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 extraction, absorption and distillation
    - In each of these processes, “phases” of different composition are brought into contact and allowed to equilibrate
    - Properties of mixtures are important for equilibrium calculations
    - Primary variables in mixtures are T, P, and *composition*

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

Today’s class: discussion of phase rules followed by discussion of phase behavior

- Phase Rule and Duhem’s theorem
- Raoult’s Law and open systems

Next Class: Modified Raoult’s Law

Equilibrium

Condition in which *macroscopic* properties are not changing with time.

- All potentials that could drive change are balanced.
- Equilibrium (w.r.t. driving forces) and steady-state (w.r.t. time) are not the same thing.
  - In chemical engineering practice, equilibrium is often *assumed*.
  - This assumption is justified when satisfactory results are obtained.
  - For example, vapor and liquid in equilibrium stage in a distillation column.
  - Another example is thermal equilibrium in a heat exchanger.

Isolated System

The system consists of 2 phases - liquid and vapor

Image from Vector Controls

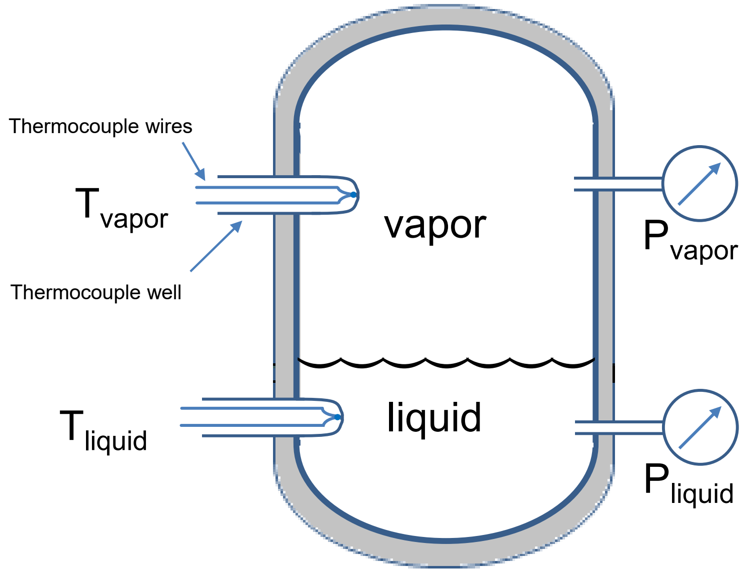


Image from Emerson US

Each phase contains multiple chemical species.

Limit discussion to two species – a "binary system."

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.

Derivation of Gibbs’ Phase Rule

Duhem's Theorem

Application - Rachford-Rice Equations

Duhem's Theorem says that we must have two specs in the flash unit (for example T and P).

Homework

Problem 13.1

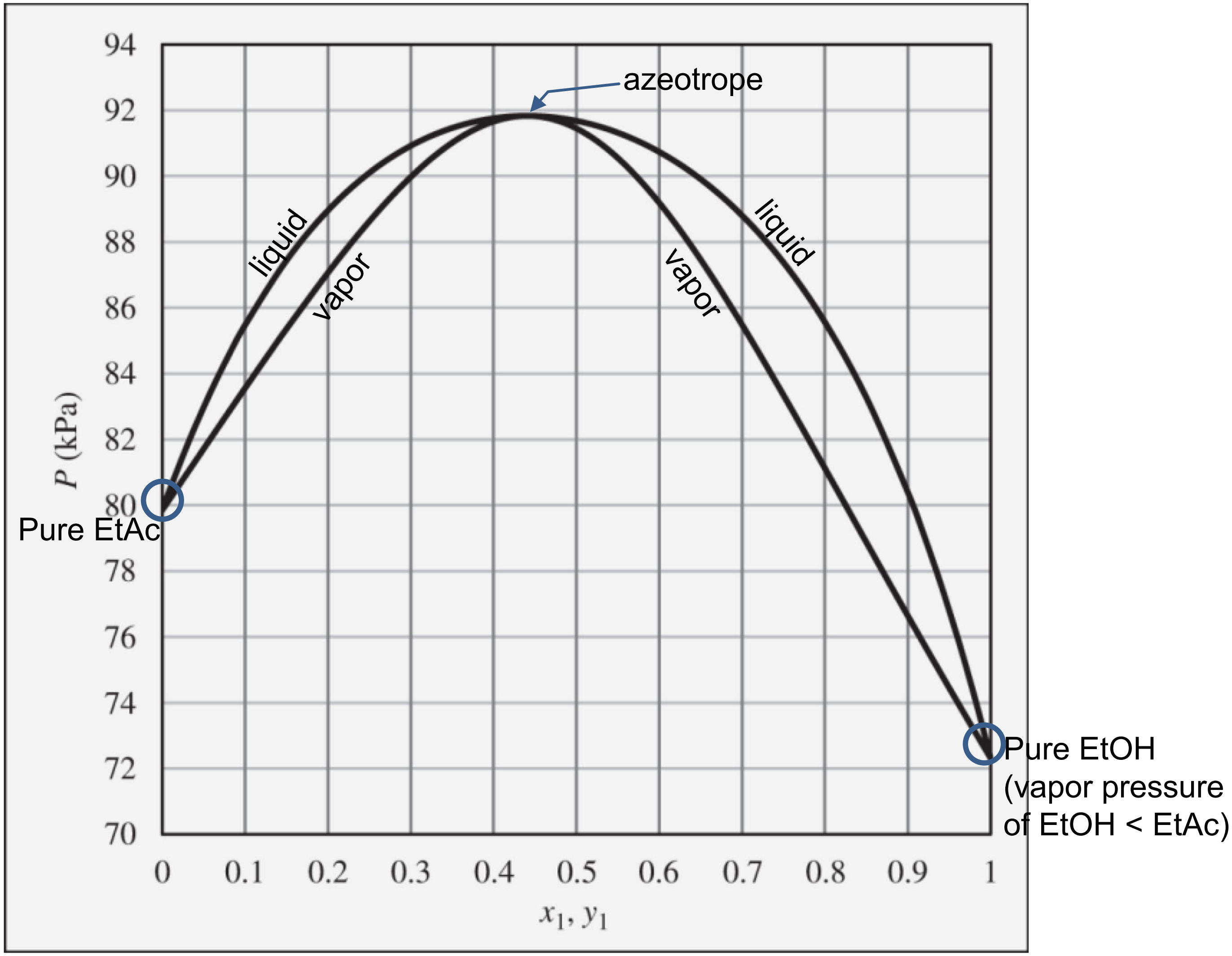
Assuming the validity of Raoult's Law, perform the following calculations for the benzene(1)/toluene(2) system:

(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)
P (kPa)
94
92
90
88
86
84
82
80
78
76
74
72
70
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x1, y1

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.