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
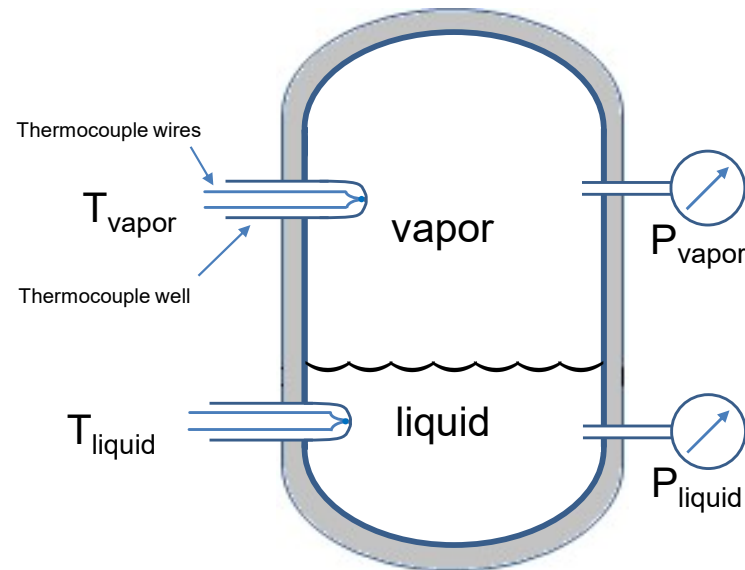

Image from Vector Controls

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."

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 flash requires two specs.

Questions?