# 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

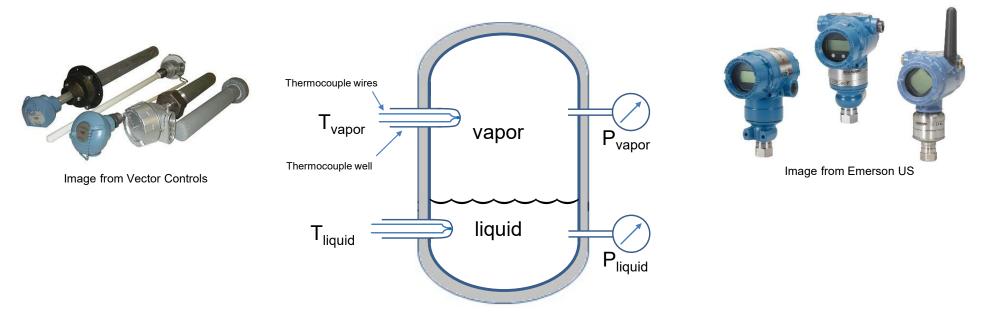
#### Equilibrium

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



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.

## Questions?