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
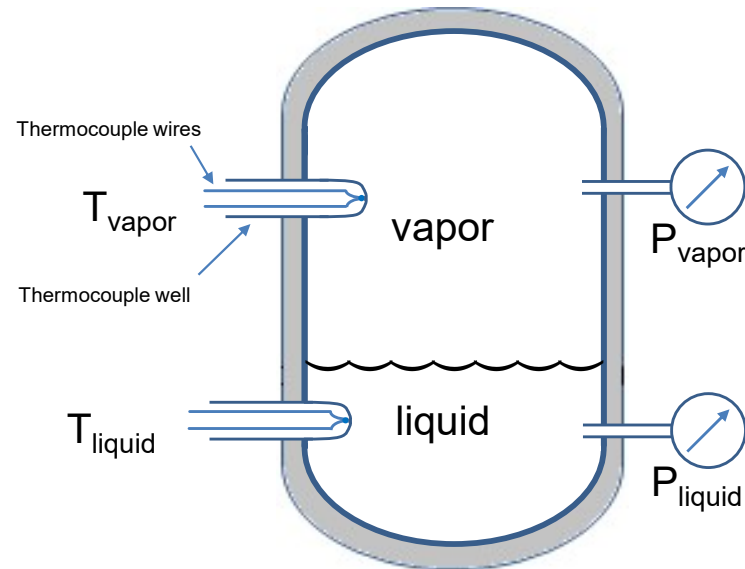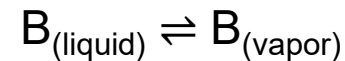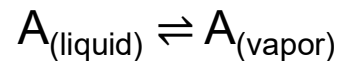

Image from Vector Controls

Thermocouple wires

T_{vapor}

Thermocouple well

vapor

P_{vapor}

T_{liquid}

liquid

P_{liquid}

Image from Emerson US

Each phase contains multiple chemical species.

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

$$A_{(liquid)} \rightleftharpoons A_{(vapor)} \qquad B_{(liquid)} \rightleftharpoons B_{(vapor)}$$

$$K_A = \frac{y_A}{x_A} \qquad\qquad K_B = \frac{y_B}{x_B}$$

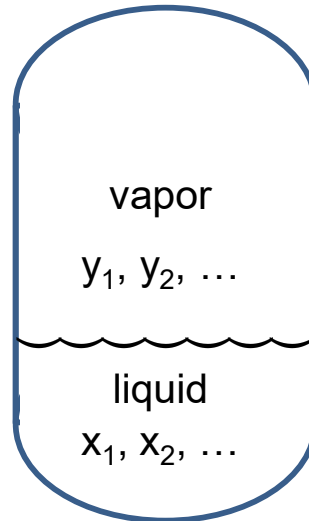Temperature and pressure of each phase are known.

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

Describes the intensive
state of a system

vapor

$y_1, y_2, \ldots$

liquid

$x_1, x_2, \ldots$

Degrees of freedom:

Difference between variables and equations

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

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

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

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

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

$$y_i = K_i \cdot x_i$$

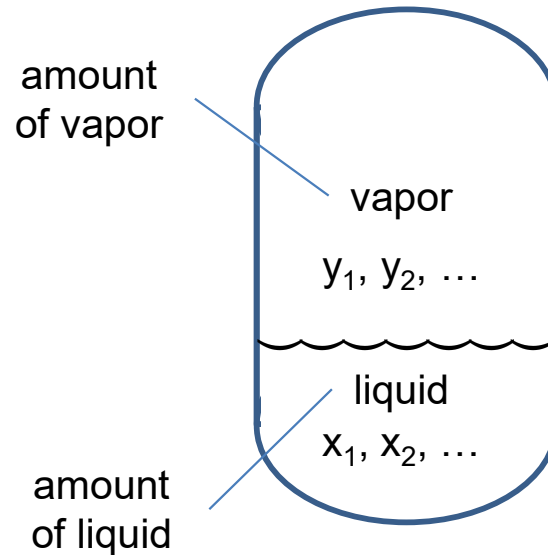number of equations:
$$(\pi - 1)\cdot N$$

Duhem's Theorem

Describes the *extensive* state of a system – how much

Applies to *open* systems - flash

Image from Wikipedia

Pierre Duhem, 1861-1916

amount of vapor

vapor

$y_1, y_2, \ldots$

liquid

$x_1, x_2, \ldots$

amount of liquid

Independent Variables Needed (IVN):

difference between variables and equations

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

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."

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

equations:

One mole balance for each species and one equation for each species equilibrating between two phases

$$y_i = K_i \cdot x_i$$

number of equations:
$(\pi - 1)\cdot N + N = \pi\cdot N$

One equation for each equilibrium   *One mole balance for each species*

Gibbs phase rule still applies

If DOF=1, then one variable must be intensive

Application - Rachford-Rice Equations

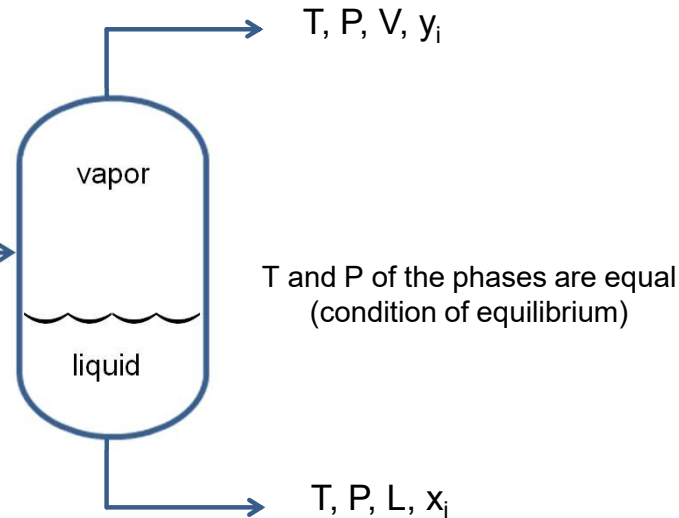Duhem's Theorem says that flash requires two specs.

- Feed mole fractions (z) are normally specified.
- T and P of feed are normally specified.
- Flow is normally specified or we can assume a basis for F.

$F, z_i, P_{feed}, T_{feed}$

Everything to the left of this line is specified.

T, P, V, y_i

vapor

liquid

T and P of the phases are equal (condition of equilibrium)

T, P, L, x_i

Definition of Ψ:

$$F = V + L$$

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

$$\Psi \equiv \frac{V}{F} \quad \Leftrightarrow \quad 1 - \Psi = \frac{L}{F}$$

Example: Binary
Number of unknowns: 7
T, P, x_1, x_2, y_1, y_2, and Ψ:

Duhem: 2
for example: P and Ψ

Unknowns Left After Duhem: 5
T, x_1, x_2, y_1, and y_2

Flash Specs.
T, P

T, $0 < \psi < 1$
P, $0 < \psi < 1$

P, $\psi = 0$ bubble point temp
P, $\psi = 1$ dew point temp

T, $\psi = 0$ bubble point pressure
T, $\psi = 1$ dew point pressure

Species Mole Balances (2):

$$Fz_i = Vy_i + Lx_i$$

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

$$\psi = 0 \;\Rightarrow\; z_i = x_i \;\Rightarrow\; \text{bubble point}$$

$$\psi = 1 \;\Rightarrow\; z_i = y_i \;\Rightarrow\; \text{dew point}$$

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

Equilibrium Expressions (2):

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

$$P_i^{sat} = e^{a_i - b_i/(T + c_i)}$$

Summation of Mole Fractions (1):

$$1 = \sum_i x_i$$

$$1 = \sum_i y_i$$

$$0 = \sum_i x_i - \sum_i y_i \quad ✓$$

(Rachford-Rice)

Equations: 2+2+1=5 (red ✓'s)

Solvable!

Questions?