1.5 Real Gases and the Virial Equation

- The compressibility factor $Z$ depends not only on temperature, but also the pressure.

- In the case of nitrogen gas at 100 bar, as the temperature is reduced, the effect of intermolecular attraction increases because the molar volume is smaller at lower temperatures and the molecules are closer together.

- If the temperature is low enough, all gases show a minimum in the plot of $Z$ vs. $P$. Hydrogen and helium exhibit this minimum only at temperature well below 0 °C. Why?
The Virial Equation: (Virial: derived from the Latin word for ‘force’):

- In 1901 H. Kamerlingh–Omnes proposed an equation of state for real gases in $Z$ as a power series in terms of $1/V_m$ for a pure gas:

$$Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots$$

For over wider range of $P$, add more terms in power series ($1/V_m$).
B and C: the second and third virial coefficients, and both are temperature dependent, but not on the pressure.
Table 1.1 Second and Third virial Coefficients at 298.15 K

<table>
<thead>
<tr>
<th>Gas</th>
<th>$B/10^{-6}$ m$^3$ mol$^{-1}$</th>
<th>$C/10^{-12}$ m$^6$ mol$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>14.1</td>
<td>350</td>
</tr>
<tr>
<td>He</td>
<td>11.8</td>
<td>121</td>
</tr>
<tr>
<td>N$_2$</td>
<td>−4.5</td>
<td>1100</td>
</tr>
<tr>
<td>O$_2$</td>
<td>−16.1</td>
<td>1200</td>
</tr>
<tr>
<td>Ar</td>
<td>−15.8</td>
<td>1160</td>
</tr>
<tr>
<td>CO</td>
<td>−8.6</td>
<td>1550</td>
</tr>
</tbody>
</table>
1.5 Real Gases and the Virial Equation

Fig. 1.9 Second virial coefficient $B$. 

![Graph showing second virial coefficient $B$ for different gases as a function of temperature $T$.]
1.5 Real Gases and the Virial Equation

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>273 K</td>
<td>600 K</td>
</tr>
<tr>
<td>Ar</td>
<td>-21.7</td>
<td>11.9</td>
</tr>
<tr>
<td>H$_2$</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>12.0</td>
<td>10.4</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-10.5</td>
<td>21.7</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-22.0</td>
<td>12.9</td>
</tr>
<tr>
<td>Ne</td>
<td>10.4</td>
<td>13.8</td>
</tr>
<tr>
<td>Xe</td>
<td>-153.7</td>
<td>-19.6</td>
</tr>
</tbody>
</table>

Table 1.1’ Second virial Coefficients, B ($10^{-6}$ m$^3$ mol$^{-1}$)
Example Comparison of the ideal gas law with the virial equation

What is the molar volume of N\textsubscript{2}(g) at 600 K and 600 bar according to (a) the ideal gas law and (b) the virial equation?

**Answer:** (a) The virial coefficient B of N\textsubscript{2}(g) at 600 K is 0.0217 L mol\textsuperscript{-1}

\[ \frac{RT}{P} = V_m[\text{ideal}] = \frac{(8.3145 \times 10^{-2} \text{L bar K}^{-1} \text{mol}^{-1})(600 \text{K})}{600 \text{bar}} = 8.3145 \times 10^{-2} \text{ L mol}^{-1} \]

(b) \[ Z = 1 + \frac{BP}{RT} = 1 + \frac{(0.0217 \text{ L mol}^{-1})}{(8.3145 \times 10^{-2} \text{ L mol}^{-1})} = 1.261 \]

\[ V_m = \frac{ZRT}{P} = (1.261)(8.3145 \times 10^{-2} \text{L mol}^{-1}) = 0.1048 \text{ L mol}^{-1} \]
The virial Equation:

It is more convenient by using $P$ as an independent variable.

$$PV_m[\text{real}] = RT(1 + B'P + C'P^2 + \ldots)$$

or

$$Z = \frac{PV_m[\text{real}]}{RT} = 1 + B'P + C'P^2 + \ldots$$

$B'$ and $C'$: both coefficients are temperature dependent; usually $B'P \gg C'P^2$. For over wider range of $P$, just add more terms in power series of $P$. 
Example 1.5 Derive the relationships between two types of virial coefficients.

**Answer:** The pressures can be eliminated from equations using the following forms:

\[
P = \frac{RT}{V_m} + \frac{BRT}{V_m^2} + \frac{CRT}{V_m^3} + \ldots \quad P^2 = \left(\frac{RT}{V_m}\right)^2 + \frac{2B(RT)^2}{V_m^3} + \ldots
\]

\[
Z = 1 + B'P + C'P^2 + \ldots = 1 + B'\left(\frac{RT}{V_m}\right) + \frac{B'BRT + C'(RT)^2}{V_m^2} + \ldots
\]

\[
B = B'RT \quad B' = \frac{B}{RT}
\]

\[
C = BB'RT + C'(RT)^2 \quad C' = \frac{C - B^2}{(RT)^2}
\]
Compression Factor $Z$

The variation of the compression factor, $Z = \frac{PV_m}{RT}$ with pressure for several gases at 0 °C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \to 0$, they do so with different slopes.
Boyle Temperature

Boyle Temperature $T_B$

- A plot of $Z$ vs. $P$ with a slope of $dZ/dP$:
  \[
  \frac{dZ}{dP} = B' + 2CP' + \ldots \quad (\text{The slope is } B' \text{ at } P = 0)\.
  \]
- Although for a real gas $Z \sim 1$ at $P \sim 0$, the slope of $Z$ against $P$ does not approach zero.
- The properties of real gas may not always coincide with the perfect gas values at low $P$.
- There may be a temperature at which $Z \sim 1$ with zero slope $B = 0$ at $P \sim 0$, this temperature is called the Boyle temperature, $T_B$.
- At the Boyle temperature $T_B$, the properties of real gas do coincide with the perfect gas values as $P \sim 0$.
- Since the second virial coeff. $B$ vanished and the third virial coeff. $C$ and higher terms are negligibly small, then $PV_m \sim RT_B$ over a more extended range of $P$ than at other temperature.
The compression factor $Z$ approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.
1.5 Real Gases and the Virial Equation

Fig. 1.10

At the Boyle temperature (B=0), a gas behaves nearly ideally over a range of pressures.
### Table 1.2 Critical Constants and Boyle Temperatures

<table>
<thead>
<tr>
<th>Gas</th>
<th>T&lt;sub&gt;c&lt;/sub&gt;/K</th>
<th>P&lt;sub&gt;c&lt;/sub&gt;/bar</th>
<th>V&lt;sub&gt;c&lt;/sub&gt;/L mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Z&lt;sub&gt;c&lt;/sub&gt;</th>
<th>T&lt;sub&gt;B&lt;/sub&gt;/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>4He</td>
<td>5.2</td>
<td>2.27</td>
<td>0.0573</td>
<td>0.301</td>
<td>22.64</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>33.2</td>
<td>13.0</td>
<td>0.0650</td>
<td>0.306</td>
<td>110.04</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>126.2</td>
<td>34.0</td>
<td>0.0895</td>
<td>0.290</td>
<td>327.22</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>154.6</td>
<td>50.5</td>
<td>0.0734</td>
<td>0.288</td>
<td>405.88</td>
</tr>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>417</td>
<td>77.0</td>
<td>0.124</td>
<td>0.275</td>
<td></td>
</tr>
<tr>
<td>Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>584</td>
<td>103.0</td>
<td>0.127</td>
<td>0.269</td>
<td></td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>304.2</td>
<td>73.8</td>
<td>0.094</td>
<td>0.274</td>
<td>714.81</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>647.1</td>
<td>220.5</td>
<td>0.056</td>
<td>0.230</td>
<td></td>
</tr>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>405.6</td>
<td>113.0</td>
<td>0.0725</td>
<td>0.252</td>
<td>995</td>
</tr>
</tbody>
</table>
A region of the $PV,T$ surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.
Paths on Surface

Sections through the surface at constant temperature give the isotherms, and the isobars shown in here too.
1.6 P–V–T Surface for a one-component system

Fig 1.11
P–V–T surface for a one-component system that contracts on freezing.
1.7 Critical Phenomena

**Fig. 1.12 The Critical Point**

Pressure–molar volume relations (e.g. isotherms) in the region of the critical point. The dashed horizontal lines in the two–phase region are called **tie lines**.
Fig. 1.12 The Critical Point

The path 1–2–3–4 shows how a liquid can be converted to a gas without the appearance of a meniscus. If liquid at point 4 is compressed isothermally, the volume decreases until the two–phase region is reached. At this point there is a large decrease in volume at constant pressure (the vapor pressure of the liquid) until all of the gas has condensed to liquid. As the liquid is compressed, the pressure rises rapidly.
The Critical Point

Experimental isotherms of carbon dioxide at several temperatures. The `critical isotherm`, the isotherm at the critical temperature, is at 31.04 °C. The critical point is marked with a star(*).
1.8 The van der Waals Equation

- For real gas, van der Waals equation is written as

\[ p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]

where \( a \) and \( b \) are van der Waals coefficients, specific to each gas. Term \( a \) is adjusted to represent the attractive forces of the molecules, without giving any specific physical origin to these forces; \( V-nb \), not \( V \), now represents the volume in which molecules can move.
1.8 The van der Waals Equation

The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown before.

\[ P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]
a and b : van der Waals coefficients

The VDW coefficients $a$ and $b$ are found by fitting the calculate curves to experimental curves. They are characteristic of each gas but independent of the temperature.

<table>
<thead>
<tr>
<th></th>
<th>a / atm L$^2$ mol$^{-2}$</th>
<th>b / 10$^{-2}$ L mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.337</td>
<td>3.20</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.610</td>
<td>4.29</td>
</tr>
<tr>
<td>He</td>
<td>0.0341</td>
<td>2.38</td>
</tr>
<tr>
<td>Xe</td>
<td>4.137</td>
<td>5.16</td>
</tr>
</tbody>
</table>

Table 1.3 van der Waals Constants
The van der Waals Equation (1873):

- Virial Equation are not convenient for too many constants and all are temperature dependent.

- Van der Waals modified the ideal gas law by taking account two effects: a). intermolecular forces, and b). molecular size.

- VDW equation has only two constants a, b. And both are independent of temperature.

- Only “free volume” follows ideal gas law; p above ideal value by size effect, $P = \frac{RT}{(V_m - b)}$,

- Constant b as parameter for excluded volume, $b \sim 4x$(molecular size);
The van der Waals Equation (1873):

- Real $P$ are less than ideal value by the attraction force from interior of the gas (internal pressure), pressure on wall depends on both collision frequency and collision force, both related to the molar concentration ($n/V = 1/V_m$), so $P$ reduced by a correction term which is square of molar conc. $a/V_m^2$

$$P_{[\text{real}]} = P - \text{correction term}$$

$$= \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 = \frac{RT}{V_m-b} - \frac{a}{V_m^2} \quad \text{or} \quad \left(P + \frac{a}{V_m^2}\right)(V_m-b)=RT$$

- Also $(\partial P/\partial T)_V = R/(V_m-b)$, constant $b$ may be determined from the slope of $P$ vs. $T$ at constant $V$.

- $T(\partial P/\partial T)_V = P + a/V_m^2$, constant $a$ may be determined from the $P$–$V$–$T$ data.
Example  Calculate the molar volume of Ar in 373 K and 100 bar by treating it as a VDW gas.

\( a = 1.35 \text{ L}^2 \text{ bar} / \text{ mol}^2 \) and \( b = 0.0322 \text{ L} / \text{ mol}^2 \) for Ar

**Ans:** multiply by \( (V_m^2 / P) \) and rearrange as

\[
V_m^3 - \left( b + \frac{RT}{P} \right) V_m^2 + \left( \frac{a}{P} \right) V_m - \left( \frac{ab}{P} \right) = 0
\]

\[\Rightarrow V_m = 0.298 \text{ L/mol}\]
Liquefaction and the VDW Equation

\[ P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]

- The ideal gas isotherms are only at high temperature and large molar volumes \((V_m \gg b)\).

- VDW loop: the calculate oscillations below the critical temperature.

- First term from kinetic energy and repulsive force, second term for the attractive effect. VDW loop occurs when both terms have similar magnitudes, liquids and gases coexist when cohesive and dispersing effects are in balance.

- Maxwell construction: horizontal line drawn with equal areas above and below the line at VDW loop.
1.8 The van der Waals Equation

van der Waals loops

The van der Waals equation predicts the real gas isotherms with oscillations below the critical temperature which is unrealistic.

\[ V^3_M - \left( b + \frac{RT}{P} \right) V^2_M + \left( \frac{a}{P} \right) V_M - \left( \frac{ab}{P} \right) = 0 \]
1.8 The van der Waals Equation

Fig. 1.13 van der Waals loops

Isotherms calculated from the van der Waals equation. The dashed line is the boundary of the L + G region.

\[
V_M^3 - \left( b + \frac{RT}{P} \right) V_M^2 + \left( \frac{a}{P} \right) V_M - \left( \frac{ab}{P} \right) = 0
\]
Z for the VDW gas:

- Compressibility factor \( Z = \frac{PV_m}{RT} \)

\[
Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} \frac{a}{RT V_m} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RT V_m}
\]

- At moderate pressure, \( \frac{b}{V_m} < 1 \); expanding the first term using:

\[
\frac{1}{(1-x)} = 1 + x + x^2 + \cdots
\]

\[
1/(1 - \frac{b}{V_m}) = 1 + (\frac{b}{V_m}) + (\frac{b}{V_m})^2 + (\frac{b}{V_m})^3 + \ldots
\]

substituted for \( Z \), then yield the virial equation in terms of volume:

\[
Z = 1 + \left( \frac{b - \frac{a}{RT}}{V_m} \right) \frac{1}{V_m} + \left( \frac{b}{V_m} \right)^2 + \cdots
\]
Example 1.6 Expansion of \((1-x)^{-1}\) using the Maclaurin series

Since we will use series like \((1-x)^{-1} = 1 + x + x^2 + \ldots\)
a number of times, it is important to realize that functions can often be expressed as series by use of the Maclaurin series

\[
f(x) = f(0) + \left( \frac{df}{dx} \right)_{x=0} x + \frac{1}{2!} \left( \frac{d^2 f}{dx^2} \right)_{x=0} x^2 + \ldots.
\]

Ans: In this case,

\[
f(0) = 1, \quad \left( \frac{df}{dx} \right) = \frac{1}{(1-x)^2} \quad \text{and} \quad \left( \frac{df}{dx} \right)_{x=0} = 1
\]

\[
\left( \frac{d^2 f}{dx^2} \right) = 2(1-x)^{-3} \quad \text{and} \quad \left( \frac{d^2 f}{dx^2} \right)_{x=0} = 2
\]
1.8 The van der Waals Equation

\[ Z = 1 + \left( b - \frac{a}{RT} \right) \frac{1}{V_m} + \left( \frac{b}{V_m} \right)^2 + \ldots \]

- The second virial coefficient \( B = b - a/RT, \ C = b^2 \)
  the value of \( a \) is relatively more important at low \( T \),
  the value of \( b \) is relatively more important at high \( T \).

- To obtain the virial equation in \( P \), replace \((1 / V_m) = P / RTZ\) and
  \[ Z = 1 + B' P + C' P^2 + \ldots \]
  \[ = 1 + (b - a/RT) (1 / RTZ) P + (b / RTZ)^2 P^2 + \ldots \]
  \[ = 1 + B' P + C' P^2 + \ldots \]

- In the limit of zero pressure, \( Z = 1 \) and
  \[ B' = (1/RT) (b - a/RT) = B / RT \]
1.8 The van der Waals Equation

Z for the VDW gas:

\[ Z = 1 + B'(1/Z) \frac{P}{RTZ} + \left(\frac{b}{RTZ}\right)^2 P^2 + \ldots \]

\[ = 1 + B' \frac{P}{Z} + C' P^2 + \ldots \]

now \[ B' \left(\frac{1}{Z} - 1\right) \frac{P}{Z} + \left(\frac{b}{RTZ}\right)^2 P^2 = C' P^2 \]

or \[ B' \left[ \frac{(1-Z)}{Z} \right] \left(\frac{1}{P}\right) + \left(\frac{b}{RTZ}\right)^2 = C' \]

• in the limit of zero pressure, \( Z = 1 \) and \( (Z-1)/P = B' \)

\[ C' = \left(\frac{b}{RT}\right)^2 - B'^2 = (C - B^2) \left(\frac{1}{RT}\right)^2 \]

\[ C' = a \left(\frac{1}{RT}\right)^3 \left(2b - a/RT\right) \]

\[ Z = 1 + \left(\frac{1}{RT}\right) \left(\frac{b - a/RT}{RT}\right) P + a \left(\frac{1}{RT}\right)^3 \left(2b - a/RT\right) P^2 + \ldots \]
1.8 The van der Waals Equation

- let \((1 / RT) = \beta\)

\[
Z = 1 + \beta (b - a/RT) P + a \beta^3 (2b - a \beta) P^2 + ... 
\]

\[
(dZ / dP) = \beta (b - a \beta) + 2a \beta^3 (2b - a \beta) P + ... 
\]

- At \(P = 0\), the initial slope

\[
\left( \frac{\partial Z}{\partial P} \right)_{p=0} = \beta (b - a \beta)
\]

\[
= (1 / RT) (b - a/RT)
\]

\[
= b (1/RT) - a (1/RT)^2
\]

- if \(bRT < a\), attractive force dominated, (negative slope)

- if \(bRT > a\), repulsive force dominated, (positive slope)

- at Boyle temperature, the second term vanished, \(B = 0\);
  \(bRT = a\), then \(T_B = a/bR\)

- the Boyle temperature is relate to the VDW coefficients.
**Exercise**

Given the van der Waals constants for ethane gas as \( a = 5.562 \text{ L}^2 \text{ bar/mol}^2 \), \( b = 0.06380 \text{ L/mol} \), for 10.0 mol of ethane at 300 K and under 30 bar,

(a) find the second virial coefficient \( B \) at this temperature.

(b) calculate the compressibility factor \( Z \) from the first two terms.

(c) estimate the approximate molar volume from \( Z \).

(d) what is its Boyle temperature \( T_B \)?

**Ans:**

(a) \( B = b - \frac{a}{RT} \)

\[
= 0.06380 \text{ L/mol} - \frac{5.562 \text{ L}^2 \text{ bar/mol}^2}{(0.0831451 \text{ L-bar/K-mol} \times 300 \text{ K})} \\
= -0.159 \text{ L/mol}
\]

(b) \( Z = 1 + B \left( \frac{p}{RT} \right) + ... \)

\[
= 1 + (-0.159 \text{ L/mol}) \left( \frac{30 \text{ bar}}{(300 \text{ K} \times 0.0831451 \text{ L-bar/K-mol})} \right) = 0.81
\]

(c) \( \frac{V}{n} = ZRT/p \)

\[
= (0.81) \left( 0.0831451 \text{ L-bar/K-mol} \right) \left( 300 \text{ K} \right) / 30 \text{ bar} = 0.67 \text{ L/mol}
\]

(d) \( T_B = \frac{a}{bR} \)

\[
= \frac{5.562 \text{ L}^2 \text{ bar/mol}^2}{(0.06380 \text{ L/mol} \times 0.0831451 \text{ L-bar/K-mol})} \\
= 1049 \text{ K}
\]
1.8 The van der Waals Equation

vdw Isotherms

Van der Waals isotherms at several values of $T/T_c$. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$. For $T < T_c$, the calculated isotherms oscillates from min $\rightarrow$ max and converges as $T \rightarrow T_c$ then coincide at $T = T_c$ with flat inflection.
Critical Constants from vdw Isotherms.

As \( T/T_C \rightarrow 1 \), the vdw isotherm becomes the critical isotherm with a flat inflexion when both the first and second derivatives are zero.

\[
\left( \frac{\partial P}{\partial V} \right)_{T=T_c} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0
\]

\[
\left( \frac{\partial^2 P}{\partial V^2} \right)_{T=T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0
\]
1.8 The van der Waals Equation

Critical Constants at inflexion point

At inflexion point, the critical constants can be derived from the VDW equation and related to the VDW coefficients.
Example 1.7 VDW constants expressed in terms of critical constants

The van der Waals equation may be written as 

\[ P = \frac{RT}{V_m} - \frac{a}{V_m^2} - \frac{b}{V_m} \]

Differentiating wrt molar volume and evaluating these equations at the critical point to obtain \( a \) and \( b \) in terms of \( T_c \), \( P_c \) or \( T_c \), \( V_c \)

Answer:

\[
P_c = \frac{RT_c}{V_c} - \frac{a}{V_c^2} = \frac{RT_c}{V_c} - \frac{a}{V_c^2}
\]

\[
\left( \frac{\partial p}{\partial V} \right)_{T_c} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0
\]

\[
\left( \frac{\partial^2 p}{\partial V^2} \right)_{T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0
\]

\[
\Rightarrow \begin{cases} 
    a = \frac{27R^2T_c^2}{64P_c} = \frac{9}{8}RT_c^2V_c \\
    b = \frac{RT_c}{8P_c} = \frac{V_c}{3}
\end{cases}
\]
Example 1.8 Critical constants expressed in terms of VDW constants.

Derive the expression for the molar volume \((V_c)\) temperature \((T_c)\) and pressure \((P_c)\) at the critical point in terms of the van der Waals constants.

Answer:

\[
\begin{align*}
a &= \frac{27R^2T_c^2}{64P_c} = \frac{9}{8}RT_c^2V_c \\
b &= \frac{RT_c}{8P_c} = \frac{\bar{V}_c}{3}
\end{align*}
\]

\[
\Rightarrow \begin{cases}
T_c = \frac{8a}{9R\bar{V}_c} = \frac{8a}{27Rb} \\
\bar{V}_c = 3b \\
P_c = \frac{RT_c}{8P_c} = \frac{a}{27b^2}
\end{cases}
\]
1.8 The van der Waals Equation

Critical Constants:

\[ V_c = 3b \]
\[ P_c = \frac{a}{27b^2} \]
\[ Z_c = \frac{P V_c}{R T_c} = \frac{3}{8} \]
\[ T_c = \frac{8a}{27Rb} \]
Example 1.9 Calculation of the molar volume using the VDW equation.

What is the molar volume of ethane at 350 K and 70 bar according to (a) the ideal gas law and (b) the van der Waals equation?

\( a = 5.562 \text{ L}^2 \text{ bar} / \text{ mol}^2 \text{ and } b = 0.0638 \text{ L} / \text{ mol} \text{ for C}_2\text{H}_6 \)

Ans:

a) \( V_m = \frac{RT}{P} = (0.083145 \text{ L bar}/\text{K mol})(350 \text{ K})(70 \text{ bar}) = 0.416 \text{ L/mol} \)

b) VDW equation:

\[
P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}
\]

70 = \( \frac{(0.083145)(350 \text{ K})}{(V_m - 0.0638) - 5.562/ V_m^2} \)

solve a cubic equation using successive approximations, starting with ideal gas molar volume:

\[
V_m = \frac{RT}{P + \frac{a}{V_m^2}} + b
\]

This yields \( V_m = 0.23 \text{ L/mol} \) (Comparing with the real root: 0.2297 L/ mol)
Reduced Variables Plot

The compression factors of four gases, plotted using reduced variables. The use of reduced variables organizes the data on to single curves.

\[ P_r = \frac{P}{P_c} \quad V_r = \frac{V_m}{V_c} \quad T_r = \frac{T}{T_c} \]