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: $Z = \frac{PV}{RT}$ = function of '

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

or Z = F(Tr, Pr); one example $= Z^0 + \omega Z^1$; ω 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

$$\left(P + \frac{a}{\tilde{V}^2}\right)(\tilde{V} - b) = RT$$

$$P = \frac{RT}{(\tilde{V} - b)} - \frac{a}{\tilde{V}^2}$$

Parameters for the Van der Waals Equation

Gas	a, *Pa-m^6/mol^2*	b, *m^3/mol x 10^3*
O_2	0.1381	3.184
N_2	0.1368	3.864
H_2O	0.5542	3.051
CH_4	0.2303	4.306
CO	0.1473	3.951
CO_2	0.3658	4.286
NH_3	0.4253	3.737
H_2	0.0248	2.660
He	0.00346	2.376

Redlich-Kwong Equation

$$P = \frac{R\,T}{(\tilde{V} - b)} - \frac{a}{T^{1/2}\,\tilde{V}(\tilde{V} + b)}$$

Peng-Robinson Equation

$$P = \frac{R\,T}{(\tilde{V} - b)} - \frac{a(T)}{\tilde{V}(\tilde{V} + b) + b(\tilde{V} - b)}$$

Generalized Cubic Equation

$$P = \frac{R\,T}{(\tilde{V} - b)} - \frac{(\tilde{V} - \eta)\theta}{(\tilde{V} + b)(\tilde{V}^2 - \delta\tilde{V} + \varepsilon)}$$

Note that if Z = PV/NRT, the equation can be written as a cubic eqation 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 paramers α, β, γ and the parameters for the respective equations of state.

	van der Waals	*Redlich-Kwong*	*Peng-Robinson*
α	$-1 - B$	-1	$-1 + B$
β	A	$A - B - B^2$	$A - 3B^2 - 2B$
γ	$-AB$	$-AB$	$-AB + B^2 + B^3$

where

$$Z = \frac{P\,\tilde{V}}{R\,T} \quad \text{and} \quad B = \frac{P\,b}{R\,T}$$

$$A = \frac{aP}{(R\,T)^2} \quad \text{for van der Waals and Peng-Robinson}$$

$$A = \frac{a\,P}{(R\,T)^2\,\sqrt{T}} \quad \text{for Redlich-Kwong}$$

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

$$Z = \frac{P\tilde{V}}{RT}$$

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

$$A = \frac{0.45724 P_r}{T_r^2}\sigma(T_r) \qquad B = 0.07780 \frac{P_R}{T_R}$$

with other parameters appropriately defined

$$\sigma(T_r) = 1 + \kappa\left(1 - \sqrt{T_r}\right)$$

$$\kappa = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

So that the parameters in the cubic form are given by

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

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

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

To relate the two types of Representation:

$$P = \frac{RT}{v - b} - \frac{a}{v(v+b) + b(v-b)} \text{ where } b = \frac{BRT}{P} \;\&\; a = \frac{A(RT)^2}{P}$$

$$P = \frac{RT}{v - \frac{BRT}{P}} - \frac{A(RT)^2/P}{v\left(v+\frac{BRT}{P}\right) + \frac{BRT}{P}\left(v-\frac{BRT}{P}\right)}$$

gathering P in denominator

$$P = \frac{RTP}{Pv - BRT} - \frac{A(RT)^2/P}{\frac{v}{P}(Pv+BRT) + \frac{BRT}{P^2}(Pv-BRT)}$$

Multiply byV/RT and elim. /P in second term:

$$\frac{Pv}{RT} = \frac{Pv}{Pv - BRT} - \frac{A(RT)*Pv}{Pv(Pv+BRT) + BRT(Pv-BRT)}$$

Sub. for Z; top & bottom by 1/RT; top & bottom by 1/RTPV

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

$$Z = \frac{Z}{Z - B} - \frac{AZ}{Z^2 + 2BZ - B^2} \qquad 1 = \frac{1}{Z - B} - \frac{A}{Z^2 + 2BZ - B^2}$$

$$0 = (Z - B)(Z^2 + 2BZ - B^2) - Z^2 - 2BZ + B^2 + A(Z - B)$$

$$0 = Z^3 + Z^2(-B + 2B - 1) + Z(-B^2 - 2B^2 + A - 2B) + B^3 + B^2 - AB$$

$$0 = Z^3 + Z^2(B - 1) + Z(A - 3B^2 - 2B) + B^3 + B^2 - AB$$

$$0 = Z^3 + Z^2\alpha + Z\beta + \gamma \;\; : \text{where } \alpha = (B - 1);\; \beta = (A - 3B^2 - 2B);\; \gamma = (B^3 + B^2 - AB)$$

One approach to the use of the Peng-Robinson:

using ω, Tc and Pc

define

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$\sqrt{\alpha} = 1 + \kappa\left(1 - T_r^{1/2}\right)$$

$$a = \alpha\,(0.45724)\frac{R^2 T_c^2}{P_c}$$

$$b = 0.0778\frac{RT_c}{P_c}$$

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

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

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

calculate $\left(\frac{v+b}{v-b}\right)$ then $v\left(\frac{v+b}{v-b}\right) + b$ then $\frac{a/P}{v\left(\frac{v+b}{v-b}\right) + b}$

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 :

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

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 :

$$s_1 = \left[r + 3*\sqrt{(q^3 + r^2)}\right]^{\frac{1}{3}} \quad ; \quad s_2 = \left[r - 3\sqrt{(q^3 + r^2)}\right]^{\frac{1}{3}}$$

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.

$$Z_1 + Z_2 + Z_3 = -\alpha \quad ; \quad Z_1Z_2 + Z_1Z_3 + Z_2Z_3 = \beta$$

$$Z_1Z_2Z_3 = \gamma$$