

# Lecture 5.

## Single Equilibrium Stages (1)

### [Ch. 4]

- Phase Separation
- Degree of Freedom Analysis
  - Gibbs phase rule  $F = C - P + 2$
  - General analysis
- Binary Vapor–Liquid Systems
  - Examples of binary system
  - Phase equilibrium diagram
  - q–line
  - Phase diagram for constant relative volatility
- Azeotropic Systems

# Phase Separation

- Simplest separation processes
  - Two phases in contact → physical equilibrium → phase separation
  - If the separation factor is large, a single contact stage may be sufficient
  - If the separation factor is not large, multiple stages are required

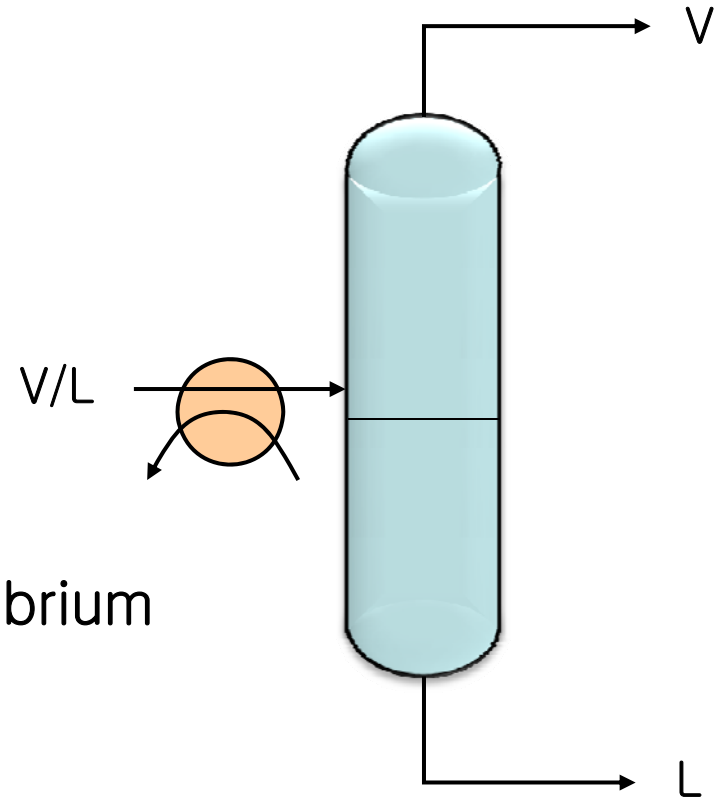
- Separation factor for vapor–liquid equilibrium

$$\alpha_{LK, HK} (\text{relative volatility}) = \frac{K_{LK}}{K_{HK}}$$

$\alpha = 10,000$  : almost perfect separation in a single stage

$\alpha = 1.10$  : almost perfect separation requires hundreds of stages

- Calculation for separation operations : **material balances, phase equilibrium relations, and energy balance**



# Gibbs Phase Rule

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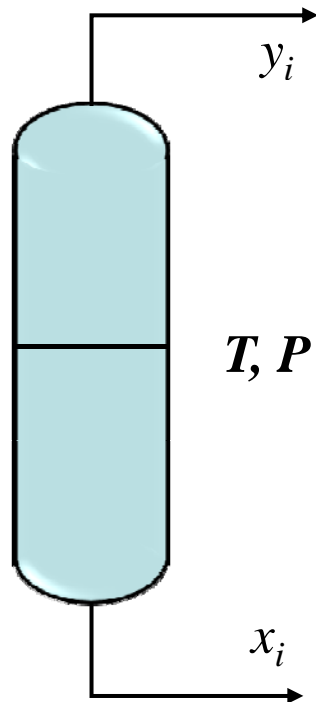
- Variables
  - **Intensive variables** : Do not depend on system size; temperature, pressure, phase compositions
  - **Extensive variables** : Depend on system size; mass, moles, energy; mass or molar flow rates, energy transfer rates
- **Degree of freedom,  $F$**   
Number of independent variables (variance)
- **Gibbs phase rule**  
Relation between the number of independent intensive variables at equilibrium

$$F = C - P + 2$$

$C$  : Number of components at equilibrium  
 $P$  : Number of phases at equilibrium

# Degree of Freedom Analysis (1)

- Gibbs phase rule : consider equilibrium **intensive** variables only



## Variables

T, P : **2** variables

$x_i, y_i, \dots$  : **C × P** variables

## Equations

$$\sum_{i=1}^C x_i = 1 \quad \text{and} \quad \sum_{i=1}^C y_i = 1 \quad \text{P equations}$$

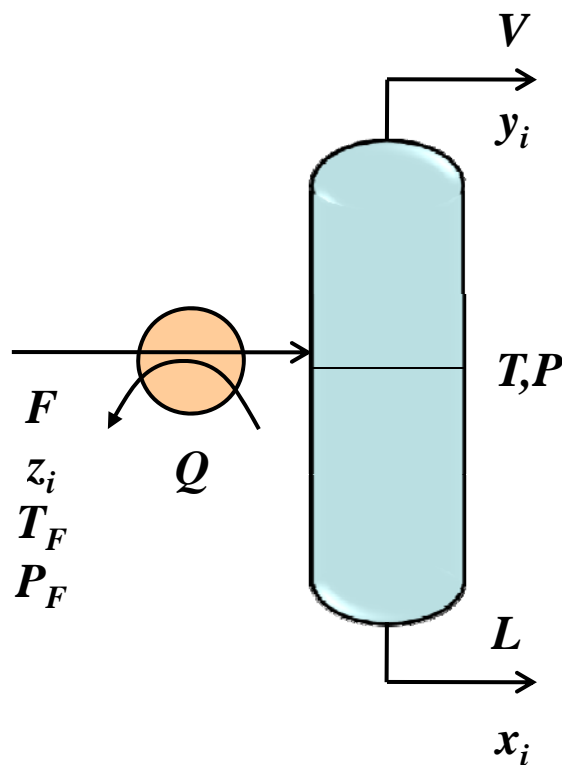
$$f_i^L = f_i^V \quad \text{or} \quad K_i = \frac{y_i}{x_i} \quad \text{C} \times (\text{P}-1) \text{ equations}$$

$$F = (2 + CP) - P - C(P - 1) = C - P + 2$$

For a binary VLE system (F=2) : given T, P → determine x and y

# Degree of Freedom Analysis (2)

- General analysis: consider all **intensive** and **extensive** variables



## Variables

$$\begin{array}{l}
 T, P : 2 \\
 x_i, y_i, \dots : C \times P
 \end{array}
 +
 \begin{array}{l}
 z_i, T_F, P_F, \\
 F, Q, \\
 [V, L, \dots]
 \end{array}
 \begin{array}{l}
 C+P+4 \text{ in general} \\
 (C+6 \text{ for VLE})
 \end{array}$$

## Equations

$$P + C(P-1) \text{ equations}$$

+

$$Fz_i = Vy_i + Lx_i$$

$C+1$  equations

$$Fh_F + Q = Vh_V + Lh_L$$

$$\begin{aligned}
 F &= (2+CP) + (C+P+4) - [P+C(P-1)] - (C+1) \\
 &= C + 5
 \end{aligned}$$

$$\text{If we consider } \sum_{i=1}^C z_i = 1 \rightarrow F = C + 4$$

# Binary Vapor–Liquid Systems

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- Experimental vapor–liquid equilibrium data for binary systems (A and B) are widely available  
e.g. Perry's handbook
- Types of equilibrium data
  - Isothermal : P–y–x
  - Isobaric : T–y–x
- If P and T are fixed → **phase compositions** are completely defined  
⇒ separation factor (relative volatility for vapor–liquid) is also fixed

$$\alpha_{A,B} = \frac{K_A}{K_B} = \frac{(y_A / x_A)}{(y_B / x_B)} = \frac{(y_A / x_A)}{(1 - y_A) / (1 - x_A)}$$

A is the more-volatile component ( $y_A > x_A$ )

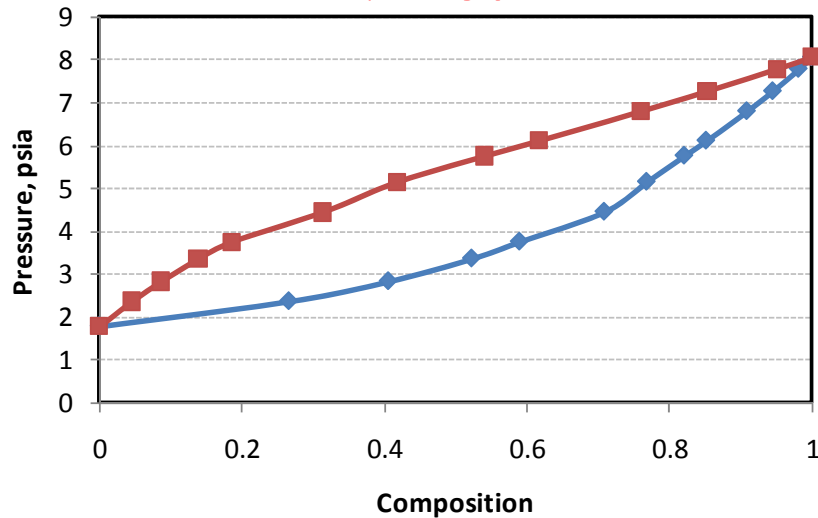
# Examples of Binary System

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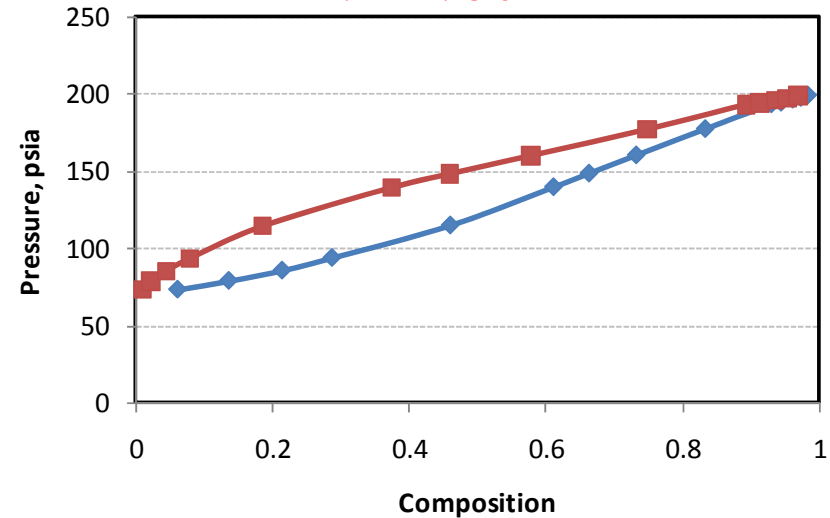
- Water + Glycerol
  - Normal boiling point difference : 190 °C
  - Relative volatility : very high
  - ⇒ Good separation in a single equilibrium stage
- Methanol + Water
  - Normal boiling point difference : 35.5 °C
  - Relative volatility : intermediate
  - ⇒ About 30 trays are required for an acceptable separation
- p-xylene + m-xylene
  - Normal boiling point difference : 0.8 °C
  - Relative volatility : close to 1.0
  - Distillation separation is impractical : about 1,000 trays are required
  - ⇒ Crystallization or adsorption is preferred

# Equilibrium Data for Methanol–Water System (1)

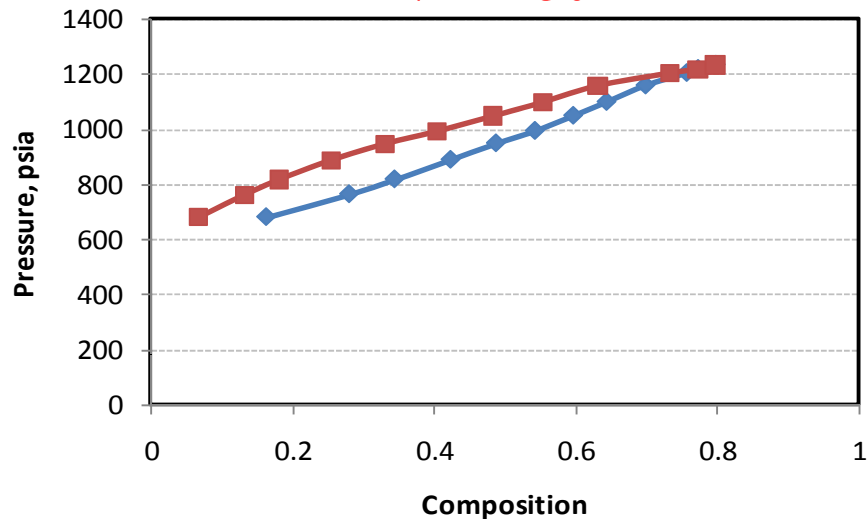
$T = 50\text{ }^{\circ}\text{C}$



$T = 150\text{ }^{\circ}\text{C}$



$T = 250\text{ }^{\circ}\text{C}$



- As  $T$  becomes higher, relative volatility becomes smaller  
→ Separation becomes difficult
- At  $250\text{ }^{\circ}\text{C}$  → no separation by distillation when  $x \geq 0.772$



# Equilibrium Data for Methanol–Water System (2)

c. Methanol (A)–Water (B) System

$T = 250^\circ\text{C}$

Data of Griswold and Wong, *Chem. Eng. Prog. Symp. Ser.*, **48** (3), 18 (1952)

Pressure, psia	$y_A$	$x_A$	$\alpha_{A,B}$
681	0.163	0.066	2.76
764	0.280	0.132	2.56
818	0.344	0.180	2.39
889	0.423	0.254	2.15
949	0.487	0.331	1.92
994	0.542	0.404	1.75
1049	0.596	0.483	1.58
1099	0.643	0.553	1.46
1159	0.698	0.631	1.35
1204	0.756	0.732	1.13
1219	0.772	0.772	1.00
1234	0.797	0.797	1.00

- $\alpha$  (relative volatility) = 1.0

→ The separation by distillation is not possible

∴ The compositions of the vapor and liquid are identical and two phases become **one phase**

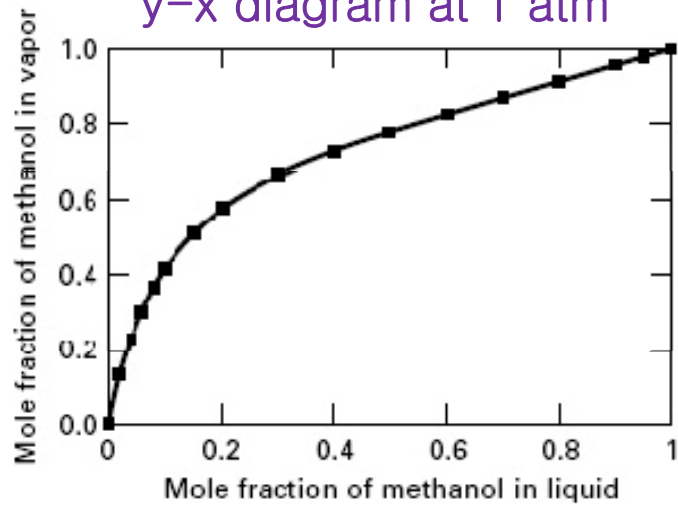
$y_A = x_A$	$T_c$ ( $^\circ\text{C}$ )	$P_c$ (psia)
0.000	374.1	3,208
0.772	250	1,219
1.000	240	1,154

In industry, distillation columns operate at pressures below  $P_c$

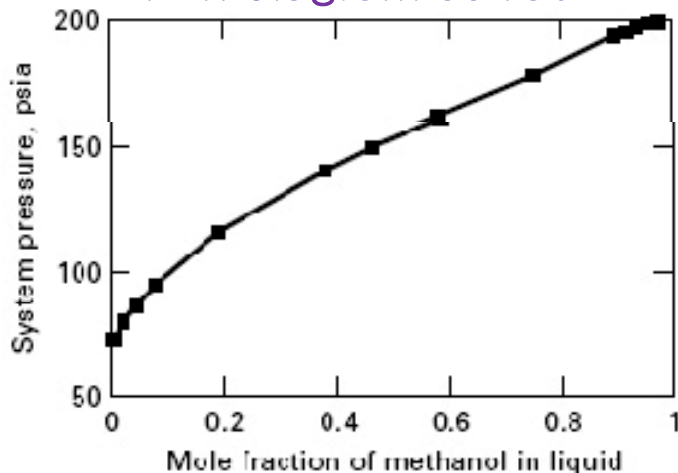
# Phase Equilibrium Diagram

Methanol–water system

y-x diagram at 1 atm

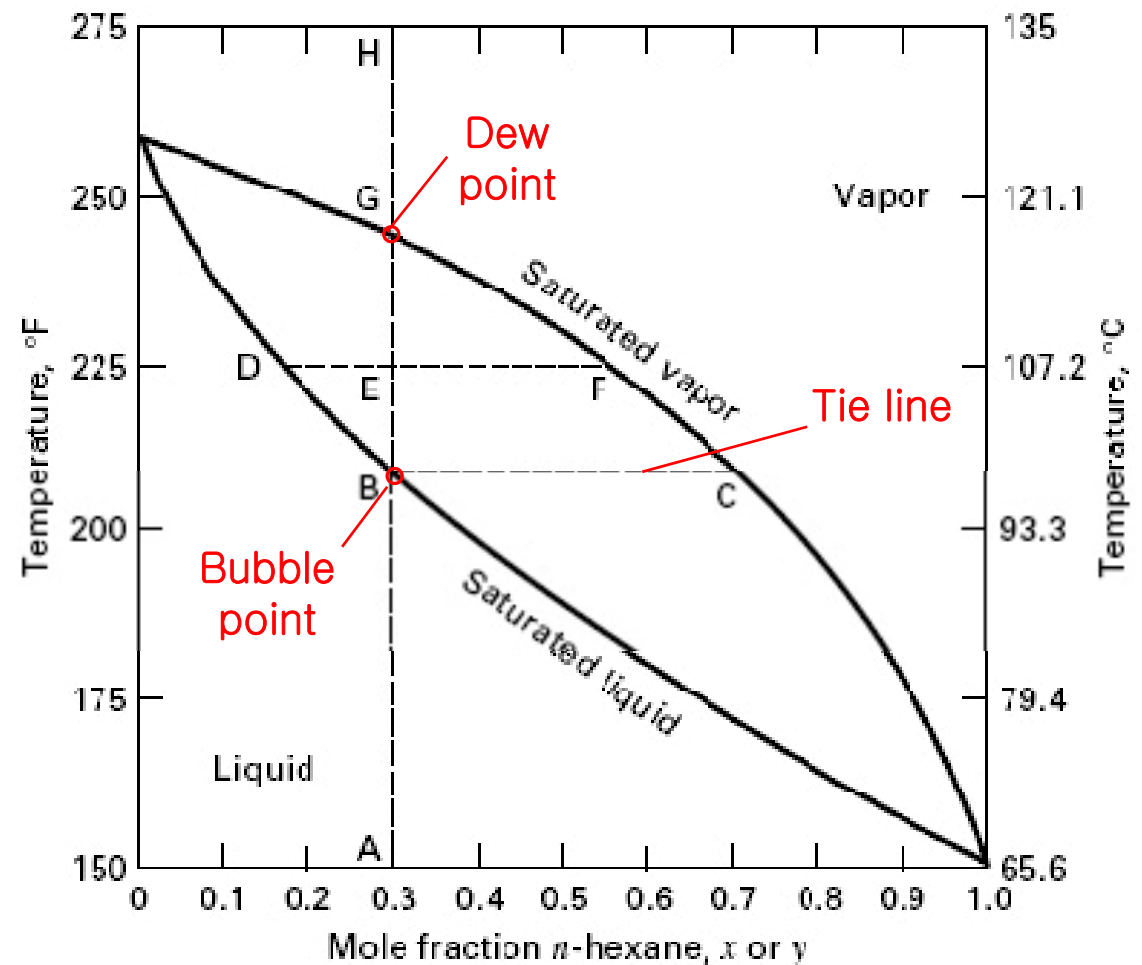


P-x diagram at 150 °C



n hexane–n octane system

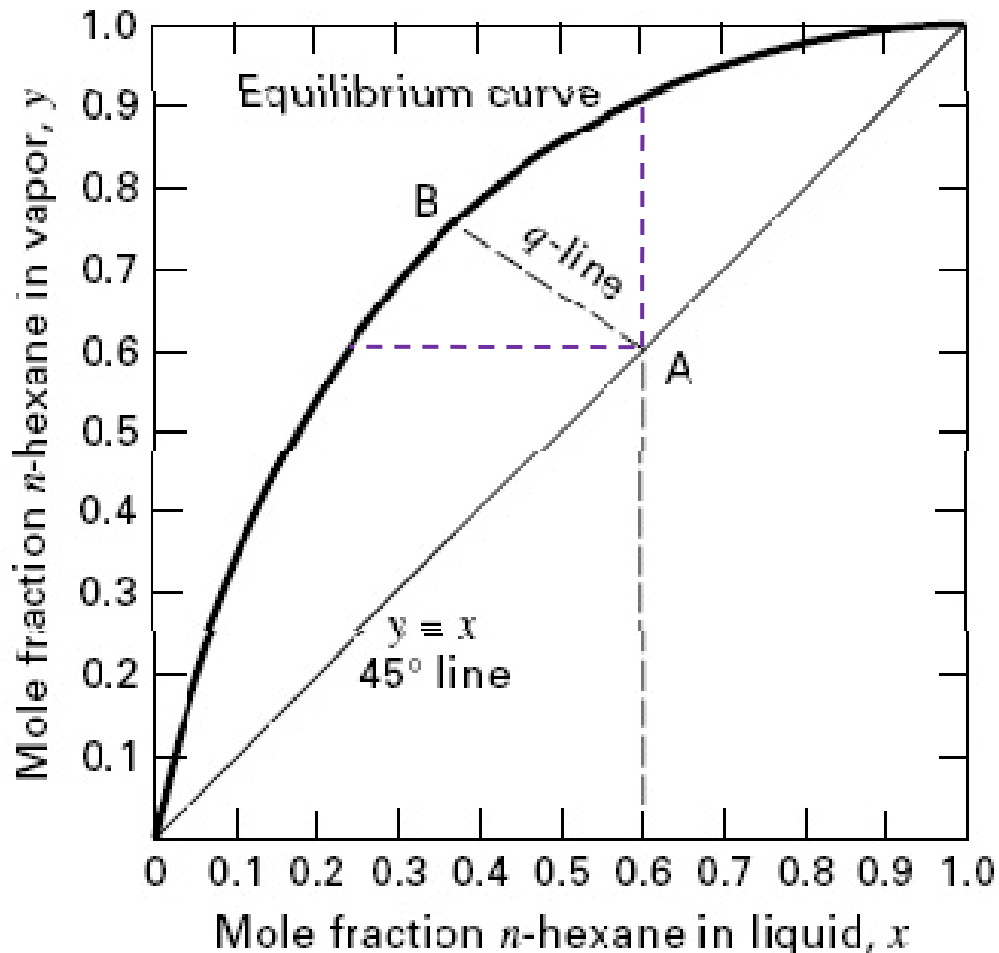
T-y-x diagram at 1 atm



# q-line

n hexane–n octane system

y–x phase diagram at 1 atm



$$Fz_H = Vy_H + Lx_H$$

$$F = V + L$$

$$y_H = \left[ \frac{(V/F) - 1}{(V/F)} \right] x_H + \frac{1}{(V/F)} z_H$$

Feed mixture, F with overall composition  $z_H = 0.6$

For 60 mol% vaporization, slope =  $(0.6 - 1)/0.6 = -2/3$

⇒ **Equilibrium composition** from equilibrium curve :  $y_H = 0.76$  and  $x_H = 0.37$

Slope=0,  $(V/F)=1$  : vapor only

Slope= $\infty$ ,  $(V/F)=0$  : liquid only

# y-x Phase Diagram for Constant Relative Volatility

- Relative volatility

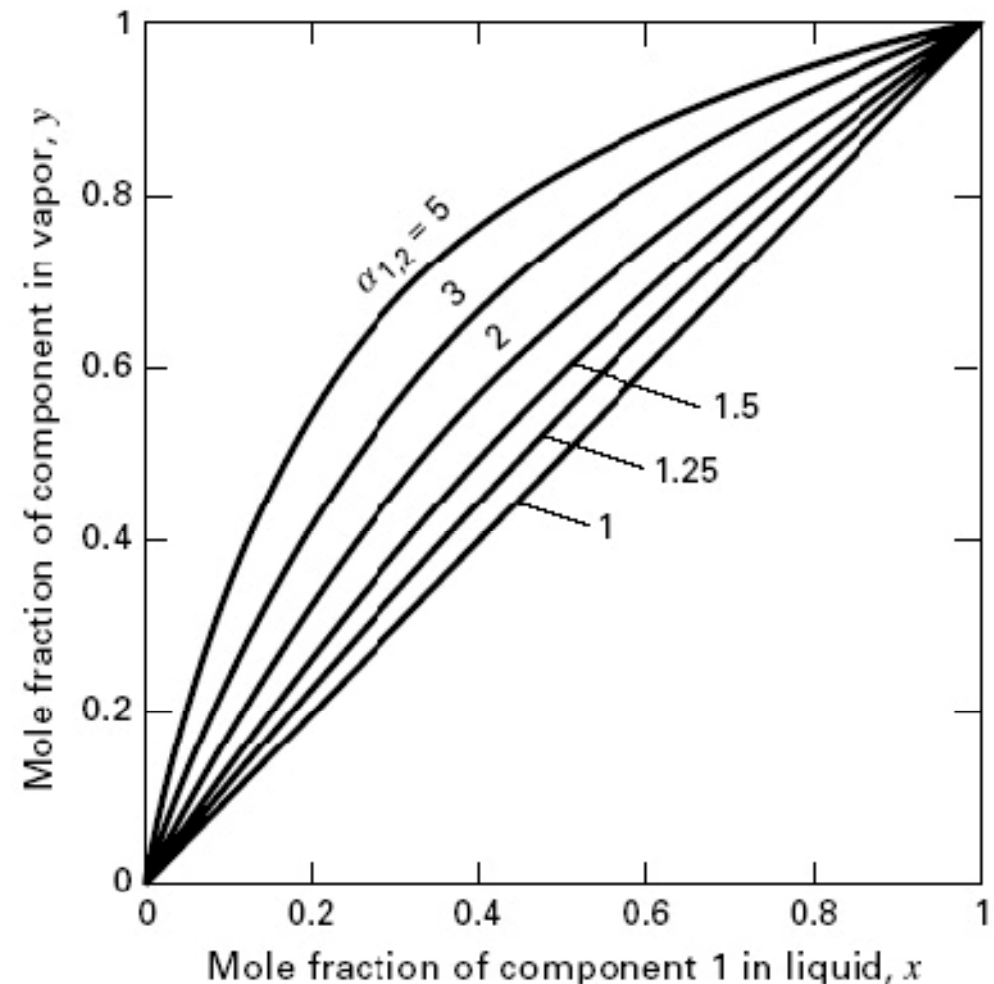
$$\alpha_{A,B} = \frac{y_A / x_A}{y_B / x_B} = \frac{y_A / x_A}{(1 - y_A) / (1 - x_A)}$$

If  $\alpha_{A,B}$  is assumed constant over the entire composition range, the y-x phase equilibrium curve can be determined using  $\alpha_{A,B}$

$$y_A = \frac{\alpha_{A,B} x_A}{1 + x_A (\alpha_{A,B} - 1)}$$

For an ideal solution,  $\alpha_{A,B}$  can be approximated with Raoult's law

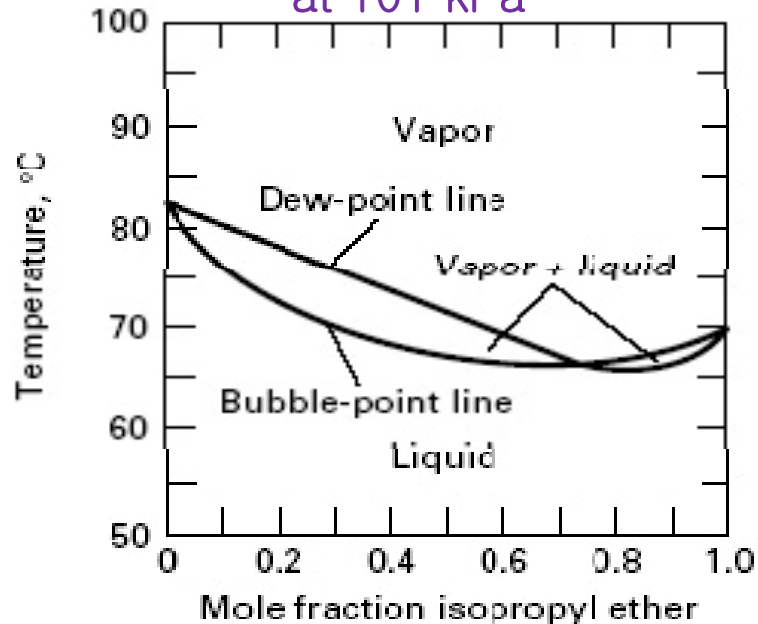
$$\alpha_{A,B} = \frac{K_A}{K_B} = \frac{P_A^{sat} / P}{P_B^{sat} / P} = \frac{P_A^{sat}}{P_B^{sat}}$$



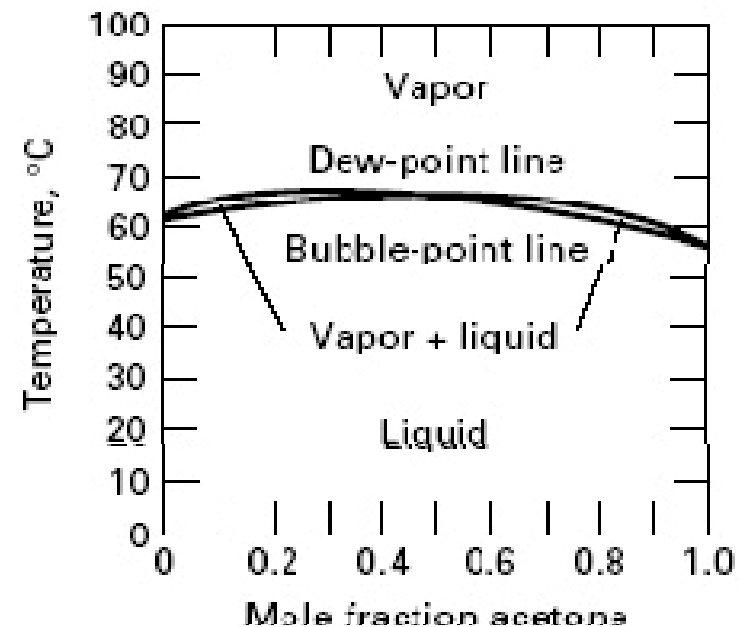
# Azeotropic systems (1)

- **Azeotropes** : formed by liquid mixtures exhibiting minimum- or maximum-boiling points
  - Homogeneous or heterogeneous azeotropes

Isopropyl ether–isopropyl alcohol  
at 101 kPa



Acetone–chloroform at 101 kPa



- Identical vapor and liquid compositions at the azeotropic composition  
→ all K-values are 1 → **no separation** by ordinary distillation

# Azeotropic systems (2)

- Azeotropes limit the separation achievable by ordinary distillation
  - ⇒ Changing pressure sufficiently : shift the equilibrium to break the azeotrope or move it
- Azeotrope formation can be used to achieve difficult separations

An **entrainer** (MSA) is added  
→ combining with one or more of the components in the feed  
→ forming a minimum-boiling azeotrope  
→ recover as the distillate

e.g. heterogeneous azeotropic distillation: addition of benzene to an alcohol–water mixture

