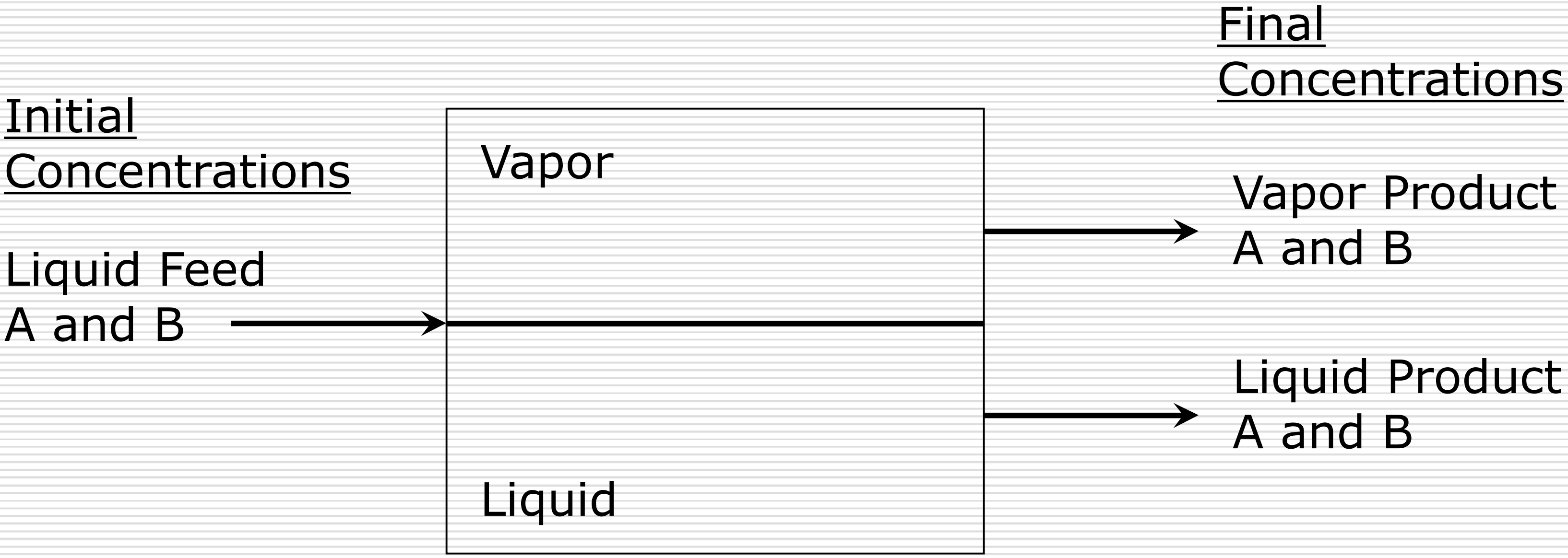
In Name of God

Unit Operation I

Lecture 2

Binary Separation by Phase Creation – A Single Stage



Initial Concentrations

Liquid Feed
A and B

Vapor

Liquid

Final Concentrations

Vapor Product
A and B

Liquid Product
A and B

What we need…

- In order to begin our analyses, we need to determine how we can relate the concentrations (the mole fractions) of components in the vapor phase to their concentrations in the liquid phase.
- We do so by assuming a "standard condition" of the system, which is known as the " vapor-liquid equilibrium condition".
- By assuming vapor-liquid equilibrium, we will have a known relationship between the concentrations in the liquid and the vapor.
- We can then utilize this "equilibrium curve".

Vapor-Liquid Equilibrium

- **Thermal Equilibrium** – there is no net heat transfer and the temperature of the vapor and liquid phases are equal.

$$T^L = T^V$$

- **Mechanical Equilibrium** – the forces between vapor and liquid are balanced and the pressure of vapor and liquid phases are equal.

$$P^L = P^V$$

- **Chemical Equilibrium** –the rates of vaporization of liquid and the condensation of vapor are equal and the chemical potentials between the vapor and liquid and phases are equal; thus, the compositions of the vapor and liquid phases do not change at a given temperature and pressure.

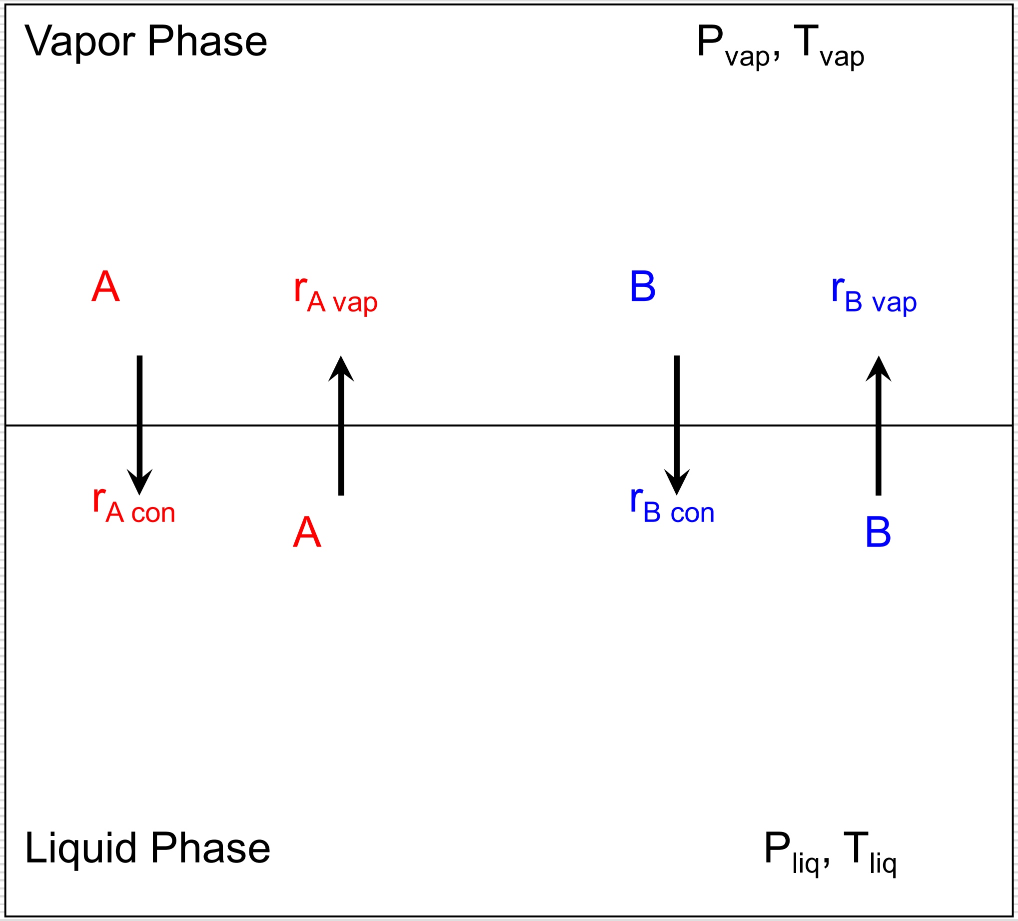
$$\mu_i^L = \mu_i^V \, ;$$

$$i = 1, \ldots, C$$

Two Component System – The Binary System

- ☐ Suppose that we add two components to a container, seal the container, and place it in a constant temperature bath.
- ☐ The system can be represented by a two-component mixture, a binary system, in the closed container at a particular temperature and pressure:

Two Component System – The Binary System



Thermal and Mechanical Equilibrium

- After a suitable period of time, the system will reach equilibrium, and the temperature and pressure of the system cease to change. Thus, we have:

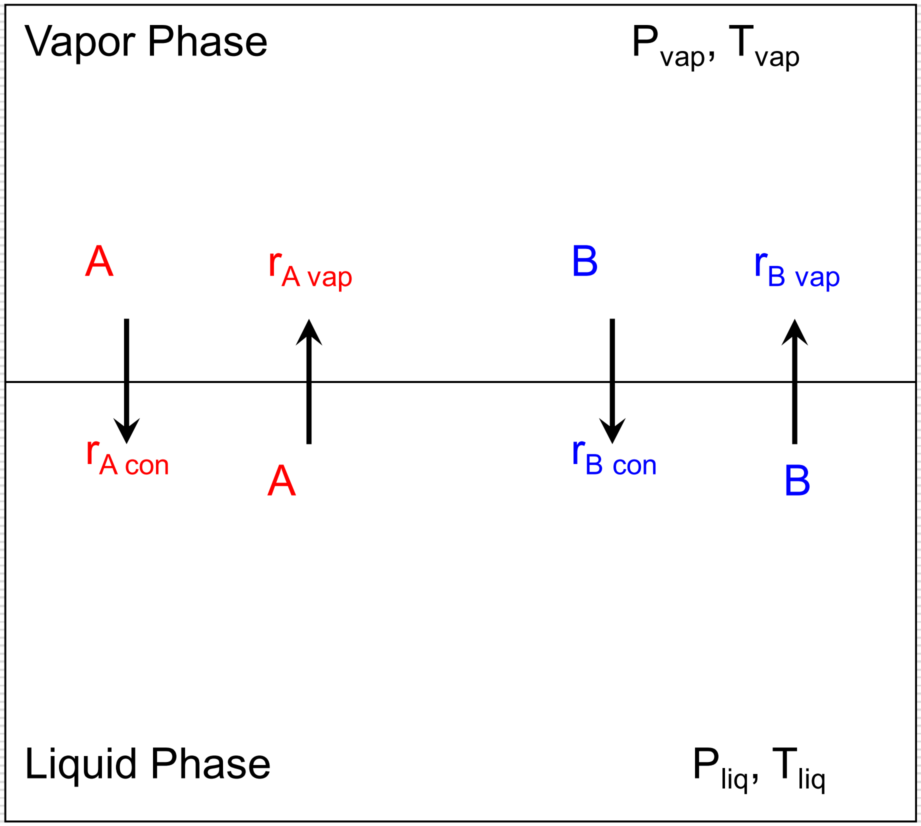
1.) Temperature (Thermal) Equilibrium

$$T_{liq} = T_{vap}$$

2.) Pressure (Mechanical) Equilibrium

$$P_{liq} = P_{vap}$$

Thermal and Mechanical Equilibrium



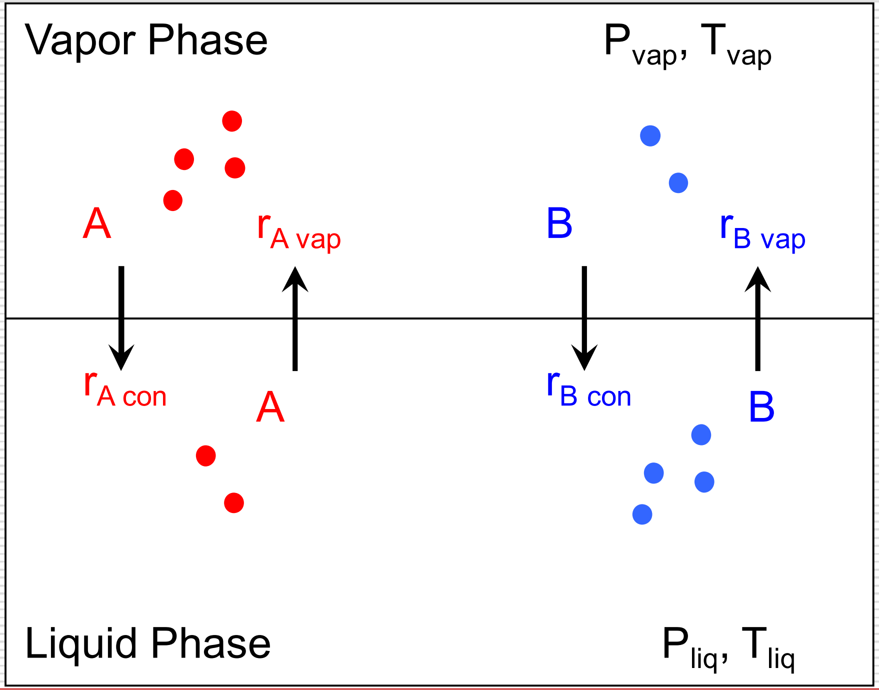
$$T_{vap} = T_{liq} \text{ and } P_{vap} = P_{liq}$$

Chemical Equilibrium

- Let’s assume component A is more volatile than component B.
- Over a suitable period of time, one will reach equilibrium in the distribution between the vapor and liquid phase of each component...

Phase Equilibrium – Overall

- Overall, at equilibrium, one will have more of component A than B in the vapor phase and more of B than A in the liquid phase:



Phase Equilibrium – Chemical Potentials

- ☐ At equilibrium, these rates, and, thus the vapor and liquid concentrations of each component, are governed by the minimum thermodynamic free energy of system – the minimum Gibbs' Free Energy.

- ☐ Another way to express this is by the chemical potentials, of each component *i* in the vapor and liquid phases, or:

$$(\mu_i)_{\text{liq}} = (\mu_i)_{\text{vap}}$$

- ☐ We will not be dealing with how to determine these chemical potentials in this course – we will use equilibrium data and analytical expressions representing the equilibrium curve in the design of separation processes.

Vapor-Liquid Phase Equilibrium

☐ Summarizing the definition of equilibrium:

1.) Temperature (Thermal) Equilibrium

$$T_{liq} = T_{vap} \qquad \text{Eq. (2-1)}$$

2.) Pressure (Mechanical) Equilibrium

$$P_{liq} = P_{vap} \qquad \text{Eq. (2-2)}$$

3.) Chemical Equilibrium

$$(\mu_i)_{liq} = (\mu_i)_{vap} \qquad \text{Eq. (2-3)}$$

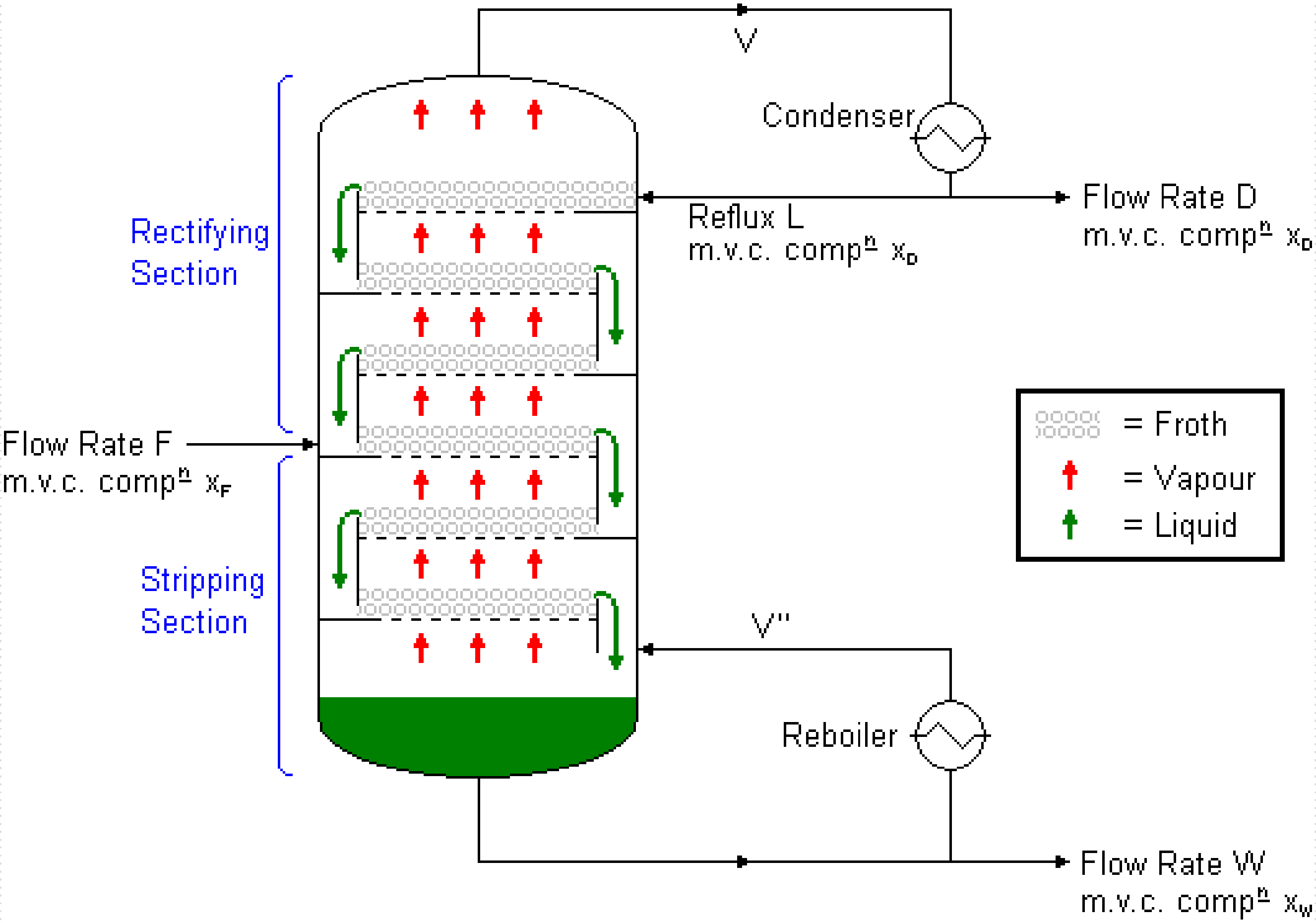
When can we assume equilibrium?

- We assume that the vapor-liquid equilibrium system is well mixed and that there is a great amount of contact between the vapor and liquid phases – this promotes thermal and mechanical equilibrium between the vapor and liquid with no mass transfer limitations, which promotes phase equilibrium.
- We assume that the time to reach equilibrium is almost instantaneous relative to the other times involved in the system – we thus have temperature and pressure equilibrium, as well phase equilibrium.

Also Remember…

- We can obtain separation by taking advantage of the differences in volatilities between components.
- We obtain a larger concentration of the more volatile component in the vapor and a larger concentration of the less volatile component in the liquid.
- We can then separate the liquid and vapor.

Staged Separations – Distillation



Equilibrium Summary

- We assume thermodynamic equilibrium for a given temperature and pressure.
- This sets the equilibrium relationship between the components in each phase.
- The distribution between phase for each component will be different, with one component enriched in the vapor phase and the other in the liquid phase.
- The next task is to determine what the equilibrium relationships are and how to handle them…

Equilibrium Mole-Fraction Relationship – Binary System

- ☐ We will start by considering the concentrations of the components in the vapor and liquid phase for a binary system.
- ☐ However, it is convenient to use mole fractions, instead of concentrations, since the sum of the mole fractions conveniently equals one. For a binary system comprised of component A and B, this can be written as:

$$x_A + x_B = 1.0$$

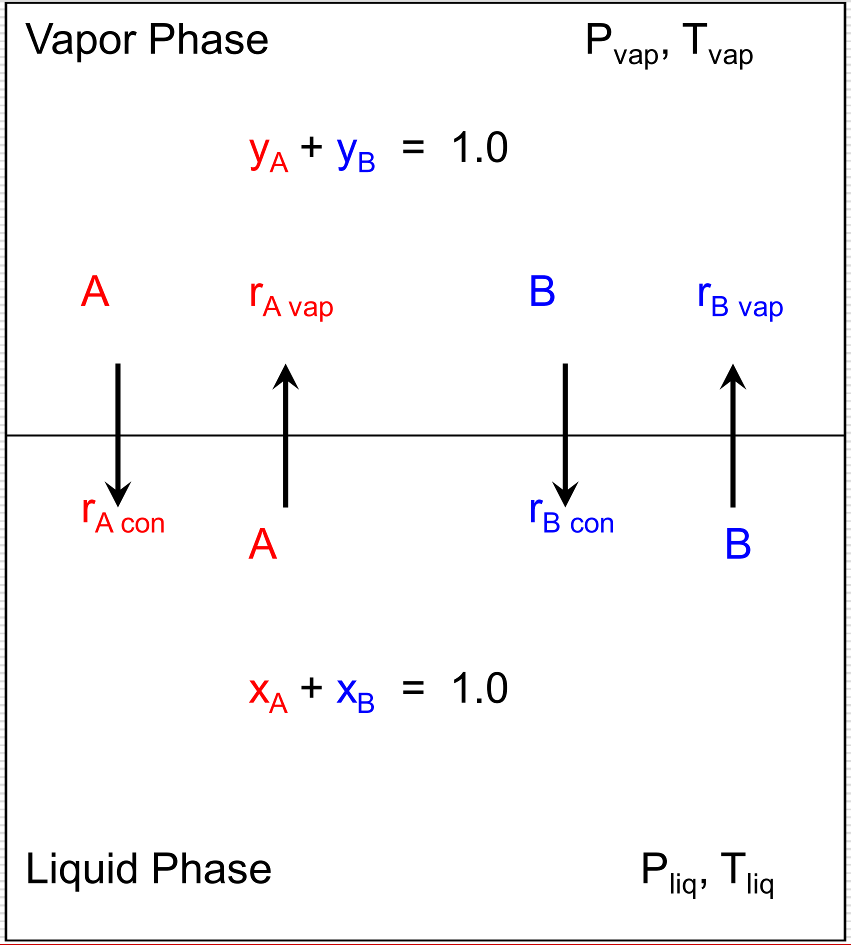
and Eq. (2-4)

$$y_A + y_B = 1.0$$

where

x_A = mole fraction of component A in the liquid phase
x_B = mole fraction of component B in the liquid phase
y_A = mole fraction of component A in the gas phase
y_B = mole fraction of component B in the gas phase

Equilibrium Mole-Fraction Relationship – Binary System



Vapor Phase

P_{vap}, T_{vap}

$y_A + y_B = 1.0$

A

$r_{A\ vap}$

B

$r_{B\ vap}$

$r_{A\ con}$

A

$r_{B\ con}$

B

$x_A + x_B = 1.0$

Liquid Phase

P_{liq}, T_{liq}

Equilibrium Mole-Fraction Relationship – Multi-Component System

- We can also extend this analysis to multi-component systems containing an *i* number of components:

$$\sum x_i = 1.0$$

Eq. (2-4)

$$\sum y_i = 1.0$$

Equilibrium Mole-Fraction Relationship

- We now have a method to conveniently relate the concentrations (as mole fractions) in the liquid and vapor phases – we now need a relationships <u>between</u> the mole fractions in the liquid and vapor phases…
- We can do this via phase equilibrium relationships which “tie” the mole fractions in the liquid together with those in the vapor.
- Phase equilibrium is dependent upon the temperature and pressure of the system, the mole fractions of the components, as well as the components of the system.
- Where do we get this equilibrium information or how do we determine it?

Equilibrium Data – Where to Find?

- Available from many sources including:
  - Perry’s Handbook (all editions)
  - Literature (see Table 2-3, p. 14, Wankat)
  - Industry monographs (often hard to obtain)

- Thermodynamic methods based upon vapor pressures, activity coefficients, etc. (such as the methods available in Aspen).

- Actually perform the experiment and determine the equilibrium data.

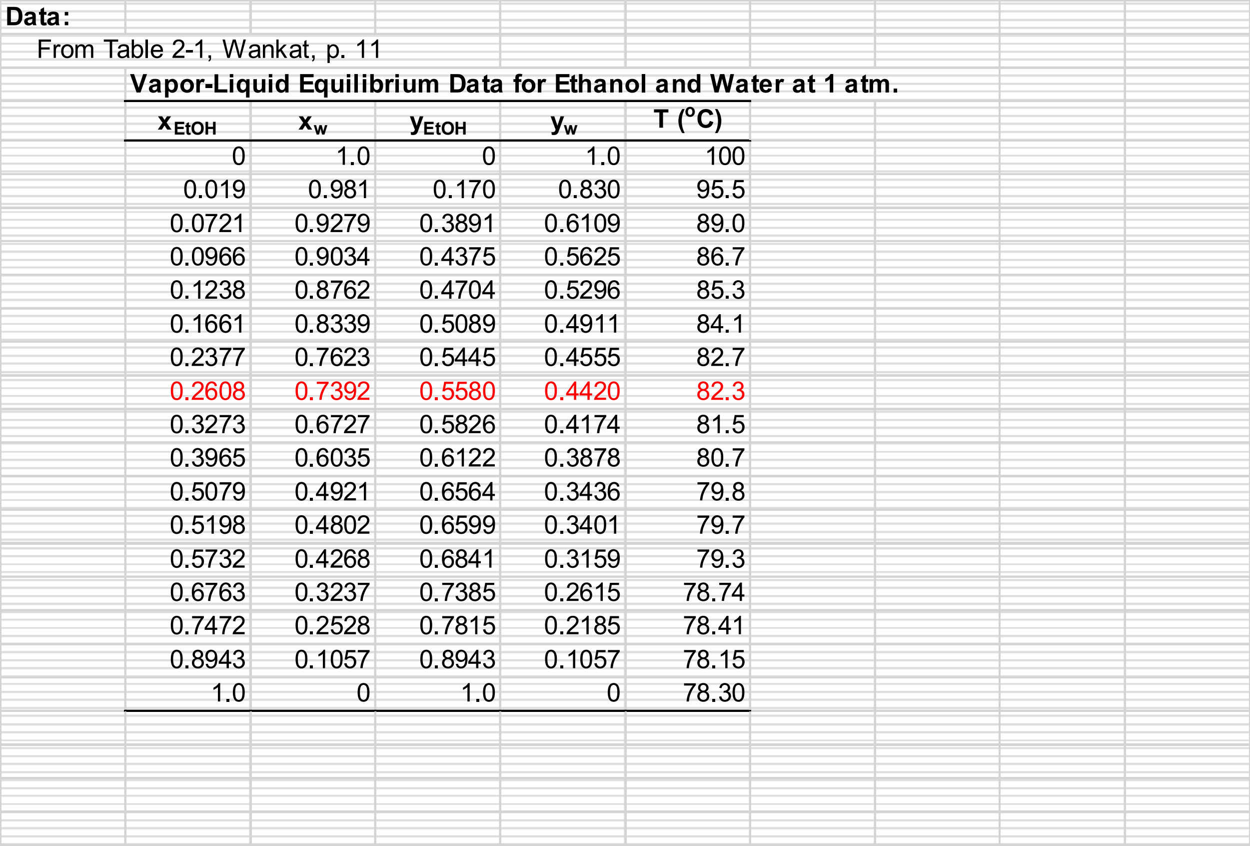
Equilibrium Data – How to Handle?

- Tabular Data
  - Generate graphical plots
  - Generate analytical expressions (curve fit)

- Graphical
  - y vs. x (P constant) – McCabe-Thiele Pot
  - T vs. x,y (P constant) – Saturated Liquid, Vapor Plot
  - Enthalpy vs. composition (P constant, T) – Ponchon-Savarit Plot

- Analytical expressions
  - Distribution coefficient
  - Relative volatility
  - DePriester charts
  - Curve fit of data

Vapor-Liquid Equilibrium Data – Ethanol-Water, P =1 atm



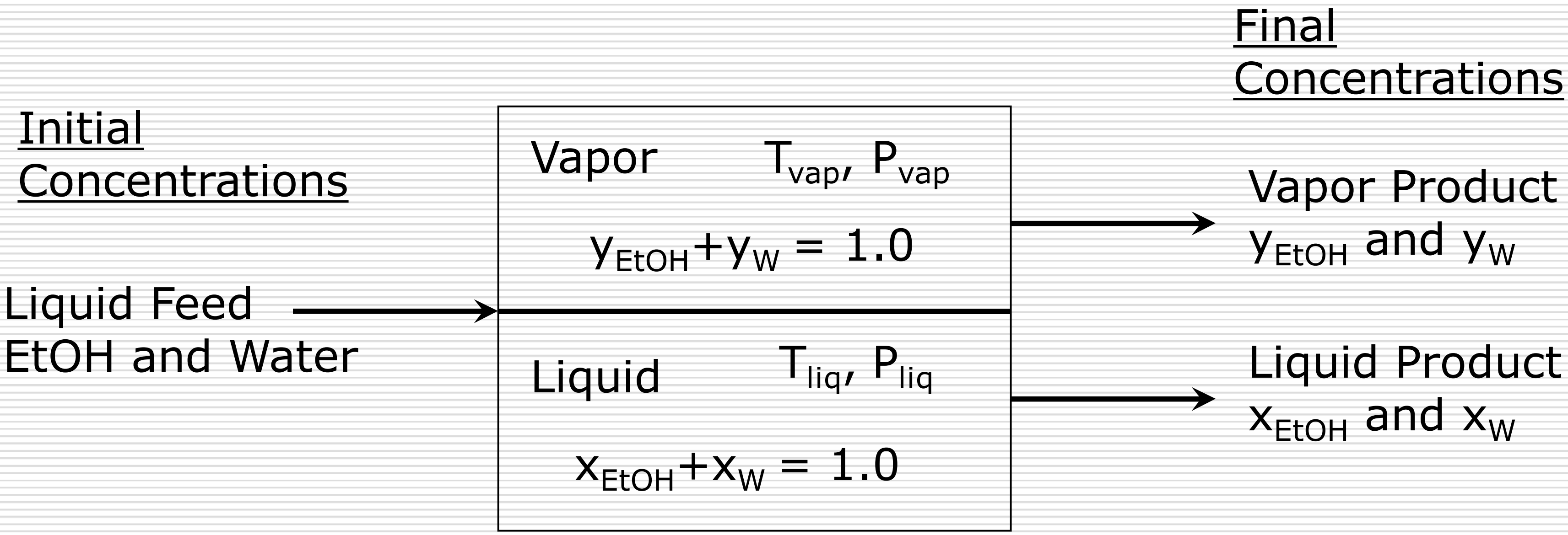
Data:

From Table 2-1, Wankat, p. 11

Vapor-Liquid Equilibrium Data for Ethanol and Water at 1 atm.

x_{EtOH}	x_w	y_{EtOH}	y_w	T (°C)
0	1.0	0	1.0	100
0.019	0.981	0.170	0.830	95.5
0.0721	0.9279	0.3891	0.6109	89.0
0.0966	0.9034	0.4375	0.5625	86.7
0.1238	0.8762	0.4704	0.5296	85.3
0.1661	0.8339	0.5089	0.4911	84.1
0.2377	0.7623	0.5445	0.4555	82.7
0.2608	0.7392	0.5580	0.4420	82.3
0.3273	0.6727	0.5826	0.4174	81.5
0.3965	0.6035	0.6122	0.3878	80.7
0.5079	0.4921	0.6564	0.3436	79.8
0.5198	0.4802	0.6599	0.3401	79.7
0.5732	0.4268	0.6841	0.3159	79.3
0.6763	0.3237	0.7385	0.2615	78.74
0.7472	0.2528	0.7815	0.2185	78.41
0.8943	0.1057	0.8943	0.1057	78.15
1.0	0	1.0	0	78.30

Binary Separation by Phase Creation – A Single Stage



Initial Concentrations

Liquid Feed
EtOH and Water

Vapor T_{vap}, P_{vap}

$y_{EtOH}+y_W = 1.0$

Liquid T_{liq}, P_{liq}

$x_{EtOH}+x_W = 1.0$

Final Concentrations

Vapor Product
y_{EtOH} and y_W

Liquid Product
x_{EtOH} and x_W

Let's Assume Equilibrium at P = 1 atm and T = 82.3 °C

- What is the mole fraction of ethanol in the liquid phase?
- What is the mole fraction of ethanol in the vapor phase?
- What is the mole fraction of water in the liquid phase?
- What is the mole fraction of water in the vapor phase?

Other Important Information

- ☐ One can determine from the data alone what the boiling points are of each pure component…
- ☐ What are the boiling points of each pure component from the data?
- ☐ Which is the more volatile component?

A Potential Trap!

- Note the mole fraction relationship between the liquid and the vapor phase for each component…
- One requires a higher mole fraction in the liquid to obtain a higher mole fraction in the vapor phase or vice-versa.
- Don’t expect that as one decreases the mole fraction of a component in one phase that it will increase in the other phase.
- We are talking about equilibrium here!

More Important Points

- In order to alter the equilibrium mole fractions, one can alter the temperature of the system at a given pressure or alter the pressure of the system at a given temperature.
- However, remember that if one changes the pressure, one will need a whole other set of equilibrium data at that pressure – always check the pressure of your equilibrium data.

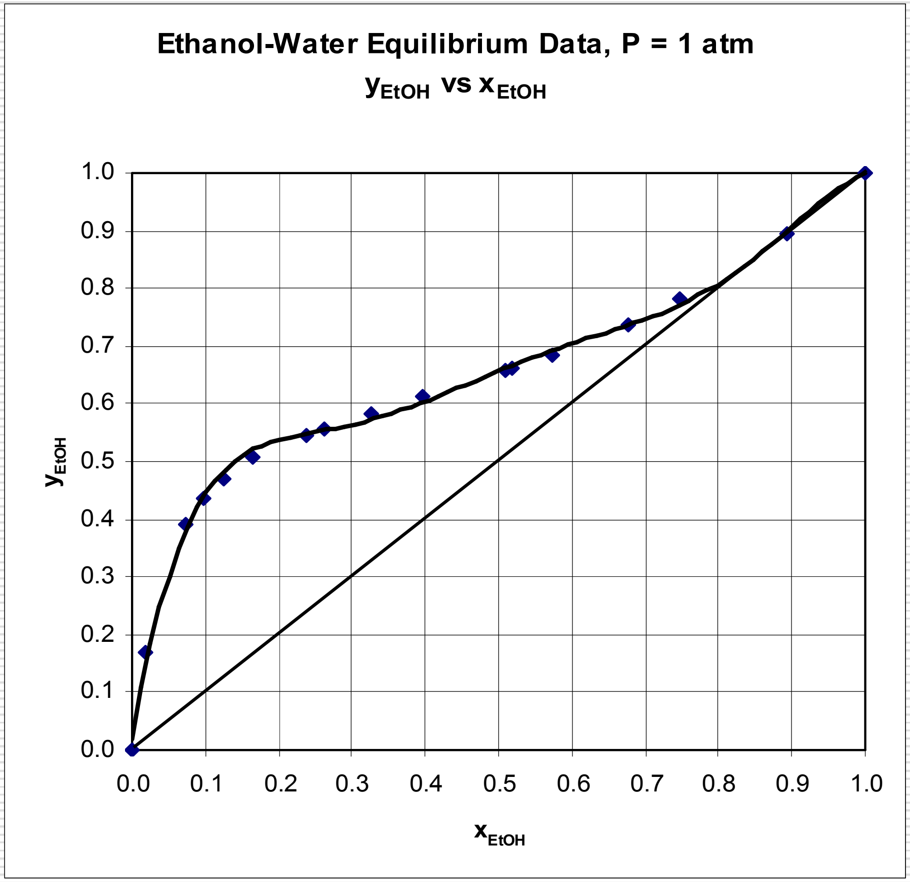
Question

- Inspection of the data indicates what relatively odd behavior occurs in the ethanol-water system at P = 1 atm?
- What happens at this point?

Graphical Plots of Equilibrium Data

- Let's now look at a way to plot this equilibrium data…
- One usually plots the more volatile component – in this case it is ethanol.

y vs. x –
McCabe-Thiele Plot



More Important Points

- Note that the more volatile component, ethanol, generally has a higher mole fraction, y_{EtOH}, in the vapor phase for a given liquid phase mole fraction, x_{EtOH}.
- What would this plot look like if one plotted the less volatile component?