

Cubic Equation of State

A cubic equation of state takes the general form:

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + vb(1+c) - cb^2} \quad (2)$$

or

$$p = \frac{RT}{v-b} - \frac{a}{(v+\delta_1 b)(v+\delta_2 b)} \quad (3)$$

where:

$$2\delta_1 = (1+c) - \sqrt{(1+c)^2 + 4c}$$

$$\delta_1 \delta_2 = -c$$

When $c = 1$, equation (2) becomes the Peng-Robinson Equation of State and when $c = 0$, it becomes the Soave-Redlich-Kwong Equation of State.

For pure components, parameters a and b are expressed in terms of the critical properties and the acentric factor:

$$\begin{aligned} \sqrt{a} &= \sqrt{a_c \alpha} \\ \sqrt{a_c} &= \sqrt{\Omega_a (RT_c)} / \sqrt{p_c} \\ \sqrt{\alpha} &= 1 + \kappa \left(1 - \sqrt{T/T_c} \right) \\ b &= \Omega_b RT_c / p_c \end{aligned} \quad (4)$$

Define:

$$A \equiv ap / (RT)^2$$

and

$$B \equiv bp / RT$$

The compressibility factor $Z = bp / RT$ can be expressed as:

$$E \equiv Z^3 - Z^2 (1 - cB) + Z [A - B(1+c) - B^2 (1+2c)] - [AB - c(B^3 + B^2)] = 0 \quad (5)$$

For mixtures, parameters a and b are defined using the following mixing rule:

$$\begin{aligned} a &= \sum_i x_i S_i \\ S_i &= \sqrt{a_i} \sum_j x_j (1 - d_{ij}) \sqrt{a_j} \\ b &= \sum x_i b_i \end{aligned} \quad (6)$$

where d_{ij} is an empirically determined interaction coefficient.

The fugacity coefficient is derived from the equation of state (Michelsen, 1981)

$$\ln \phi = \left(\frac{\partial \tilde{F}}{\partial n} \right)_{T,v} - \ln Z$$

where:

$$\tilde{F} = \int_v^{\infty} \left(\frac{p}{RT} - \frac{N}{V} \right) dV \quad (7)$$

Resulting in:

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln (Z - B) - \frac{1}{\delta_2 - \delta_1} \frac{A}{B} \left(\frac{2S_i}{a} - \frac{b_i}{b} \right) \ln \left(\frac{Z + \delta_2 B}{Z + \delta_1 B} \right) \quad (8)$$

Calculation of Parameters

The above equations require knowledge of Ω_a , Ω_b , and κ . Parameters Ω_a and Ω_b are obtained from the critical condition. At the critical point, the compressibility factor will have three real and equal roots (Martin, 1979).

$$(Z - Z_c)^3 = 0$$

Comparing this with equation (8) results in:

$$\Omega_b = 1 / (3Z_1 + c)$$

$$\Omega_b = (Z_1^3 + c + c/\Omega_b) \Omega_b^2$$

$$Z_c = \Omega_b Z_1$$

where:

$$Z_1 \equiv 1 + Z_2 + 2/Z_2$$

$$Z_2 \equiv (3 + c + Z_3)^{1/3}$$

$$Z_3 \equiv c^2 + 6c + 1$$

Setting the value of c results in the usual equation of state:

Equation of State						
Peng-Robinson (PR)	1	-0.4142	2.4142	0.45724	0.07780	0.307
Soave-Redlich-Kwong (SRK)	0	0	1	0.42747	0.08664	0.333

(9)

The value of κ is obtained from the following empirical correlations.

For the PR equation of state, Peng and Robinson (1976) proposes:

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

$$\kappa = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3$$

For the SRK equation of state, Soave (1972) proposes:

$$\kappa = 0.480 + 1.574\omega - 0.176\omega^2$$

While the following equation is suggested by Grabowski and Daubert (1978)

$$\kappa = 0.48508 + 1.55171\omega - 0.15613\omega^2$$

Selection of Compressibility Root and Vapor/Liquid Identification

The cubic Z-factor equation may yield two real roots. In which case, the one that results in the lowest Gibbs free energy (i.e. most stable) will be selected. Let Z_A and Z_B be the two real roots resulting in free energy G_A and G_B respectively. Since free energy:

$$G = \sum_i x_i \ln f_i$$

$$G_A - G_B = \ln \left(\frac{Z_B - B}{Z_A - B} \right) + \frac{1}{\delta_2 - \delta_1} \frac{A}{B} \ln \left(\frac{Z_B + \delta_2 B}{Z_A + \delta_2 B} \frac{Z_A + \delta_1 B}{Z_B + \delta_1 B} \right) - (Z_B - Z_A) \quad (10)$$

If $G_A - G_B > 0$, Z_B will be selected and vice versa. For single-phase fluids, if the above scheme selects the largest Z root, the fluid is said to be vapor. Similarly, if the smallest positive Z root is chosen, the fluid is said to be liquid.

In cases where the Z -factor equation yields only one real root, the naming of the phase to be vapor or liquid is irrelevant. For identification purposes, the criteria according to Gosset et al. (1986) is used.

The fluid is designated as liquid when $A/B > \Omega_a/\Omega_b$ and $Z < (Z_c/\Omega_b)B$, else it is designated as vapor.

For simplicity, the EOS Z_C as shown in equation (9) is used in the above criteria. For multiphase fluids, the phases are identified according to their mass densities. The lower density phase is arbitrarily denoted as vapor.

Volume Translation Technique

The volume translation technique of Peneloux et al. (1982) is used to improve the density prediction capability of the SRK and PR equation of states.

Consider pressure-explicit equation of state of the form:

$$p = p(T, V, n_1, n_2, n_3, \dots)$$

The fugacity of component i is:

$$\ln f_i = \int_0^p \left(\frac{v_i}{RT} - \frac{1}{p} \right) dp + \ln(x_i p) \quad (11)$$

where v_i is the partial molar volume. The equilibrium conditions require that:

$$\ln f_i^L = \ln f_i^v \quad (12)$$

A volume translation modifies the molar volume of the system v predicted by the equation of state as follows:

$$v^t = v^0 - \tilde{v} \quad (13)$$

$$\tilde{v} = \sum x_i r_i$$

and

$$B_{ci} = \Omega_b \frac{RT_c}{p_c}$$

where t_i is the dimensionless individual translation value for each component and the superscripts o and t correspond respectively to the results before and after the volume translation. B_{ci} is the hard core molecular volume of component i . By using equation (13), the fugacities of component i after the volume translation become:

$$\ln(f_i^L) = \ln(f_i^o) - pr_i/RT \quad (14)$$

Thus if:

$$\ln(f_i^L) = \ln(f_i^v)$$

then:

$$\ln(f_i^L)^t = \ln(f_i^v)^t$$

i.e. the volume translation has no effect on the equilibrium conditions. Therefore, it will not alter the saturation pressures, saturation temperatures, equilibrium compositions, etc. However, it will modify the molar volumes, compressibility factors and densities of the fluid.

The following equations show the effect of equation (13) on the parameters of interest to petroleum engineers.

Compressibility:

$$Z^t = Z^o (v^o/v^t) \quad (15)$$

Gas oil ratio, GOR :

$$GOR^t = GOR^o (v^o/v^t)_{stc} \quad (16)$$

Mass density, ρ :

$$\rho^t = \rho^o (v^o/v^t) \quad (17)$$

where subscript **stc** denotes the stock tank (standard) conditions. Other equations of interest can be derived easily using equation (13).

The use of the volume translation technique requires the knowledge of r_i for each component. These can be estimated from equation (15) at the critical conditions:

$$(Z_c)_i = (Z_c)_{EOS} (v_{ci} - r_i)/v_{ci}$$

where $(Z_c)_{EOS}$ is the compressibility factor from the equation of state, as shown in equation (9). Peneloux et al. (1982) have tabulated values of t_i for the first ten components in the alkane series. Jhaveri et al. (1984) have also developed empirical equations for t_i . Generally, for phase behavior matching, it is advantageous to treat t_i as regression variables. Experience shows that it is sufficient to introduce non-zero t_i 's for the C_{6+} components and methane only. Furthermore, for the C_{6+} components, it is preferable to have one t_i value for all components, for example:

$$t_{C6-C12} = t_{C13-C20} = t_{C20+}$$

Enthalpy and Heat Capacity

The excess enthalpy, H^E , of a fluid which follows the EOS in Equations (2) and (3) is given by:

$$H^E \equiv H - H^* = pv - RT + \frac{T(\partial a / \partial T) - a}{(\delta_2 - \delta_1)} \ln \left(\frac{v + \delta_2 b}{v + \delta_1 b} \right) \quad (18)$$

and the excess capacity is:

$$C_p^E \equiv \left(\partial H^E / \partial T \right)_p \quad (19)$$

where H is the system enthalpy and H^* is the enthalpy at the ideal gas state, calculated from:

$$H^* = \sum_i x_i H_i^*$$

H_i^* is a function of temperature only and cannot be derived from the EOS and has to be input by the user in the form of a polynomial:

$$H_i^* = H_A + H_B T + H_C T^2 + H_D T^3 + H_E T^4 + H_F T^5$$

with T in deg. R and H_i^* in Btu/lb. H_A through H_F are user specified parameters. Passut and Danner (1972) have compiled the values of H_A through H_F for components commonly encountered in Petroleum Engineering.

In most practical uses, the important variables are the enthalpy differences and not the absolute enthalpies. Thus, the reference point for H can be chosen arbitrarily. In WinProp enthalpy is assigned zero when the component is at ideal gas state at zero Kelvin.