Equations of State

For non ideal gases we will need a relationship for work and this requires a relationship for PVT (an equation of state):

What are the assumptions for an Ideal Gas and their interactions?
How will real gases differ?

Q and T (above)
V for T and P

Many first approximations start with a compressibility factor, Z:

\[ PV = nZRT \]

where for one mole: \( Z \frac{PV}{RT} = \text{function of} \)

\[ Z = 1 + B'P + C'P + D'T + \ldots \text{ or } = \frac{B}{V} + \frac{C}{V^2} + \ldots \]

or \( Z = F(Tr, Pr) \); one example \( Z^0 + \omega Z^1 \); \( \omega \) for gas (tables)

or [Virial] \( PV = a + bP + cP^2 + \ldots \)

or van der Waals

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

\( a \) and \( b \) for gas (tables)

**Van der Waals equation**

\[ \left( P + \frac{a}{V^2} \right) \left( \frac{1}{V - b} \right) = RT \]

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

**Parameters for the Van der Waals Equation**

<table>
<thead>
<tr>
<th>Gas</th>
<th>( a, \text{Pa-m}^3/\text{mol}^2 )</th>
<th>( b, \text{m}^3/\text{mol} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0.1381</td>
<td>3.184</td>
</tr>
<tr>
<td>N₂</td>
<td>0.1368</td>
<td>3.864</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.5542</td>
<td>3.051</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.2303</td>
<td>4.306</td>
</tr>
<tr>
<td>CO</td>
<td>0.1473</td>
<td>3.951</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.3658</td>
<td>4.286</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.4253</td>
<td>3.737</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0248</td>
<td>2.660</td>
</tr>
<tr>
<td>Element</td>
<td>Density</td>
<td>Volume</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>He</td>
<td>0.00346</td>
<td>2.376</td>
</tr>
</tbody>
</table>
Redlich-Kwong Equation

\[ P = \frac{RT}{(\tilde{V} - \frac{a}{RT})} - \frac{a}{T^{1/2} \tilde{V} (\tilde{V} + \frac{b}{RT})} \]

Peng-Robinson Equation

\[ P = \frac{RT}{(\tilde{V} - \frac{a}{RT})} - \frac{a(T)}{\tilde{V} \tilde{V} + \frac{b}{RT} + \frac{b}{RT} - \frac{b}{RT}} \]

Generalized Cubic Equation

\[ P = \frac{RT}{(\tilde{V} - \frac{a}{RT})} - \frac{(\tilde{V} - \eta)\theta}{(\tilde{V} + \frac{b}{RT} - \frac{b}{RT} + \frac{b}{RT} - \frac{b}{RT})} \]

Note that if \( Z = PV/NRT \), the equation can be written as a cubic equation in \( Z \)

\[ Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \]

Solution for Selected Equations of State

The usual cubic equations of state can all be expressed in the same form:

\[ Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \]

For the van der Waals, Redlich-Kwong, and Peng-Robinson equations, the Table below gives the relationship between the parameters \( \alpha, \beta, \gamma \) and the parameters for the respective equations of state.

<table>
<thead>
<tr>
<th></th>
<th>van der Waals</th>
<th>Redlich-Kwong</th>
<th>Peng-Robinson</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>- 1 - B</td>
<td>- 1</td>
<td>- 1 + B</td>
</tr>
<tr>
<td>( \beta )</td>
<td>A</td>
<td>A - B - B^2</td>
<td>A - 3B^2 - 2B</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-AB</td>
<td>-AB</td>
<td>-AB + B^2 + B^3</td>
</tr>
</tbody>
</table>

where

\[ Z = \frac{P \tilde{V}}{RT} \quad \text{and} \quad B = \frac{Pb}{RT} \]

\[ A = \frac{aP}{(RT)^2 \sqrt{T}} \quad \text{for Redlich-Kwong} \]

\[ A = \frac{aP}{(RT)^2} \quad \text{for van der Waals and Peng-Robinson} \]
Peng-Robinson Equation of State

The cubic form of the Peng-Robinson equation is the following

\[ Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \]

noting that the definitions of \( Z \), \( A \), and \( B \) are

\[ Z = \frac{P \sqrt{V}}{RT} \]

Using the generalized form for the parameters in the Peng-Robinson Equation, we obtain a simplified set of parameters to use in the equation

\[ A = \frac{0.45724 P_r}{T_r^2} \sigma(T_r) \quad B = 0.07780 \frac{P_r}{T_R} \]

with other parameters appropriately defined

\[ \sigma(T_r) = 1 + \kappa(1 - \sqrt{T_r}) \]

\[ \kappa = 0.37464 + 1.542 \omega - 0.26992 \omega^2 \]

So that the parameters in the cubic form are given by

\[ \alpha = -1 + 0.07780 \frac{P_r}{T_r} \]

\[ \beta = \frac{0.45724 P_r}{T_r^2} \sigma(T_r) - 2 \left( 0.07780 \frac{P_r}{T_r} \right) - 3 \left( 0.07780 \frac{P_r}{T_r} \right)^2 \]

\[ \gamma = \left( 0.07780 \frac{P_r}{T_r} \right)^2 \left( 0.45724 P_r \right) \sigma(T_r) + \left( 0.07780 \frac{P_r}{T_r} \right)^3 \]

\[ + \left( 0.07780 \frac{P_r}{T_r} \right)^2 \]
To relate the two types of Representation:

\[
P = \frac{RT}{v - b} - \frac{a}{v(v+b) + b(v-b)} \quad \text{where} \quad b = \frac{BRT}{P} \quad \text{and} \quad a = \frac{A(\text{RT})^2}{P}
\]

\[
P = \frac{RT}{v - \frac{BRT}{P}} - \frac{A(\text{RT})^2}{P} \quad \frac{1}{v(\frac{v+BRT}{P}) + \frac{BRT}{P}(\frac{v-BRT}{P})}
\]

gathering \( P \) in denominator

\[
P = \frac{\text{RTP}}{Pv - BRT} - \frac{A(\text{RT})^2}{P} \quad \frac{1}{P(\frac{Pv+BRT}{P} + \frac{BRT}{P^2}(P-BRT))}
\]

Multiply by \( \text{V}/\text{RT} \) and eliminate \( /P \) in second term:

\[
\frac{\text{PV}}{\text{RT}} = \frac{\text{PV}}{\text{Pv} - BRT} - \frac{A(\text{RT})^2 \text{PV}}{P(\text{Pv+BRT}) + BRT(\text{Pv-BRT})}
\]

Sub. for \( Z \); top & bottom by \( 1/\text{RT} \); top & bottom by \( 1/\text{RTPV} \)

\[
Z = \frac{Z}{Z - B} - \frac{A}{\frac{[Pv+BRT]}{RT} + \frac{B(Pv-BRT)}{PV}} = \frac{Z}{Z - B} - \frac{A}{(Z+B)+B - \frac{B^2}{Z}}
\]

\[
Z = \frac{Z}{Z - B} - \frac{AZ}{Z^2 + 2BZ - B^2} \quad \therefore 1 = \frac{1}{Z - B} - \frac{A}{Z^2 + 2BZ - B^2}
\]

\[
0 = (Z - B)(Z^2 + 2BZ - B^2) - Z^2 - 2BZ + B^2 + A(Z - B)
\]

\[
\]

\[
\]

\[
0 = Z^3 + Z^2\alpha + Z\beta + \gamma \quad \text{where} \quad \alpha = (B - 1); \quad \beta = (A - 3B^2 - 2B); \quad \gamma = (B^3 + B^2 - AB)
\]
One approach to the use of the Peng-Robinson:

using \( \omega, T_c \) and \( P_c \)

define

\[
\kappa = 0.37464 + 1.54226 \omega - 0.26992 \omega^2
\]

\[
\overline{\alpha} = 1 + \kappa \left( 1 - T_r^{1/2} \right)
\]

\[
a = \alpha \left( 0.45724 \frac{R^2 T_c}{P_c} \right)
\]

\[
b = 0.0778 \frac{R T_c}{P_c}
\]

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

to iterate multiply by \((v-b)/P\) and rearrange:

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

calculate \( \frac{v+b}{v-b} \) then \( \frac{v+b}{v-b} \) + b then \( \frac{a/P}{\sqrt{\frac{v+b}{v-b}} + b} \)

This then gives \( v \), the next guess

Proceed until \( v \) does not vary
The solution of a Cubic Equation

If a cubic equation is stated as below:

\[ Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \]

its roots can be obtained if we examine the following forms:

\[ q = \frac{1}{3} \beta - \frac{1}{9} \alpha^2 \]
\[ r = \frac{1}{6} (\alpha \beta - 3 \gamma) - \frac{1}{27} \alpha^3 \]

If \( q^3 + r^2 > 0 \), there will be one real root and a pair of complex conjugate roots.

If \( q^3 + r^2 = 0 \), all roots are real and at least two will be equal.

If \( q^3 + r^2 < 0 \), all roots are real (irreducible case, i.e., no analytical solution)

The roots can be expressed using the following definitions:

\[ s_1 = \left[ r + 3 \sqrt[3]{(q^3 + r^2)} \right]^{1/3} \]
\[ s_2 = \left[ r - 3 \sqrt[3]{(q^3 + r^2)} \right]^{1/3} \]

and the roots are:

\[ Z_1 = (s_1 + s_2) - \frac{\alpha}{3} \]
\[ Z_2 = \frac{(s_1 + s_2)}{2} - \frac{\alpha}{3} + \frac{i \sqrt{3}}{2} (s_1 - s_2) \]
\[ Z_3 = \frac{(s_1 + s_2)}{2} - \frac{\alpha}{3} - \frac{i \sqrt{3}}{2} (s_1 - s_2) \]

You should note some interesting and useful properties of the roots.

\[ Z_1 + Z_2 + Z_3 = \alpha \]
\[ Z_1 Z_2 + Z_1 Z_3 + Z_2 Z_3 = \beta \]
\[ Z_1 Z_2 Z_3 = \gamma \]