Equilibrium Diagrams and Saturated Liquid/Vapor Systems

• In equilibrium, different phases of matter
  – gas, liquid, solid (also multiple solid phases, e.g., different crystalline structures of steel)

• So far looked at individual phases of simple (homogeneous) substances

• Multiple phases can exist simultaneously in equilibrium

• Consider heating simple compressible substance at constant pressure
Phase Transitions - Constant Pressure

Start with solid

Small change in v until gas

2 → 3: Melting
4 → 5: Evaporation
3 → 2: Freezing/Fusion
5 → 4: Condensation
Typical T-\(v\) Diagram

- Solid + Gas/vapor
- Liquid + Gas
- (Saturated) Vapor Dome
- (Subcooled) Liquid
- Triple Line
- Solid
- Critical Point
- Supercritical States
- \(P_{\text{crit}}\)
- \(P_{\text{hi}}\)
- \(P_{\text{low}}\)

Saturation States = Phase Transitions
Phases of Compressible Substances

- **Triple Line**
  - all 3 phases can coexist at same T and P

- **Critical Point**
  - maximum T and p at which distinct liquid and gas phases can coexist

- **Supercritical States** (or supercritical fluid)
  - for \( p > p_{\text{crit}} \), no distinct transition from liquid to gas, fluid can have characteristics of both
Surface View

- Phase space not just 2 dimensional
Mixed Phase Regions

- Independent TD properties
  - \( p \) and \( T \) not independent
  - phase transition at const. \( p, \ T \)
    (e.g., given \( T_{\text{sat}} \), know \( p_{\text{sat}} \))

- Can define new intensive variable to characterize composition
  - describe how much of each phase present
  - should not depend on total mass
Quality of Saturated Liquid-Vapor

- For saturated liquid-vapor region (vapor dome)
  - new variable is quality, $x$
    
    $$x \equiv \frac{m_g}{m_{\text{mixture}}} = \frac{m_g}{m_f + m_g}$$

  - $x$ gives fraction of mass that is gas ($g$)
  - $(1-x)$ is fraction of mass that is liquid ($f$)
  - $0 < x < 1$ (0 for liquid, 1 for gas)
Volume of Saturated Liquid-Vapor Mixture

- Get TD properties of saturated mixture by summing up proper amount of property for each phase, e.g.,

\[ V_{\text{mix}} = m_g v_g + m_f v_f = m_{\text{mix}} \left[ \frac{m_g v_g}{m_{\text{mix}}} + \frac{m_f v_f}{m_{\text{mix}}} \right] \]

\[ = m_{\text{mix}} \left[ x v_g + (1 - x) v_f \right] \]

or

\[ v_{\text{mix}} = x v_g + (1 - x) v_f \]

\[ = v_f + x(v_g - v_f) \]

- where

\[ g \rightarrow \text{gas}, \ f \rightarrow \text{liquid} \]
Saturated Liquid-Vapor Mixture Properties

- For general intensive property $y$ that obeys sum rule,

$$y_{\text{mix}} = xy_g + (1-x)y_f$$

or

$$y_{\text{mix}} = y_f + x y_{fg}$$

with $y_{fg} = y_g - y_f$

- $y_{\text{mix}}$ always bounded by $y_f$, $y_g$
- does not work for $\rho$ ($\rho \neq \rho_1 + \rho_2$)

Does $T_{\text{mix}}$ obey sum rule?
Example 1:

- **Given:** 3 kg of water at 200°C with quality \( x = 0.6 \)
- **Find:** Volume (V) and internal energy (U)
- **Assume:** phase equilibrium
Example 1:

- **Analysis:**

\[
V = m\left[\nu_f + x\nu_{fg}\right] \\
= 3\text{kg}\left[0.0011564 + 0.6(0.1262)\right]\frac{m^3}{kg} \\
= 3\text{kg}\left[0.07688 \text{m}^3/\text{kg}\right] \\
= 0.231\text{m}^3
\]

\[
U = m\left[u_f + xu_{fg}\right] \\
= 3\text{kg}\left[850.58 + 0.6(1744.1)\right]\frac{kJ}{kg} \\
= 5691kJ
\]

**Note:** \(\nu_{mix} \gg \nu_f\) (~70×)

because \(\nu_g \gg \nu_f\)

or \(\rho_g << \rho_f\)

What is pressure of mixture?

\[m = 3 \text{ kg} \]

\[T = 200\degree\text{C}\]

\[x = 0.6\]
Example 2:

• **Given:** 5 lb\textsubscript{m} of water initially at 700°F and 2000 psia in rigid container

• **Find:** How much energy loss required to cool water to 300°F

• **Assume:** equilibrium initial and final state

• **Analysis:**

\[
Q = \Delta U = m(u_1 - u_2)
\]

Need \(u_2\) and \(u_1\)
Example 2:

\[ V = \text{const} \]

\[ T_1 = 700^\circ F \]
\[ p_1 = 2000 \text{ psi} \]
\[ m = 5 \text{ lb}_m \]

\[ Q \]

\[ u_1 = ? \]

\[ T > T_{\text{sat}} \]

superheated vapor

\[ u_1 = 1147.2 \text{ BTU/lb}_m \]
Example 2:

\[ V = \text{const} \]

\[ T_2 = 300^\circ\text{F} \]

\[ v_2 = 0.249\text{ft}^3/\text{lb}_m \]

\[ m = 5 \text{ lb}_m \]

\[ \Delta U = m(u_1 - u_2) = Q \]

\[ = 4240\text{BTU} \left( 4.47\text{MJ} \right) \]

\[ v_2 = v_f + x_2 v_{fg} \]

\[ u_2 = 299\text{ BTU}/\text{lb}_m \]
Example 2:

Do phases always coexist in equilibrium?

\[ T_1 = 700^\circ F \]
\[ p_1 = 2000 \text{psi} \]
\[ v_1 = 0.25 \text{ft}^3/\text{lb}_m \]
\[ m = 5 \text{ lb}_m \]

\[ T_2 = 300^\circ F \]
\[ p_2 = 66.97 \text{psi} \]
\[ v_2 = 0.25 \text{ft}^3/\text{lb}_m \]
\[ m = 5 \text{ lb}_m \]