

CH365 Chemical Engineering Thermodynamics

Lesson 38 Vapor-Liquid Fundamentals

Block 6 – Solution Thermodynamics

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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

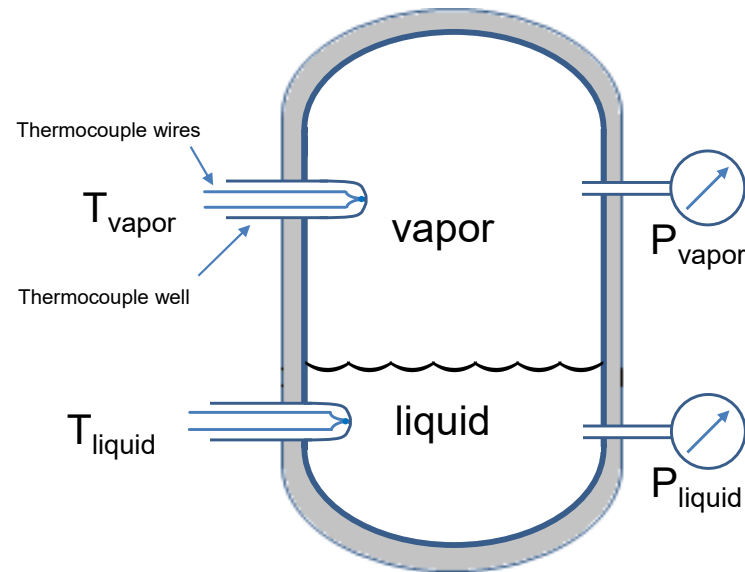


Image from Emerson US

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”



Image from Vector Controls

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

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

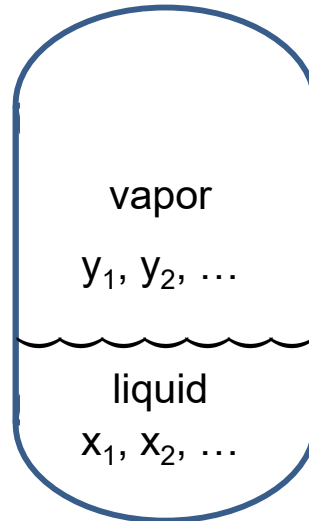
$$C_i = \frac{\dot{n}_i}{q} = \frac{\text{molar flow rate of } i}{\text{volumetric flow rate}}$$

molar mass of mixture

$$M \equiv \sum_i x_i M_i$$

Derivation of Gibbs' Phase Rule

Describes the intensive state of a system



Degrees of freedom:

Difference between variables and equations

$$\text{DOF} = 2 + (N - 1)\pi - (\pi - 1)N$$

$$\text{DOF} = 2 - \pi + N \quad (\text{eq 3.1})$$

variables:

temperature T

pressure P

N chemical species

π phases

$N-1$ mole fractions in each phase

number of variables:

$$2 + (N - 1) \cdot \pi$$

equations:

Species 1 in liquid \rightleftharpoons Species 1 in vapor

$$K_i = \frac{\text{concentration of product } i}{\text{concentration of reactant } i} \quad K_1 = \frac{y_1}{x_1}$$

one equilibrium expression can be written for each component for each pair of phases

$$y_i = K_i \cdot x_i$$

number of equations:

$$(\pi - 1) \cdot N$$

Duhem's Theorem

Open Systems - Flash



Image from Wikipedia

Pierre Duhem, 1861-1916

amount
of vapor

vapor

 y_1, y_2, \dots

liquid

 x_1, x_2, \dots amount
of liquid

Describes the extensive state of a system – how much

variables:

temperature T pressure P N chemical species π phases $N-1$ mole fractions in each phase

number of variables:

$$2 + (N - 1) \cdot \pi + \pi = 2 + N \cdot \pi$$

How much of each phase

Independent Variables Needed (IVN):

difference between variables and equations

$$\text{IVN} = 2 + N\pi - N\pi = 2$$

$$\text{IVN} = 2$$

“For any closed system formed initially from given masses of prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed.”

equations:

Count one material balance for each component and one equilibrium expression for each component for each pair of phases

$$y_i = K_i \cdot x_i$$

number of equations:

$$(\pi - 1) \cdot N + N = \pi \cdot N$$

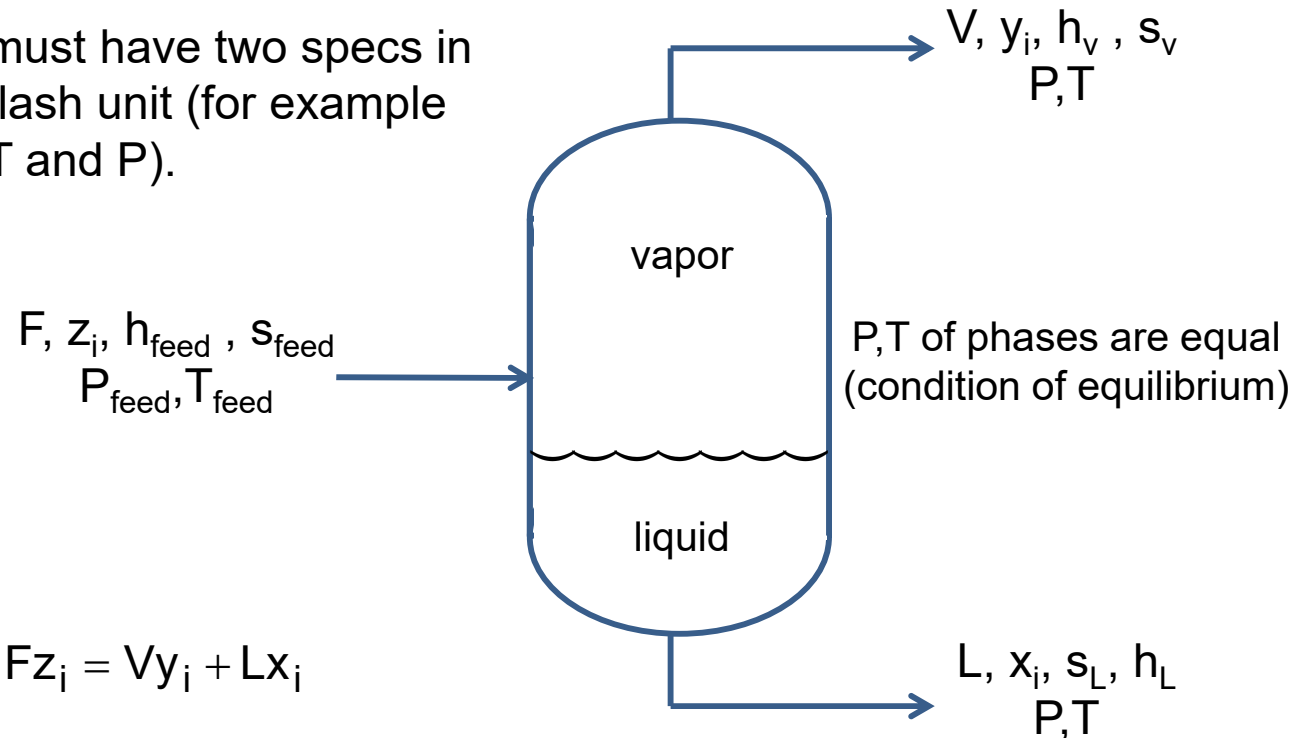
How much of each species

Gibbs phase rule still applies

If $\text{DOF}=1$, then one variable must be intensive

Application - Rachford-Rice Equations

- must have two specs in flash unit (for example T and P).



$$F = V + L$$

$$1 = \frac{V}{F} + \frac{L}{F}$$

$$\psi = \frac{V}{F}$$

$$(1 - \psi) = \frac{L}{F}$$

$$Fz_i = Vy_i + Lx_i$$

$$z_i = \psi y_i + (1 - \psi)x_i$$

$$y_i = K_i \cdot x_i \quad K_i = \frac{y_i}{x_i} = \frac{P_i^{\text{sat}}}{P}$$

T can be specified

P can be specified

$$z_i = \psi K_i x_i + (1 - \psi)x_i = \psi K_i x_i + x_i - \psi x_i = \psi K_i x_i + x_i - \psi x_i = (\psi(K_i - 1) + 1)x_i$$

$$x_i = \frac{z_i}{1 + \psi(K_i - 1)}$$

$$f(\psi) = \sum_i x_i - \sum_i y_i$$

Homework

Problem 13.1

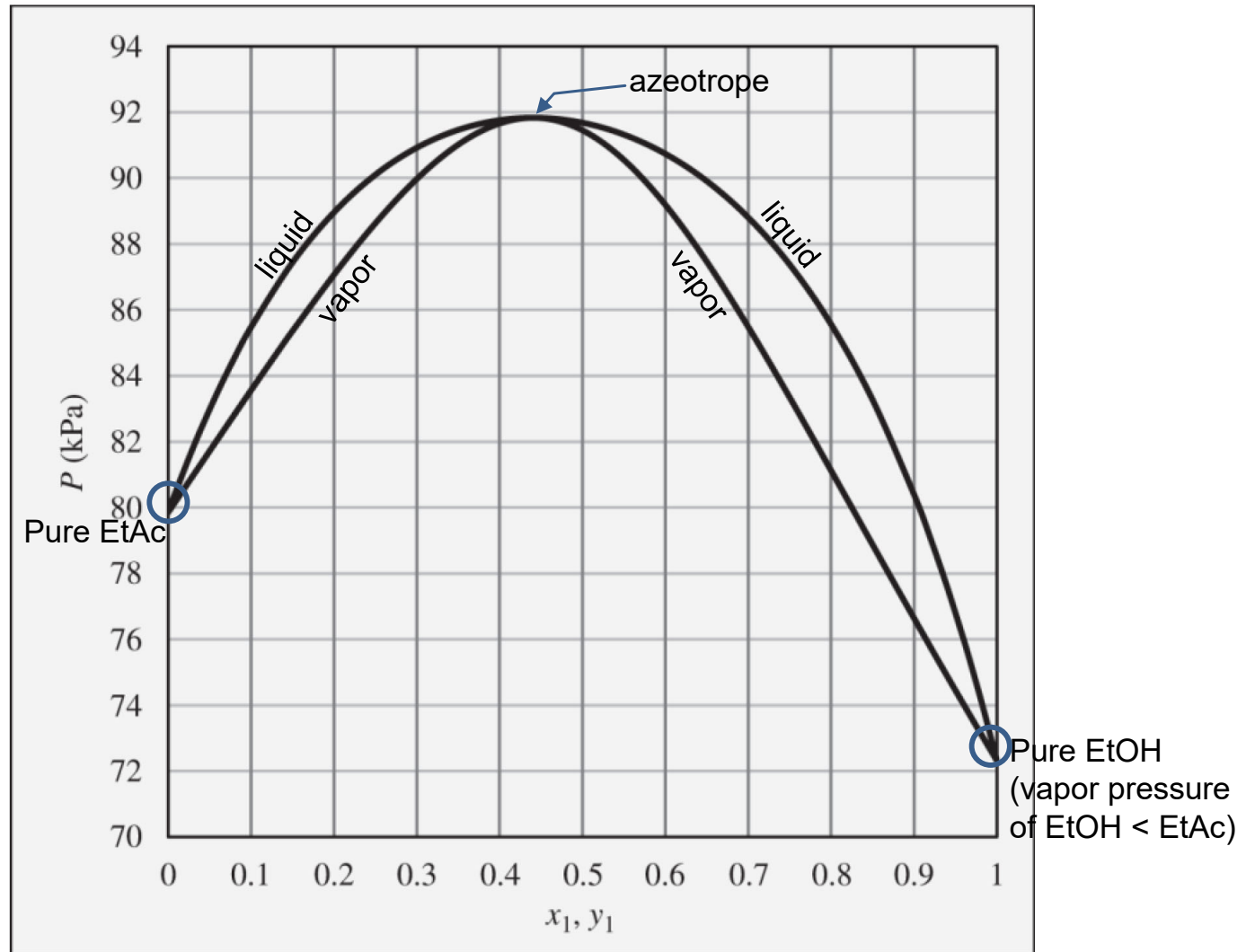
Assuming the validity of Raoult's Law, perform the following calculations for the benzene(1)/toluene(2) system:

- (a) Given $x_1=0.33$ and $T = 100$ deg C, find y_1 and P .
- (c) Given $x_1=0.33$ and $P = 120$ kPa, find y_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.



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.