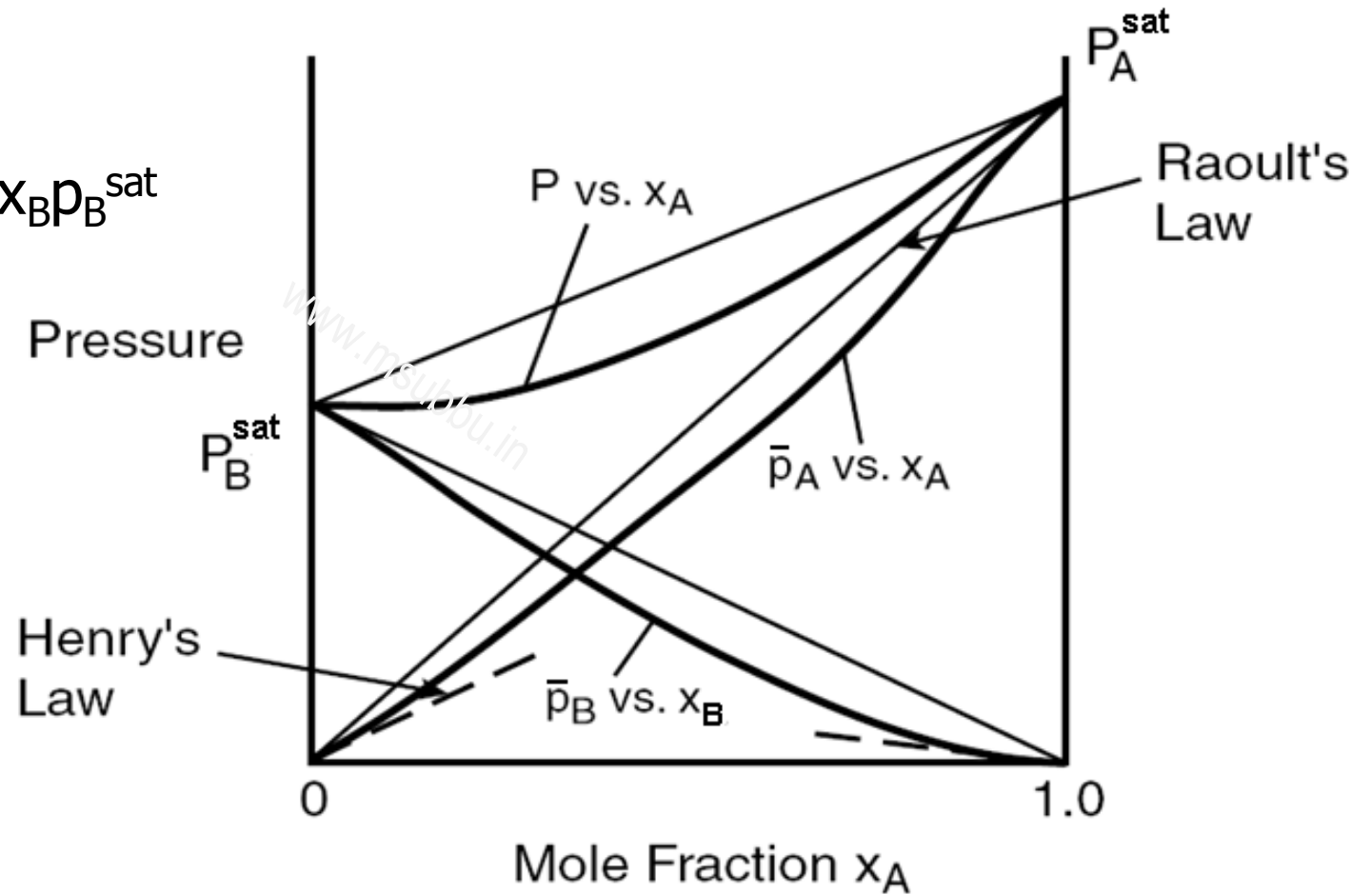


# Negative Deviation From Raoult's Law

$$P = \gamma_A x_A p_A^{\text{sat}} + \gamma_B x_B p_B^{\text{sat}}$$

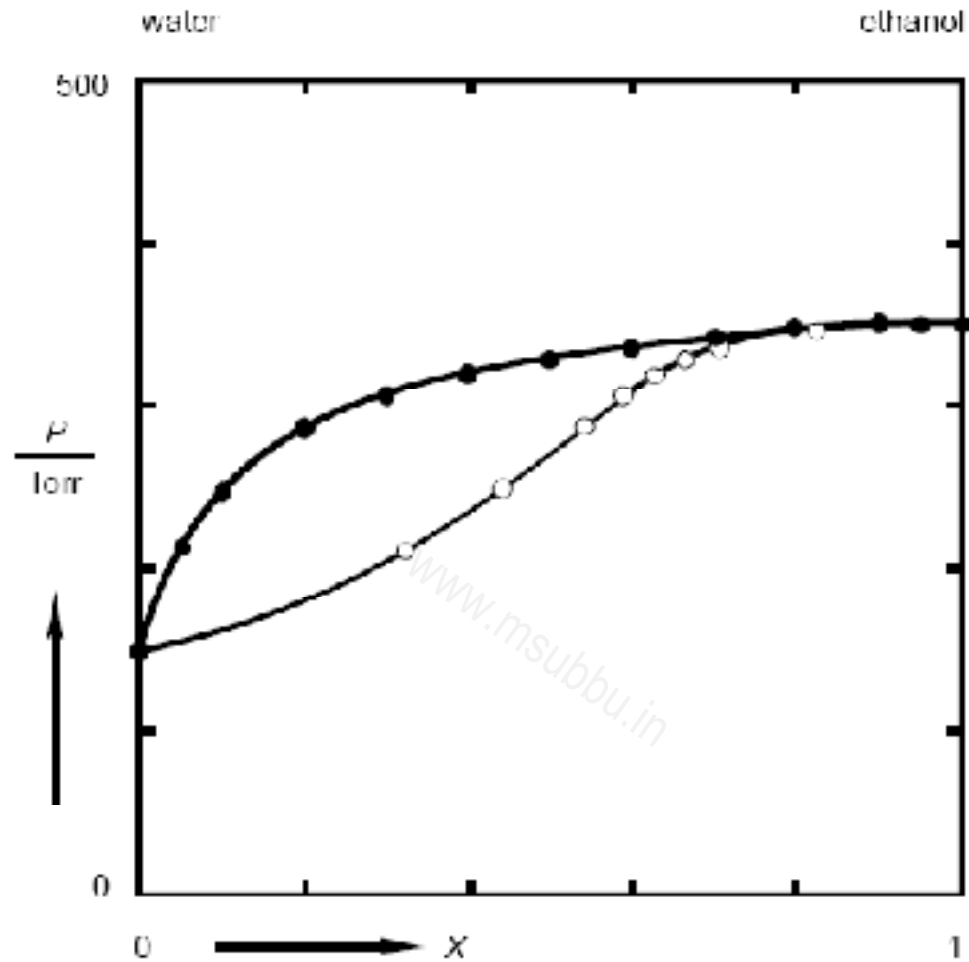
$\gamma_i$  less than 1

$\ln \gamma_i$  negative

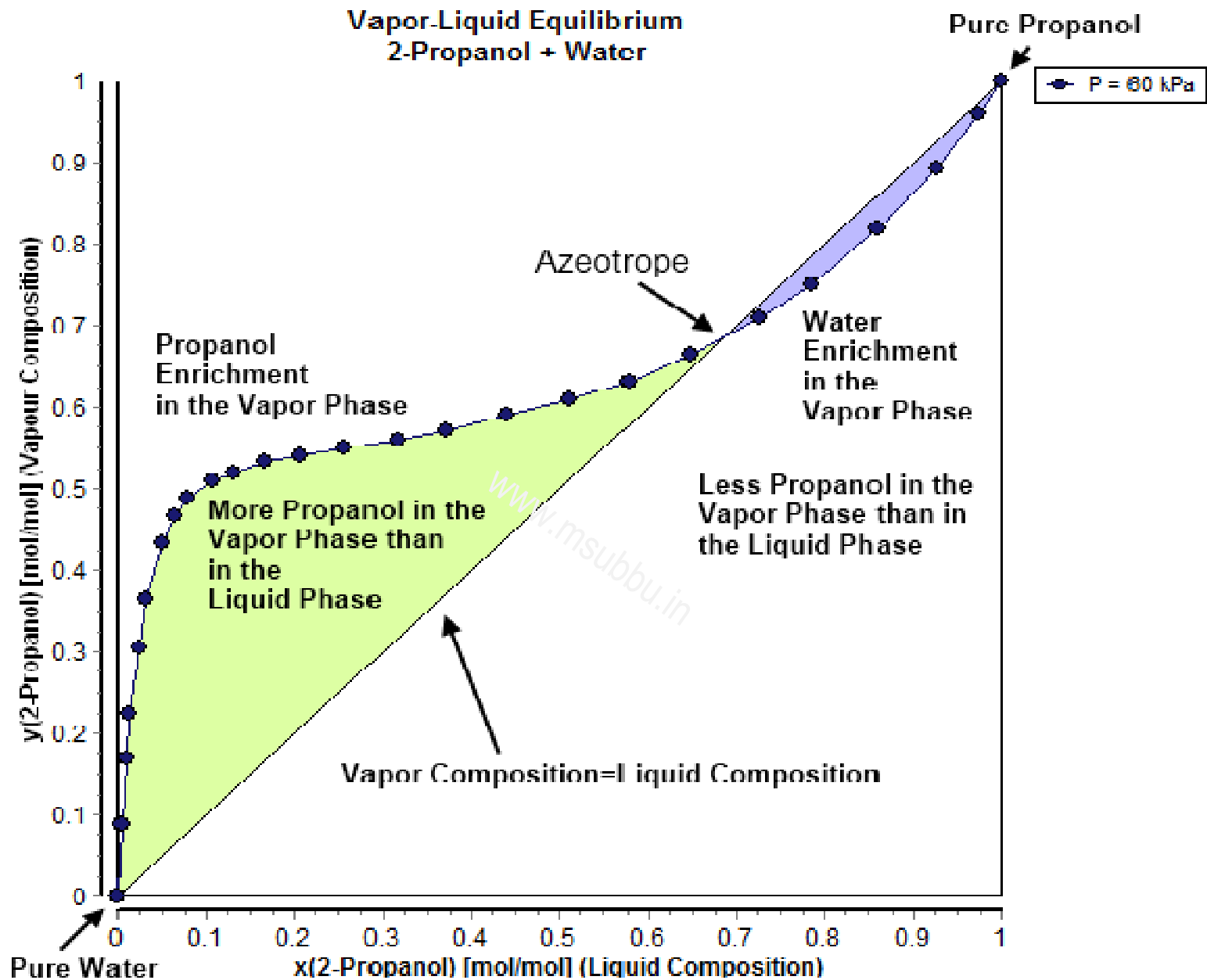


# Azeotropes

- If azeotropes are not present, a fractional distillation can eventually separate the mixture into the pure components, with the component with the higher vapor pressure ending up as the distillate and the less volatile component (known as the residue) left in the distillation pot.
- For a minimum boiling azeotrope, a fractional distillation can produce a distillate with the azeotropic composition and a residue that is one of the pure components, depending on the composition of the starting mixture.
- For a maximum boiling azeotrope a fractional distillation can produce one of the pure components as the distillate, and a residue with the azeotropic composition.



Liquid + vapour equilibrium in the system water + ethanol at 60 °C. Filled circles represent liquid phase; open circles vapour phase

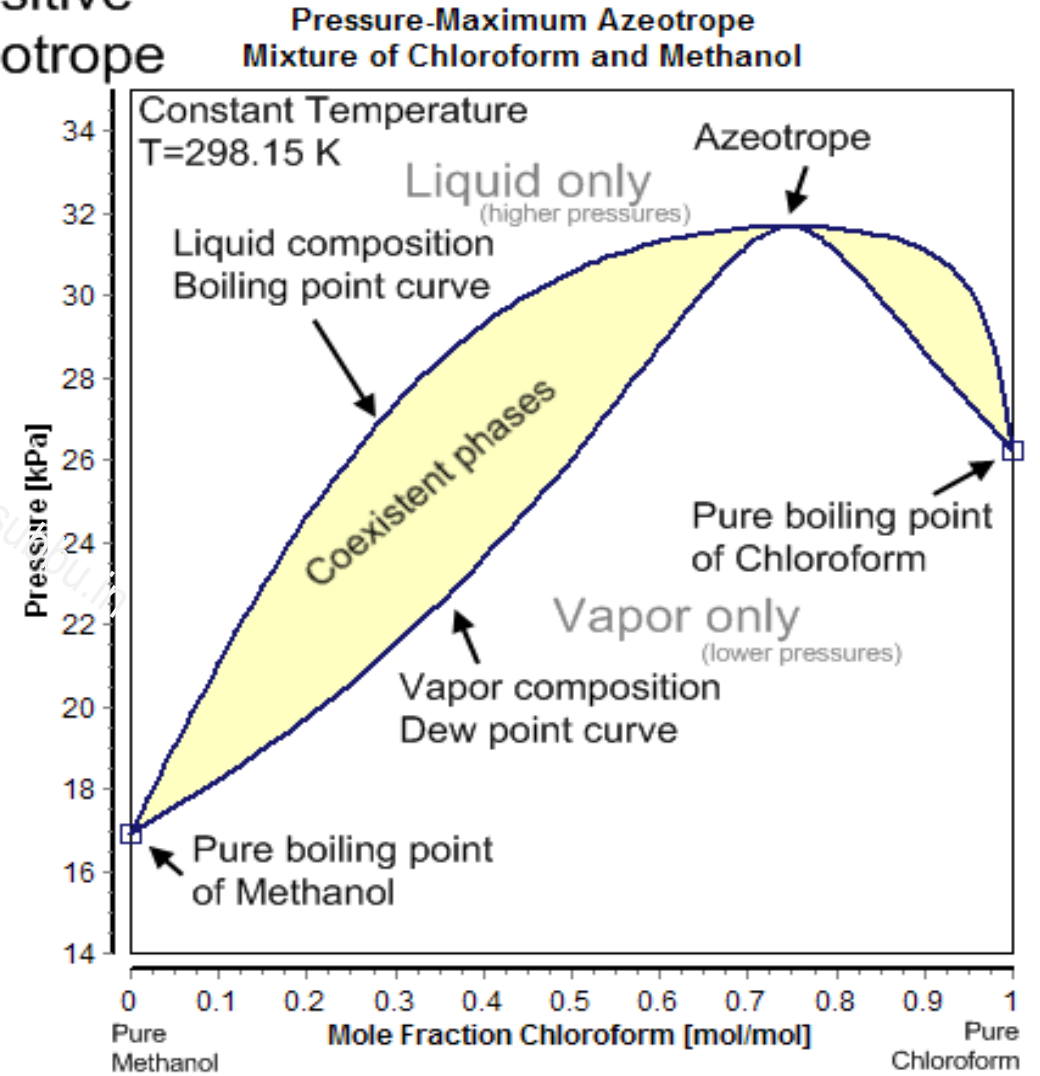
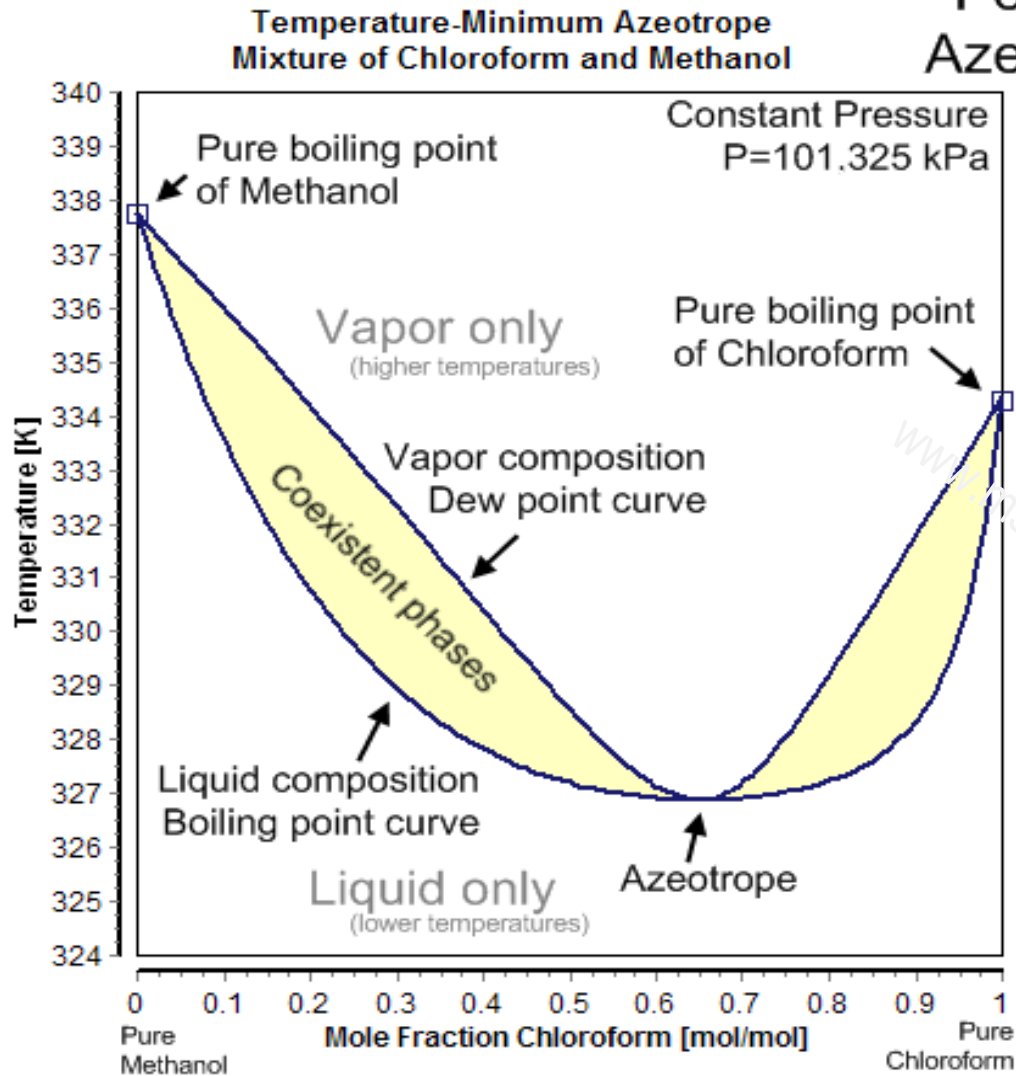


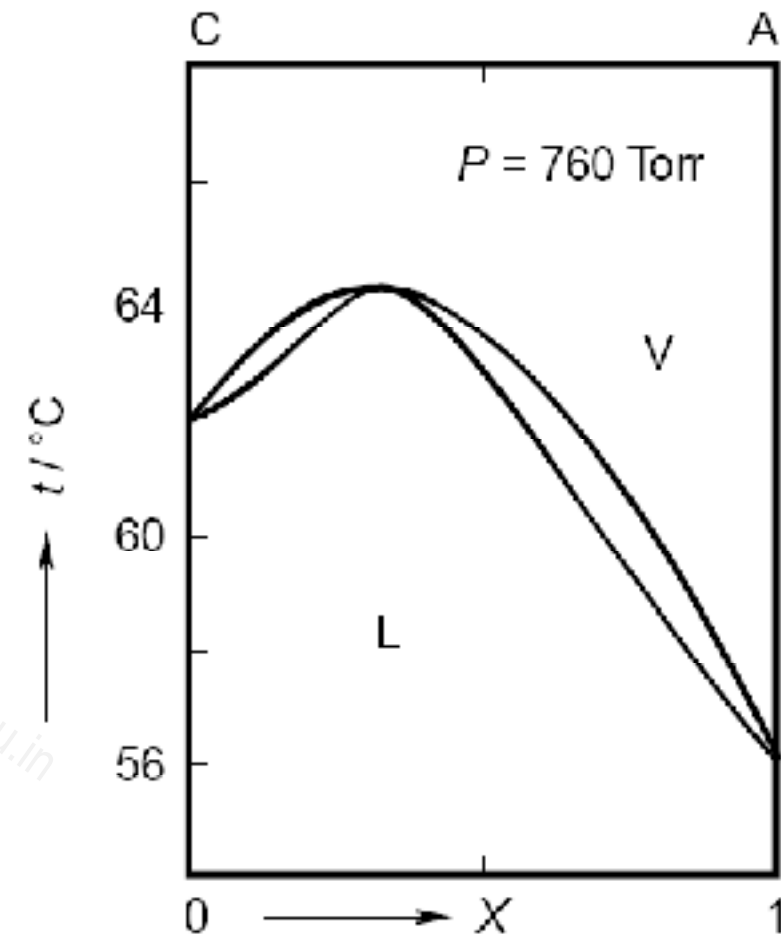
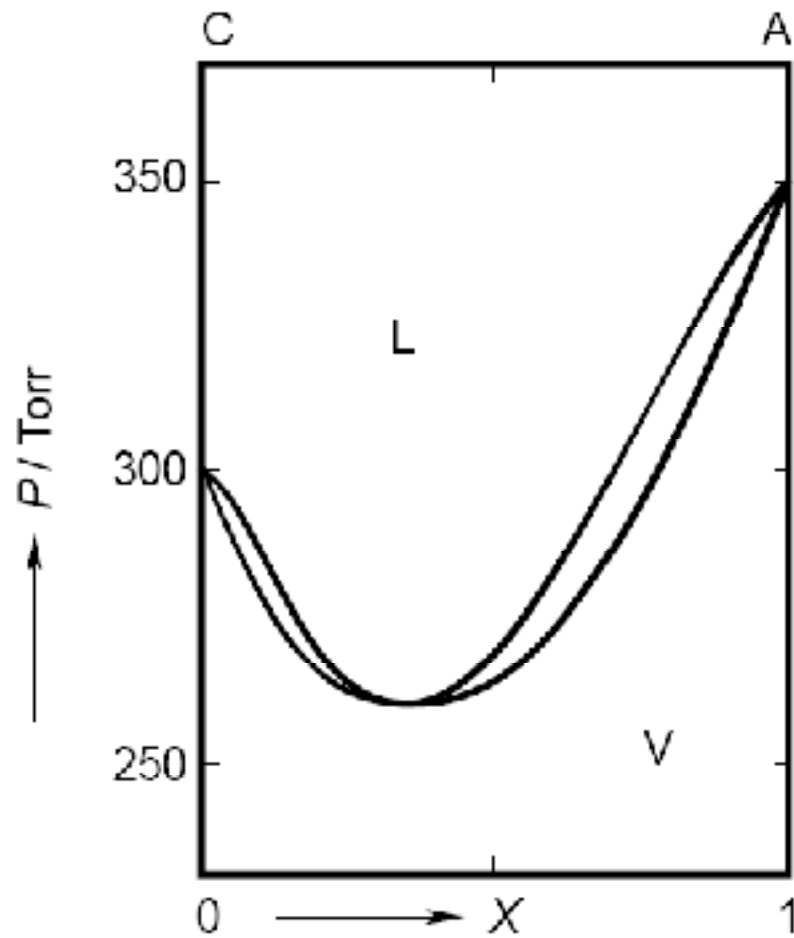
Data taken from Dortmund Data Bank

Original Source: Marzal P., Monton J.B., Rodrigo M.A., J.Chem.Eng.Data, 41(3), 608-611, 1996

Curves calculated by mod. UNIFAC (Dortmund)

## Positive Azeotrope





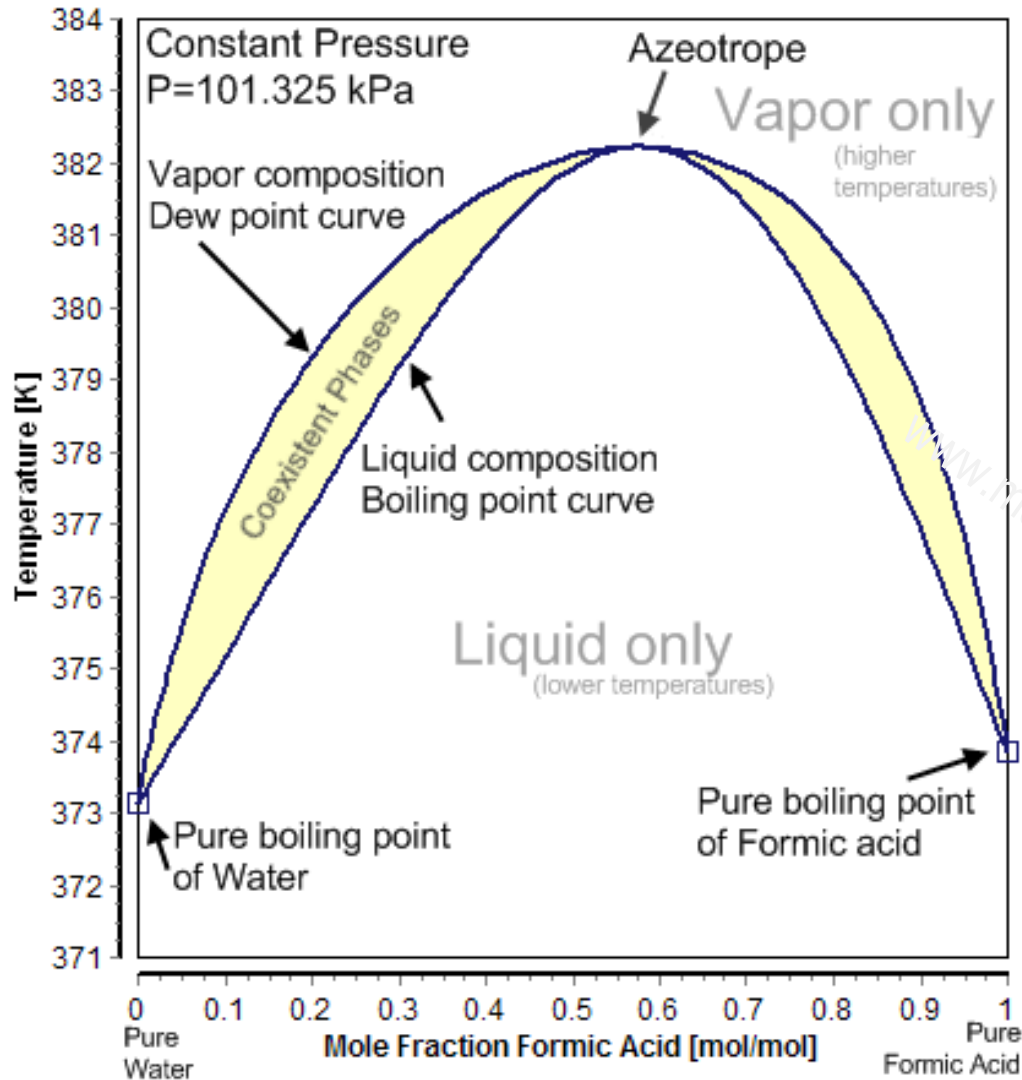
For the (liquid + vapour) equilibrium in the system {chloroform (C) + acetone (A)}, a minimum in the isothermal diagram ( $t = 35.2\text{ }^{\circ}\text{C}$ , left, Apelblat et al. 1980), goes together with a maximum in the isobaric diagram (right, Reinders and de Minjer 1940)



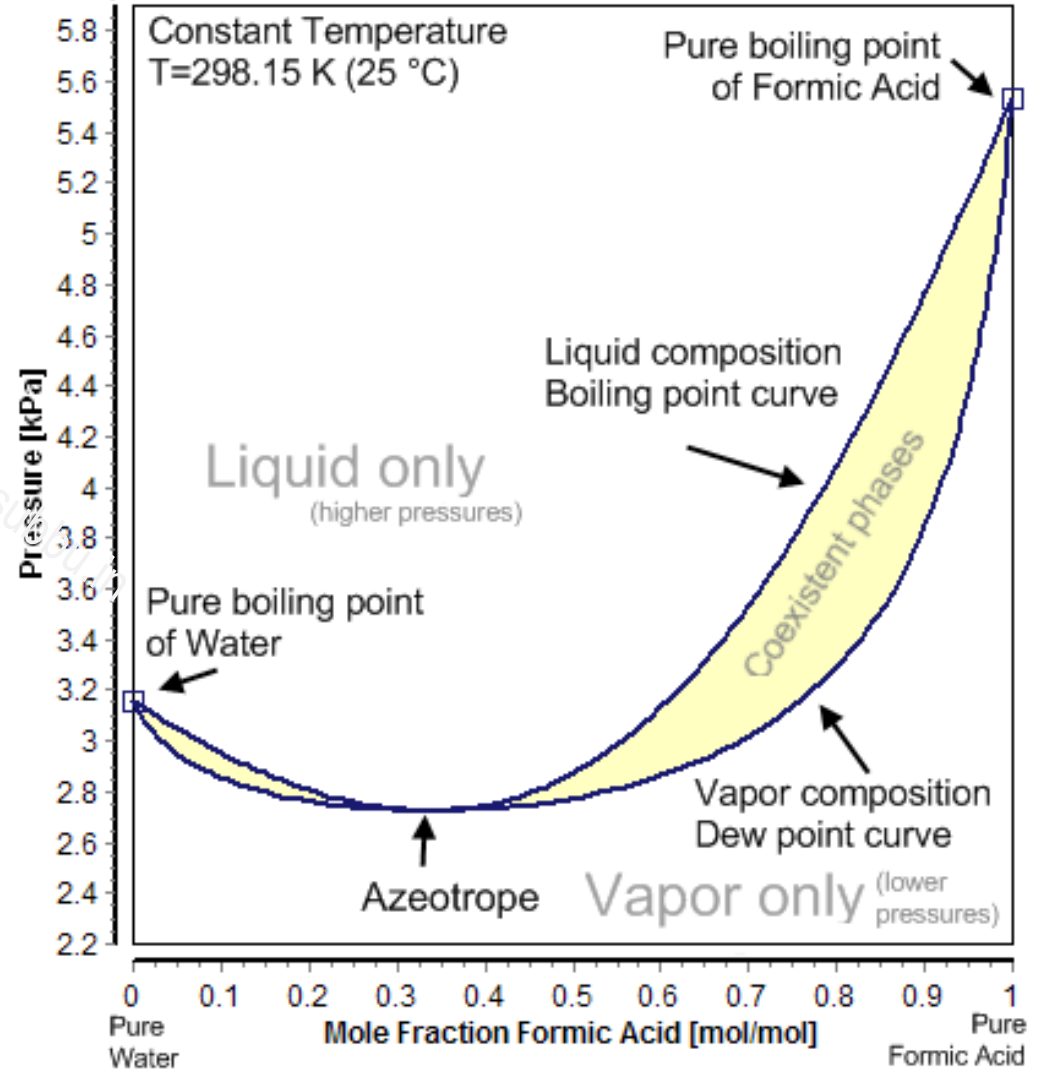
Curve calculated with mod. UNIFAC (Dortmund)

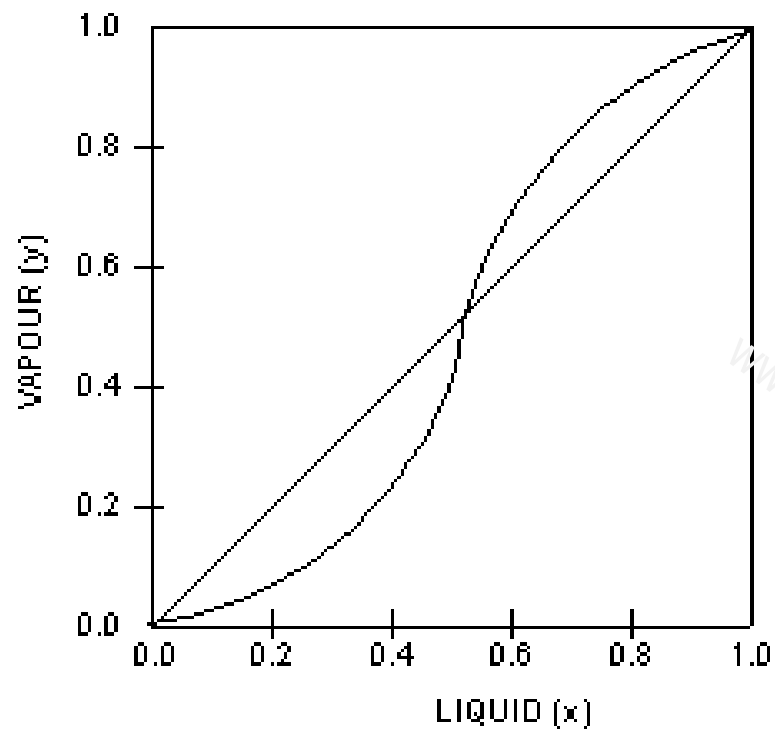
## Negative Azeotrope

### Temperature-Maximum Azeotrope Mixture of Water and Formic Acid

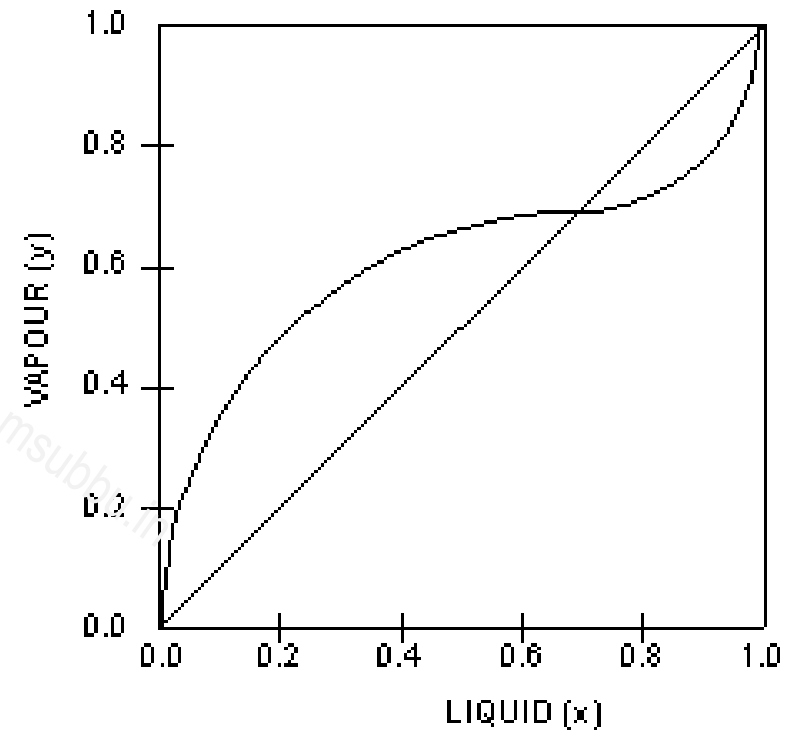


### Pressure-Minimum Azeotrope Mixture of Water and Formic Acid



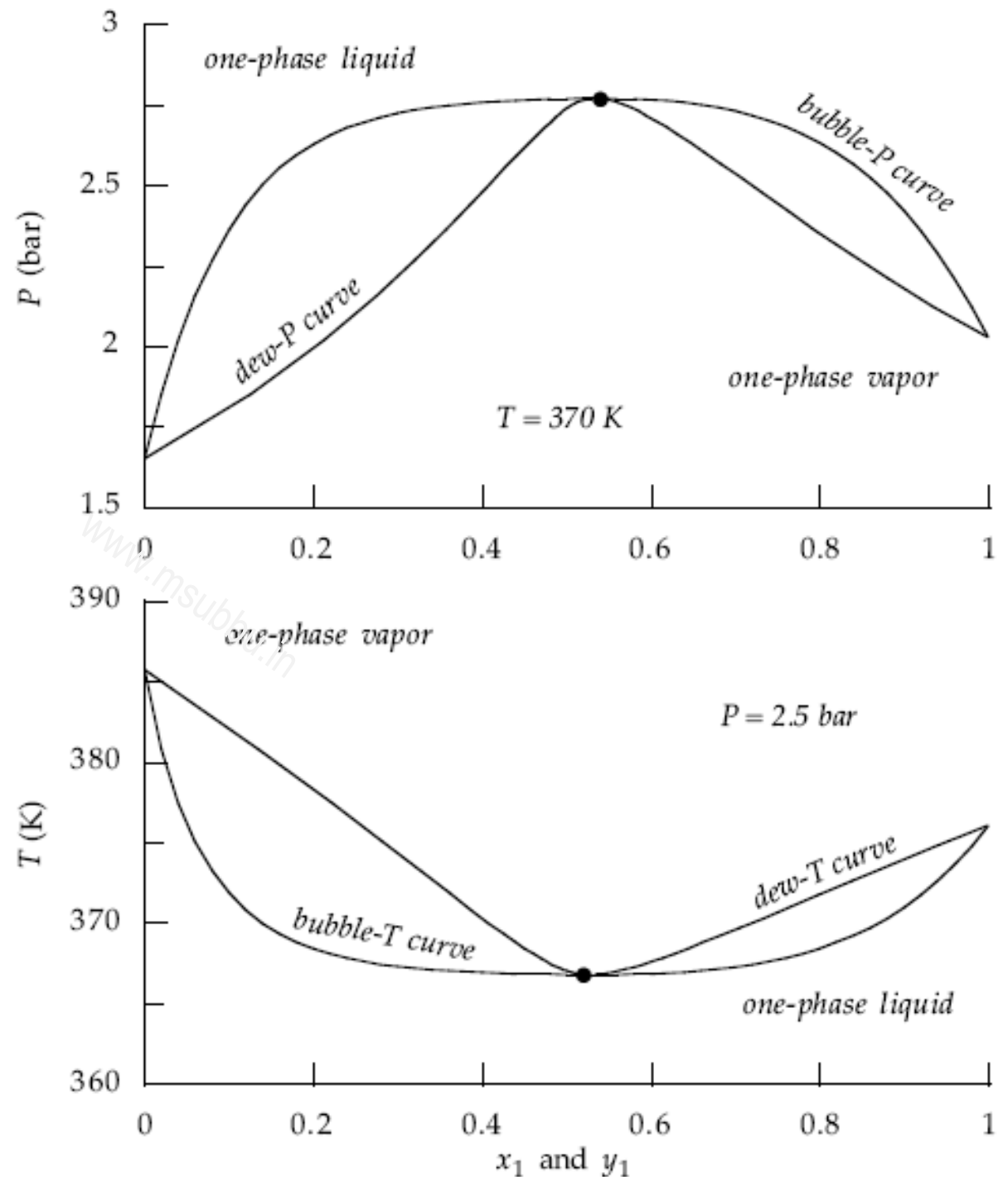


Maximum Boiling Point

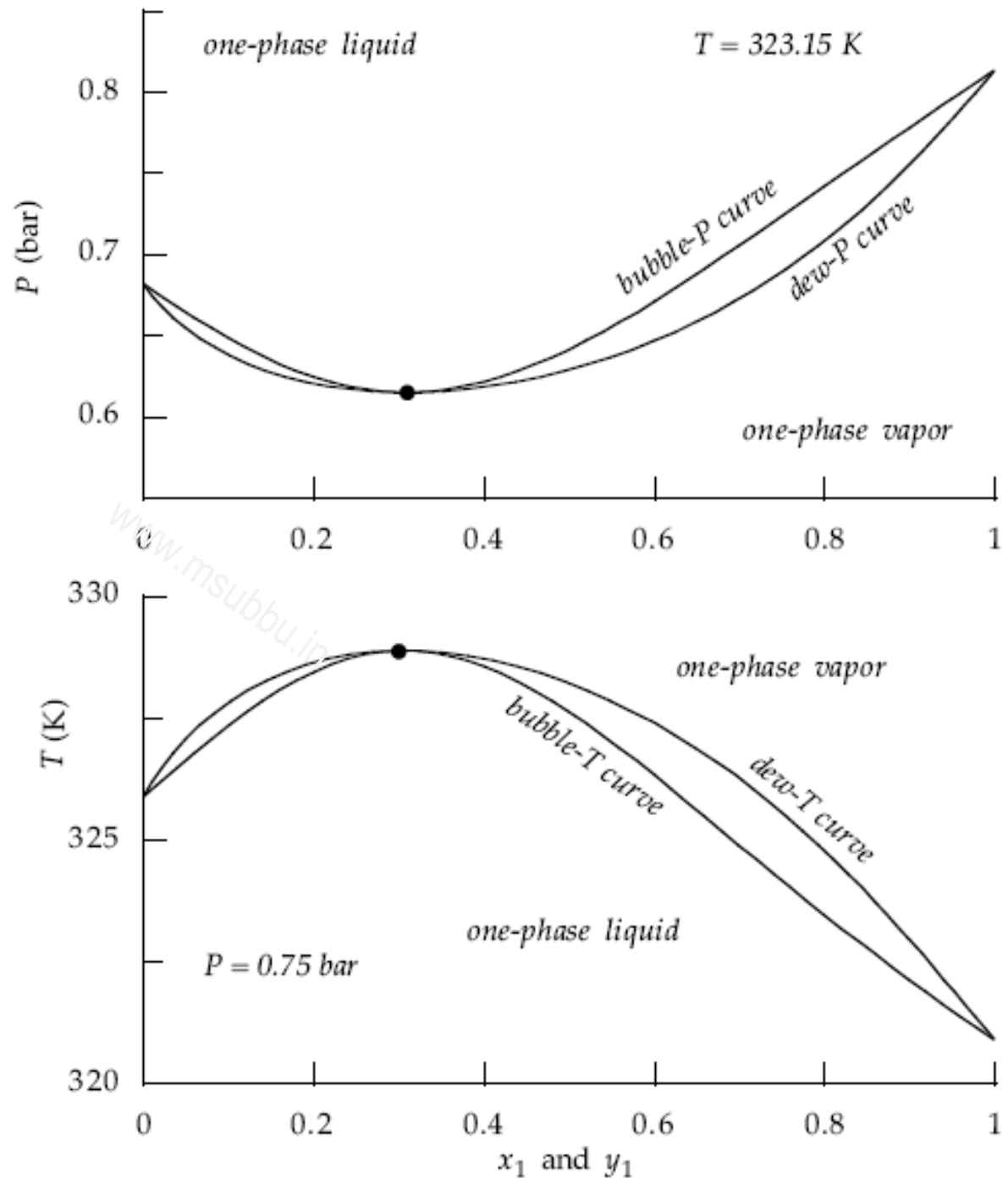


Minimum Boiling Point

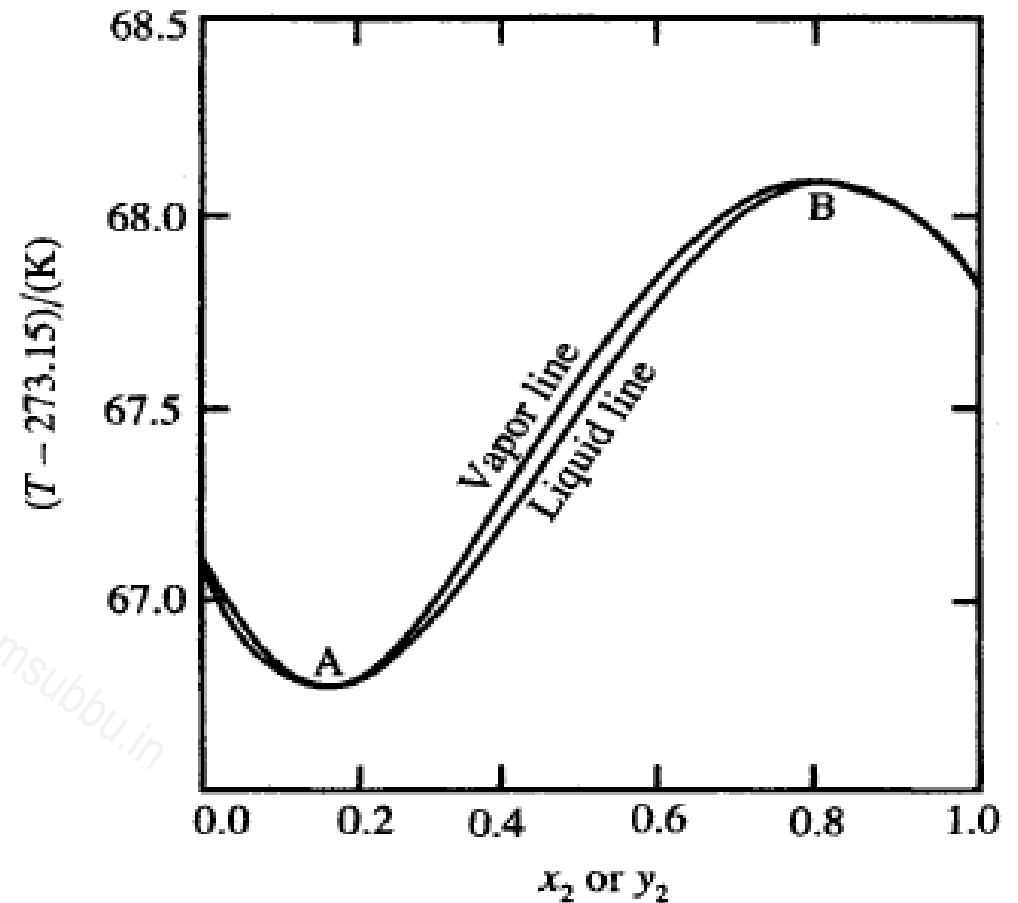
Positive homogeneous azeotropes in mixtures of ethanol(1) and benzene(2). The  $Pxy$  diagram is at 370 K, and the  $Txy$  diagram is at 2.5 bar. Filled circles locate the azeotropes.



Negative homogeneous azeotropes (dots) in mixtures of acetone(1) and chloroform(2). The  $Pxy$  diagram is at  $50^\circ\text{C}$ ; the  $Txy$  diagram is at  $0.75$  bar.



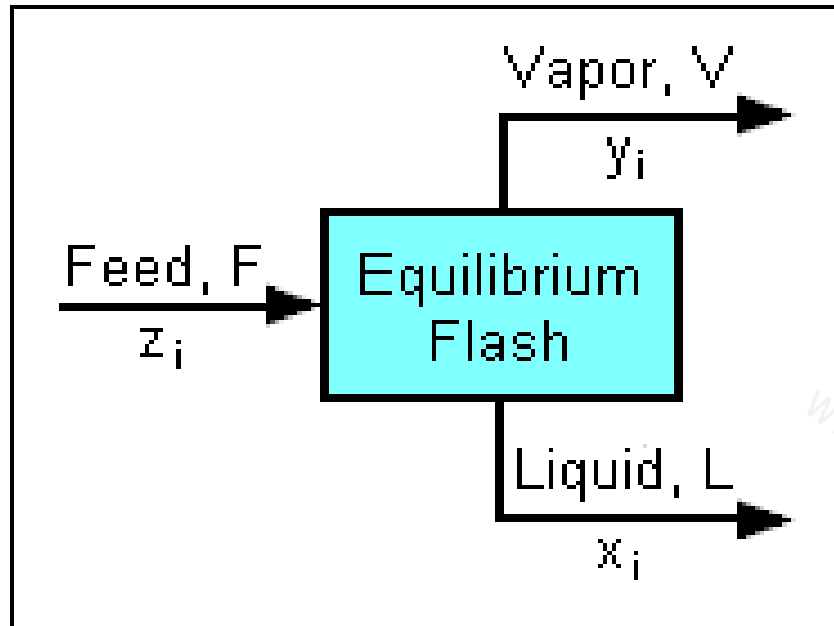
# Double Azeotrope



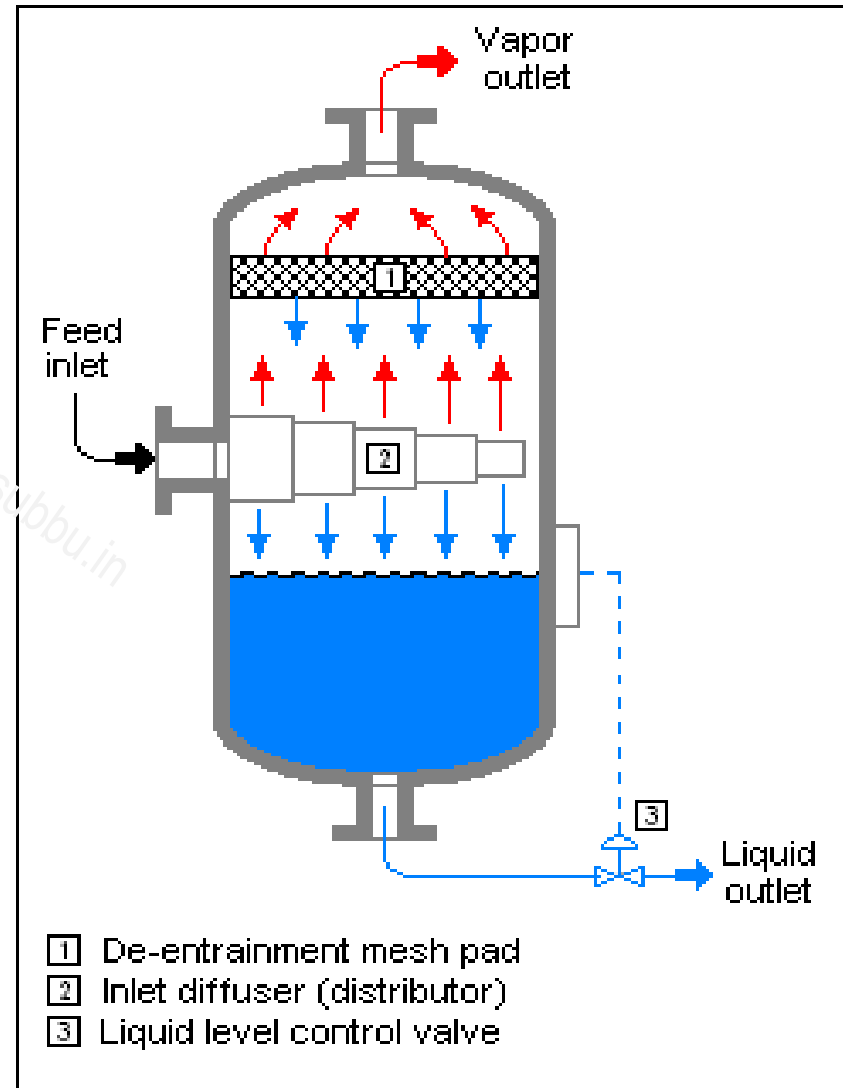
**Figure 14.3** Boiling temperature against composition phase diagram for  $\{(x_1 \text{ or } y_1) \text{ C}_6\text{F}_6 + (x_2 \text{ or } y_2) \text{ C}_6\text{H}_6\}$  at a pressure of 0.664 MPa. Evident in the diagram is a minimum boiling azeotrope at point A and a maximum boiling azeotrope at point B. Reprinted with permission from W. J. Gaw and F. L. Swinton, "Occurrence of a Double Azeotrope in the Binary System Hexafluorobenzene + Benzene"; *Nature (London)*, **212**, 284 (1966). Copyright MacMillan Magazines Ltd.

# VLE Calculations of Non-ideal Solutions

- Obtain  $\gamma_i$  from azeotropic composition data
- Evaluate model parameters of  $\gamma_i$ - $x_i$  models based on the above data
- Make VLE calculation with  $y_i P = \gamma_i x_i P_i^{\text{sat}}$



The **equilibrium flash** of a multi-component liquid is also an isenthalpic process and may be visualized as a simple distillation process using a single equilibrium stage.



# VLE Problems

Problem Name	Knowns	Unknowns to find
Bubble P	$T, x_i$	$P, y_i$
Dew P	$T, y_i$	$P, x_i$
Bubble T	$P, x_i$	$T, y_i$
Dew T	$P, y_i$	$T, x_i$
Flash	$T, P, z_i$	$x_i, y_i, n^v/n$



# Henry's Law & Raoult's Law

- As early as in 1803 William Henry showed empirically that the vapor pressure of a solute  $i$  is proportional to the concentration of solute  $i$ :

$$p_i = x_i k_{H,i}$$

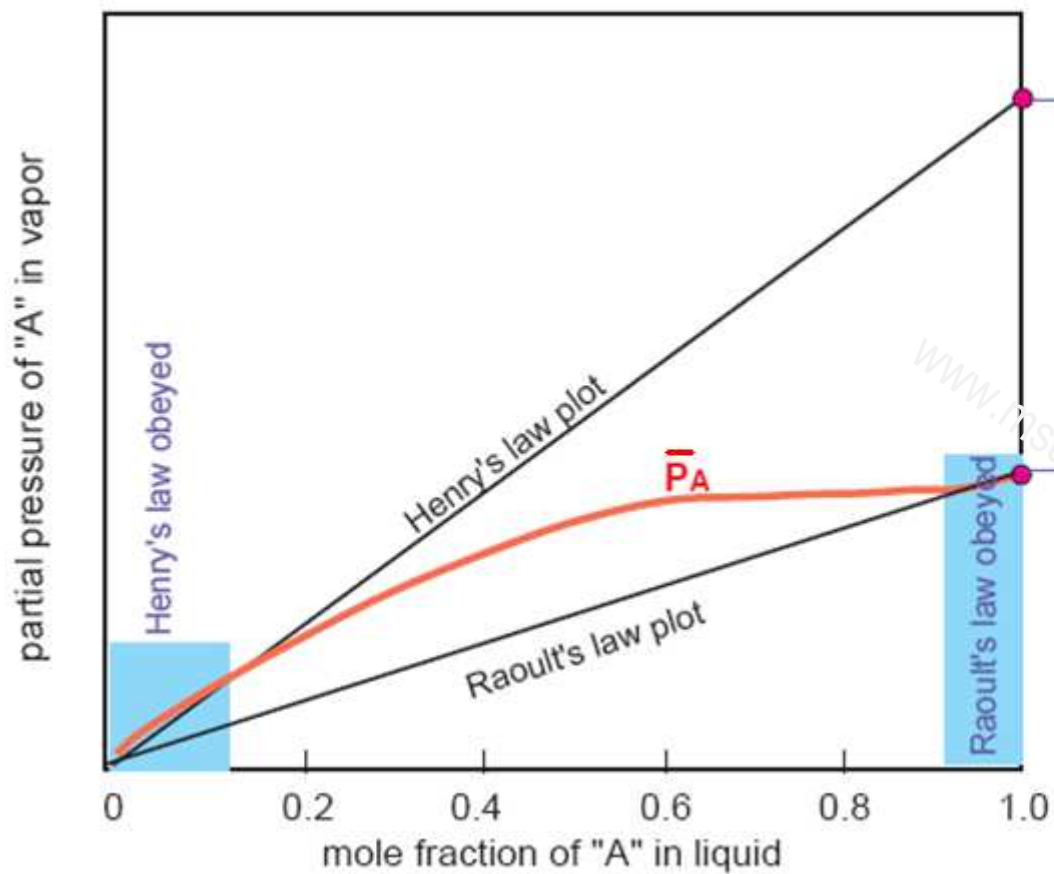
where  $x_i$  is the mole fraction solute and  $k_{H,i}$  is known as the **Henry's law constant**.

- More than 80 years later François Raoult demonstrated that at low concentrations of a solute, the vapor pressure of the solvent is simply

$$p_i = x_i p_i^*$$

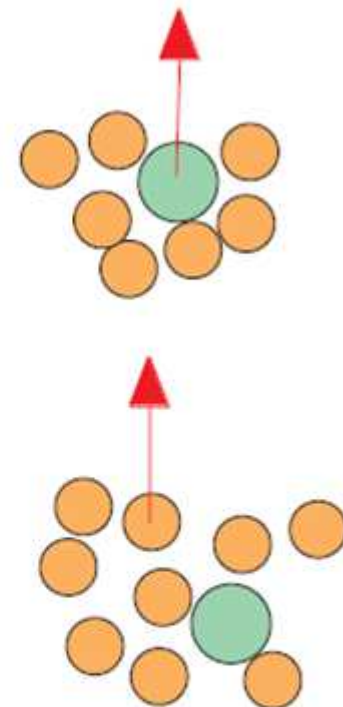
where  $x_i$  is the mole fraction solvent and  $p_i^*$  is the vapor pressure of the pure solvent.

- Raoult's and Henry's laws are often termed 'limiting laws'. This use reflects that real solutions often follow these laws at infinite dilution only.

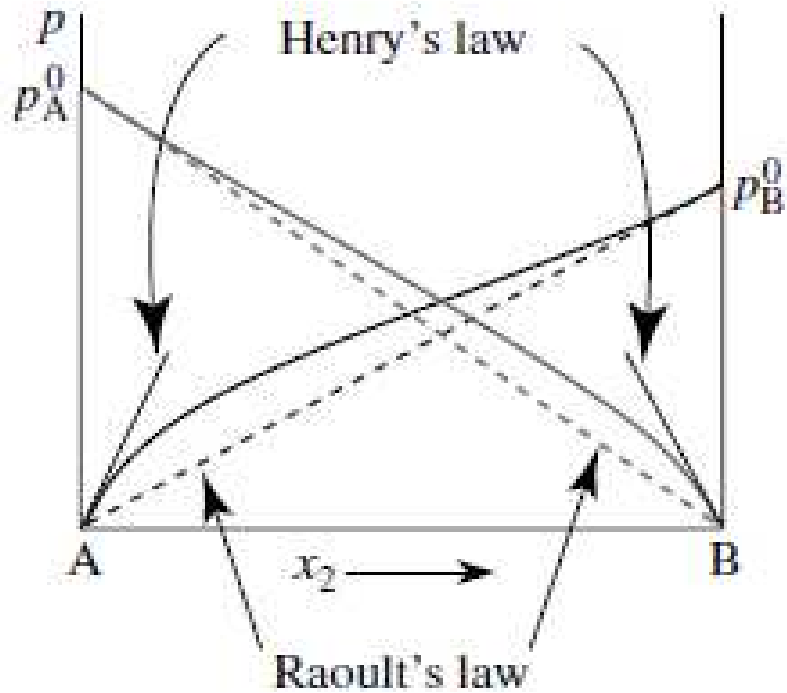


$K_A$  (Henry's law constant) measures escaping tendency of "A" molecules from an environment of "B" molecules, and thus reflects attractive forces between unlike molecules.

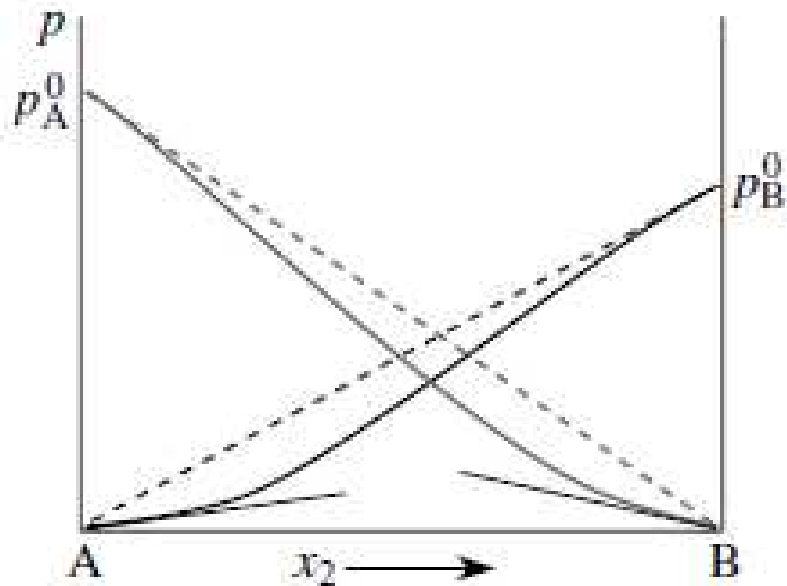
$P_A^0$  ("Raoult's law constant") measures escaping tendency of "A" molecules from a phase of pure "A", and thus reflects attractive forces between molecules of like kind.



Comparison of Raoult's law and Henry's law



Schematic illustrations of the saturated vapor pressures above two different non-ideal solutions.



The continuous solid curves represent the behavior of the real solutions, the dashed lines represent Raoult's law and short solid lines represent Henry's law.

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**Example 7.22 pT-flash.** A feed  $F$  is split into a vapor product  $V$  and a liquid product  $L$  in a flash tank (see Figure 7.4 on page 189). The feed is 50% pentane, 30% hexane and 20% cyclohexane (all in mol-%). In the tank,  $T = 390\text{K}$  and  $p = 5$  bar. For example, we may have a heat exchanger that keeps constant temperature and a valve on the vapor product stream that keeps constant pressure. We want to find the product split and product compositions. Assume ideal liquid mixture and ideal gas (Raoult's law).

**Comment.** This is a quite close-boiling mixture and we have already found that at 5 bar the bubble point temperature is  $382.64\text{ K}$  (Example 7.18) and the dew point temperature is  $393.30\text{ K}$  (Example 7.20). The temperature in the flash tank must be between these temperatures for a two-phase solution to exist (which it does in our case since  $T = 390\text{ K}$ ).

**Solution.** The feed mixture of pentane (1), hexane (2) and cyclohexane (3) is

$$z_1 = 0.5; \quad z_2 = 0.3; \quad z_3 = 0.2$$

We have  $K_i = p_i^{\text{sat}}(T)/p$  and at  $T = 390\text{K}$  and  $p = 5$  bar, we find with the Antoine parameters in Table 7.2:

$$K_1 = 1.685, \quad K_2 = 0.742, \quad K_3 = 0.532$$

Now,  $z_i$  and  $K_i$  are known, and the Rachford-Rice equation (7.50) is solved numerically to find the vapor split  $V/F = 0.6915$ . The resulting liquid and vapor compositions are (for details see the MATLAB code below):

$$x_1 = 0.3393, \quad x_2 = 0.3651, \quad x_3 = 0.2956$$

$$y_1 = 0.5717, \quad y_2 = 0.2709, \quad y_3 = 0.1574$$

**Example 7.23** Condenser and flash drum for ammonia synthesis. *The exit gas from an ammonia reactor is at 250 bar and contains 61.5% H<sub>2</sub>, 20.5% N<sub>2</sub> and 18% NH<sub>3</sub>. The gas is cooled to 25°C (partly condensed), and is then separated in a flash drum into a recycled vapor stream V and a liquid product L containing most of the ammonia. We want to calculate the product compositions (L and V) from the flash drum.*

**Data.** *In spite of the high pressure, we assume for simplicity ideal gas. Use vapor pressure data for ammonia from Table 7.2 and Henry's law coefficients for N<sub>2</sub> and H<sub>2</sub> from page 187. For ammonia, we assume ideal liquid mixture, i.e.,  $\gamma_{\text{NH}_3} = 1$  (which is reasonable since the liquid phase is almost pure ammonia).*

**Solution.** *The feed mixture of H<sub>2</sub> (1), N<sub>2</sub> (2) and NH<sub>3</sub> (3) is*

$$z_1 = 0.615, \quad z_2 = 0.205, \quad z_3 = 0.18$$

*For ammonia, we have at  $T = 298.15 \text{ K}$  and  $p = 250 \text{ bar}$  (Raoult's law):*

$$K_3 = \frac{p_3^{\text{sat}}(T)}{p} = \frac{9.83 \text{ bar}}{250 \text{ bar}} = 0.0393$$

For  $H_2$  and  $N_2$ , we have from the given data for Henry's coefficient at  $25^\circ C$  (298.15 K):

$$K_1 = \frac{H_1(T)}{p} = \frac{15200 \text{ bar}}{250 \text{ bar}} = 60.8$$

$$K_2 = \frac{H_2(T)}{p} = \frac{8900 \text{ bar}}{250 \text{ bar}} = 35.6$$

Now,  $z_i$  and  $K_i$  are known, and the Rachford-Rice equation (7.50) is solved numerically to find the vapor split  $V/F = 0.8500$ . The resulting liquid and vapor compositions of the products are

$$\begin{aligned} x_1 &= 0.0119, & x_2 &= 0.0067, & x_3 &= 0.9814 \\ y_1 &= 0.7214, & y_2 &= 0.2400, & y_3 &= 0.0386 \end{aligned}$$

This agrees well with flow sheet data from a commercial ammonia plant.