Equations of States (EOS) – Volume Shift – SRK & PR EOS

A **comparison** of the **predicted** liquid molar volume by leading ***two parameter EOS*** with **experimental** data of **pure compounds** generally shows a systematic deviation.

$$V^{\mathrm{L}}_{\mathrm{corr}} = V^{\mathrm{L}} - \sum_i (x_i c_i)$$

$$V^{\mathrm{v}}_{\mathrm{corr}} = V^{\mathrm{v}} - \sum_i (y_i c_i)$$

$$c_i = (0.0115831168 + 0.411844152\omega_i)\left(\frac{T_{\mathrm{ci}}}{p_{\mathrm{ci}}}\right)$$

Component	PR EOS	SRK EOS
N_2	−0.1927	−0.0079
CO_2	−0.0817	0.0833
H_2S	−0.1288	0.0466
C_1	−0.1595	0.0234
C_2	−0.1134	0.0605
C_3	−0.0863	0.0825
i-C_4	−0.0844	0.0830
n-C_4	−0.0675	0.0975
i-C_5	−0.0608	0.1022
n-C_5	−0.0390	0.1209
n-C_6	−0.0080	0.1467
n-C_7	0.0033	0.1554
n-C_8	0.0314	0.1794
n-C_9	0.0408	0.1868
n-C_{10}	0.0655	0.2080

Equations of States (EOS) – Volume Shift – SRK & PR EOS – Example 10

Rework Example 9 by incorporating volume corrections.

$$c_i = (0.0115831168 + 0.411844152\omega_i)\left(\frac{T_{ci}}{p_{ci}}\right)$$

Component	x_i	p_c	T_c	ω_i	c_i	$c_i x_i$	y_i	$c_i y_i$
C_1	0.45	666.4	343.33	0.0104	0.00839	0.003776	0.86	0.00722
C_2	0.05	706.5	549.92	0.0979	0.03807	0.001903	0.05	0.00190
C_3	0.05	616.0	666.06	0.1522	0.07729	0.003861	0.05	0.00386
C_4	0.03	527.9	765.62	0.1852	0.1265	0.00379	0.02	0.00253
C_5	0.01	488.6	845.8	0.2280	0.19897	0.001989	0.01	0.00198
C_6	0.01	453	923	0.2500	0.2791	0.00279	0.005	0.00139
C_{7+}	0.40	285	1160	0.5200	0.91881	0.36752	0.005	0.00459
$\sum$						0.38564		0.02349

$$V^{v} = \frac{RTZ^{v}}{p} = \frac{(10.73)(620)(0.9267)}{4000} = 1.54119\,\text{ft}^3/\text{mol}$$

$$V^{L} = \frac{RTZ^{L}}{p} = \frac{(10.73)(620)(1.4121)}{4000} = 2.3485\,\text{ft}^3/\text{mol}$$

$$V^{L}_{corr} = V^{L} - \sum_i (x_i c_i) = 2.3485 - 0.38564 = 1.962927\,\text{ft}^3/\text{mol}$$

$$V^{v}_{corr} = V^{v} - \sum_i (y_i c_i) = 1.54119 - 0.02394 = 1.5177\,\text{ft}^3/\text{mol}$$

Equations of States (EOS) – Volume Shift – SRK & PR EOS – Example 10 – Cont.

$$Z^{v}_{corr} = \frac{(4000)(1.5177)}{(10.73)(620)} = 0.91254$$

$$Z^{L}_{corr} = \frac{(4000)(1.962927)}{(10.73)(620)} = 1.18025$$

$$\rho = \frac{pM_a}{RTZ}$$

$$\rho^{v} = \frac{(4000)(20.89)}{(10.73)(620)(0.91254)} = 13.767\,\text{lb/ft}^3$$

$$\rho^{L} = \frac{(4000)(100.25)}{(10.73)(620)(1.18025)} = 51.07\,\text{lb/ft}^3$$

Equations of States (EOS) – Summary

EOS	$p_{repulsion}$	$p_{attraction}$	a	b
Ideal	$\frac{RT}{V}$	0	0	0
vdW	$\frac{RT}{V-b}$	$\frac{a}{V^2}$	$\Omega_a \frac{R^2 T_c^2}{p_c}$	$\Omega_b \frac{R T_c}{p_c}$
RK	$\frac{RT}{V-b}$	$\frac{a}{V(V+b)\sqrt{T}}$	$\Omega_a \frac{R^2 T_c^{2.5}}{p_c}$	$\Omega_b \frac{R T_c}{p_c}$
SRK	$\frac{RT}{V-b}$	$\frac{a\alpha(T)}{V(V+b)}$	$\Omega_a \frac{R^2 T_c^2}{p_c}$	$\Omega_b \frac{R T_c}{p_c}$
PR	$\frac{RT}{V-b}$	$\frac{a\alpha(T)}{V(V+b)+b(V-b)}$	$\Omega_a \frac{R^2 T_c^2}{p_c}$	$\Omega_b \frac{R T_c}{p_c}$

Fugacity – I

- The **fugacity "f"** is a **measure of the molar Gibbs energy of a real gas**.
- The tendency of the molecules from one phase to escape into the other.

$$f^{\mathrm{o}} = p \exp\left[\int_o^p \left(\frac{Z-1}{p}\right) dp\right]$$

$f^{\mathrm{o}} =$ fugacity of a pure component, psia
$p =$ pressure, psia
$Z =$ compressibility factor

Fugacity – II

- Physically, the fugacity of a **component *i*** in one phase with respect to the fugacity of the component in a second phase is a measure of ***the potential for transfer of the component between phases***.
- The phase with the ***lower component fugacity*** **accepts the component** ***from the phase with a higher component fugacity***.
- ***Equal fugacities*** of a component in the two phases results in a ***zero net transfer***.
- ***A zero transfer for all components*** implies that the hydrocarbon system is in ***thermodynamic equilibrium***.

$$f_i^{\mathrm{v}} = f_i^{\mathrm{L}}, \quad 1 \le i \le n$$

f_i^{v} = fugacity of component i in the gas phase, psi
f_i^{L} = fugacity of component i in the liquid phase, psi
n = number of components in the system

Fugacity Coefficient (ϕ)

The ratio of the *fugacity to the pressure*. The fugacity coefficient of component *i* in a hydrocarbon liquid mixture or hydrocarbon gas mixture is ***a function of the system pressure, mole fraction, and fugacity of the component***.

For a component ***i*** in the **gas phase**: $\phi_i^v = \frac{f_i^v}{y_i p}$

For a component ***i*** in the **liquid phase**: $\phi_i^L = \frac{f_i^L}{x_i p}$

Fugacity Coefficient (ϕ) - K_i

$$\boldsymbol{K_i = \frac{y_i}{x_i}}$$

When ***two phases exist in equilibrium***, it suggests that $\boldsymbol{f_i^L = f_i^v}$, which leads to redefining the ***K-value in terms of the fugacity of components*** as:

$$\xRightarrow{y_i=\frac{f_i^v}{p\phi_i^v} \quad \& \quad x_i=\frac{f_i^L}{p\phi_i^L}} \boldsymbol{K_i = \frac{\phi_i^L}{\phi_i^v}} \quad \xRightarrow{Where} \quad \ln \phi_i = \left(\frac{1}{RT}\right)\left[\int_V^\infty \left(\frac{\partial p}{\partial n_i} - \frac{RT}{V}\right)\right] dV - \ln Z$$

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Fugacity Coefficient (ϕ) – Calculations – SRK EOS

$$\ln\left(\Phi_i^{\mathrm{L}}\right) = \frac{b_i(Z^{\mathrm{L}}-1)}{b_{\mathrm{m}}} - \ln\left(Z^{\mathrm{L}}-B\right) - \left(\frac{A}{B}\right)\left[\frac{2\Psi_i}{(a\alpha)_{\mathrm{m}}} - \frac{b_i}{b_{\mathrm{m}}}\right]\ln\left[1+\frac{B}{Z^{\mathrm{L}}}\right]$$

$$\Psi_i = \sum_j \left[x_j\sqrt{a_i a_j \alpha_i \alpha_j}\left(1-k_{ij}\right)\right]$$

$$(a\alpha)_{\mathrm{m}} = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j}\left(1-k_{ij}\right)\right]$$

$$\ln\left(\Phi_i^{\mathrm{v}}\right) = \frac{b_i(Z^{\mathrm{v}}-1)}{b_{\mathrm{m}}} - \ln(Z^{\mathrm{v}}-B) - \left(\frac{A}{B}\right)\left[\frac{2\Psi_i}{(a\alpha)_{\mathrm{m}}} - \frac{b_i}{b_{\mathrm{m}}}\right]\ln\left[1+\frac{B}{Z^{\mathrm{v}}}\right]$$

$$\Psi_i = \sum_j \left[y_j\sqrt{a_i a_j \alpha_i \alpha_j}\left(1-k_{ij}\right)\right]$$

$$(a\alpha)_{\mathrm{m}} = \sum_i \sum_j \left[y_i y_j \sqrt{a_i a_j \alpha_i \alpha_j}\left(1-k_{ij}\right)\right]$$

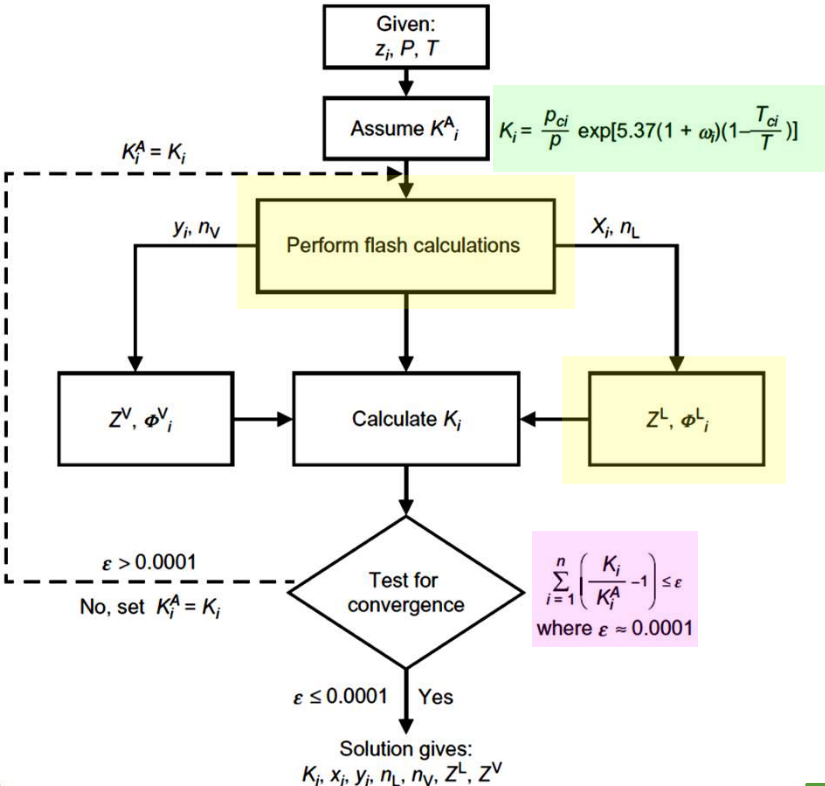
Fugacity Coefficient (ϕ) – Calculations – PR EOS

$$\overset{\boldsymbol{L}}{\Rightarrow} \ln \phi_i^L = \frac{b_i(Z^L - 1)}{b_m} - \ln(Z^L - B) - \frac{A}{2\sqrt{2}B}\left[\frac{2\psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right] \ln\left[\frac{Z^L + \left(1 + \sqrt{2}B\right)}{Z^L + \left(1 - \sqrt{2}B\right)}\right]$$

$$\overset{\boldsymbol{v}}{\Rightarrow} \ln \phi_i^v = \frac{b_i(Z^v - 1)}{b_m} - \ln(Z^v - B) - \frac{A}{2\sqrt{2}B}\left[\frac{2\psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right] \ln\left[\frac{Z^v + \left(1 + \sqrt{2}B\right)}{Z^v + \left(1 - \sqrt{2}B\right)}\right]$$

The parameters are the same as before.

EOS – Applications - Equilibrium Ratio



EOS – Applications – Bubble Point

A saturated vapor exists for a given temperature at the pressure at which an **infinitesimal amount of liquid** first appears.

$$n_t = n_L + n_v$$

$$z_i n_t = x_i n_L + y_i n_v$$

$$z_i = x_i n_L + y_i n_v$$

$$z_i = x_i n_L + y_i n_v$$

$$z_i = x_i(1) + y_i(0)$$

$$z_i = x_i$$

$$z_i = \frac{k_i}{y_i}$$

$$\sum \frac{z_i}{k_i} = 1 \xrightarrow{K_i = \frac{\phi_i^L}{\phi_i^v}} \sum \frac{z_i}{\phi_i^L / \phi_i^v}$$

EOS – Applications – Dew Point – Cont.

$$\sum \frac{z_i}{k_i} = 1 \xrightarrow{K_i=\frac{\phi_i^L}{\phi_i^v}} \sum \frac{z_i}{\phi_i^L/\phi_i^v} = 1 \xrightarrow{\phi_i^v=\frac{f_i^v}{y_i p}} \sum \left[\left(\frac{z_i}{\phi_i^L}\right)\frac{f_i^v}{z_i p}\right] = 1$$

$$\Rightarrow p_d = \sum \left[\frac{f_i^v}{\phi_i^L}\right] \Rightarrow f(p_d) = \sum \left[\frac{f_i^v}{\phi_i^L}\right] - p_d = 0$$

It can be solved for the **dew-point** pressure by using **the Newton-Raphson iterative method**.