Unit one – Properties of Pure Substances

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Mechanical Engineering 370
Thermodynamics
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Outline

• Extensive, $E$, $m$, intensive, $T$, $P$, $\rho$, and specific, $e = E/m$, variables
• $\rho = m/V = 1/v$ => density $= 1/(\text{sp. vol.})$
• Look at $P$-$v$-$T$ data for real substances
• Ideal gases $PV = nR_uT = mRT$
  – Engineering gas constant: $R = R_u / M$
  – With $v = V/m$, $Pv = RT$
  • Use of $V$ or $v = V/m$ gives difference between $PV = mRT$ and $Pv = RT$

Thermodynamic Variables

• Extensive variables (volume, mass, energy) depend on size of system
• Intensive variables (pressure, temperature, density) do not
• Specific variables are ratio of an extensive variable to mass (e.g. specific volume, $v = V/m$)
• General notation, if $E$ is an extensive variable, $e = E/m$ is specific variable

Thermodynamic System

• Basic unit of analysis defined by boundaries where all interactions occur
• State of system defined by properties
• Interaction of system with surroundings
  – Can interchange energy and mass
  – Open/closed systems: Have/Do not have mass addition or removal
  • Open system called control volume
  – Isolated system: constant energy and mass
  – All interactions across boundaries

Thermodynamic State

• Two independent intensive properties determine the state of a simple compressible system
• Once the state of a system is determined all other properties are known
• Thermodynamic processes are a continuous series of states known as a quasi-equilibrium process

Ideal Gas Equations

• From chemistry: $PV = nR_uT$
• $R_u = \text{Universal gas constant} = 8.314 \text{ kJ/kmol·K} = 8.314 \text{ kPa · m}^3/\text{kmol·K} = 10.73 \text{ psia · ft}^3/\text{lbmol · K}$
• Engineering gas constant, $R = R_u / M$
• Definition of mol, $n = m / M$
• $PV = (m/M)(MR)T = mRT$
• $P(T/m) = P = RT$
• $P(v/m) = P = RT$
**Why Use Ideal Gas?**

- Simple equations
- Real gas behavior close to ideal gas for low pressure (or high temperature)
- Want $P$ low compared to $P_c$
- Example calculation: find specific volume of water at $1,000^\circ C$ and $10$ kPa
  
  - Compare to property table value of $v = 58.758 \text{ m}^3/\text{kg}$ for water (page 918)

**Finding R**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$M$ kg/kmol</th>
<th>$R$ kJ/kg·K</th>
<th>Gas constant, $R$ = kPa·m$^3$/kg·K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$\text{N}_2$</td>
<td>28.97</td>
<td>0.2870</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3$</td>
<td>17.03</td>
<td>0.8882</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>$\text{Ar}$</td>
<td>39.948</td>
<td>0.2081</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>$\text{C}_6\text{H}_6$</td>
<td>78.115</td>
<td>0.0106</td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td>$\text{Br}_2$</td>
<td>159.808</td>
<td>0.0520</td>
<td></td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>$\text{CCl}_3$</td>
<td>137.37</td>
<td>0.0505</td>
<td></td>
</tr>
<tr>
<td>Trichlorofluoromethane (R-11)</td>
<td>$\text{CCl}_2\text{F}_2$</td>
<td>137.37</td>
<td>0.0505</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>$\text{H}_2\text{O}$</td>
<td>18.015</td>
<td>0.4614</td>
<td></td>
</tr>
<tr>
<td>Xenon</td>
<td>$\text{Xe}$</td>
<td>131.30</td>
<td>0.0633</td>
<td></td>
</tr>
</tbody>
</table>

**Ideal Gas Calculation II**

- A volume of 20 ft$^3$ at a pressure of 300 psia contains 20 lbm of Helium; what is the temperature?
  
  - $T = \frac{PV}{(mR)}$
  - $R = 2.6809 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R}$ (page 958)
  
  $$T = \frac{PV}{mR} = \frac{(300 \text{ psia})(20 \text{ ft}^3)}{2.6809 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R}} = 111.9 \text{ R} = -347.7^\circ F$$

**P-v-T for Real Substances**

- Three phases: gas, liquid and solid
- Look at gas and liquid
- Thought experiment
  - Add heat to a liquid at constant pressure; measure $T$ and $v$
  - After a while vapor starts to form
    - Heat addition increases volume by converting liquid to gas while $T$ is constant (at constant $P$)
    - Finally have only gas that expands readily
  - Ideal gas has $vT = \text{const}$ (at constant $P$)
Thought Experiment II

- States 2 to 4 are liquid vapor transition
  - Liquid and vapor have same properties (P, \( v_l = 1/\rho_l \), \( v_g = 1/\rho_g \), and T) during transition; only relative proportions change

Figures 3-6 to 3-10 from Çengel, Thermodynamics An Engineering Approach, 2008

Thought Experiment III

- Repeat experiment with difference in variables
- Hold temperature constant
- Add heat and measure pressure, P, and specific volume \( v \)
- Have same liquid-vapor transition
  - P is constant if T is constant
  - Liquid and vapor properties constant in transition only relative proportions change

Thought Experiment Results

- A constant temperature line on P-v
  - Looks like a hyperbola in the gas region
  - Has constant pressure during the transition from liquid to gas
  - Is nearly vertical in the liquid region
- The points where the transition between liquid and gas take place for different temperatures: saturation curve
- Results of “experiment” on next slide

Critical P-v Diagram for Water

Superheat P-v Diagram for Water
What We Have to Do

- Find all intensive thermodynamic properties when we are given only two intensive properties
  - Two independent, intensive properties define state
- Here we will discuss only four intensive properties, P, v, T, and fraction of vapor in mixed region called the quality, x
- Approach used here will be applied to finding other properties: internal energy, enthalpy, and entropy

Finding Properties

- When we have a mixture of liquid and gas T and P are not independent
- For a single phase (liquid or gas) T and P are independent (can specify state)
- In the mixed region we use vapor mass fraction, called quality, x

\[
x = \frac{m_g}{m_g + m_f} = \frac{v_f - v_g}{v_g - v_f} \quad \text{• } v_f \text{ and } v_g \text{ are found from either } T \text{ or } P
\]

Quality Derived

- Mixed region volume is sum of liquid and vapor volumes

\[
V = \frac{m_g v_g + m_f v_f}{m} \implies V = \frac{m_g}{m} v_g + \frac{m_f}{m} v_f = \frac{m}{m} v_g + \frac{m}{m} v_f
\]

- Use quality: 

\[
x = \frac{m_g}{m_g + m_f} = \frac{m_g}{m}
\]

\[
v = \frac{m}{m} v_g + \frac{m}{m} v_f = x v_g + (1 - x) v_f = v_f + x(v_g - v_f)
\]

- Will apply this later to other properties

Saturation Properties

Saturated liquid (f) and saturated vapor (g) properties can be found if P or T are known

Use quality, x, in mixed region

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

Saturation Tables

- See steam tables, pp 914–923
- Saturation tables
  - Table A-4 has T as lookup variable
  - Table A-5 has P as lookup variable
  - Same results in each table
- Other variables besides specific volume have saturated liquid (f) and gas (g)
- Example: what are P and v if T = 220°C and x = 0.25?

- Use Table A-4, Page 915, T = 220°C
- Find P = 2319.6 kPa, v_f = 0.001190 m³/kg and v_g = 0.086094 m³/kg
What is $v$ for $x = 0.25$?

- Found from Table A-4 with lookup $T$
  - $P = P_{\text{sat}}(T = 220^\circ C) = 2319.6 \text{ kPa}$
  - $v_f(T = 220^\circ C) = 0.001190 \text{ m}^3/\text{kg}$
  - $v_g(T = 220^\circ C) = 0.086094 \text{ m}^3/\text{kg}$

$$
v = (1-x)v_f + xv_g = (1-0.25)v_f + 0.25v_g = 0.001190 \text{ m}^3/\text{kg} + 0.022416 \text{ m}^3/\text{kg}
$$

What if $P$ and $T$ are Given?

- If these are independent properties then they define a state
- The “superheat” (gas) tables for water (Table A-6, pp 918 – 921) have a set of tables for $P$ with rows of data for $v$
- Data are also given for other properties
- Basic question: Given $T$ and $P$, how do we know if we have a liquid or a gas?

### Table A-6

![Image of Table A-6](image)

#### General Rules

- When we are given $T$ and $P$ we have a single phase. Is it gas or liquid?
  - It is a gas if $T > T_{\text{sat}}(P)$ or $P < P_{\text{sat}}(T)$
  - It is a liquid if $T < T_{\text{sat}}(P)$ or $P > P_{\text{sat}}(T)$
  - “Superheat” tables have $T_{\text{sat}}$ by $P$
- Can guess superheat and check
  - Example: R134a at 0°C and $P = 100 \text{ kPa}$, 400 kPa
  - Guess superheat and find at 100 kPa and 0°C, $v = 0.21630 \text{ m}^3/\text{kg}$; at 400 kPa there is no 0°C entry
  - Data from page 929
Results

- $v(0^\circ C, 100 \text{ kPa}) = 0.21630 \text{ m}^3/\text{kg}$
- What is $v(0^\circ C, 100 \text{ kPa})$? Page 929

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>$v$ (m$^3$/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.051201</td>
<td>235.07</td>
</tr>
<tr>
<td>10</td>
<td>0.051506</td>
<td>235.97</td>
</tr>
<tr>
<td>20</td>
<td>0.054213</td>
<td>244.18</td>
</tr>
<tr>
<td>30</td>
<td>0.056796</td>
<td>252.36</td>
</tr>
</tbody>
</table>

- Why are there no data at $T = 0^\circ C$ and $P = 400 \text{ MPa} (= 0.4 \text{ MPa})$?

General Rules Continued

- The example did not find a $0^\circ C$ entry at 400 kPa because this is a liquid
  - The header 0.4 MPa ($T_{sat} = 8.91^\circ C$ confirms that $T = 0^\circ C < T_{sat} = 8.91^\circ C$
- Approximation for compressed liquid: $v(T,P) \approx v_f(T)$ Note it’s $v_f(T)$
  - To get answer for 400 kPa and $0^\circ C$ look at saturation table for $T = 0^\circ C$, A-11, page 926
  - $v(0^\circ C, 400 \text{ kPa}) = v_f(0^\circ C) = 0.0007723 \text{ m}^3$/kg

Two More Problems

- What is the specific volume for refrigerant 134a (R-134a) when the pressure is 90 psia and the temperature is 240°F
  - R-134a tables in English units: pp. 976-979
  - Guess that this is gas and look in “superheated” tables on page 979
  - $v = 0.77796 \text{ ft}^3/\text{lb}_m$ at given $T$ and $P$
- What is $P$ when $T = 240^\circ F$ and $v = 0.77796 \text{ ft}^3/\text{lb}_m$?

Review Last Problem

- What is the specific volume for refrigerant 134a (R-134a) when the pressure is 90 psia and the temperature is 240°F
  - R-134a tables in English units: pp. 978-81
  - What if we could not guess that this is gas or made a wrong guess?
    - Use general rule that gas occurs when $P < P_{sat}(T)$ or $T > T_{sat}(P)$
    - For this problem $T = 240^\circ F > T_{sat}(90 \text{ psi}) = 72.83^\circ F$
    - Also $P = 90 \text{ psi} < P_{sat}(240^\circ F) = 138.79 \text{ psi}$

Find State Given $v$ and $(T$ or $P)$

- Determine state: find $v_f$ and $v_g$ from saturation tables for given $T$ or $P$
  - If $v > v_g$ it is a gas; use superheat table
  - If $v < v_f$ it is a liquid; see below
  - If $v_l < v < v_g$ it is in mixed region. Can find $x$
- For liquid to use $v = v_f(T)$ we must be given $v-P$; find $T$ for which $v_f(T) = v_{given}$
- Compressed liquid tables for water

Given $T$-$v$ (or $P$-$v$); Find $P$ (or $T$)

- Determine state: find $v_f$ and $v_g$ from saturation tables for given $T$ (or $P$)
  - If $v > v_g$ it is a gas; use superheat table
  - If $v < v_f$ it is a liquid; see below
  - If $v_l < v < v_g$ it is in mixed region. Can find $x$
- For liquid to use $v = v_f(T)$ we must be given $v-P$; find $T$ for which $v_f(T) = v_{given}$
- Compressed liquid tables for water
Interpolation

- Can use interpolation function on your calculator if you have one
- Basic idea is that you have a table with data pairs \((x_1, y_1)\) and \((x_2, y_2)\)
- You want to find a value of \(y\) for some value of \(x\) between \(x_1\) and \(x_2\)
- Simplest idea is to assume a straight line between \(x_1\) and \(x_2\)

![Interpolation](image)

Interpolation II

- For a straight line any two points on the line can give slope
- \[ y = y_1 + \frac{y_2 - y_1}{x_2 - x_1}(x - x_1) \]

Example Problem

- For \(H_2O\) at \(P = 2\) MPa, what is \(T\) when \(v(m^3/kg) = (a) 0.00115, (b) 0.01, (c) 0.2\)?
- Table A-5, p 917 At 2000 kPa, \(v_f = 0.001177 \text{ m}^3/\text{kg}, v_g = 0.099587 \text{ m}^3/\text{kg}\)
  - Thus (a) is liquid, (b) is mixed, (c) is gas
  - For compressed liquid state (a), correct \(T\) is one for which \(v_f(T) = 0.00115 \text{ m}^3/\text{kg}\)
  - Extract from Table A-4, next slide, shows that this \(v_f\) is between \(T = 195^oC\) and \(T = 200^oC\)

Data and Interpolation

- We want to find \(T\) for \(v = 0.00115 \text{ m}^3/\text{kg}\)
  - Between 195°C and 200°C
- For this interpolation \(x_1 = 0.001149 \text{ m}^3/\text{kg}, x_2 = 0.001157 \text{ m}^3/\text{kg}, y_1 = 195^oC\) and \(y_2 = 200^oC\)

Example: (b) Mixed, (c) Gas

- \(b)\) for mixed region, \(T = T_{sat}(2\ \text{Mpa}) = 212.38^oC\); can find quality
  \[ x = \frac{v - v_f}{v_g - v_f} = \frac{0.01m^3/kg - 0.001177m^3/kg}{0.099587m^3/kg - 0.001177m^3/kg} = 0.8896 = 8.96% \]
- \(c)\) \(v = .2 \text{ m}^3/\text{kg}\) at \(P = 2\ \text{MPa}\) found on p. 921 between \(T = 600^oC\) and \(700^oC\)
- \(T = 600^oC\) \[ 700^oC - 600^oC = 0.4^oC \]

- \(T = 700^oC\) \[ 700^oC - 600^oC = 10^oC \]
- \(T = 800^oC\) \[ 700^oC - 600^oC = 100^oC \]
- \(T = 900^oC\) \[ 700^oC - 600^oC = 300^oC \]
Compressed Liquid Table

- Not a common table, use here to check approximation that \( v(P, T) \approx v_f(T) \)
- Table A-7, page 922, gives \( v(50 \text{ MPa, } 100^\circ\text{C}) = 0.0010201 \text{ m}^3/\text{kg} \)
- Table A-4, page 914, gives \( v_f(100^\circ\text{C}) = 0.001043 \text{ m}^3/\text{kg} \)
- Error is about 2% even for a pressure difference of 49.9 MPa between the actual pressure and saturation pressure

More on Compressed Liquid

- Check approximation that \( v(P, T) \approx v_f(T) \) for previous problem: \( v = 0.00115 \text{ m}^3/\text{kg} \) and \( P = 2 \text{ MPa} \)
- Do not have data for compressed liquid at 2 MPa in table on page 922
  - First entry is at 5 MPa
- Have to use double interpolation and interpolation with saturation points
  - Interpolate between \( P_{\text{sat}} \) and 5 MPa

Interpolations

- We are looking for \( v = 0.00115 \text{ m}^3/\text{kg} \) which is between 180°C and 200°C in compressed liquid table at 5 MPa
- We have to find data at these temperatures and 2 MPa
  - Because 5 MPa is the first table entry we use saturation as the lower data point
  
  \[
  v(T, 2 \text{ MPa}) = v_f(T) + \frac{v_f(5 \text{ MPa}) - v_f(T)}{5 \text{ MPa} - P_{\text{sat}}(T)} [2 \text{ MPa} - P_{\text{sat}}(T)]
  \]

Table

Compressed liquid data shown here

<table>
<thead>
<tr>
<th>( T )</th>
<th>( v )</th>
<th>( u )</th>
<th>( h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°C</td>
<td>0.0012862</td>
<td>1148.1</td>
<td>1154.5</td>
</tr>
<tr>
<td>190°C</td>
<td>0.0012937</td>
<td>1154.6</td>
<td>1159.1</td>
</tr>
<tr>
<td>200°C</td>
<td>0.0012996</td>
<td>1159.6</td>
<td>1163.7</td>
</tr>
<tr>
<td>210°C</td>
<td>0.0013045</td>
<td>1164.3</td>
<td>1167.9</td>
</tr>
<tr>
<td>220°C</td>
<td>0.0013089</td>
<td>1168.9</td>
<td>1172.3</td>
</tr>
<tr>
<td>230°C</td>
<td>0.0013129</td>
<td>1172.9</td>
<td>1176.3</td>
</tr>
<tr>
<td>240°C</td>
<td>0.0013166</td>
<td>1176.2</td>
<td>1179.9</td>
</tr>
<tr>
<td>250°C</td>
<td>0.0013200</td>
<td>1179.4</td>
<td>1182.7</td>
</tr>
<tr>
<td>260°C</td>
<td>0.0013231</td>
<td>1182.2</td>
<td>1185.0</td>
</tr>
<tr>
<td>270°C</td>
<td>0.0013259</td>
<td>1184.5</td>
<td>1187.3</td>
</tr>
<tr>
<td>280°C</td>
<td>0.0013284</td>
<td>1186.6</td>
<td>1189.5</td>
</tr>
<tr>
<td>290°C</td>
<td>0.0013306</td>
<td>1188.4</td>
<td>1190.6</td>
</tr>
</tbody>
</table>

Interpolations II

- Apply formula for \( T = 180^\circ\text{C} \) and 200°C

\[
\begin{align*}
v(180^\circ\text{C}, 2 \text{ MPa}) &= 0.001127 m^3/kg + \\
&\frac{0.001125 m^3/kg - 0.001127 m^3/kg}{5 \text{ MPa} - 1.0021 \text{ MPa}} (2 \text{ MPa} - 1.0021 \text{ MPa}) = 0.001126501 m^3/kg
\end{align*}
\]

\[
\begin{align*}
v(200^\circ\text{C}, 2 \text{ MPa}) &= 0.001157 m^3/kg + \\
&\frac{0.001153 m^3/kg - 0.001157 m^3/kg}{5 \text{ MPa} - 1.5538 \text{ MPa}} (2 \text{ MPa} - 1.5538 \text{ MPa}) = 0.00115648 m^3/kg
\end{align*}
\]

Interpolations III

- Now interpolate between results for two different \( T \)'s to find \( T \) at desired \( v \)

\[
T = 180^\circ\text{C} + \frac{200^\circ\text{C} - 180^\circ\text{C}}{0.00115648 m^3/kg - 0.001126501 m^3/kg} = 195.7^\circ\text{C}
\]

- Previous result using \( v(T, P) = v_f(T) \) was 195.6°C