# CH365 Chemical Engineering Thermodynamics

## Lesson 38
## Vapor-Liquid Fundamentals

Block 6 – Solution Thermodynamics

# Overview

Chemical engineering is concerned with changes in composition

- Chemical reactions and reactors
- Mass transfer operations such as extractions, absorption and distillation
    - Phases of different composition are brought into contact and allowed to equilibrate

Properties of mixtures are important

- Primary variables are temperature, pressure, and *composition*

Vapor/liquid systems are the most common, although gas/liquid, liquid/liquid, liquid/solid, and vapor/solid are also encountered

Discussion of phase rules followed by discussion of phase behavior

- Raoult's Law
- Henry's law
- Modified Raoult's Law

# Equilibrium

Condition in which no changes with time occur in *macroscopic* properties

- All potentials that could lead to a change are balanced

- In chemical engineering practice, equilibrium is often assumed
    - Justified when satisfactory results are obtained
    - For example, an equilibrium stage in a distillation column
    - Reboiler in a distillation column with finite vaporization rate

# Isolated System

The system consists of liquid and vapor – 2 phases

Image from Vector Controls

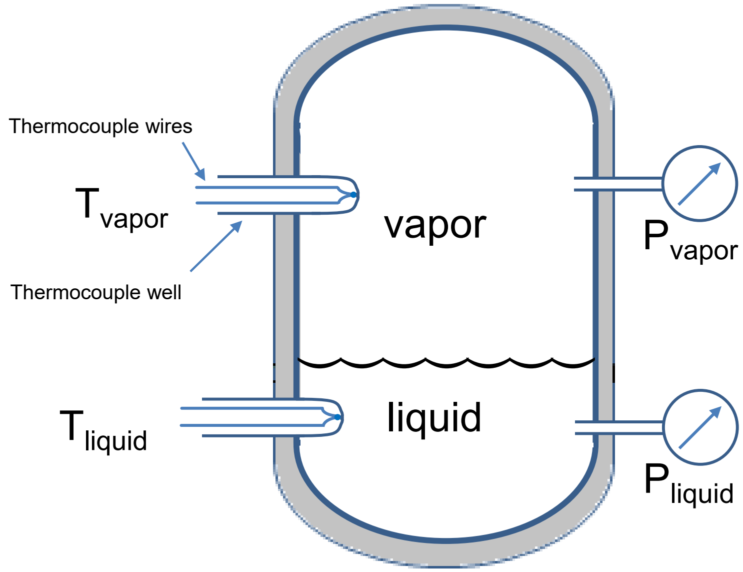



Image from Emerson US

Each phase may contain more than one chemical species

Temperature and pressure of each phase are known

On the *macroscopic* level, all properties are constant with time

On the *microscopic* level, molecules are exchanging between phases

Molecules with sufficiently high velocity escape surface forces in the liquid

Limit discussion to two species a “Binary system”

# Measures of Composition

mass fraction

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}}$$

mole fraction

$$x_i \equiv \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$$

molar concentration

$$C_i \equiv \frac{x_i}{V} = \frac{\text{mole fraction}}{\text{molar volume}}$$

$$C_i = \frac{\dot{n}_i}{q} = \frac{\text{molar flow rate of i}}{\text{volumetric flow rate}}$$

molar mass of mixture

$$M \equiv \sum_i x_i M_i$$

# Derivation of Gibbs' Phase Rule

# Duhem's Theorem

# Application - Rachford-Rice Equations

# Homework

# Problem 13.1

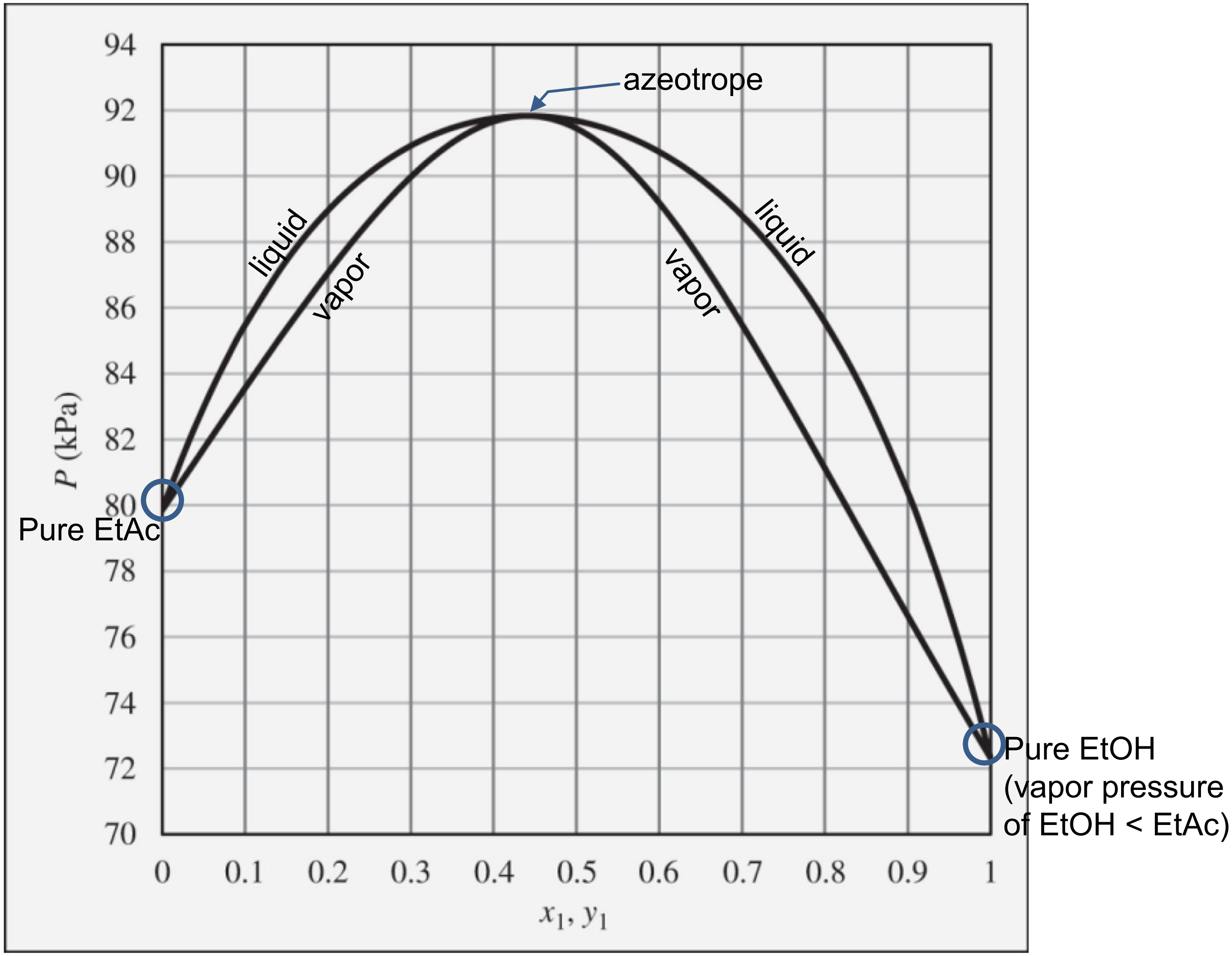
Assuming the validity of Raoult's Law, perform the following calculations for the benzene(1)/toluene(2) system:

(c) Given $x_1$=0.33 and P =120 kPa, find $y_1$ and T.
(d) Given $y_1$=0.33 and P =120 kPa, find $x_1$ and T.

# Problem 12.4

The pressure above a mixture of ethanol and ethyl acetate at 70 deg C is measured to be 78 kPa.  What are the possible compositions of the liquid and vapor phases?

The Pxy diagram is shown on page 443.  Ethanol is component 1.



azeotrope
liquid
vapor
vapor
liquid
Pure EtAc
Pure EtOH
(vapor pressure
of EtOH < EtAc)
94
92
90
88
86
84
82
80
78
76
74
72
70
P (kPa)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
$x_1$, $y_1$

# Problem 12.3

The pressure above a mixture of ethanol and ethyl acetate at 70 deg C is measured to be 86 kPa.  What are the possible compositions of the liquid and vapor phases?

The Pxy diagram is shown on page 443.

# Problem 13.6

Of the following liquid/vapor systems, which can be approximately modeled by Raoult's Law? For those which cannot, why? Table B.1 in Appendix B may be useful.

(a) Benzene/toluene at 1 atm.
(b) n-Hexane/n-heptane at 25 bar.
(c) Hydrogen/propane at 200 K.
(d) Isooctane/n-octane at 100 degC.
(e) Water/n-decane at 1 bar.