Chapter 3

PROPERTIES OF PURE SUBSTANCES

Mehmet Kanoglu
Objectives

• Introduce the concept of a pure substance.
• Discuss the physics of phase-change processes.
• Illustrate the $P-v$, $T-v$, and $P-T$ property diagrams and $P-v-T$ surfaces of pure substances.
• Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.
• Describe the hypothetical substance “ideal gas” and the ideal-gas equation of state.
• Apply the ideal-gas equation of state in the solution of typical problems.
• Introduce the compressibility factor, which accounts for the deviation of real gases from ideal-gas behavior.
• Present some of the best-known equations of state.
**PURE SUBSTANCE**

- **Pure substance**: A substance that has a fixed chemical composition throughout.
- Air is a mixture of several gases, but it is considered to be a pure substance.

Nitrogen and gaseous air are pure substances.

A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.
PHASES OF A PURE SUBSTANCE

The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.

In a solid, the attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.

The arrangement of atoms in different phases: (a) molecules are at relatively fixed positions in a solid, (b) groups of molecules move about each other in the liquid phase, and (c) molecules move about at random in the gas phase.
PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

- **Compressed liquid (subcooled liquid):** A substance that it is not about to vaporize.
- **Saturated liquid:** A liquid that is about to vaporize.

At 1 atm and 20°C, water exists in the liquid phase **(compressed liquid)**.

At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize **(saturated liquid)**.
- **Saturated vapor**: A vapor that is *about to condense*.
- **Saturated liquid–vapor mixture**: The state at which the *liquid and vapor phases coexist* in equilibrium.
- **Superheated vapor**: A vapor that is *not about to condense* (i.e., not a saturated vapor).

As more heat is transferred, part of the saturated liquid vaporizes (saturated liquid–vapor mixture).

At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (saturated vapor).

As more heat is transferred, the temperature of the vapor starts to rise (superheated vapor).
If the entire process between state 1 and 5 described in the figure is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during the heating process.

*T-v diagram for the heating process of water at constant pressure.*
Saturation Temperature and Saturation Pressure

• The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.

• Water boils at 100°C at 1 atm pressure.

• **Saturation temperature** $T_{\text{sat}}$: The temperature at which a pure substance changes phase at a given pressure.

• **Saturation pressure** $P_{\text{sat}}$: The pressure at which a pure substance changes phase at a given temperature.

![Image of liquid-vapor saturation curve of a pure substance (numerical values are for water).](image)

### Table 3–1

<table>
<thead>
<tr>
<th>Temperature, $T$, °C</th>
<th>Saturation pressure, $P_{\text{sat}}$, kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>0.26</td>
</tr>
<tr>
<td>-5</td>
<td>0.40</td>
</tr>
<tr>
<td>0</td>
<td>0.61</td>
</tr>
<tr>
<td>5</td>
<td>0.87</td>
</tr>
<tr>
<td>10</td>
<td>1.23</td>
</tr>
<tr>
<td>15</td>
<td>1.71</td>
</tr>
<tr>
<td>20</td>
<td>2.34</td>
</tr>
<tr>
<td>25</td>
<td>3.17</td>
</tr>
<tr>
<td>30</td>
<td>4.25</td>
</tr>
<tr>
<td>40</td>
<td>7.39</td>
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<tr>
<td>50</td>
<td>12.35</td>
</tr>
<tr>
<td>100</td>
<td>101.4</td>
</tr>
<tr>
<td>150</td>
<td>476.2</td>
</tr>
<tr>
<td>200</td>
<td>1555</td>
</tr>
<tr>
<td>250</td>
<td>3976</td>
</tr>
<tr>
<td>300</td>
<td>8588</td>
</tr>
</tbody>
</table>
• **Latent heat**: The amount of energy absorbed or released during a phase-change process.

• **Latent heat of fusion**: The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.

• **Latent heat of vaporization**: The amount of energy absorbed during vaporization and it is equivalent to the energy released during condensation.

• The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs.

• At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

• The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

**TABLE 3–2**

<table>
<thead>
<tr>
<th>Elevation, m</th>
<th>Atmospheric pressure, kPa</th>
<th>Boiling temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>101.33</td>
<td>100.0</td>
</tr>
<tr>
<td>1,000</td>
<td>89.55</td>
<td>96.5</td>
</tr>
<tr>
<td>2,000</td>
<td>79.50</td>
<td>93.3</td>
</tr>
<tr>
<td>5,000</td>
<td>54.05</td>
<td>83.3</td>
</tr>
<tr>
<td>10,000</td>
<td>26.50</td>
<td>66.3</td>
</tr>
<tr>
<td>20,000</td>
<td>5.53</td>
<td>34.7</td>
</tr>
</tbody>
</table>
Some Consequences of $T_{\text{sat}}$ and $P_{\text{sat}}$ Dependence

The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from 25°C to 0°C.

The temperature of liquid nitrogen exposed to the atmosphere remains constant at -196°C, and thus it maintains the test chamber at 1-96°C.

In 1775, ice was made by evacuating the air space in a water tank.
The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the $T$-$v$, $P$-$v$, and $P$-$T$ diagrams for pure substances.
- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid–vapor mixture region (wet region)

At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

**Critical point**: The point at which the saturated liquid and saturated vapor states are identical.
$P$-$v$ diagram of a pure substance. The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.
Extending the Diagrams to Include the Solid Phase

At triple-point pressure and temperature, a substance exists in three phases in equilibrium.

For water, $T_{tp} = 0.01^\circ C$ and $P_{tp} = 0.6117$ kPa.

$P$-$v$ diagram of a substance that contracts on freezing.

$P$-$v$ diagram of a substance that expands on freezing (such as water).
**Sublimation**: Passing from the solid phase directly into the vapor phase.

At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

*P-T* diagram of pure substances.
The $P$-$v$-$T$ surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the $P$-$v$ and $T$-$v$ diagrams.

$P$-$v$-$T$ surface of a substance that contracts on freezing.

$P$-$v$-$T$ surface of a substance that expands on freezing (like water).
PROPERTY TABLES

- For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Therefore, properties are frequently presented in the form of tables.
- Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties.
- The results of these measurements and calculations are presented in tables in a convenient format.

Enthalpy—A Combination Property

\[ h = u + P\nu \quad \text{(kJ/kg)} \]

\[ H = U + P\nu \quad \text{(kJ)} \]

The combination \( u + P\nu \) is frequently encountered in the analysis of control volumes.

The product \( pressure \times volume \) has energy units.

\begin{align*}
\text{kPa} \cdot \text{m}^3 & \equiv \text{kJ} \\
\text{kPa} \cdot \text{m}^3/\text{kg} & \equiv \text{kJ/kg} \\
\text{bar} \cdot \text{m}^3 & \equiv 100 \ \text{kJ} \\
\text{MPa} \cdot \text{m}^3 & \equiv 1000 \ \text{kJ} \\
\text{psi} \cdot \text{ft}^3 & \equiv 0.18505 \ \text{Btu}
\end{align*}
Saturated Liquid and Saturated Vapor States

- **Table A–4**: Saturation properties of water under temperature.
- **Table A–5**: Saturation properties of water under pressure.

A partial list of Table A–4.

<table>
<thead>
<tr>
<th>Temp. press. °C</th>
<th>Sat. press. kPa</th>
<th>Specific volume m³/kg</th>
<th>Specific volume m³/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>T Sat. press. P&lt;sub&gt;sat&lt;/sub&gt;</td>
<td>Sat. liquid ν&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Sat. vapor ν&lt;sub&gt;g&lt;/sub&gt;</td>
<td>ν&lt;sub&gt;f&lt;/sub&gt; = specific volume of saturated liquid</td>
</tr>
<tr>
<td>85</td>
<td>57.868</td>
<td>0.001032</td>
<td>2.8261</td>
</tr>
<tr>
<td>90</td>
<td>70.183</td>
<td>0.001036</td>
<td>2.3593</td>
</tr>
<tr>
<td>95</td>
<td>84.609</td>
<td>0.001040</td>
<td>1.9808</td>
</tr>
</tbody>
</table>

**Enthalpy of vaporization,**<sub>fg</sub> **(Latent heat of vaporization):** The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.
Examples:
Saturated liquid and saturated vapor states of water on $T$-$v$ and $P$-$v$ diagrams.
**Saturated Liquid–Vapor Mixture**

**Quality, \( x \)**: The ratio of the mass of vapor to the total mass of the mixture. Quality is between 0 and 1 → 0: sat. liquid, 1: sat. vapor

The properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor.

\[
x = \frac{m_{\text{vapor}}}{m_{\text{total}}}
\]

\[
m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_j + m_g
\]

Temperature and pressure are dependent properties for a mixture.

The relative amounts of liquid and vapor phases in a saturated mixture are specified by the **quality** \( x \).

A two-phase system can be treated as a homogeneous mixture for convenience.
$v_{\text{avg}} = v_f + xv_{fg}$ (m$^3$/kg)

$x = \frac{m_g}{m_t}$

$u_{\text{avg}} = u_f + xu_{fg}$ (kJ/kg)

$h_{\text{avg}} = h_f + xh_{fg}$ (kJ/kg)

$y \rightarrow v, u, \text{ or } h$

$y_{\text{avg}} = y_f + xy_{fg}$

$y_f \leq y_{\text{avg}} \leq y_g$

Quality is related to the horizontal distances on $P$-$v$ and $T$-$v$ diagrams.

The $v$ value of a saturated liquid–vapor mixture lies between the $v_f$ and $v_g$ values at the specified $T$ or $P$. 

Sat. liquid $v_g$

Sat. liquid $v_f$
Examples: Saturated liquid-vapor mixture states on $T$-$v$ and $P$-$v$ diagrams.

- $T = 90^\circ\text{C}$
- $m_g = 2 \text{ kg}$
- $m_f = 8 \text{ kg}$

- $P = 70.183 \text{ kPa}$
- $P = 160 \text{ kPa}$
- $T = -15.60^\circ\text{C}$

- $v_f = 0.001036 \text{ m}^3/\text{kg}$
- $v_g = 2.3593 \text{ m}^3/\text{kg}$
- $v_f = 0.0007437 \text{ m}^3/\text{kg}$
- $v_g = 0.12348 \text{ m}^3/\text{kg}$

- $h_f = 31.21 \text{ kJ/kg}$
- $h_g = 241.11 \text{ kJ/kg}$
- $R-134a$
- $m = 4 \text{ kg}$
In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor. In this region, temperature and pressure are independent properties.

### Superheated Vapor

Compared to saturated vapor, superheated vapor is characterized by

- Lower pressures ($P < P_{\text{sat}}$ at a given $T$)
- Higher temperatures ($T > T_{\text{sat}}$ at a given $P$)
- Higher specific volumes ($\nu > \nu_g$ at a given $P$ or $T$)
- Higher internal energies ($u > u_g$ at a given $P$ or $T$)
- Higher enthalpies ($h > h_g$ at a given $P$ or $T$)

At a specified $P$, superheated vapor exists at a higher $h$ than the saturated vapor.

A partial listing of Table A–6.

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$\nu$, m³/kg</th>
<th>$u$, kJ/kg</th>
<th>$h$, kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sat.</td>
<td>1.6941</td>
<td>2505.6</td>
<td>2675.0</td>
</tr>
<tr>
<td>100</td>
<td>1.6959</td>
<td>2506.2</td>
<td>2675.8</td>
</tr>
<tr>
<td>150</td>
<td>1.9367</td>
<td>2582.9</td>
<td>2776.6</td>
</tr>
<tr>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
<tr>
<td>1300</td>
<td>7.2605</td>
<td>4687.2</td>
<td>5413.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$P = 0.1$ MPa (99.61 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sat.</td>
</tr>
<tr>
<td>0.37483</td>
</tr>
<tr>
<td>0.42503</td>
</tr>
<tr>
<td>0.47443</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$P = 0.5$ MPa (151.83 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sat.</td>
</tr>
<tr>
<td>0.37483</td>
</tr>
<tr>
<td>0.42503</td>
</tr>
<tr>
<td>0.47443</td>
</tr>
</tbody>
</table>
The compressed liquid properties depend on temperature much more strongly than they do on pressure.

\[ y \approx y_f @ T \] \[ y \rightarrow v, u, \text{ or } h \]

A more accurate relation for \( h \)

\[ h \approx h_f @ T + v_f @ T (P - P_{sat} @ T) \]

**Compressed Liquid**

Compressed liquid is characterized by:

- Higher pressures \((P > P_{sat} \text{ at a given } T)\)
- Lower temperatures \((T < T_{sat} \text{ at a given } P)\)
- Lower specific volumes \((v < v_f \text{ at a given } P \text{ or } T)\)
- Lower internal energies \((u < u_f \text{ at a given } P \text{ or } T)\)
- Lower enthalpies \((h < h_f \text{ at a given } P \text{ or } T)\)

**Given: \( P \) and \( T \)**

\[ v \approx v_f @ T \]
\[ u \approx u_f @ T \]
\[ h \approx h_f @ T \]

A compressed liquid may be approximated as a saturated liquid at the given temperature.

At a given \( P \) and \( T \), a pure substance will exist as a compressed liquid if

\[ T < T_{sat} @ P \]
Reference State and Reference Values

- The values of $u$, $h$, and $s$ cannot be measured directly, and they are calculated from measurable properties using the relations between properties.
- However, those relations give the changes in properties, not the values of properties at specified states.
- Therefore, we need to choose a convenient reference state and assign a value of zero for a convenient property or properties at that state.
- The reference state for water is 0.01°C and for R-134a is -40°C in tables.
- Some properties may have negative values as a result of the reference state chosen.
- Sometimes different tables list different values for some properties at the same state as a result of using a different reference state.
- However, in thermodynamics we are concerned with the changes in properties, and the reference state chosen is of no consequence in calculations.

<table>
<thead>
<tr>
<th>Temp., $T$ °C</th>
<th>Sat. press., $P_{sat}$ kPa</th>
<th>Sat. liquid, $u_l$</th>
<th>Sat. vapor, $u_g$</th>
<th>Sat. liquid, $h_l$</th>
<th>Sat. vapor, $h_g$</th>
<th>Sat. liquid, $s_l$</th>
<th>Sat. vapor, $s_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.6117</td>
<td>0.001000</td>
<td>206.00</td>
<td>0.000</td>
<td>2374.9</td>
<td>0.001</td>
<td>2500.9</td>
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<tr>
<td>5</td>
<td>0.8725</td>
<td>0.001000</td>
<td>147.03</td>
<td>21.019</td>
<td>2360.8</td>
<td>21.020</td>
<td>2489.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp., $T$ °C</th>
<th>Sat. press., $P_{sat}$ kPa</th>
<th>Sat. liquid, $u_l$</th>
<th>Sat. vapor, $u_g$</th>
<th>Sat. liquid, $h_l$</th>
<th>Sat. vapor, $h_g$</th>
<th>Sat. liquid, $s_l$</th>
<th>Sat. vapor, $s_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40</td>
<td>51.25</td>
<td>0.0007054</td>
<td>0.36081</td>
<td>-0.036</td>
<td>207.40</td>
<td>0.000</td>
<td>225.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
THE IDEAL-GAS EQUATION OF STATE

• **Equation of state**: Any equation that relates the pressure, temperature, and specific volume of a substance.

• The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state. This equation predicts the \( P-v-T \) behavior of a gas quite accurately within some properly selected region.

\[
P = R \left( \frac{T}{V} \right) \quad P \, V = R \, T
\]

**Ideal gas equation of state**

\[
R = \frac{R_u}{M} \quad \text{kJ/kg \cdot K or kPa \cdot m^3/kg \cdot K}
\]

- \( R \): gas constant
- \( M \): molar mass (kg/kmol)
- \( R_u \): universal gas constant

\[
R_u = \begin{cases} 
8.31447 \text{ kJ/kmol} \cdot \text{K} \\
8.31447 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\
0.0831447 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\
1.98588 \text{ Btu/lbmol} \cdot \text{R} \\
10.7316 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{R} \\
1545.37 \text{ ft} \cdot \text{lbf/} \text{lbmol} \cdot \text{R}
\end{cases}
\]

Different substances have different gas constants.
Mass = Molar mass × Mole number

\[ m = MN \quad \text{(kg)} \]

\[ \frac{P_1 \nu_1}{T_1} = \frac{P_2 \nu_2}{T_2} \]

Various expressions of ideal gas equation

\[ \nu = m \bar{\nu} \quad \rightarrow \quad P \nu = mRT \]

\[ mR = (MN)R = NR_u \quad \rightarrow \quad P \nu = NR_u T \]

\[ \nu = N \bar{\nu} \quad \rightarrow \quad P \bar{\nu} = R_u T \]

Ideal gas equation at two states for a fixed mass

Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

Properties per unit mole are denoted with a bar on the top.

Properties per unit mass:

- \( \nu \, \text{m}^3/\text{kg} \)
- \( u \, \text{kJ/kg} \)
- \( h \, \text{kJ/kg} \)

Properties per unit mole:

- \( \bar{\nu} \, \text{m}^3/\text{kmol} \)
- \( \bar{u} \, \text{kJ/kmol} \)
- \( \bar{h} \, \text{kJ/kmol} \)
Is Water Vapor an Ideal Gas?

- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).
- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.
- In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why?
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

Percentage of error ([|v_{table} - v_{ideal}|/v_{table}] \times 100) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.
Compressibility factor $Z$

A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

\[ P\nu = ZRT \]

\[ Z = \frac{P\nu}{RT} \]

\[ Z = \frac{\nu_{\text{actual}}}{\nu_{\text{ideal}}} \]

The farther away $Z$ is from unity, the more the gas deviates from ideal-gas behavior.

*Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).*

**Question:** What is the criteria for low pressure and high temperature?

**Answer:** The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.

The compressibility factor is unity for ideal gases.

At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).
Reduced pressure

\[ P_R = \frac{P}{P_{cr}} \]

Reduced temperature

\[ T_R = \frac{T}{T_{cr}} \]

Pseudo-reduced specific volume

\[ v_R = \frac{v_{\text{actual}}}{RT_{cr}/P_{cr}} \]

\[ Z = \ldots \]

(Fig. A–15)

Z can also be determined from a knowledge of \( P_R \) and \( v_R \).

Comparison of Z factors for various gases.

Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.
OTHER EQUATIONS OF STATE

Several equations have been proposed to represent the $P$-$v$-$T$ behavior of substances accurately over a larger region with no limitations.

**Van der Waals Equation of State**

\[
\left( P + \frac{a}{v^2} \right) (v - b) = RT
\]

\[
a = \frac{27R^2T^2}{64P_{cr}} \quad b = \frac{RT_{cr}}{8P_{cr}}
\]

This model includes two effects not considered in the ideal-gas model: the intermolecular attraction forces and the volume occupied by the molecules themselves. The accuracy of the van der Waals equation of state is often inadequate.

Critical isotherm of a pure substance has an inflection point at the critical state.

\[
\left( \frac{\partial P}{\partial v} \right)_{T=T_{cr}=\text{const}} = 0
\]

\[
\left( \frac{\partial^2 P}{\partial v^2} \right)_{T=T_{cr}=\text{const}} = 0
\]
Beattie-Bridgeman Equation of State

\[ P = \frac{R_u T}{\nu^2} \left( 1 - \frac{c}{\nu T^3} \right) (\nu + B) - \frac{A}{\nu^2} \]

\[ A = A_0 \left( 1 - \frac{a}{\nu} \right) \quad B = B_0 \left( 1 - \frac{b}{\nu} \right) \]

The constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about 0.8\( \rho_{cr} \).

Benedict-Webb-Rubin Equation of State

\[ P - \frac{R_u T}{\nu} + \left( B_0 R_u T - \Lambda_0 - \frac{C_0}{T^2} \right) \frac{1}{\nu^2} + \frac{b R_u T - a}{\nu^3} + \frac{a \alpha}{\nu^6} + \frac{c}{\nu^3 T^2} \left( 1 + \frac{\gamma}{\nu^2} \right) e^{-\gamma/\nu^2} \]

The constants are given in Table 3–4. This equation can handle substances at densities up to about 2.5 \( \rho_{cr} \).

Virial Equation of State

\[ P = \frac{RT}{\nu} + \frac{a(T)}{\nu^2} + \frac{b(T)}{\nu^3} + \frac{c(T)}{\nu^4} + \frac{d(T)}{\nu^5} + \ldots \]

The coefficients \( a(T) \), \( b(T) \), \( c(T) \), and so on, that are functions of temperature alone are called \textit{virial coefficients}. 
Complex equations of state represent the $P$-$v$-$T$ behavior of gases more accurately over a wider range.

**van der Waals**: 2 constants. Accurate over a limited range.

**Beattie-Bridgeman**: 5 constants. Accurate for $\rho \leq 0.8\rho_{cr}$.

**Benedict-Webb-Rubin**: 8 constants. Accurate for $\rho \leq 2.5\rho_{cr}$.

**Strobridge**: 16 constants. More suitable for computer calculations.

**Virial**: may vary. Accuracy depends on the number of terms used.

Percentage of error involved in various equations of state for nitrogen ($\%$ error $= \left[\left|\frac{v_{\text{table}} - v_{\text{equation}}}{v_{\text{table}}}\right|\right] \times 100$).
Summary

• Pure substance
• Phases of a pure substance
• Phase-change processes of pure substances
  ✓ Compressed liquid, Saturated liquid, Saturated vapor, Superheated vapor
  ✓ Saturation temperature and Saturation pressure
• Property diagrams for phase change processes
  ✓ The T-v diagram, The P-v diagram, The P-T diagram, The P-v-T surface
• Property tables
  ✓ Enthalpy
  ✓ Saturated liquid, saturated vapor, Saturated liquid vapor mixture, Superheated vapor, compressed liquid
  ✓ Reference state and reference values
• The ideal gas equation of state
  ✓ Is water vapor an ideal gas?
• Compressibility factor
• Other equations of state