Chapter 4: Equations of States
Chapter 5: Phase Behavior Calculations

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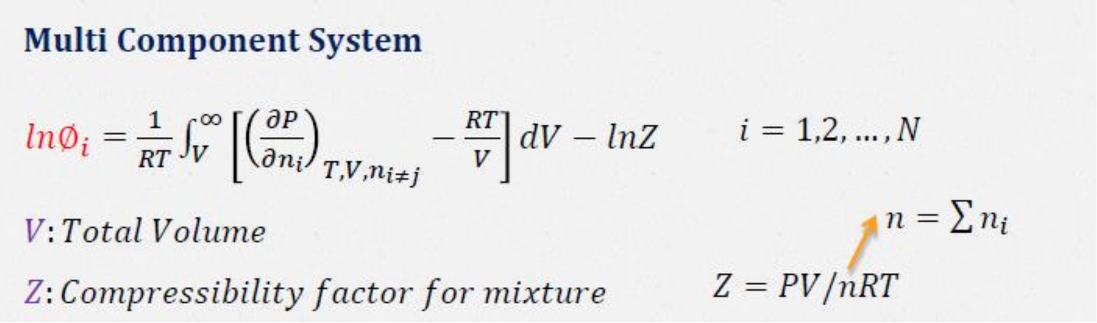
Home works: 1, 3, 5, 7, 12, 13 15

Chapter 4: Equations of States



Multi Component System

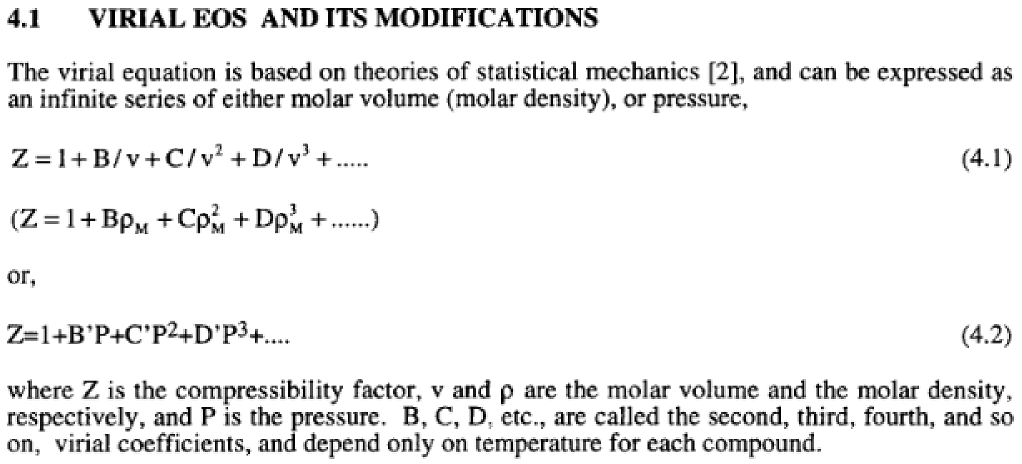
$$ln\emptyset_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} - \frac{RT}{V}\right] dV - lnZ \qquad i = 1,2,\dots,N$$

$V: Total\ Volume$

$n = \sum n_i$

$Z: Compressibility\ factor\ for\ mixture$

$Z = PV/nRT$



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:

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \qquad V=V(P, T)$$

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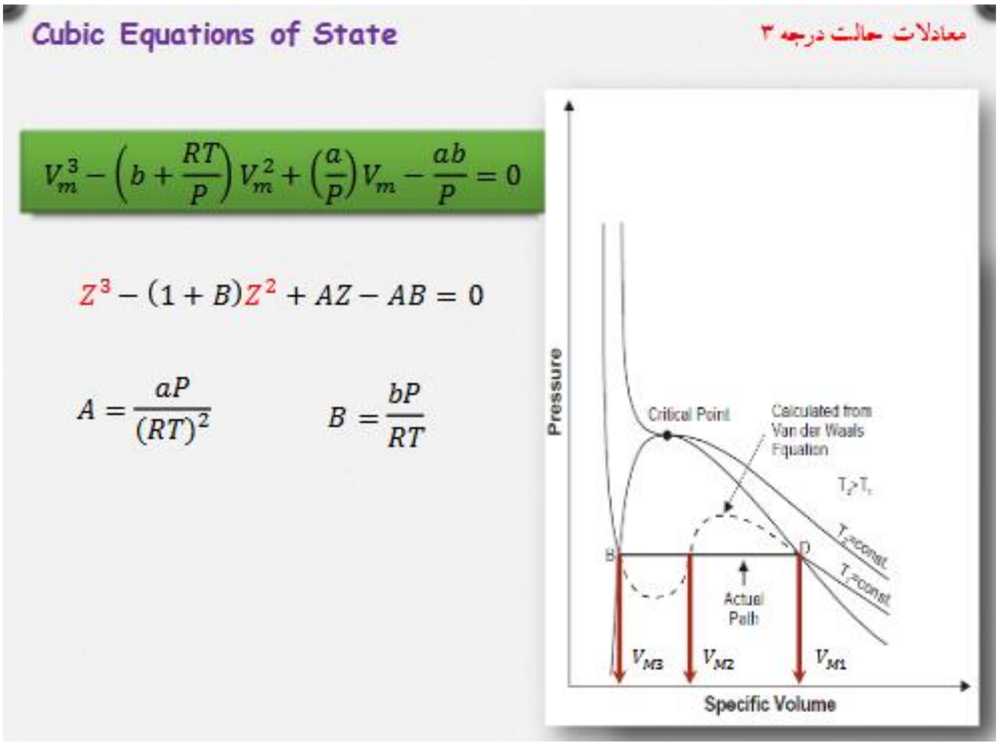
$$Z=\frac{PV}{RT}=1+\frac{B}{V}+\frac{C}{V^2}+\ldots \qquad P=P(T, V)$$

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

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

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

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



Cubic Equations of State

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

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

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

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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,

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

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

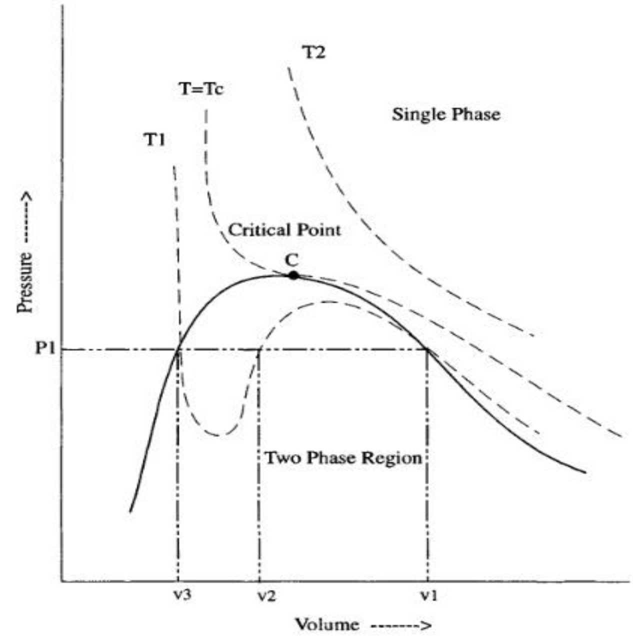

Figure 4.1. Volumetric behaviour of pure compound as predicted by cubic EOS of van der Waals type.

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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

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,

$Z=1.49069$

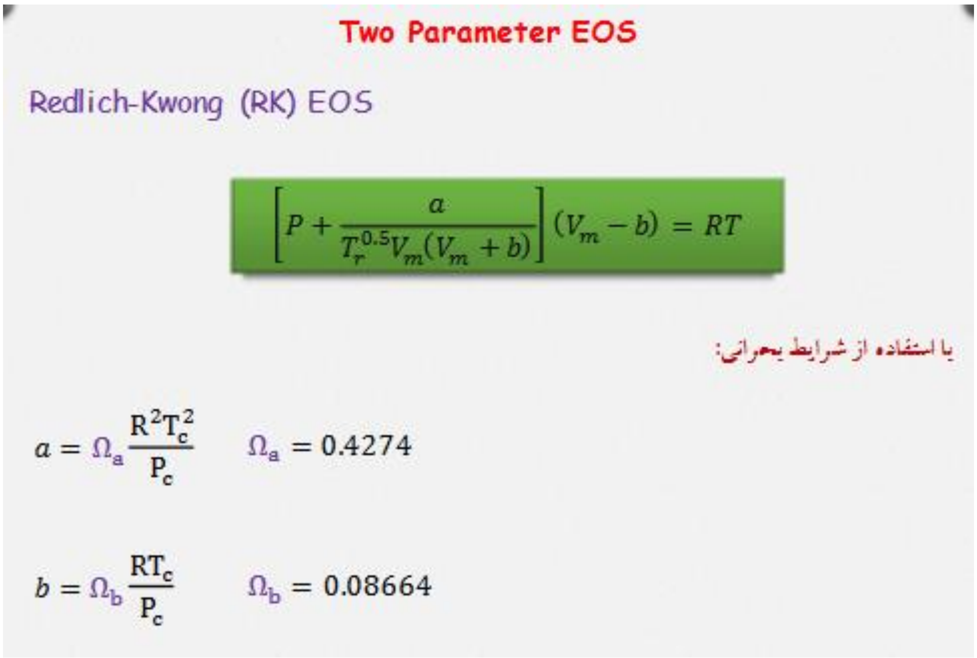
Substituting the above value of the compressibility factor in the fugacity expression results in,

$\phi=0.97779$

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

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

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



Two Parameter EOS

Redlich-Kwong (RK) EOS

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

با 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,

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

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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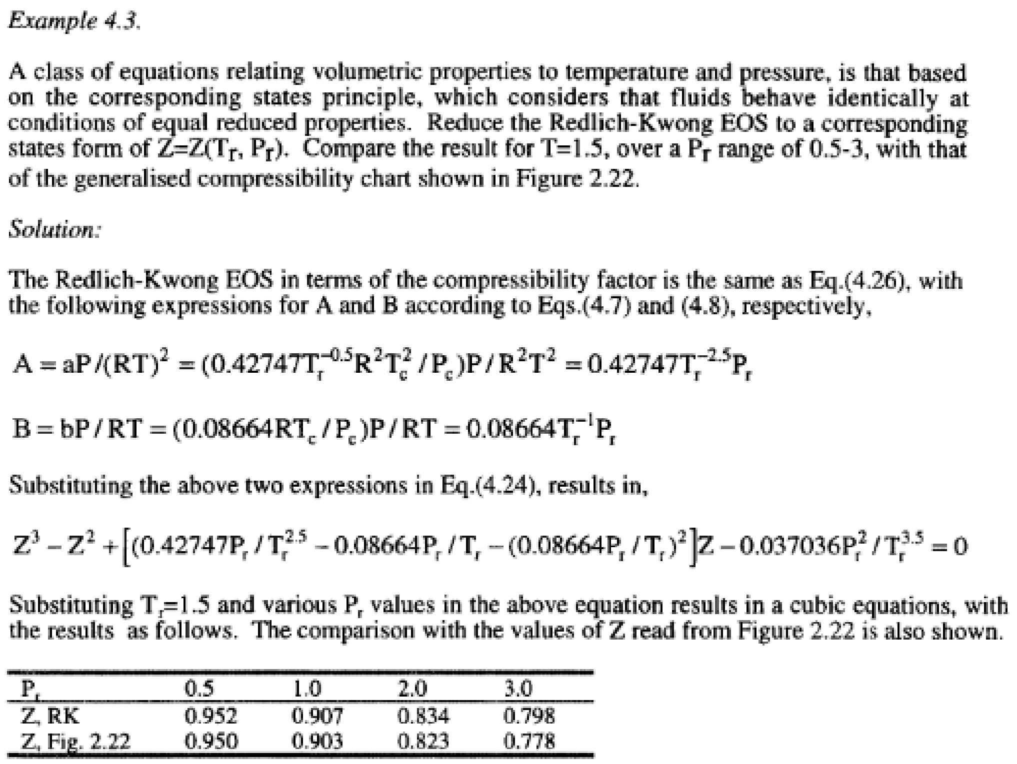


Example 4.3.

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,

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

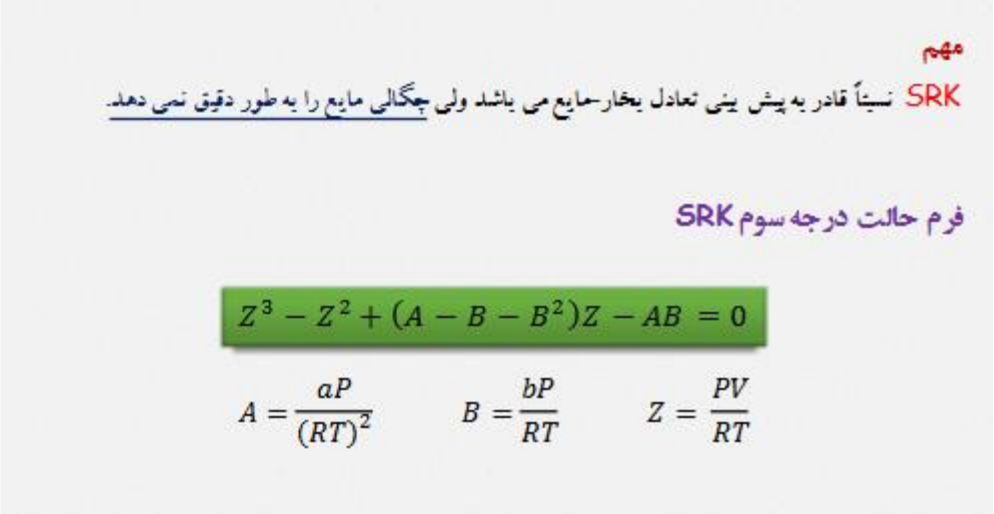
$$B = bP/RT = (0.08664RT_c/P_c)P/RT = 0.08664T_r^{-1}P_r$$

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



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

$$\boxed{Z^3 - Z^2 + (A - B - B^2)Z - AB = 0}$$

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

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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:

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

where

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

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

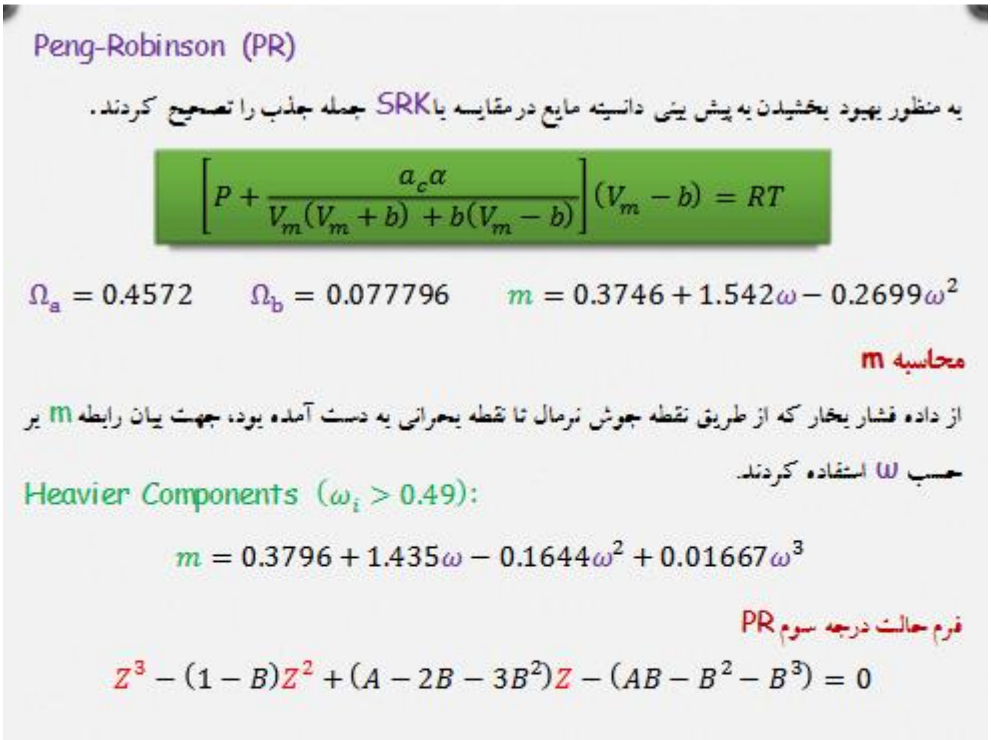
and

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

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

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{4.24}$$

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



Peng-Robinson (PR)

به منظور بهبود بخشیدن به پیش بینی دانسیته مایع درمقایسه با SRK 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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22. Soave, G., Barolo, M. and Bertucco, A: "Estimation of High Pressure Fugacity Coefficients of Pure Gaseous Fluids by a Modified SRK Equation of State", J. Fluid Phase Equilibria, 91, 87-100 (1993).

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28. Mathias, P.M., Naheiri, T. and Oh, E.M: "A Density Correction for the Peng-Robinson Equation of State", J. Fluid Phase Equilibria, 47, 77-87 (1989).

Peng-Robinson EOS (PR)

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

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

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,

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

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

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

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

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

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,

$$v^{cor} = v - c \tag{4.31}$$

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:

$$c = \sum^{N} x_i c_i \tag{4.32}$$

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

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

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

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

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

$$S_E = 1 - \psi / M^{\chi} \tag{4.36}$$

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

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,

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

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

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,

$c=S_Eb=-0.01478\times0.108539=-0.001604$ 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.

vdW: $u=0$ $\quad w=0$
SRK: $u=b$ $\quad w=0$
PR: $u=2b$ $\quad w=b$

یک شکل عمومی برای معادلت حالت درجه ۳

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

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,

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

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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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,

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

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 $\theta=6$ 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,

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

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,

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

Chapter 4: Equations of States
Chapter 5: Phase Behavior Calculations

Home works: 1, 2, 4, 5, 7, 10

Chapter 5: Phase Behavior Calculations

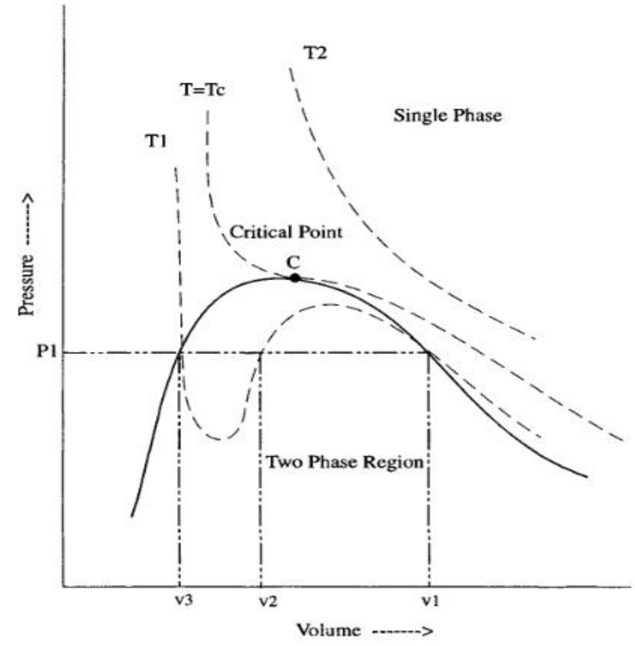
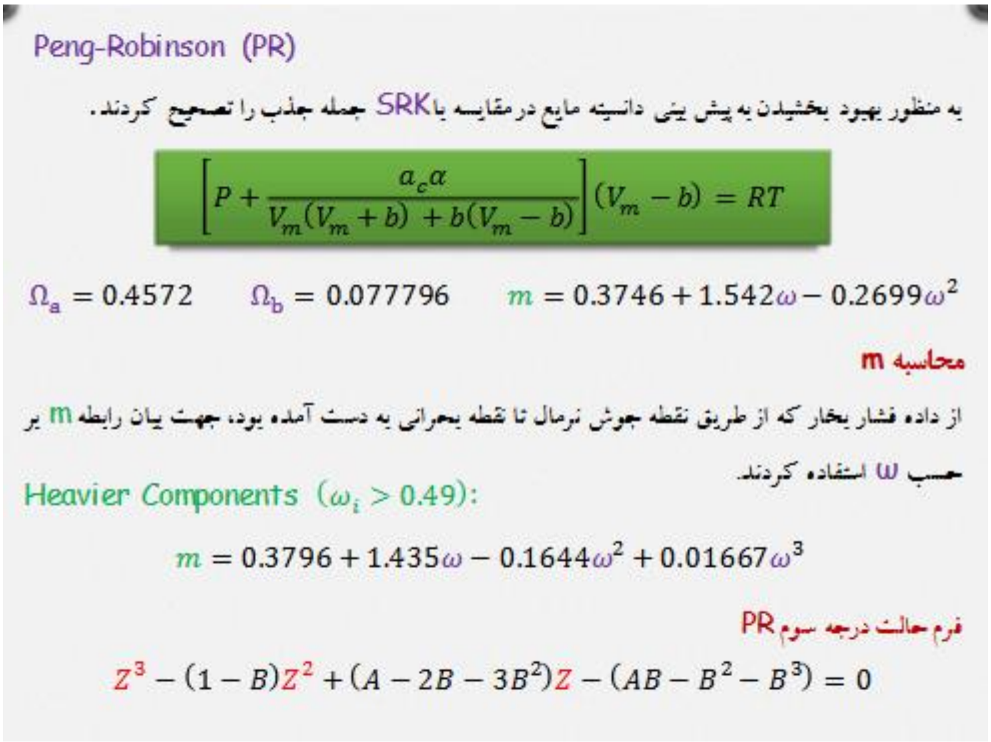


Figure 4.1. Volumetric behaviour of pure compound as predicted by cubic EOS of van der Waals type.



Peng-Robinson (PR)

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

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

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

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

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

Chapter 4: Equations of States
Chapter 5: Phase Behavior Calculations

Pure component fugacity coefficient

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

یک شکل عمومی برای معادلت حالت درجه ۳

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

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,

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

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

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,

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

Fugacity coefficient for component *i*th in mixture

4.3 Mixing Rules

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

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

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,

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

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

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

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

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

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Example 4.5.

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Solution:

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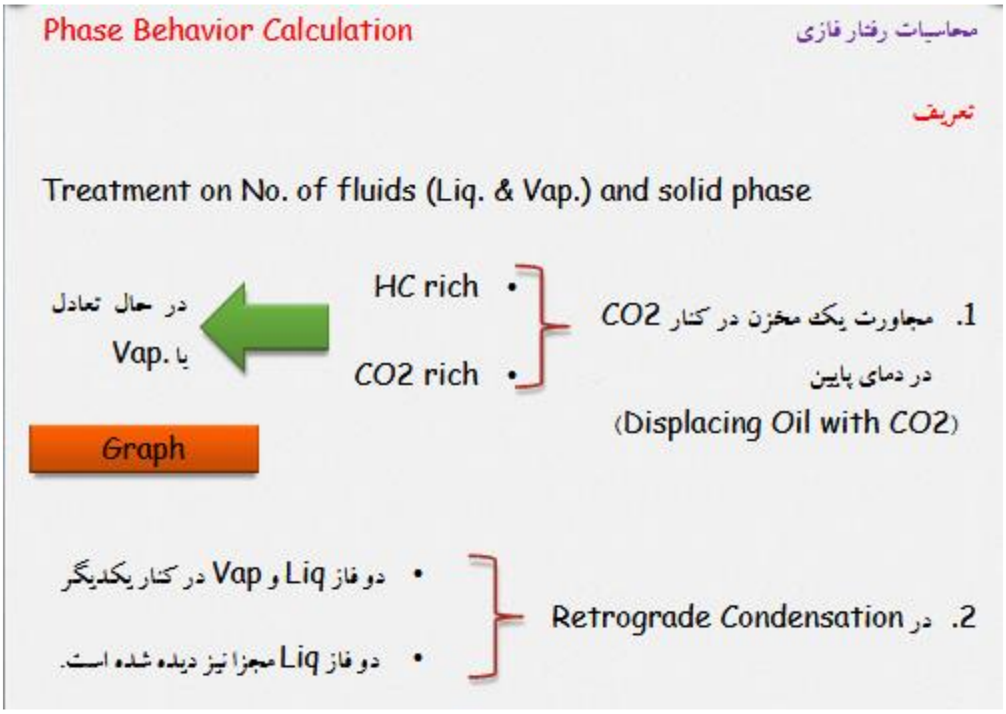
$$\ln\phi_i = \frac{1}{RT}\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} - RT/V\right]dV - \ln Z \tag{3.31}$$

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,

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

Vapor – Liquid – Solid Phases



Phase Behavior Calculation محاسبات رفتار فازی

تعریف

Treatment on No. of fluids (Liq. & Vap.) and solid phase

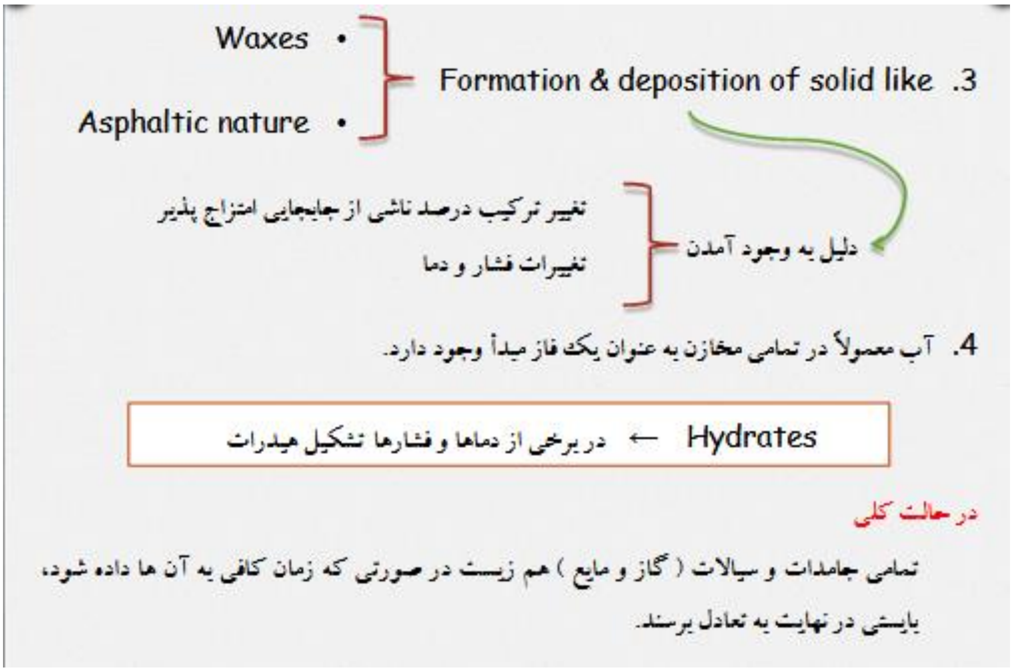
1. مجاورت یک مخزن در کنار CO2 در دمای پایین (Displacing Oil with CO2)
   - HC rich
   - CO2 rich

در حال تعادل با .Vap

Graph

2. در Retrograde Condensation
   - دو فاز Liq و Vap در کنار یکدیگر
   - دو فاز Liq مجزا نیز دیده شده است.

Chapter 4: Equations of States
Chapter 5: Phase Behavior Calculations



3. Formation & deposition of solid like
   - Waxes
   - Asphaltic nature

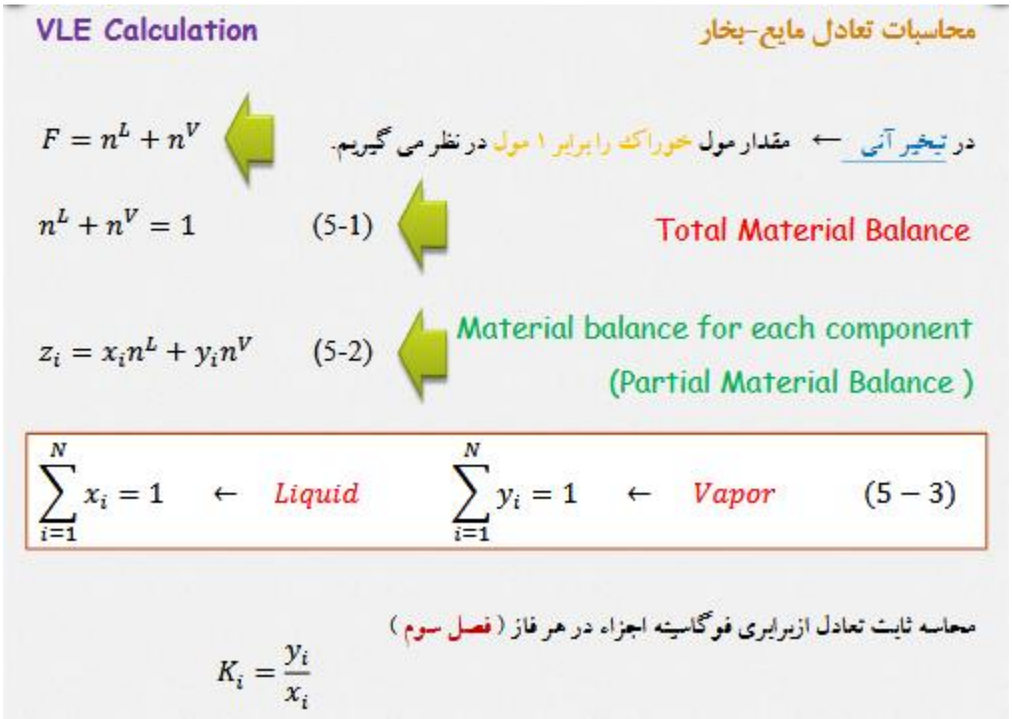
دلیل به وجود آمدن
- تغییر ترکیب درصد ناشی از جابجایی امتزاج پذیر
- تغییرات فشار و دما

4. آب معمولاً در تمامی مخازن به عنوان یک فاز مبدأ وجود دارد.

Hydrates ← در برخی از دماها و فشارها تشکیل هیدرات

در حالت کلی

تمامی جامدات و سیالات (گاز و مایع) هم زیست در صورتی که زمان کافی به آن ها داده شود، بایستی در نهایت به تعادل برسند.



VLE Calculation — محاسبات تعادل مایع-بخار

$F = n^L + n^V$ ← در تبخیر آنی ← مقدار مول خوراک را برابر ۱ مول در نظر می گیریم.

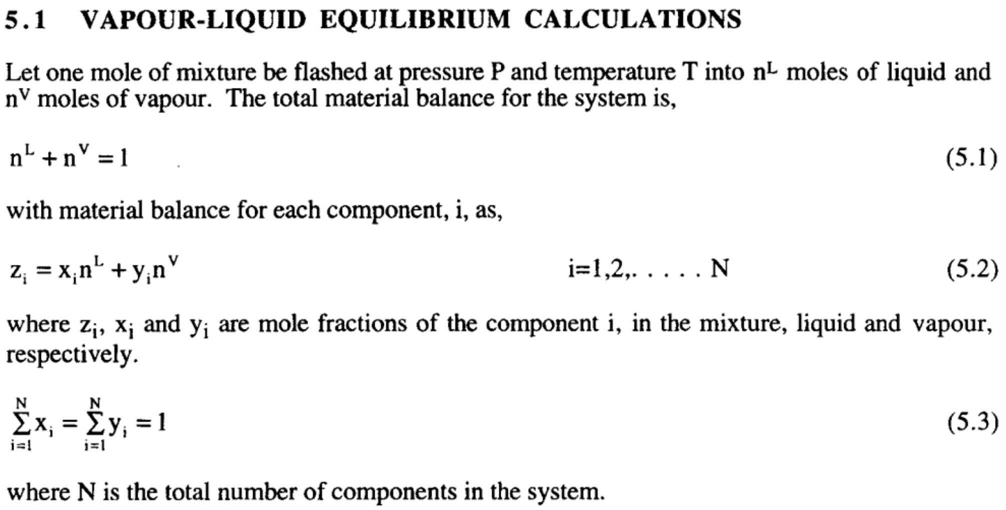
$n^L + n^V = 1$ (5-1) ← Total Material Balance

$z_i = x_i n^L + y_i n^V$ (5-2) ← Material balance for each component (Partial Material Balance)

$$\sum_{i=1}^{N} x_i = 1 \leftarrow \text{Liquid} \qquad \sum_{i=1}^{N} y_i = 1 \leftarrow \text{Vapor} \qquad (5-3)$$

محاسبه ثابت تعادل ازبرابری فوگاسیته اجزاء در هر فاز (فصل سوم)

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



5.1 VAPOUR-LIQUID EQUILIBRIUM CALCULATIONS

Let one mole of mixture be flashed at pressure P and temperature T into n^L moles of liquid and n^V moles of vapour. The total material balance for the system is,

$$n^L + n^V = 1 \qquad (5.1)$$

with material balance for each component, i, as,

$$z_i = x_i n^L + y_i n^V \qquad i=1,2,.\ .\ .\ .\ .\ N \qquad (5.2)$$

where z_i, x_i and y_i are mole fractions of the component i, in the mixture, liquid and vapour, respectively.

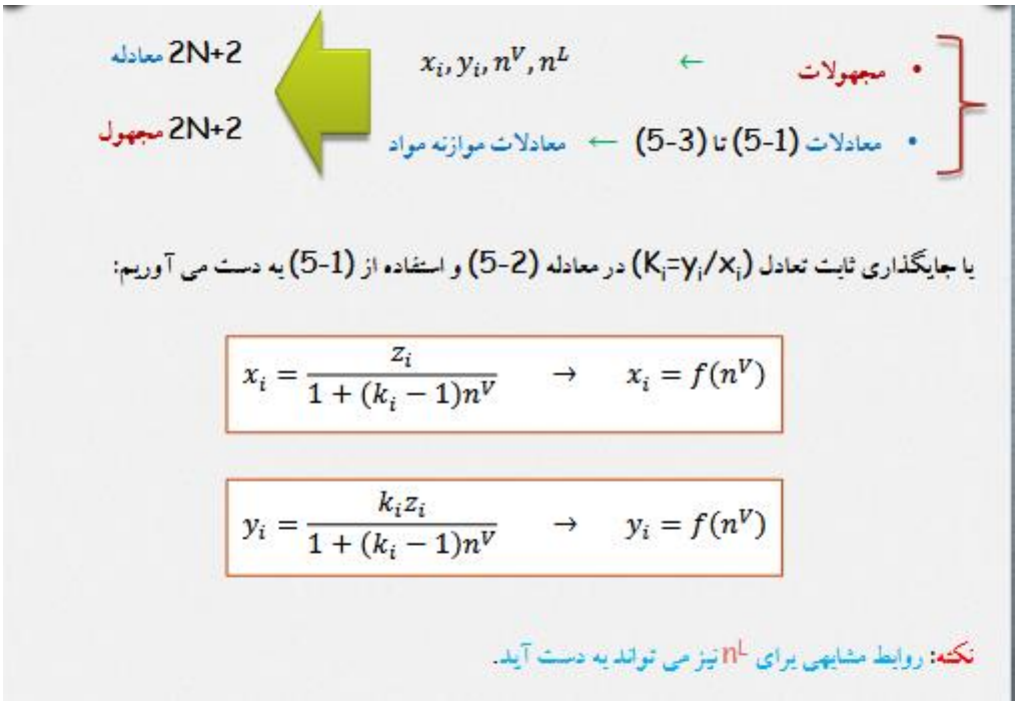
$$\sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = 1 \qquad (5.3)$$

where N is the total number of components in the system.

No. of Equation (5-2) =N

Chapter 4: Equations of States

Chapter 5: Phase Behavior Calculations



- مجهولات ← x_i, y_i, n^V, n^L
- معادلات (5-1) تا (5-3) ← معادلات موازنه مواد

2N+2 معادله

2N+2 مجهول

با جایگذاری ثابت تعادل $(K_i=y_i/x_i)$ در معادله (5-2) و استفاده از (5-1) به دست می آوریم:

$$x_i = \frac{z_i}{1+(k_i-1)n^V} \quad \rightarrow \quad x_i = f(n^V)$$

$$y_i = \frac{k_i z_i}{1+(k_i-1)n^V} \quad \rightarrow \quad y_i = f(n^V)$$

نکته: روابط مشابهی برای n^L نیز می تواند به دست آید.

At equilibrium, the fugacity of any component, i, in the vapour is equal to that in the liquid. The equality of fugacity can be expressed by the equilibrium ratio, K_i, as given by Eq.(3.43),

$$K_i = y_i / x_i \qquad i=1,2,.\;.\;.\;.\;.\;N \qquad (3.43)$$

The material balance equations, Eqs.(5.1-3), and the equilibrium requirement, Eq.(3.43) provide the required 2N+2 independent equations to determine the 2N+2 unknowns of x_i, y_i, n^L and n^V. The number of variables can be reduced, however, by combining the above equations.

Substituting the equilibrium ratio $K_i = y_i/x_i$ into Eq.(5.2), and solving for x_i and y_i using Eq.(5.1) results in,

$$x_i = \frac{z_i}{1+(K_i-1)n^V} \qquad (5.4)$$

No. of Equation (3-43) =N

EoS for for Liquid and Vapor =2

Total No. of Eqs.=2N+2

$$y_i = \frac{K_i z_i}{1+(K_i-1)n^V} \tag{5.5}$$

Similar equations can also be derived in terms of n^L instead of n^V.

For known values of K_i, any of the above two equations can be substituted in Eq.(5.3) to determine the value of n^V (or n^L). An iterative method is required to solve the resulting equation. The following equation, known as the Rachford-Rice [1] equation, is generally the preferred form, as its value monotonically decreases with increasing n^V,

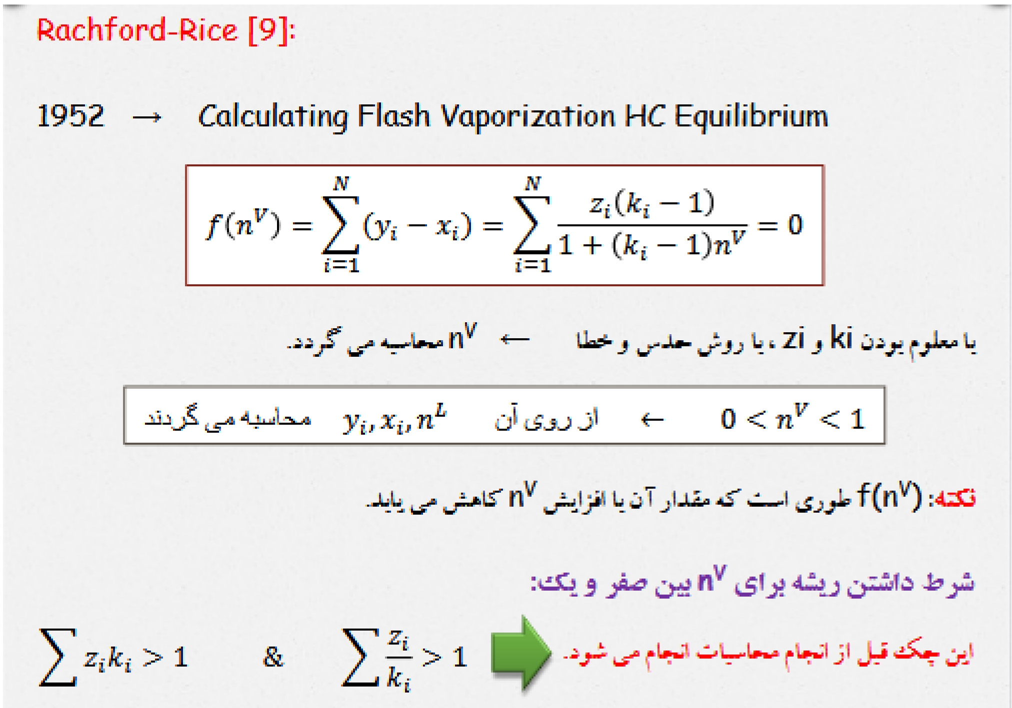
$$f(n^V) = \sum_{i=1}^{N}(y_i - x_i) = \sum_{i=1}^{N}\frac{z_i(K_i-1)}{1+(K_i-1)n^V} = 0 \tag{5.6}$$

The above equation yields a physically correct root for n^V between 0 and 1, provided that,

$$\sum_{i=1}^{N} K_i z_i > 1 \tag{5.7}$$

and

$$\sum_{i=1}^{N} z_i / K_i > 1 \tag{5.8}$$



Rachford-Rice [9]:

1952 → Calculating Flash Vaporization HC Equilibrium

$$\boxed{f(n^V) = \sum_{i=1}^{N}(y_i - x_i) = \sum_{i=1}^{N}\frac{z_i(k_i-1)}{1+(k_i-1)n^V} = 0}$$

با معلوم بودن ki و zi ، با روش حدس و خطا ← n^V محاسبه می گردد.

$0 < n^V < 1$ ← از روی آن y_i, x_i, n^L محاسبه می گردند

نکته: $f(n^V)$ طوری است که مقدار آن با افزایش n^V کاهش می یابد.

شرط داشتن ریشه برای n^V بین صفر و یک:

این چک قبل از انجام محاسبات انجام می شود.

$$\sum z_i k_i > 1 \qquad \& \qquad \sum \frac{z_i}{k_i} > 1$$

The mixture is at its bubble point when n^V approaches zero. Hence Eq.(5.6) reduces to,

$$\sum_{i=1}^{N} z_i K_i = 1 \tag{5.9}$$

and

$$y_i = K_i x_i = K_i z_i \tag{5.10}$$

At any temperature the bubble point pressure can be determined as the pressure at which K-values satisfy Eq.(5.9). The bubble point is most sensitive to the mixture light components, which exhibit large K values.

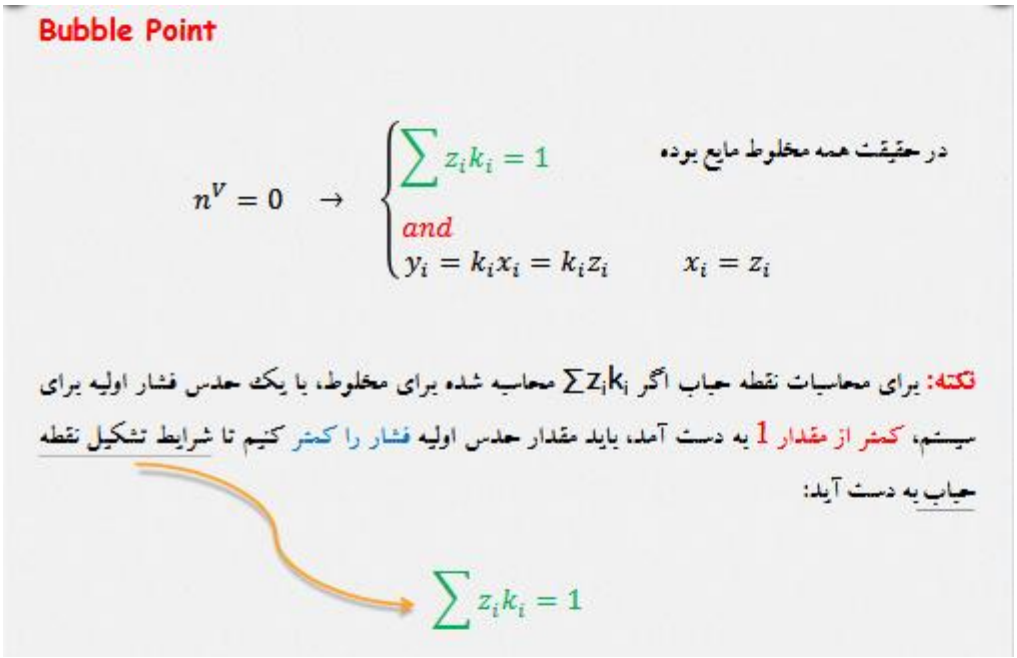
At the dew point, n^V approaches 1. Hence Eq.(5.6) reduces to,

$$\sum_{i=1}^{N} z_i / K_i = 1 \tag{5.11}$$

and

$$x_i = y_i / K_i = z_i / K_i \tag{5.12}$$

The dew point pressure is that at which K-values satisfy Eq.(5.11). The dew point is most sensitive to the mixture heavy components, which exhibit small K-values.



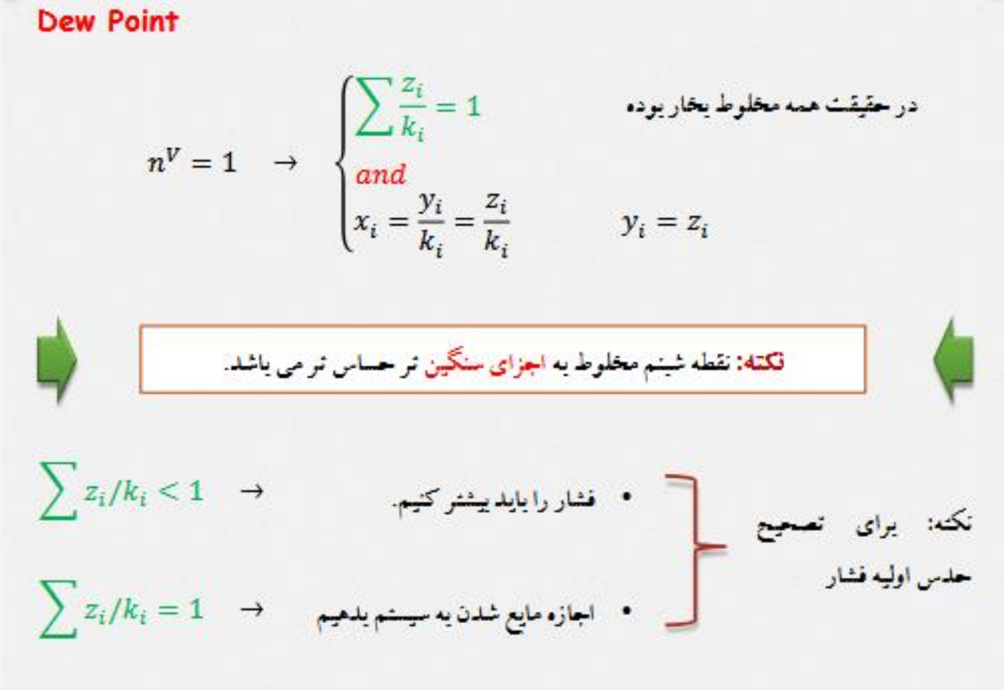
Bubble Point

$$n^V = 0 \quad \rightarrow \quad \begin{cases} \sum z_i k_i = 1 \\ and \\ y_i = k_i x_i = k_i z_i \end{cases} \qquad x_i = z_i$$

در حقیقت همه مخلوط مایع بوده

نکته: برای محاسبات نقطه حباب اگر $\sum z_i k_i$ محاسبه شده برای مخلوط، با یک حدس فشار اولیه برای سیستم، کمتر از مقدار 1 به دست آمد، باید مقدار حدس اولیه فشار را کمتر کنیم تا شرایط تشکیل نقطه حباب به دست آید:

$$\sum z_i k_i = 1$$



Dew Point

$$n^V = 1 \rightarrow \begin{cases} \sum \frac{z_i}{k_i} = 1 \\ and \\ x_i = \frac{y_i}{k_i} = \frac{z_i}{k_i} \end{cases}$$

در حقیقت همه مخلوط بخار بوده

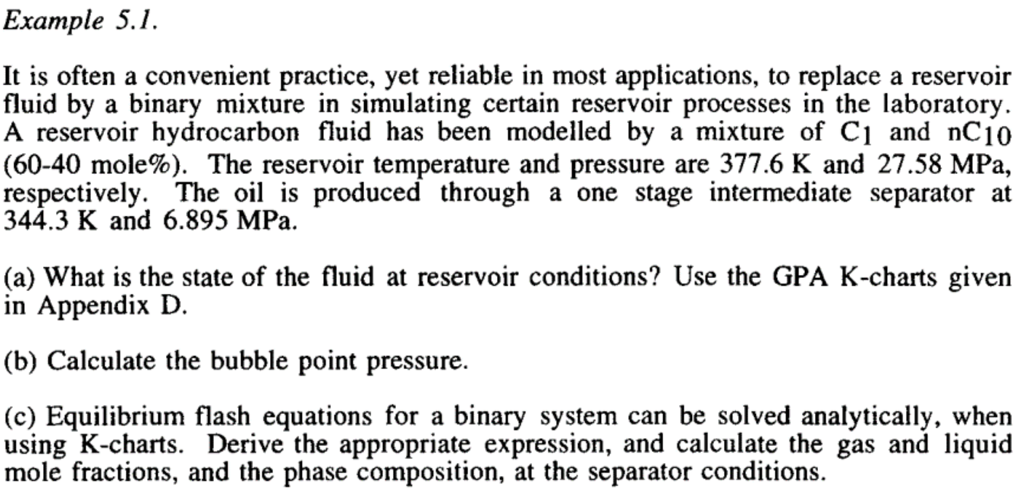
$y_i = z_i$

نکته: نقطه شبنم مخلوط به **اجزای سنگین** تر حساس تر می باشد.

نکته: برای تصحیح حدس اولیه فشار

$\sum z_i/k_i < 1 \rightarrow$ • فشار را باید بیشتر کنیم.

$\sum z_i/k_i = 1 \rightarrow$ • اجازه مایع شدن به سیستم بدهیم



Example 5.1.

It is often a convenient practice, yet reliable in most applications, to replace a reservoir fluid by a binary mixture in simulating certain reservoir processes in the laboratory. A reservoir hydrocarbon fluid has been modelled by a mixture of C_1 and nC_{10} (60-40 mole%). The reservoir temperature and pressure are 377.6 K and 27.58 MPa, respectively. The oil is produced through a one stage intermediate separator at 344.3 K and 6.895 MPa.

(a) What is the state of the fluid at reservoir conditions? Use the GPA K-charts given in Appendix D.

(b) Calculate the bubble point pressure.

(c) Equilibrium flash equations for a binary system can be solved analytically, when using K-charts. Derive the appropriate expression, and calculate the gas and liquid mole fractions, and the phase composition, at the separator conditions.

Solution:

Component 1: C_1 Component 2: nC_{10}

(a)
The convergence pressure at 377.6 K (220 °F) is estimated from Figure D.1 (Appendix D): P_k=5000 psia (34.47 MPa).

The equilibrium ratios of C_1 and nC_{10} are then read from Figures D.2 and D.13 (Appendix D), respectively, at 377.6 K and 27.58 MPa (4000 psia):

$K_1=1.4$ $K_2=0.13$

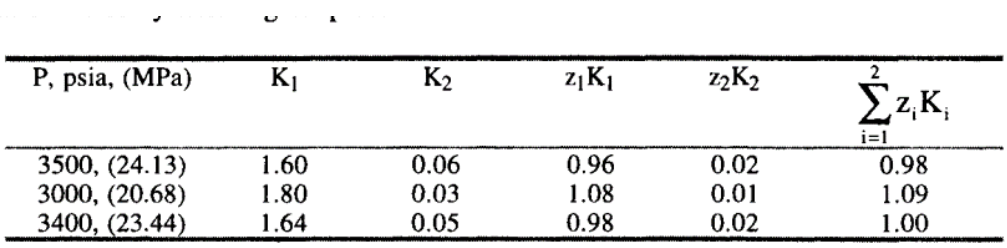
Checking $\sum_{i=1}^{N} z_i K_i$,

$$\sum_{i=1}^{2} z_i K_i = 0.6\times1.4+0.4\times0.13=0.89<1.$$

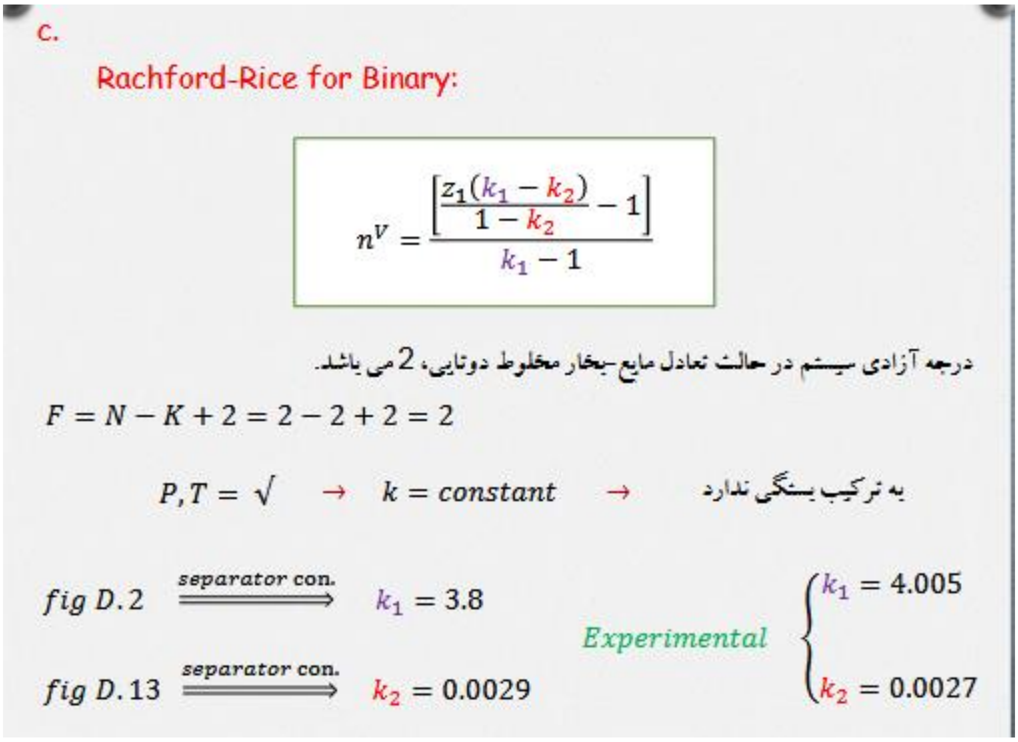
Hence, the fluid is a compressed (undersaturated) liquid.

For an undersaturated vapour, $\sum_{i=1}^{N} z_i / K_i < 1$, whereas for a two phase system both Eq.(5.7) and Eq.(5.8) should be satisfied.

(b)
At the bubble point Eq.(5.9) must be satisfied. The K-values are read from the charts at 377.6 K by iterating on pressure:



P, psia, (MPa)	K_1	K_2	z_1K_1	z_2K_2	$\sum_{i=1}^{2} z_iK_i$
3500, (24.13)	1.60	0.06	0.96	0.02	0.98
3000, (20.68)	1.80	0.03	1.08	0.01	1.09
3400, (23.44)	1.64	0.05	0.98	0.02	1.00



c.

Rachford-Rice for Binary:

$$n^V = \frac{\left[\frac{z_1(k_1-k_2)}{1-k_2} - 1\right]}{k_1 - 1}$$

درجه آزادی سیستم در حالت تعادل مایع-بخار مخلوط دوتایی، 2 می باشد.

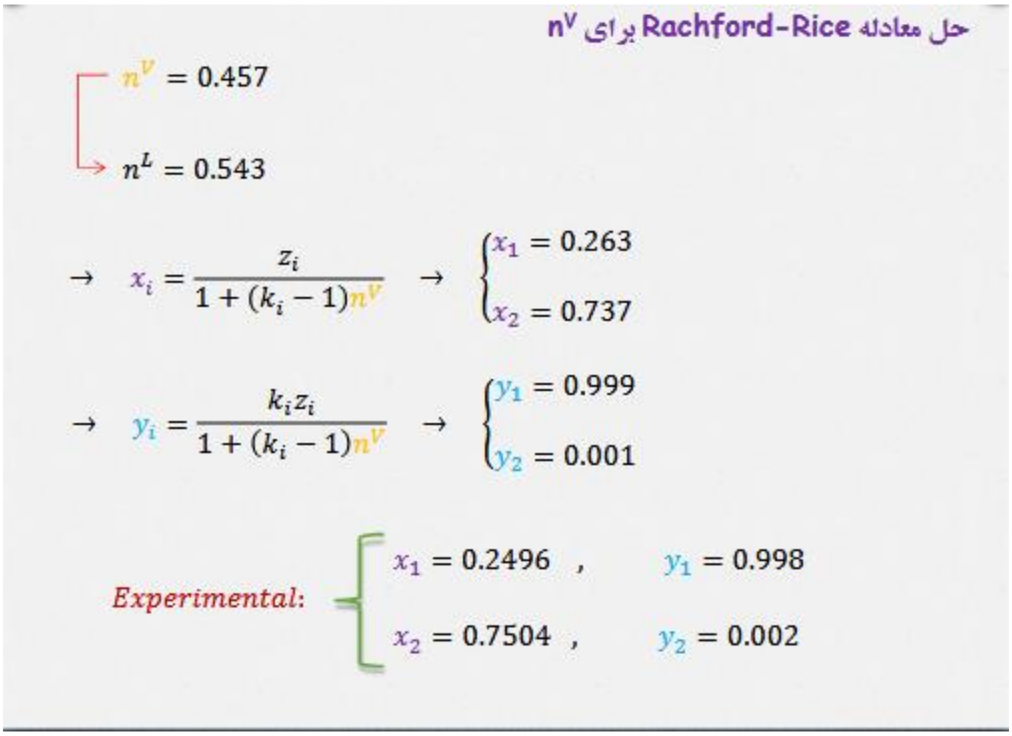
$$F = N - K + 2 = 2 - 2 + 2 = 2$$

$P,T = \surd \rightarrow k = constant \rightarrow$ به ترکیب بستگی ندارد

$fig\ D.2 \xrightarrow{separator\ con.} k_1 = 3.8$

$fig\ D.13 \xrightarrow{separator\ con.} k_2 = 0.0029$

$Experimental \begin{cases} k_1 = 4.005 \\ k_2 = 0.0027 \end{cases}$



حل معادله Rachford-Rice برای n^V

$$n^V = 0.457 \rightarrow n^L = 0.543$$

$$\rightarrow \quad x_i = \frac{z_i}{1 + (k_i - 1)n^V} \quad \rightarrow \quad \begin{cases} x_1 = 0.263 \\ x_2 = 0.737 \end{cases}$$

$$\rightarrow \quad y_i = \frac{k_i z_i}{1 + (k_i - 1)n^V} \quad \rightarrow \quad \begin{cases} y_1 = 0.999 \\ y_2 = 0.001 \end{cases}$$

$$Experimental: \begin{cases} x_1 = 0.2496 \;, & y_1 = 0.998 \\ x_2 = 0.7504 \;, & y_2 = 0.002 \end{cases}$$

The experimental value is 23.50 MPa (3408 psia) [2]. Note that $\sum_{i=1}^{N} z_i K_i$ strongly depends on the K-value of methane, due to its high volatility and concentration. A reasonable initial guess for a reservoir oil in most cases could be the pressure at which $(Kz)_{C_1}=1$.

(c)
For a binary system Eq.(5.6) reduces to:

$$n^V = [z_1(K_1 - K_2)/(1 - K_2) - 1]/(K_1 - 1) \qquad \text{(E5.1)}$$

The degrees of freedom for a binary vapour-liquid system at equilibrium conditions are only two, according to the Gibbs phase rule, Eq.(1.2). Hence at a given temperature and pressure, the K-values are constant and independent of the overall composition.

Using Figures D.2 and D.13, at 344.3 K and 6.895 MPa (1000 psia),

$K_1=3.8$, $K_2=0.0029$, (experimental values $K_1=4.005$, and $K_2=0.0027$ [49]).

Eq.(E5.1) results in, vapour mole fraction: $n^V=0.457$, liquid mole fraction: $n^L=0.543$.

Eqs.(5.4-5) give the composition of equilibrated phases as follows,

$x_1=0.263$, $x_2=0.737$, $y_1=0.999$, $y_2=0.001$

($x_1=0.2496$, $x_2=0.7504$, $y_1=0.9980$, $y_2=0.0020$, experimental values).

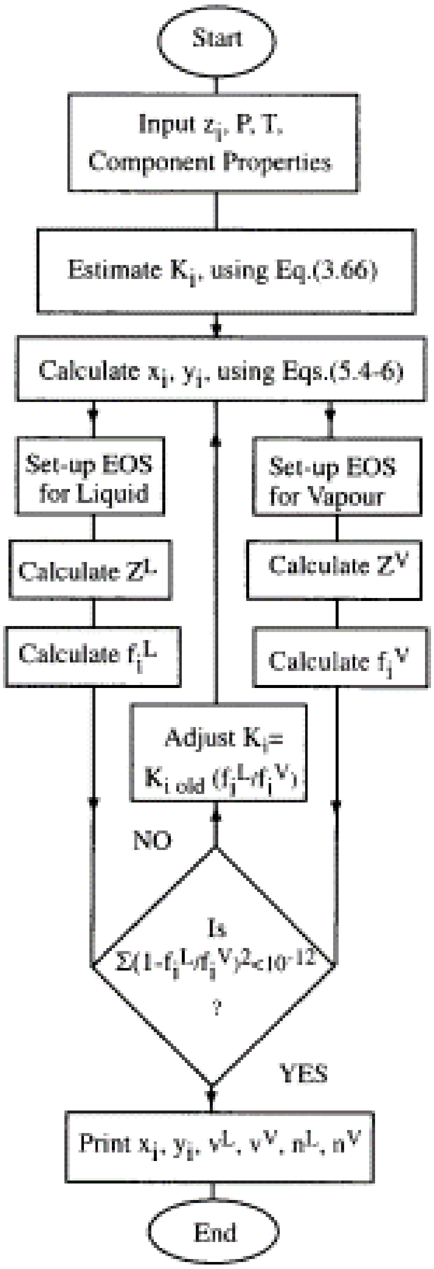
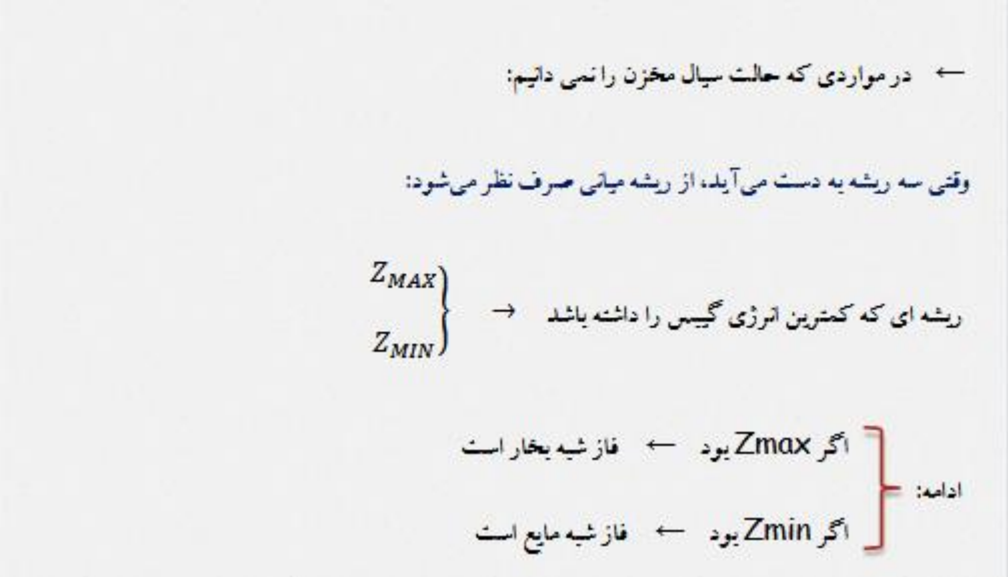


Figure 5.1. Flow chart of flash calculations using equation of state.

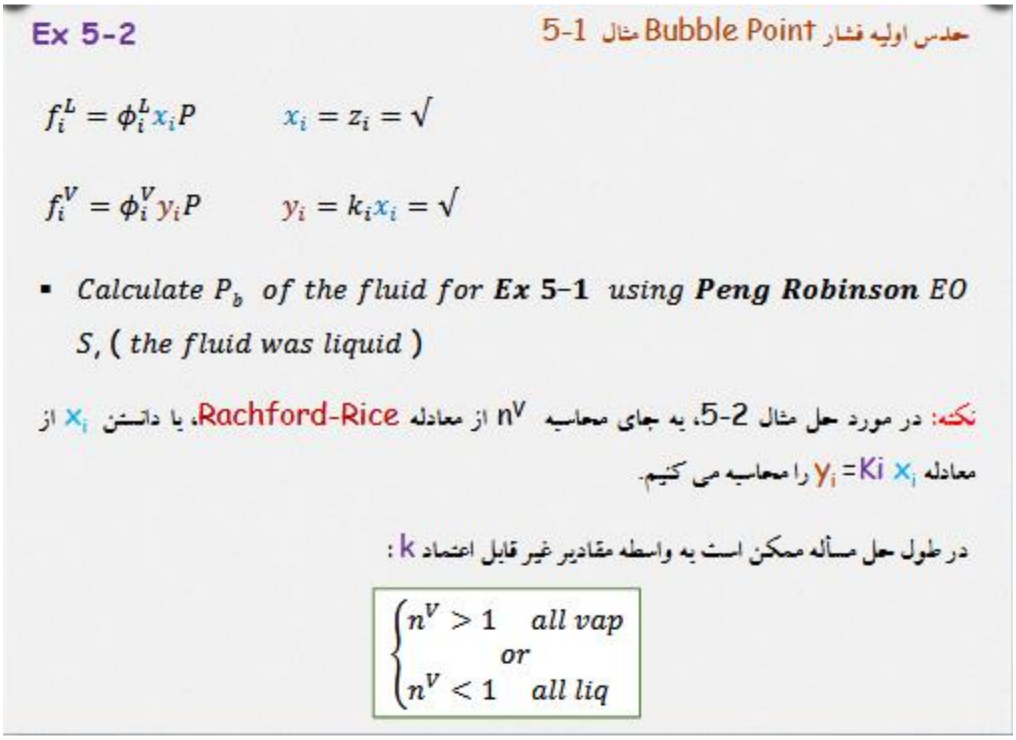


← در مواردی که حالت سیال مخزن را نمی دانیم:

وقتی سه ریشه به دست می‌آید، از ریشه میانی صرف نظر می‌شود:

$$\left.\begin{matrix} Z_{MAX} \\ \\ Z_{MIN} \end{matrix}\right\} \rightarrow$$ ریشه ای که کمترین انرژی گیبس را داشته باشد

ادامه:
اگر Zmax بود ← فاز شبه بخار است
اگر Zmin بود ← فاز شبه مایع است



Ex 5-2

حدس اولیه فشار Bubble Point مثال 5-1

$$f_i^L = \phi_i^L x_i P \qquad x_i = z_i = \surd$$

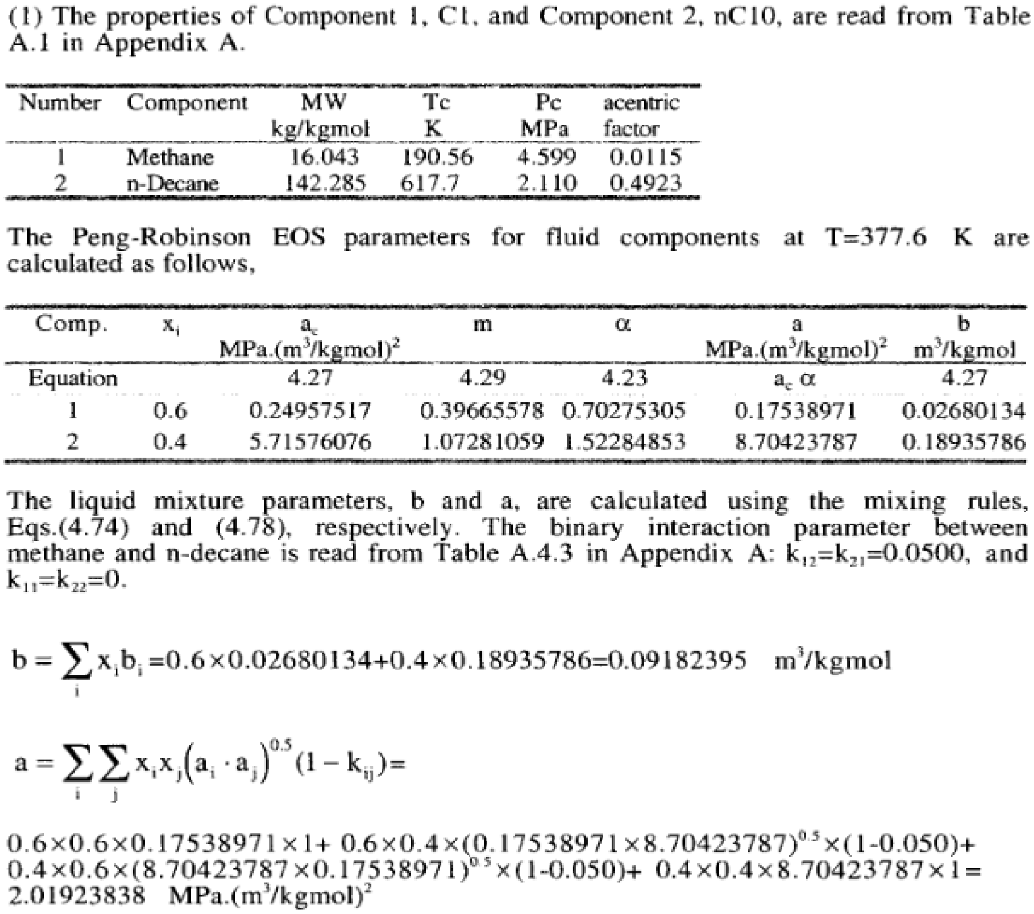
$$f_i^V = \phi_i^V y_i P \qquad y_i = k_i x_i = \surd$$

- *Calculate P_b of the fluid for **Ex 5-1** using **Peng Robinson** EOS, (the fluid was liquid)*

نکته: در مورد حل مثال 2-5، به جای محاسبه n^V از معادله Rachford-Rice، با داشتن x_i از معادله y_i =Ki x_i را محاسبه می کنیم.

در طول حل مسأله ممکن است به واسطه مقادیر غیر قابل اعتماد k :

$$\boxed{\begin{cases} n^V > 1 \quad all\ vap \\ \qquad or \\ n^V < 1 \quad all\ liq \end{cases}}$$



(1) The properties of Component 1, C1, and Component 2, nC10, are read from Table A.1 in Appendix A.

Number	Component	MW kg/kgmol	Tc K	Pc MPa	acentric factor
1	Methane	16.043	190.56	4.599	0.0115
2	n-Decane	142.285	617.7	2.110	0.4923

The Peng-Robinson EOS parameters for fluid components at T=377.6 K are calculated as follows,

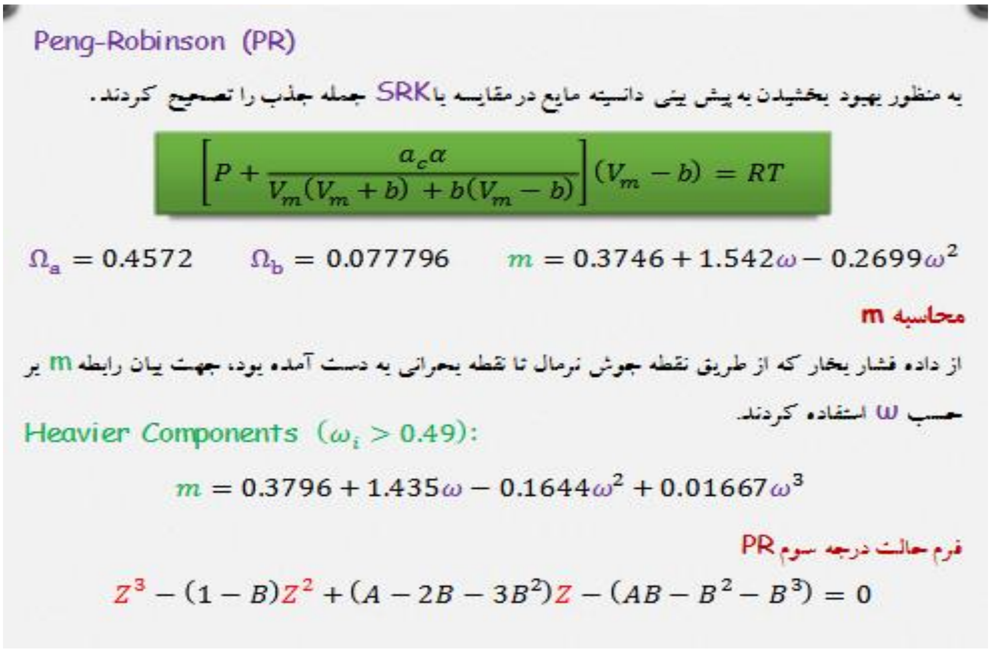
Comp.	x_i	a_c MPa.(m^3/kgmol)^2	m	α	a MPa.(m^3/kgmol)^2	b m^3/kgmol
Equation		4.27	4.29	4.23	$a_c\ \alpha$	4.27
1	0.6	0.24957517	0.39665578	0.70275305	0.17538971	0.02680134
2	0.4	5.71576076	1.07281059	1.52284853	8.70423787	0.18935786

The liquid mixture parameters, b and a, are calculated using the mixing rules, Eqs.(4.74) and (4.78), respectively. The binary interaction parameter between methane and n-decane is read from Table A.4.3 in Appendix A: $k_{12}=k_{21}=0.0500$, and $k_{11}=k_{22}=0$.

$$b=\sum_i x_i b_i = 0.6\times 0.02680134 + 0.4\times 0.18935786 = 0.09182395 \quad \text{m}^3/\text{kgmol}$$

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

$0.6\times0.6\times0.17538971\times1 + 0.6\times0.4\times(0.17538971\times8.70423787)^{0.5}\times(1-0.050) + 0.4\times0.6\times(8.70423787\times0.17538971)^{0.5}\times(1-0.050) + 0.4\times0.4\times8.70423787\times1 = 2.01923838$ MPa.(m^3/kgmol)^2



Peng-Robinson (PR)

به منظور بهبود بخشیدن به پیش بینی دانسیته مایع درمقایسه با SRK 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

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

Pure component fugacity coefficient

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

یک شکل عمومی برای معادلت حالت درجه ۳

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

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

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

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

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

(2) A bubble point pressure of 27.58 MPa (4000 psia) is assumed as the initial guess. The final result should not depend on the initially selected value.

(3) The Wilson equation, Eq.(3.66), is used to estimate the equilibrium ratios at 27.58 MPa, and 377.6 K: $K_1=2.457$, and $K_2=0.0004684$.

(4) The vapour composition is calculated using Eq.(3.43), $y_i=K_ix_i$, resulting in $y_1=1.474$, and $y_2=0.0001874$. Note that Σy_i is not equal to 1 which only occurs at the correct bubble point pressure.

(5) The Peng-Robinson EOS, Eq.(4.27), is set-up for both phases. The dimensionless values of EOS parameters are calculated from Eqs.(4.7-8).

Liquid Phase:

$A=5.6501$, and $B=0.8067$, which results in the following cubic equation for the liquid compressibility factor, Eq.(4.30):

$$Z^3-0.19332Z^2-2.08487Z-3.38239=0$$

The above equation has only one real root (Appendix C), $Z^L=1.0985$

Vapour Phase:

A procedure similar to that of liquid results in $A=1.0661$ and $B=0.3468$ for the vapour phase, with only one real root for its compressibility factor cubic equation,

$Z^V=0.89802$.

(6) The fugacity of each component is calculated in both phases, using Eq.(E4.5),

$$\ln\phi_i=\frac{b_i}{b}(Z-1)-\ln(Z-B)-\frac{A}{B(-2\sqrt{2})}\left(\frac{2\sum_{j=1}^{N}x_ja_{ij}}{a}-\frac{b_i}{b}\right)\ln\left(\frac{Z+(1-\sqrt{2})B}{Z+(1+\sqrt{2})B}\right) \qquad \text{(E5.2)}$$

where $a_{ij}=(a_ia_j)^{0.5}(1-k_{ij})$.

The calculated values of fugacity coefficients, fugacities, and equilibrium ratios are as follows:

Comp.	P, MPa	x_i	y_i	ϕ_i^L	ϕ_i^V	f_i^L, MPa	f_i^V, MPa	K_i
Equation				E5.2	E5.2	$\phi_i^L x_i P$	$\phi_i^V y_i P$	ϕ_i^L/ϕ_i^V
1	27.58	0.60000	1.474	1.3643	0.9157	22.56	37.22	1.4899
2	27.58	0.40000	0.0001874	0.003345	0.02295	0.03690	0.0001186	0.14575

Clearly the fugacity of components are not equal in the two phases at the above selected pressure. The resulting error value of $\sum_{1}^{N}(1-f_i^L/f_i^V)^2=10^5$ is far remote from the objective value of $<10^{-12}$.

(8) Now with the new pressure and equilibrium ratios, steps (4) to (7) are repeated. The results of a few initial, intermediate and final iterations are given in the following tables.

Iter. No.	Pres., MPa	y_1	y_2	Z^L	Z^V
2	26.24	0.8932	0.05829	1.0513	0.91638
3	25.59	0.9329	0.04261	1.0285	0.92134
14	24.31	0.9774	0.02225	0.9828	0.9289
29	24.294	0.97777	0.022228	0.98213	0.92877

Iter. No.	f_1^L MPa	f_1^V MPa	f_2^L MPa	f_2^V MPa	K_1	K_2	Error
2	21.86	20.92	0.03383	0.04628	1.5548	0.10653	7.43E-02
3	21.52	21.13	0.03246	0.04182	1.5841	0.082677	5.05E-02
14	20.87	20.87	0.02989	0.2991	1.6292	0.055615	4.97E-07
29	20.861	20.861	0.029834	0.029834	1.6296	0.055569	3.58E-12

The change of Gibbs energy can be calculated using Eqs.(3.14) and (3.27), with fugacities determined by EOS. For example, using the Peng-Robinson or Soave-Redlich-Kwong EOS with component fugacity coefficients as,

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

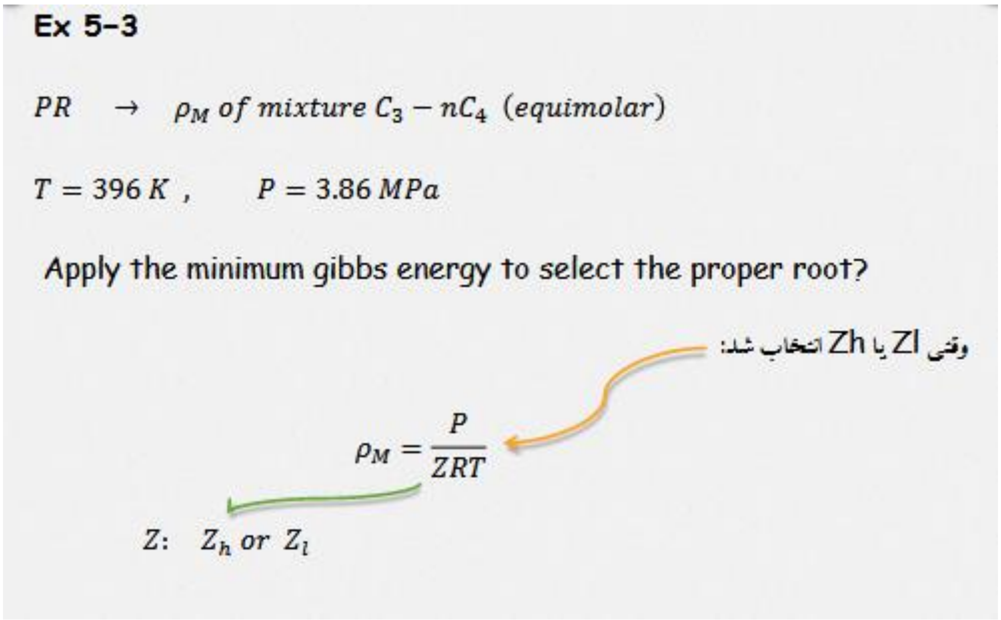
or using the total fugacity coefficient given by Eq.(4.18), the system molar Gibbs energy difference at the two roots Z_h and Z_l is determined as,

$$(G_h - G_l)/RT = (Z_h - Z_l) + \ln\left(\frac{Z_l - B}{Z_h - B}\right) - \frac{A}{B(\delta_2-\delta_1)}\ln\left[\left(\frac{Z_l+\delta_1 B}{Z_l+\delta_2 B}\right)\left(\frac{Z_h+\delta_2 B}{Z_h+\delta_1 B}\right)\right] \qquad (5.13)$$

If the above is positive, Z_l is selected, otherwise, Z_h is the correct root.

Example 5.3.

The Peng-Robinson EOS is used to predict the density of a single phase equimolar mixture of C_3 and nC_4 at 396 K and 3.86 MPa. Apply the minimum Gibbs energy concept to select the proper root.



Ex 5-3

$PR \rightarrow \rho_M$ of mixture $C_3 - nC_4$ (equimolar)

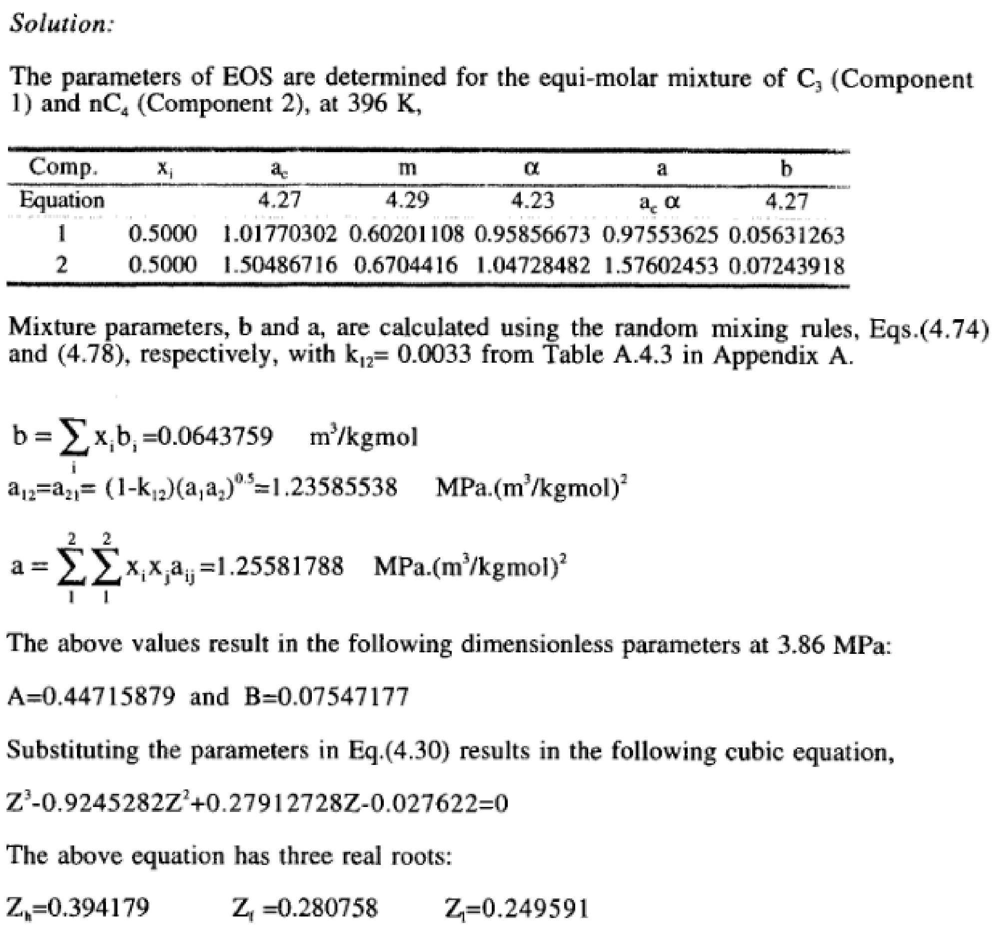
$T = 396\,K$, $P = 3.86\,MPa$

Apply the minimum gibbs energy to select the proper root?

وقتی Zl یا Zh انتخاب شد:

$$\rho_M = \frac{P}{ZRT}$$

Z: Z_h or Z_l



Solution:

The parameters of EOS are determined for the equi-molar mixture of C_3 (Component 1) and nC_4 (Component 2), at 396 K,

Comp.	x_i	a_c	m	α	a	b
Equation		4.27	4.29	4.23	$a_c\,\alpha$	4.27
1	0.5000	1.01770302	0.60201108	0.95856673	0.97553625	0.05631263
2	0.5000	1.50486716	0.6704416	1.04728482	1.57602453	0.07243918

Mixture parameters, b and a, are calculated using the random mixing rules, Eqs.(4.74) and (4.78), respectively, with k_{12}= 0.0033 from Table A.4.3 in Appendix A.

$$b = \sum_i x_i b_i = 0.0643759 \quad m^3/kgmol$$

$$a_{12}=a_{21}= (1-k_{12})(a_1 a_2)^{0.5}=1.23585538 \quad MPa.(m^3/kgmol)^2$$

$$a = \sum_1^2 \sum_1^2 x_i x_j a_{ij} = 1.25581788 \quad MPa.(m^3/kgmol)^2$$

The above values result in the following dimensionless parameters at 3.86 MPa:

$A=0.44715879$ and $B=0.07547177$

Substituting the parameters in Eq.(4.30) results in the following cubic equation,

$$Z^3-0.9245282Z^2+0.27912728Z-0.027622=0$$

The above equation has three real roots:

$Z_h=0.394179$ $\quad Z_i=0.280758$ $\quad Z_l=0.249591$

Rejecting the intermediate root, Z_r, and substituting $\delta_1=1+\sqrt{2}$, and $\delta_2=1-\sqrt{2}$ in Eq.(5.13) to obtain the expression for the Peng-Robinson EOS, we obtain,

$$(G_h - G_l)/RT = -0.00046$$

Hence, Z_h represents the stable phase with a lower energy level, and the fluid is vapour-like.

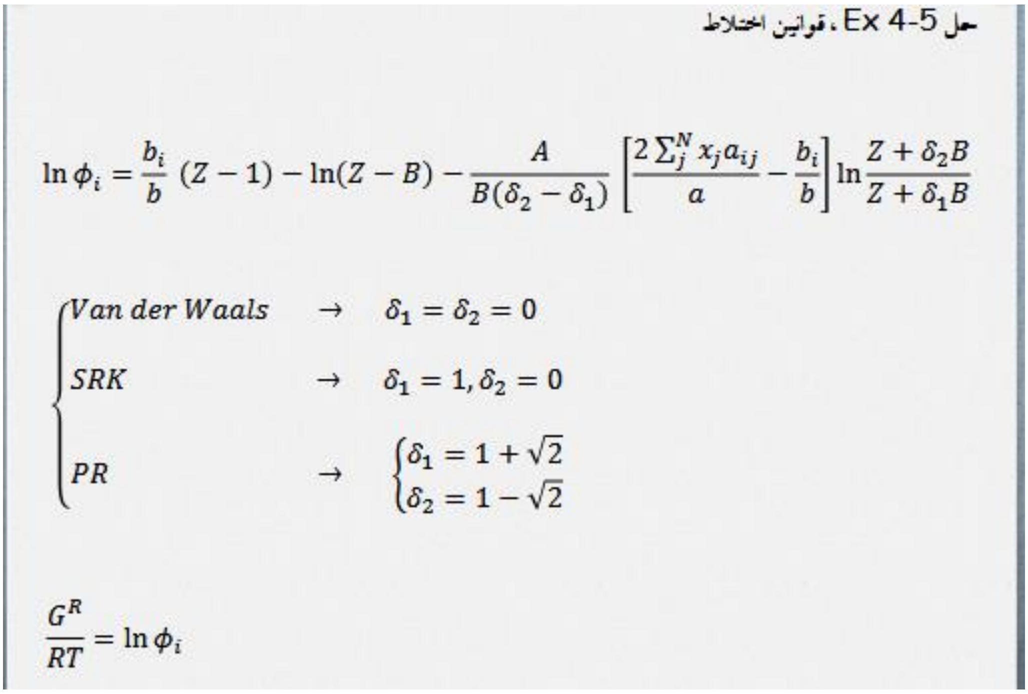
The density is calculated as,

$$\rho_M = P/(ZRT) = 3.86/(0.394179\times 0.0083144\times 396) = 2.9742 \quad \text{kgmol/m}^3$$

$$M = \sum x_i M_i = 51.109 \quad \text{kgmol/mol}$$

$$\rho = \rho_M M = 152.01 \quad \text{kg/m}^3$$

When at a selected temperature-pressure, EOS gives one real root, that root will be expected to be the correct root for the phase under consideration. Phase behaviour calculations using EOS is an iterative process as compositions of all or some of the phases, hence the parameters of EOS, are not known in advance. The initially estimated composition for a phase may provide a wrong single root, as shown schematically in Figure 5.2.

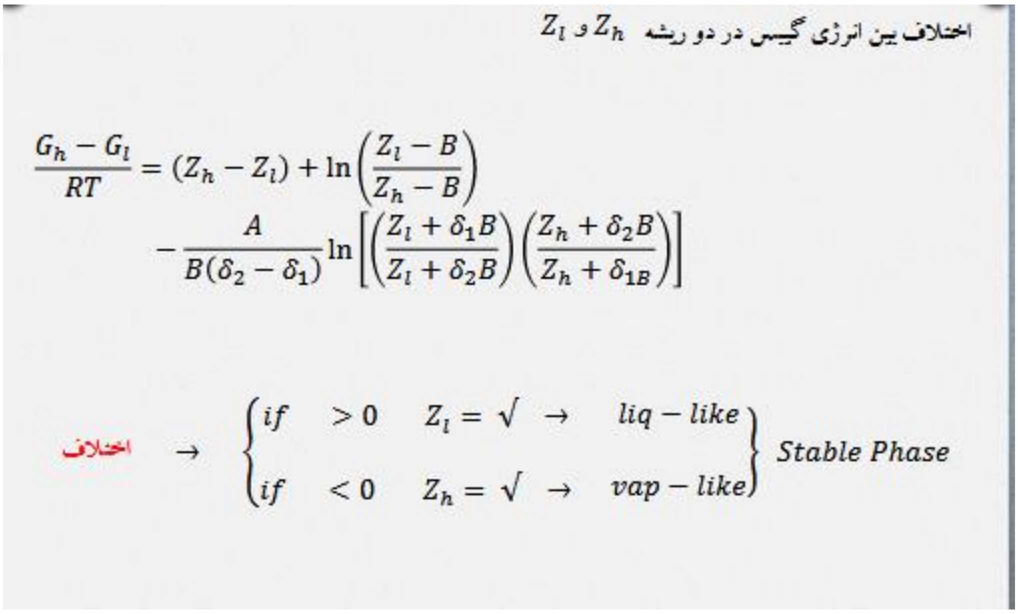


حل Ex 4-5 ، قوانین اختلاط

$$\ln\phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{B(\delta_2-\delta_1)}\left[\frac{2\sum_j^N x_j a_{ij}}{a} - \frac{b_i}{b}\right]\ln\frac{Z+\delta_2 B}{Z+\delta_1 B}$$

$$\begin{cases} Van\ der\ Waals & \rightarrow \quad \delta_1=\delta_2=0 \\ SRK & \rightarrow \quad \delta_1=1, \delta_2=0 \\ PR & \rightarrow \quad \begin{cases}\delta_1 = 1+\sqrt{2} \\ \delta_2 = 1-\sqrt{2}\end{cases} \end{cases}$$

$$\frac{G^R}{RT} = \ln\phi_i$$



اختلاف بین انرژی گیبس در دو ریشه Z_h و Z_l

$$\frac{G_h-G_l}{RT} = (Z_h-Z_l) + \ln\left(\frac{Z_l-B}{Z_h-B}\right) - \frac{A}{B(\delta_2-\delta_1)}\ln\left[\left(\frac{Z_l+\delta_1 B}{Z_l+\delta_2 B}\right)\left(\frac{Z_h+\delta_2 B}{Z_h+\delta_{1B}}\right)\right]$$

اختلاف $\rightarrow \left.\begin{cases} if \quad >0 \quad Z_l = \sqrt{} \quad \rightarrow \quad liq-like \\ if \quad <0 \quad Z_h = \sqrt{} \quad \rightarrow \quad vap-like \end{cases}\right\} Stable\ Phase$

Stability Limit

A main application of determining the intrinsic stability limit is in determination of the critical point by an equation of state. It was noted in Figure 5.8, that the binodal curve and the phase envelope meet at the critical point. This feature has been used successfully to determine the critical point of multi component systems, as both the binodal curve and the phase envelope can be expressed by energy terms, similar to those in Eqs.(3.8), and (5.41), and rigorously calculated using thermodynamic relations.

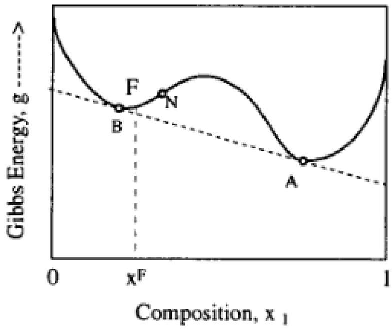


Figure 5.9. Intrinsic stability limit of a binary mixture at constant pressure and temperature.

Example 5.6.

Prove that the mechanical stability limit for a pure compound, as described in Figure 5.8, can be derived by the general energy concept. Find the stability limit of normal hexane at 473.0 K, using the Soave-Redlich-Kwong EOS (SRK).

Solution:

Describing the stability limit criterion, Eq.(5.41), in terms of the Helmholtz energy, Eq.(3.12), with variables of temperature and volume, we obtain,

$$d^2A=0$$

where,

$$dA = -SdT - PdV + \sum_i \mu_i dn_i$$

For a pure compound at constant temperature the above reduces to,

$$dA=-PdV$$

Hence,

$$(\partial^2 A/\partial V^2)_T = -\frac{1}{n}(\partial P/\partial v)_T = 0$$

That is, the stability limits for the vapour and liquid phases of a pure compound lie at the maximum and minimum pressure values, respectively, on the isotherm as described by EOS.

Calculating the derivative of pressure with respect to volume at constant temperature, using SRK, we obtain,

$$v^4 + (2b - 2a/RT)v^3 + (b^2 + 3ab/RT)v^2 - ab^3/RT = 0$$

The EOS parameters for normal hexane are calculated at 473.0 K as follows:

Tc K	Pc MPa	ω	a_c MPa.(m^3/kgmol)^2	m	α	a MPa.(m^3/kgmol)^2	b m^3/kgmol
Equation			4.22	4.25	4.23	a_c α	4.22
507.6	3.025	0.2659	2.517012	0.938436	1.066155	2.683527	0.120877

Substituting the values of a and b in the above equation results in,

$$v^4-1.1229661v^3+0.26205757v^2-0.00120518=0$$

with the roots as:

v_1=-0.06014 m^3/kgmol
v_2= 0.08275 m^3/kgmol
v_3= 0.30412 m^3/kgmol
v_4= 0.79623 m^3/kgmol

The first two roots are not acceptable, i.e., one negative and the other smaller than b=0.120877 m^3/kgmol, whereas the third and fourth roots represent the volume limits for liquid and vapour phases, respectively. The associated pressures at the stability limits can simply be determined from SRK by substituting the values of volume and temperature,

P^L=0.6995 MPa P^V=2.148 MPa

Compositional grading

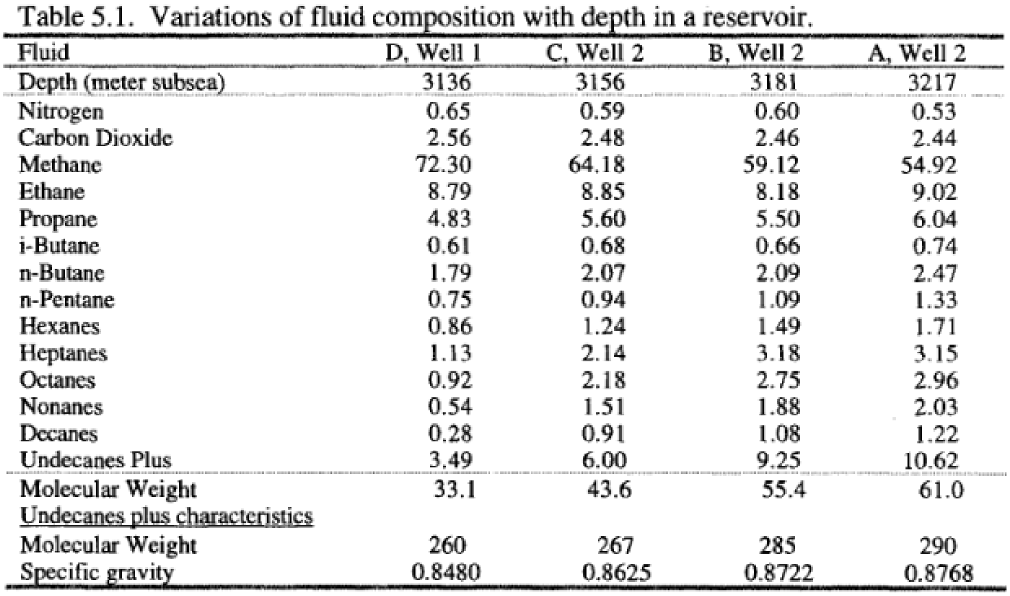


Table 5.1. Variations of fluid composition with depth in a reservoir.

Fluid	D, Well 1	C, Well 2	B, Well 2	A, Well 2
Depth (meter subsea)	3136	3156	3181	3217
Nitrogen	0.65	0.59	0.60	0.53
Carbon Dioxide	2.56	2.48	2.46	2.44
Methane	72.30	64.18	59.12	54.92
Ethane	8.79	8.85	8.18	9.02
Propane	4.83	5.60	5.50	6.04
i-Butane	0.61	0.68	0.66	0.74
n-Butane	1.79	2.07	2.09	2.47
n-Pentane	0.75	0.94	1.09	1.33
Hexanes	0.86	1.24	1.49	1.71
Heptanes	1.13	2.14	3.18	3.15
Octanes	0.92	2.18	2.75	2.96
Nonanes	0.54	1.51	1.88	2.03
Decanes	0.28	0.91	1.08	1.22
Undecanes Plus	3.49	6.00	9.25	10.62
Molecular Weight	33.1	43.6	55.4	61.0
Undecanes plus characteristics				
Molecular Weight	260	267	285	290
Specific gravity	0.8480	0.8625	0.8722	0.8768

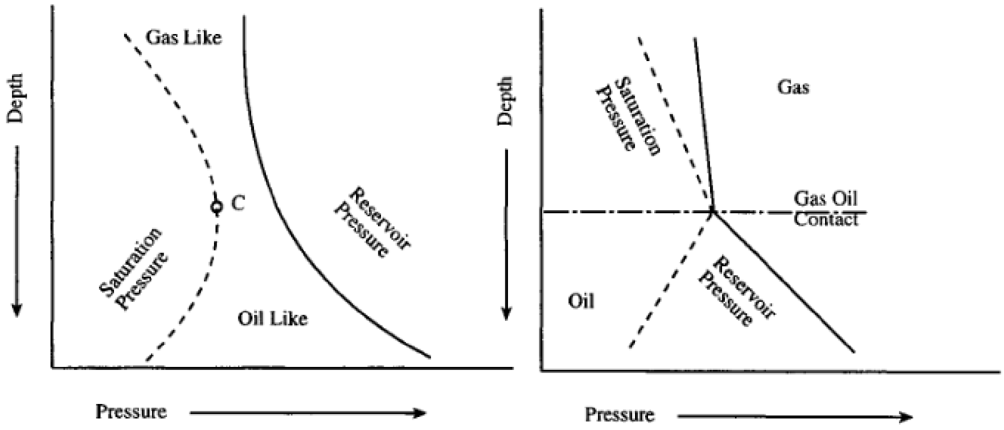
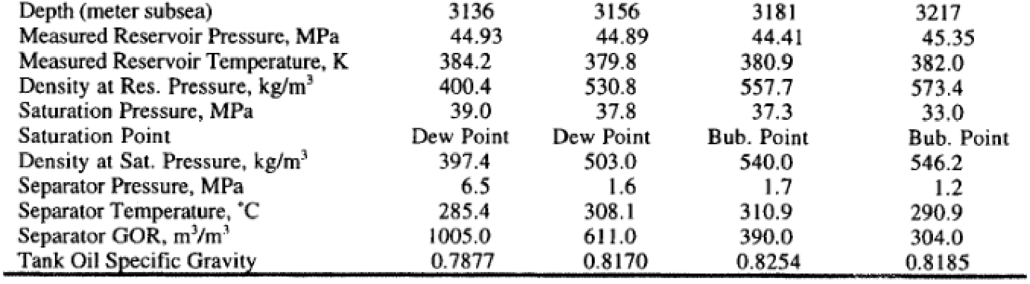


Figure 5.10. Phase variations in reservoirs with compositional grading.

Table 5.2. Properties of fluids at different depths in the North Sea reservoir.



Fluid	D, Well 1	C, Well 2	B, Well 2	A, Well 2
Depth (meter subsea)	3136	3156	3181	3217
Measured Reservoir Pressure, MPa	44.93	44.89	44.41	45.35
Measured Reservoir Temperature, K	384.2	379.8	380.9	382.0
Density at Res. Pressure, kg/m^3	400.4	530.8	557.7	573.4
Saturation Pressure, MPa	39.0	37.8	37.3	33.0
Saturation Point	Dew Point	Dew Point	Bub. Point	Bub. Point
Density at Sat. Pressure, kg/m^3	397.4	503.0	540.0	546.2
Separator Pressure, MPa	6.5	1.6	1.7	1.2
Separator Temperature, °C	285.4	308.1	310.9	290.9
Separator GOR, m^3/m^3	1005.0	611.0	390.0	304.0
Tank Oil Specific Gravity	0.7877	0.8170	0.8254	0.8185