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

<table>
<thead>
<tr>
<th>Transition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>Melting</td>
</tr>
<tr>
<td>2→3</td>
<td>Evaporation</td>
</tr>
<tr>
<td>3→2</td>
<td>Freezing/Fusion</td>
</tr>
<tr>
<td>4→5</td>
<td>Condensation</td>
</tr>
</tbody>
</table>

Small change in v until gas
Phase Equilibrium and Saturated Liquid/Gas Systems

Typical T-$\nu$ Diagram

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

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Phase Equilibrium and Saturated Liquid/Gas Systems

- 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.,
  \[
  V_{\text{mix}} = m_g v_g + m_f v_f = m_{\text{mix}} \left[ \frac{m_g v_g + m_f v_f}{m_{\text{mix}}} \right]
  \]
  or
  \[
  v_{\text{mix}} = x v_g + (1-x) v_f = v_f + x(v_g - v_f)
  \]
  - where
    $g \rightarrow$ gas, $f \rightarrow$ liquid
Saturated Liquid-Vapor Mixture Properties

- For general intensive property \( y \) that obeys sum rule,

\[
\begin{align*}
y_{\text{mix}} & = xy_g + (1-x)y_f \\
\text{or} & \\
y_{\text{mix}} & = y_f + x y_{fg}
\end{align*}
\]

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:**

\[ V = m[v_f + xv_{fg}] \]

Table B.1

\[ V = 3 \text{ kg} [0.0011564 + 0.6(0.1262)] \frac{m^3}{kg} \]

\[ V = 3 \text{ kg} [0.07688 \text{ m}^3/\text{kg}] \]

\[ V = 0.231 \text{ m}^3 \]

\[ U = m[u_f + xu_{fg}] \]

\[ U = 3 \text{ kg} [850.58 + 0.6(1744.1)] \frac{kJ}{kg} \]

\[ U = 3 \text{ kg} [585.850] \frac{kJ}{kg} \]

\[ U = 5691 \text{ kJ} \]

**Note:**

- \( v_{mix} \gg v_f \) (~70x)
- because \( v_g \gg v_f \)
- or \( \rho_g \ll \rho_f \)
- \( u_g \) only ~3\( u_f \)

What is pressure of mixture?

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### Example 2:

**Given:** 5 lb\(_m\) 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 = const

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

\[ Q \]

\[ u_1 = \ ? \]

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

– superheated vapor

\[ u_1 = 1147.2\,\text{BTU/lb}_m \]

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Example 2:

V = const

\[ T_2 = 300\,^\circ\text{F} \]
\[ u_2 = 0.249\,\text{ft}^3/\text{lb}_m \]
\[ m = 5\,\text{lb}_m \]

\[ Q \]

\[ v_2 = v_f + x_f v_f \]

\[ u_2 = 299\,\text{BTU/lb}_m \]

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

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

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Example 2: V=const

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

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

Do phases always coexist in equilibrium?