Chapter 4: Equations of States

Danesh, Ali. *PVT and phase behaviour of petroleum reservoir fluids*. Elsevier, 1998.

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Home works: 1, 3, 5, 7, 12, 13 15

Chapter 4: Equations of States

Multi Component System

$$ln\emptyset_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} - \frac{RT}{V}\right] dV - lnZ \qquad i = 1,2,\dots,N$$

V: Total Volume

Z: Compressibility factor for mixture

$$n = \sum n_i$$

$$Z = PV/nRT$$

4.1 VIRIAL EOS AND ITS MODIFICATIONS

The virial equation is based on theories of statistical mechanics [2], and can be expressed as an infinite series of either molar volume (molar density), or pressure,

$$Z = 1 + B/v + C/v^2 + D/v^3 + \dots \qquad (4.1)$$

$$(Z = 1 + B\rho_M + C\rho_M^2 + D\rho_M^3 + \dots)$$

or,

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots \qquad (4.2)$$

where Z is the compressibility factor, v and ρ are the molar volume and the molar density, respectively, and P is the pressure. B, C, D, etc., are called the second, third, fourth, and so on, virial coefficients, and depend only on temperature for each compound.

Virial EoS:

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots$$

V=V(P, T)

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$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \qquad P=P(T, V)$$

$$B' = \frac{B}{RT} \;\; ; \;\; C' = \frac{C - B'}{RT} \;\; ; \;\; D' = \frac{D - 3BC + 2B^3}{(RT)^3}$$

Starling Modification of Benedict-Webb-Rubin EOS (BWRS)

The Benedict-Webb-Rubin EOS (BWR) [1] is an empirical extension of the virial EOS. A modification of the Benedict-Webb-Rubin EOS as proposed by Starling [3] with 11 parameters has been applied successfully to petroleum reservoir fluids,

$$P = \rho_M RT + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho_M^2 + \left(bRT - a - \frac{d}{T}\right)\rho_M^3 + \alpha\left(a + \frac{d}{T}\right)\rho_M^6 + \frac{c\rho_M^3}{T^2}\left(1 + \gamma\rho_M^2\right)\exp\left(-\gamma\rho_M^2\right) \qquad (4.3)$$

where ρ_M is the molar density and the 11 coefficients can be evaluated from the following generalised equations:

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$$\rho_{Mc} B_O = 0.443690 + 0.115449\omega$$

$$\frac{\rho_{Mc} A_o}{RT_c} = 1.28438 - 0.920731\omega$$

$$\frac{\rho_{Mc} C_o}{RT^3_c} = 0.356306 + 1.70871\omega$$

$$\frac{\rho_{Mc} D_o}{RT^4_c} = 0.0307452 + 0.179433\omega$$

$$\frac{\rho_{Mc} E_o}{RT^5_c} = 0.006450 - 0.022143\omega \ \exp(-3.8\omega)$$

$$\rho^2_{Mc} b = 0.528629 + 0.349261\omega$$

$$\frac{\rho^2_{Mc} a}{RT_c} = 0.484011 + 0.754130\omega$$

$$\frac{\rho^2_{Mc} d}{RT^2_c} = 0.0732828 + 0.463492\omega$$

$$\rho^3_{Mc} \alpha = 0.0705233 \ - 0.044448\omega$$

$$\frac{\rho^2_{Mc} c}{RT^3_c} = 0.504087 + 1.32245\omega$$

$$\rho^2_{Mc} \gamma = 0.544979 \ -0.270896\omega$$

$$(P)(V) = RT$$

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

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

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cubic EoS ≡ *emprical*

Van der Waals EOS

معادله واندروالس (۱۸۷۳)

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

$\frac{a}{V_m^2}$ تصحیح نیروهای جاذبه ی بین مولکولی

مفهوم

به دلیل بیشتر بودن نیروی جاذبه مولکولی در گازهای حقیقی، فشار وارده بر دیواره ظرف از طرف گاز حقیقی به اندازه این مقدار کمتر از نیروی وارده از طرف گاز ایده آل بر دیواره ظرف می باشد.

b تصحیح حجم/ تصحیح نیروهای دافعه بین مولکولی

مفهوم

به دلیل بیشتر بودن نیروهای دافعه در گاز حقیقی، حجم مولی گاز حقیقی به اندازه b بیش تر از حجم مولی گاز ایده آل می باشد.

R ثابت جهانی گازها است.

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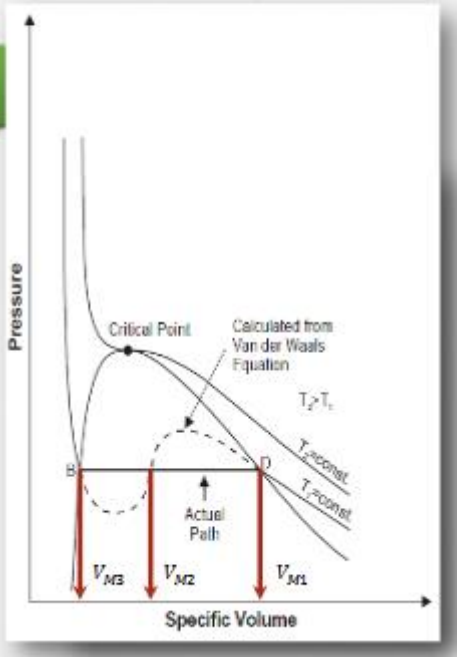
Cubic Equations of State

معادلات حالت درجه ۳

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

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

$$A = \frac{aP}{(RT)^2} \qquad B = \frac{bP}{RT}$$



با توجه به شکل در نقطه بحرانی ← Inflection Point

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

با جایگذاری معادله واندروالس در معادلات فوق خواهیم داشت:

$$a = \frac{9}{8}RT_cV_c = \frac{27}{64}\left(\frac{R^2T_c^2}{P_c}\right) \qquad \Omega_a = \frac{9}{8}Z_c$$

برای تمامی مواد $Z_c = 0.375$

$$b = \frac{1}{3}V_c = \frac{1}{8}\left(\frac{RT_c}{P_c}\right) \qquad \Omega_b = \frac{1}{3}Z_c$$

در واقعیت

ترکیبات انگشت شماری نظیر گازهای کوانتومی وجود دارند که مقدار Zc آن ها بزرگتر از 0.3 می باشد.

مثال ۴-۱

مربوط به محاسبه حلالیت متان در آب و محاسبه ضریب فوگاسیته با استفاده از معادله واندروالس است.

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4.2 CUBIC EQUATIONS OF STATE

van der Waals improved the ideal gas equation by considering the intermolecular attractive and repulsive forces, and introduced his well-known equation of state in 1873,

$$(P + \frac{a}{v^2})(v - b) = RT \tag{4.4}$$

where a/v^2 and b represent the attractive and repulsive terms respectively, and v is the molar volume.

As the pressure approaches infinity, the molar volume becomes equal to b. Hence, b is also considered as an apparent volume of the molecules and called co-volume. It should be always less than the molar volume v.

The above equation in terms of volume or compressibility factor takes a cubic form as follows:

$$v^3 - (b + \frac{RT}{P})v^2 + (\frac{a}{P})v - \frac{ab}{P} = 0 \tag{4.5}$$

or

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \tag{4.6}$$

where the dimensionless parameters A and B are defined as,

$$A \equiv \frac{aP}{(RT)^2} \tag{4.7}$$

$$B \equiv \frac{bP}{RT} \tag{4.8}$$

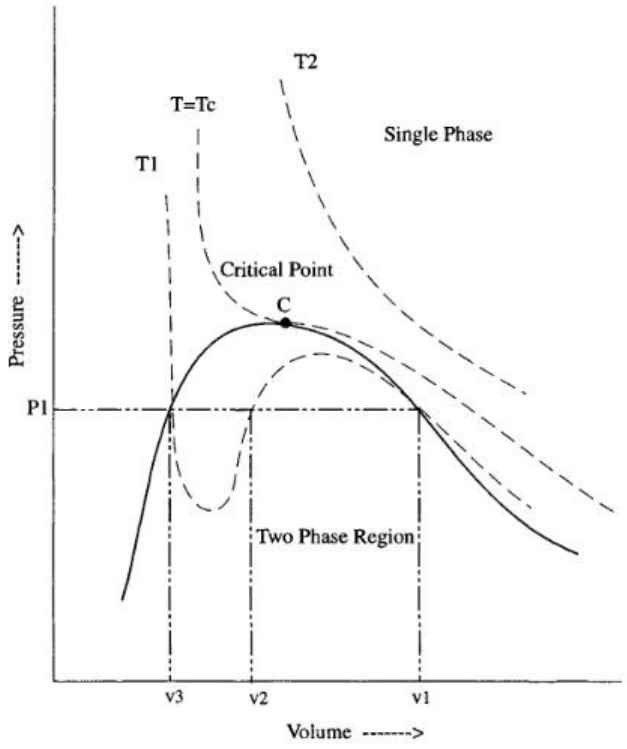

Figure 4.1. Volumetric behaviour of pure compound as predicted by cubic EOS of van der Waals type.

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Example 4.1.

In Example 3.3, the solubility of methane in water was calculated by assuming the methane fugacity coefficient equal to one. Use vdW to estimate the fugacity coefficient and improve the accuracy of predicted gas solubility.

Solution:

Substituting the pressure in the fugacity expression for pure compounds, Eq.(3.35), using vdW, we obtain,

$$\ln\phi = (Z-1) - \ln Z + \frac{1}{RT}\int_{\infty}^{v}\left(\frac{RT}{v} - P\right)dv =$$

$$= (Z-1) - \ln Z + \frac{1}{RT}\int_{\infty}^{v}\left(\frac{RT}{v} - \frac{RT}{v-b} + \frac{a}{v^2}\right)dv$$

Integration of the above equation results in,

$$\ln\phi = (Z-1) - \ln Z + \frac{1}{RT}\left[RT\ln\frac{v}{v-b} - \frac{a}{v}\right]_{\infty}^{v}$$

Implementing the limits, and making the equation dimensionless, using Eqs.(4.7-8), we obtain:

$$\ln\phi = (Z-1) - \ln(Z-B) - A/Z$$

The parameters of vdW are calculated, using Eqs.(4.9-10) and methane critical properties given in Table A.1 in Appendix A, as,

$$a = \frac{27}{64}\left(\frac{R^2T_c^2}{P_c}\right) = (27/64)\times(0.0083144\times190.56)^2/4.599 = 0.230274 \text{ MPa.}(m^3/kgmol)^2$$

$$b = \frac{1}{8}\left(\frac{RT_c}{P_c}\right) = (1/8)\times 0.0083144\times190.56/4.599 = 0.304254 \ m^3/kgmol$$

with the dimensionless values, defined in Eq.(4.7-8), as follows,

A=1.556251 B=0.902574

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Substituting the above values in Eq.(4.6), results in the following cubic equation for Z,

$Z^3-1.90257\ Z^2+1.55625\ Z-1.40463=0$

with only one real root,

$Z=1.49069$

Substituting the above value of the compressibility factor in the fugacity expression results in,

$\phi=0.97779$

Hence the concentration of dissolved methane in water, corrected for the fugacity coefficient, is,

$f_{C1}^{V}=P\times\phi=65\times0.97779$ MPa $=(1.4378\times10^{4}$ MPa/mol fraction$)\times x_{C1}$

$x_{C1}=4.42\times10^{-3}$ mole fraction of methane in water.

Two Parameter EOS

Redlich-Kwong (RK) EOS

$$\left[P+\frac{a}{T_r^{0.5}V_m(V_m+b)}\right](V_m-b)=RT$$

یا استفاده از شرایط بحرانی:

$$a=\Omega_a\frac{R^2T_c^2}{P_c}\qquad \Omega_a=0.4274$$

$$b=\Omega_b\frac{RT_c}{P_c}\qquad \Omega_b=0.08664$$

4.2.1 Two-Parameter EOS

Redlich and Kwong [10] modified the attractive term of vdW as,

$$P=RT/(v-b)-a/[T_r^{0.5}v(v+b)] \qquad (4.21)$$

The values of Ω_a and Ω_b were considered to be constant, hence, determined to be 0.42747 and 0.08664 respectively, using Eq.(4.9).

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Example 4.3.

A class of equations relating volumetric properties to temperature and pressure, is that based on the corresponding states principle, which considers that fluids behave identically at conditions of equal reduced properties. Reduce the Redlich-Kwong EOS to a corresponding states form of $Z=Z(T_r, P_r)$. Compare the result for T=1.5, over a P_r range of 0.5-3, with that of the generalised compressibility chart shown in Figure 2.22.

Solution:

The Redlich-Kwong EOS in terms of the compressibility factor is the same as Eq.(4.26), with the following expressions for A and B according to Eqs.(4.7) and (4.8), respectively,

$$A = aP/(RT)^2 = (0.42747T_r^{-0.5}R^2T_c^2/P_c)P/R^2T^2 = 0.42747T_r^{-2.5}P_r$$

$$B = bP/RT = (0.08664RT_c/P_c)P/RT = 0.08664T_r^{-1}P_r$$

Substituting the above two expressions in Eq.(4.24), results in,

$$Z^3 - Z^2 + \left[(0.42747P_r/T_r^{2.5} - 0.08664P_r/T_r - (0.08664P_r/T_r)^2\right]Z - 0.037036P_r^2/T_r^{3.5} = 0$$

Substituting T_r=1.5 and various P_r values in the above equation results in a cubic equations, with the results as follows. The comparison with the values of Z read from Figure 2.22 is also shown.

P_r	0.5	1.0	2.0	3.0
Z, RK	0.952	0.907	0.834	0.798
Z, Fig. 2.22	0.950	0.903	0.823	0.778

Soave-Redlich-Kwong (SRK)

α به جای $Tr^{0.5}$ ← به صورت تابعی عمومی تر ارائه می گردد.

$$\left[P + \frac{a_c\alpha}{V_m(V_m+b)}\right](V_m - b) = RT$$

$$\alpha = [1 + m(1 - T_r^{0.5})]^2$$

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

$$\omega = -\log(P_r^{sat})\Big|_{T_r=0.7} - 1$$

برای محاسبه m بر حسب ω از تساوی فوگاسیته های اشباع مایع و بخار در Tr=0.7 استفاده کردند.

$$f^l_{|T_r=0.7} = f^v_{|T_r=0.7}$$

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مهم

SRK نسبتاً قادر به پیش بینی تعادل بخار-مایع می باشد ولی چگالی مایع را به طور دقیق نمی دهد.

فرم حالت درجه سوم SRK

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

$$A = \frac{aP}{(RT)^2} \qquad B = \frac{bP}{RT} \qquad Z = \frac{PV}{RT}$$

Soave-Redlich-Kwong EOS (SRK)

Soave [21] replaced the temperature dependency of the attractive term in RK, $T_r^{-0.5}$, by a more general function α:

$$P = RT / (v - b) - a_c \alpha / [v(v + b)] \qquad (4.22)$$

where

$$a_c = 0.42747\ R^2T_c^2 / P_c$$

$$b = 0.08664\ R\ T_c / P_c$$

and

$$\alpha = [1 + m\ (1 - T_r^{0.5})]^2 \qquad (4.23)$$

The function α was selected, and m was correlated with the acentric factor by equating fugacities of saturated liquid and vapour phases at $T_r = 0.7$.

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \qquad (4.24)$$

Soave et al. [22], later suggested to divide the value of m determined from the above equation by 1.18 to improve the results.

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Peng-Robinson (PR)

به منظور بهبود بخشیدن به پیش بینی دانسیته مایع درمقایسه باSRK جمله جذب را تصحیح کردند.

$$\left[P+\frac{a_c\alpha}{V_m(V_m+b)+b(V_m-b)}\right](V_m-b)=RT$$

$\Omega_a = 0.4572 \qquad \Omega_b = 0.077796 \qquad m = 0.3746 + 1.542\omega - 0.2699\omega^2$

محاسبه m

از داده فشار بخار که از طریق نقطه جوش نرمال تا نقطه بحرانی به دست آمده بود، جهت بیان رابطه m بر حسب ω استفاده کردند.

Heavier Components $(\omega_i > 0.49)$:

$$m = 0.3796 + 1.435\omega - 0.1644\omega^2 + 0.01667\omega^3$$

فرم حالت درجه سوم PR

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

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Peng-Robinson EOS (PR)

Peng and Robinson [24] modified the attractive term mainly to improve the prediction of liquid density in comparison with SRK,

$$P = RT/(v - b) - a_c\alpha/[v(v + b) + b(v - b)] \quad (4.27)$$

where,

$$a_c = 0.457235\, R^2\, T_c^2 / P_c$$

and

$$b = 0.077796\, R\, T_c / P_c$$

They used a similar form of α as proposed by Soave, Eq.(4.23), but used vapour-pressure data from the normal boiling point to the critical point, and correlated m as,

$$m = 0.37464 + 1.5422\omega - 0.26992\omega^2 \quad (4.28)$$

The correlation was later modified to improve predictions for heavier components [25],

$$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 \quad (4.29)$$

PR in terms of the compressibility factor Z takes the following form,

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)\, Z - (AB - B^2 - B^3) = 0 \quad (4.30)$$

PR is obtained by substituting u and w in Eq.(4.12) by 2b and b, respectively.

Volume Shift

Peneloux et al. [26] were the first who introduced the volume shift concept, i.e. shifting the volume axis, and applied it to SRK,

$$v^{cor} = v - c \quad (4.31)$$

where v^{cor} is the corrected molar volume, and c is the correction term determined by matching the measured and predicted saturated liquid volumes at $T_r = 0.7$.

EOS are applied to multicomponent mixtures by introducing mixing rules to determine mixture parameters, as will be described in Section 4.5. The following mixing rule is used to determine c for mixtures:

$$c = \sum^{N} x_i c_i \quad (4.32)$$

where, x_i, is the mole fraction of component, i, in the mixture.

Peneloux et al. correlated the volume translation parameter c as,

$$c = 0.40768(0.29441 - Z_{RA})\, \frac{RT_c}{P_c} \quad (4.34)$$

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Volume Shift — جابجایی حجمی

انحراف بین حجم مولی مایع پیش بینی شده یا داده آزمایشگاهی ترکیبات خالص (مربوط به معادلات حالت دو پارامتری)

این انحراف ← در نواحی فشار دور از نقطه بحرانی تقریباً ثابت می باشد

Peneloux (SRK):

Corrected Molar Volume

$$V_m^{corr} = V_m - C \qquad (SRK)$$

C: Matching the measured and predicted saturated liquid volume at Tr=0.7

نکته: تأثیرات این انحراف روی حجم مولی گاز در نواحی فشار دور از منطقه بحرانی به دلیل بزرگ بودن میزان حجم مولی گاز ناچیز می باشد.

فشارپایین ومتوسط ⇒ $V_g^M \gg C$

$$C = \sum_{i=1}^{N} x_i C_i \qquad x_i: \ mole\ fraction$$

$$C = 0.40768(0.29441 - Z_{RA})\frac{RT_c}{P_c}$$

Rackett Equation

$$V^s = \left(\frac{RT_c}{P_c}\right) Z_{RA}^{\left[1+(1-T_R)^{\frac{2}{7}}\right]}$$

Jhaveri & Youngren (PR)

$$V_m^{corr} = V_m - C \qquad (PR)$$

تطبیق حجم های مولی اندازه گیری شده و پیش بینی شده برای هیدروکربون های گوناگون

$S_E = \frac{C}{b}$ ← پارامتر واندروالس در PR

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Jhaveri and Youngren [27], similarly to Peneloux et al., applied the volume shift concept to PR, and related c to the parameter b, by defining a dimensionless shift parameter, S_E,

$$S_E = c / b \tag{4.35}$$

S_E was determined by matching the predicted and measured molar volumes for various hydrocarbons. The shift parameters for light compounds are given in Table 4.1.

Table 4.1.
Values of shift parameter in Peng-Robinson equation of state.

component	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	C_6
S_E	-0.1540	-0.1002	-0.08501	-0.07935	-0.06413	-0.04350	-0.04183	-0.01478

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Light Components → Table 4.1

Component	C1	C2	C3	iC4	nC4	iC5	nC5	C6
S_E	-0.1540	-0.1002	-0.08501	-0.07935	-0.06413	-0.04350	-0.04183	-0.01478

Modify

$$S_E = 1 - \frac{\Psi}{M^x}$$

Molecular Weight

Table 4.2

Component Type	ψ	χ
Paraffins	2.258	0.1823
Naphthenes	3.004	0.2324
Aromatics	2.516	0.2008

The authors correlated the shift parameter to the molecular weight as,

$$S_E = 1 - \psi / M^{\chi} \qquad (4.36)$$

where ψ and χ are positive coefficients. Suggested values for the coefficients are given in Table 4.2.

Table 4.2.
Coefficients of shift parameter correlation, Eq.(4.36).

Component Type	ψ	χ
Paraffins	2.258	0.1823
Naphthenes	3.004	0.2324
Aromatics	2.516	0.2008

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Example 4.4.

Calculate the vapour pressure of normal hexane at 477.6 K using PR. What are the predicted values of the saturated vapour, and liquid density?

Solution:

At the saturation point, the fugacities of hexane as vapour and liquid should be equal. Hence, a pressure is assumed and the fugacities are calculated, using PR. The pressure is iterated until the two calculated fugacities become equal.

Substituting u=2b and w=b in the generalised fugacity expression for pure compounds, Eq.(4.18), results in,

$$\ln\phi = (Z-1) - \ln(Z-B) + \frac{A}{2B\sqrt{2}} \ln \frac{Z+(1-\sqrt{2})B}{Z+(1+\sqrt{2})B}$$

The parameters of PR are calculated, using Eq.(4.27), and normal hexane critical properties, Table A.1 in Appendix A, as,

$a_c = 0.457235R^2T_c^2/P_c = 0.457235\times(0.0083144\times507.6)^2/3.025 = 2.692273$ MPa.$(m^3/kgmol)^2$

$b = 0.077796\, RT_c/P_c = 0.077796\times 0.0083144\times507.6/3.025 = 0.108539$ $m^3/kgmol$

The temperature dependency factor of the attractive term, α, is calculated from Eq.(4.29), and Eq.(4.23), for ω=0.3013 at T_r=477.6/507.6=0.94089,

$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 = 0.812562$

$\alpha = [1 + m(1 - T_r^{0.5})]^2 = 1.049349$

Hence,

$a=\alpha\times a_c = 2.825135$ MPa.$(m^3/kgmol)^2$

Assuming a saturation pressure of 1.86 MPa, using Figure 1.3 or Eq.(1.10), the two dimensionless parameters, defined by Eqs.(4.7-8), are calculated as,

A=0.33324353 B=0.0508396

which results in the following cubic equation for Z, Eq.(4.6),

$Z^3 - 0.9491604\, Z^2 + 0.22381034\, Z - 0.0142259 = 0$

The above equation has three real roots, Appendix B,

Z_1=0.62954
Z_2=0.10557
Z_3=0.21405

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Substituting the above two values of the compressibility factor in the fugacity expression results in,

$\phi_1=\phi^V=0.729704$

$\phi_2=\phi^L=0.746610$

For a pure compound the equality of fugacity reduces to the equality of fugacity coefficient. The comparison of the calculated fugacity coefficients indicates that the assumed pressure is close to the saturation pressure, but requires improvement. The next pressure may be estimated as,

$$P_{(r+1)}=\left[P(\phi^L/\phi^V)\right]_{(r)}$$

where r is the iteration number.

The above approach results in a pressure equal to 1.9031 MPa, for the next step. The iteration converges to,

$P^s=1.9458$ MPa

$\phi^L=\phi^V=0.71716$

The estimated value by the Lee-Kesler equation, Eq.(1.10), is 1.936 MPa.

The cubic equation at the above pressure is as follows,

$Z^3-0.9468152\,Z^2+0.23376031\,Z-0.015562=0$

with the following roots:

$Z_1=0.60089$
$Z_2=0.10958$
$Z_3=0.23634$

Rejecting the intermediate root, and calculating the molar volume, Eq.(1.5), we obtain,

$v=ZRT/P$ $\quad v^L=0.22362\ m^3/kgmol$ $\quad v^V=1.22623\ m^3/kgmol$

The volume shift for normal hexane is calculated, Eq.(4.35), as,

$c=S_E b=-0.01478\times0.108539=-0.001604\ m^3/kgmol$

which results in the following corrected molar volumes, Eq.(4.31),

$v^{cor}=v-c$ $\quad v^{L,cor}=0.22523\ m^3/kgmol$ $\quad v^{V,cor}=1.2279\ m^3/kgmol$

The densities of the saturated phases are:

$\rho=M/v$ $\quad \rho^L=382.6\ kg/m^3$ $\quad \rho^V=70.18\ kg/m^3$

The measured values, Figure 1.5, are $\rho^L=423$, and $\rho^V=72\ kg/m^3$. The modified Rackett equation, Eq.(1.12), predicts a saturated liquid density of 424.3 kg/m^3.

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vdW: u=0 w=0
SRK: u=b w=0
PR: u=2b w=b

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$$P = \frac{RT}{v-b} - \frac{a}{v^2+uv-w^2} \tag{4.12}$$

In a two-parameter form of the equation u and w are related to b whereas in a three-parameter form u, and w are related to b, and/or a third parameter c. In a four-parameter modification u and w are related to b and/or c and a fourth parameter d.

The above general equation in terms of the compressibility factor is,

$$Z^3 - (1+B-U)Z^2 + (A-BU-U-W^2)Z - (AB-BW^2-W^2) = 0 \tag{4.13}$$

where the dimensionless parameters A and B are the same as those defined in Eqs.(4.7) and (4.8), respectively, and

$$U \equiv \frac{uP}{RT} \tag{4.14}$$

$$W \equiv \frac{wP}{RT} \tag{4.15}$$

The two-parameter EOS are the most popular equations, where the parameters are expressed by,

$$a = \Omega_a \frac{R^2 T_c^{\,2}}{P_c} \tag{4.16}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{4.17}$$

Note that the expressions for the parameters in the modified equations are similar to those of the original vdW, but the coefficients have been generalised as Ω_a and Ω_b. The other parameters, in EOS which use more than two, are generally of co-volume nature, hence, expressed by an equation similar to Eq.(4.17), but with different coefficients.

The substitution of Eq.(4.12) into the expression for fugacity of a pure substance, Eq.(3.35), results in the following generalised expression, using the same approach as in Example 4.1,

$$\ln\phi = (Z-1) - \ln(Z-B) + \frac{A}{\sqrt{U^2+4W^2}} \ln \frac{2Z+U-\sqrt{U^2+4W^2}}{2Z+U+\sqrt{U^2+4W^2}} \tag{4.18}$$

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4.3 Mixing Rules

4.3.1. Random Mixing Rules

$$B = \sum_i \sum_j x_i x_j B_{ij} \tag{4.68}$$

where B_{ij} is the coefficient due to interaction between molecules i and j.

Employing Eq.(4.1), the second coefficient is determined as,

$$B = \lim_{\rho \to 0} (\partial Z / \partial \rho)$$

Using a van der Waals type equation to describe Z at low pressures, the above equation results in,

$$B = \lim_{\rho \to 0} (\partial Z / \partial \rho) = b - (a / RT) \tag{4.69}$$

Hence, the mixing rules for a and b, at least at low pressures, should be compatible with that in Eq.(4.68), i.e., it should be of quadratic form.

$$a = \sum_i \sum_j x_i x_j \left(a_i \cdot a_j\right)^{0.5} \tag{4.73}$$

$$b = \sum_i \sum_i x_i x_j b_{ij} = \sum_i \sum_j x_i x_j \left(b_i + b_j\right)/2 = \sum_i x_i b_i \tag{4.74}$$

A mixing rule similar to that of b is also used for other parameters in EOS that contain more than two parameters, when the additional parameters are of the co-volume characteristic,

$$c = \sum_i x_i c_i \tag{4.75}$$

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$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} \qquad b = \sum_i \sum_j \frac{x_i x_j (b_i + b_j)}{2}$$

فرم های دیگر:

نکته: می توان برای b_{ij} از رابطه دقیق زیر که بر اساس در نظر گرفتن فاصله بین دو مولکول به جای میانگین حجم هایشان به دست آمده است:

$$b = \left(\frac{b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}}}{2} \right)^3$$

نکته: در معادله حالت سه پارامتری مانند (PT) ، که اغلب پارامتر سوم (خاصیت) ماهیت شبه حجم دارد:

$C = \sum x_i c_i$ ← پارامتر سوم

The attractive force between molecules i and j, represented in EOS by parameter, a_{ij}, which is of an energy nature, can be expressed in a simple geometric average form [43] as,

$$a_{ij} = (a_i a_j)^{1/2} \tag{4.70}$$

The repulsive force between molecules i and j, represented in EOS by parameter b_{ij}, which has the characteristic of volume, can be determined by arithmetic average,

$$b_{ij} = (b_i + b_j)/2 \tag{4.71}$$

Eqs.(4.70) and (4.71) describing the interaction between a pair of different molecules are more intuitive than rigorous. Other forms, perhaps with equally valid arguments, can also be considered. For example, considering the distance between the two molecules, instead of averaging their volumes results in,

$$b = \left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3 \tag{4.72}$$

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It is common to incorporate an additional parameter in Eq.(4.71) to express the attractive term between pairs of non-similar molecules,

$$a_{ij} = \left(a_i a_j\right)^{1/2}\left(1 - k_{ij}\right) \tag{4.77}$$

where k_{ij} is known as the binary interaction parameter.

Using the above description, the random mixing rule of the attractive term becomes,

$$a = \sum_i \sum_j x_i x_j \left(a_i \cdot a_j\right)^{0.5} (1 - k_{ij}) \tag{4.78}$$

The use of binary interaction parameter for the repulsive term, particularly in mixtures with high concentration of CO2 [44], has also been suggested, but has not gained popularity,

$$b_{ij} = [(b_i + b_j)/2](1-k'_{ij}) \tag{4.79}$$

where k'_{ij} are the repulsive BIP.

Correlations to estimate BIP for specific EOS, such as SRK[45] and PR[46], as well as general ones [47,48, 49] have been suggested. The most commonly used correlation [47] is,

$$k_{ij} = \vartheta_i \left[1 - \left(\frac{2\left(v_{c_i}^{1/3} v_{c_j}^{1/3}\right)^{1/2}}{v_{c_i}^{1/3} + v_{c_j}^{1/3}}\right)^{\theta}\right] \tag{4.80}$$

where the constants ϑ_i, and θ, are determined for each EOS using the available binary data, or adjusted in tuning of EOS for a particular fluid system, as will be described in Section 9.3. A default value of θ=6 may be used [50].

Example 4.5.

The Soave-Redlich-Kwong, and the Peng-Robinson EOS are the most widely used equations in the petroleum industry. It is common to express these equations by the following general form,

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

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where, δ_1, and, δ_2, are constants equal to 1 and 0 in SRK, and $1+\sqrt{2}$, and $1-\sqrt{2}$ in PR, respectively.

Prove that the fugacity of each component in a mixture, using the above EOS and the random mixing rules is given by,

$$\ln\phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{B(\delta_2-\delta_1)}\left(\left(2\sum_{j=1}^{N} x_j a_{ij}\right)/a - b_i/b\right)\ln\left(\frac{Z+\delta_2 B}{Z+\delta_1 B}\right) \tag{E4.5}$$

Solution:

The fugacity coefficient is calculated from Eq.(3.31),

$$\ln\phi_i = \frac{1}{RT}\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} - RT/V\right]dV - \ln Z \tag{3.31}$$

where V is the total volume. Hence, the equation of state is written in terms of total volume by substituting v=V/n, where n is the total number of moles,

$$n = \sum_{1}^{N} n_i$$

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$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{(V + \delta_1 nb)(V + \delta_2 nb)}$$

The derivative of pressure at constant total volume, pressure and all mole numbers except n_i is calculated as,

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \frac{RT}{V - bn} + \frac{nRT\left[\partial(nb)/\partial n_i\right]}{(V - nb)^2} - \frac{\partial(n^2 a)/\partial n_i (n^2 a)}{(V + \delta_1 nb)(V + \delta_2 nb)} +$$

$$\frac{\left\{\delta_1\delta_2\left[\partial(nb)^2/\partial n_i (nb)^2\right] + (\delta_1 + \delta_2)V\left[\partial(nb)/\partial n_i\right]\right\}(n^2 a)}{\left[(V + \delta_1 nb)(V + \delta_2 nb)\right]^2}$$

Applying the random mixing rules to calculate a and b, Eq.(4.78) and Eq.(4.74) respectively,

$$n^2 a = \sum_{i=1}^{N}\sum_{j=1}^{N} n^2 x_i x_j a_{ij} = \sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j a_{ij}$$

$$nb = \sum_{i=1}^{N} n x_i b_i = \sum_{i=1}^{N} n_i b_i$$

the derivatives of the two parameters are obtained as,

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$$\left[\partial(nb)/\partial_{ni}\right]_{T,V,n_{j\neq i}} = b_i$$

$$\left[\partial(n^2a)/\partial_{ni}\right]_{T,V,n_{j\neq i}} = 2\sum_{j=1}^{N} n_j a_{ij} = 2n\sum_{j=1}^{N} x_j a_{ij}$$

Substituting the above calculated terms in Eq.(3.31) and integrating it between the two limits will result in,

$$\ln\phi_i = -\ln Z(1-nb/V) + \frac{nb_i}{V-nb} + \frac{a}{RT(\delta_1-\delta_2)b}\left(\left(2\sum_{j=1}^{N} n_j a_{ij}\right)/na - b_i/b\right)\times \ln\frac{V+n\delta_2 b}{V+\delta_1 nb} - \frac{naVb_i}{RTb(V+\delta_1 nb)(V+\delta_2 nb)}$$

Substituting

$$\frac{-an^2}{(V+\delta_1 nb)(v+\delta_2 nb)} = P - \frac{nRT}{V-nb}$$, i.e., the equation of state, and V= nv = nbZ/B

in the above will result in Eq.(E4.5).