Chapter 5: Phase Behavior Calculations

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

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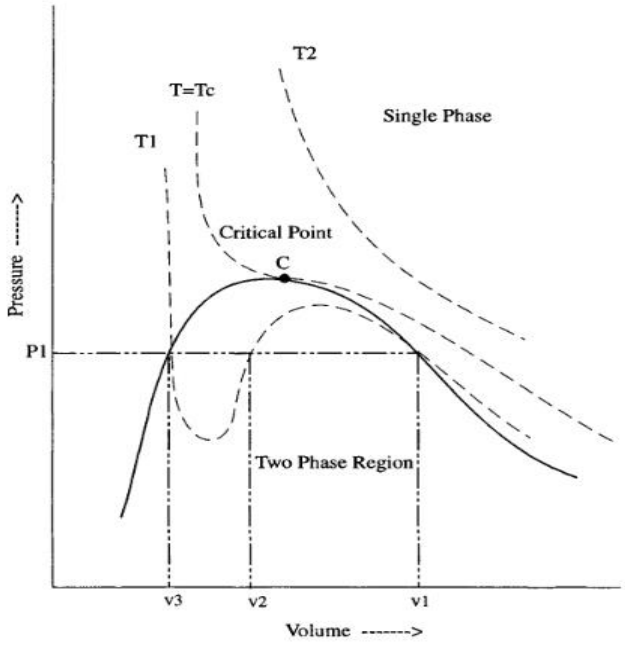
Home works: 1, 2, 4, 5, 7, 10

Chapter 5: Phase Behavior Calculations

منابع اضافی برای این فصل:

- Molecular Thermodynamics of Fluid Phase Equilibrium (Prausnitz)
- Chemical Engineering Thermodynamics (Van Ness)



Chapter 5: Phase Behavior Calculations

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 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,

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

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

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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Fugacity coefficient for component *i*th in mixture

4.3 Mixing Rules

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

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

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,

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

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.

Chapter 5: Phase Behavior Calculations

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,

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

Solution:

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

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

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 5: Phase Behavior Calculations

Vapor – Liquid – Solid Phases

Phase Behavior Calculation

محاسبات رفتار فازی

تعریف

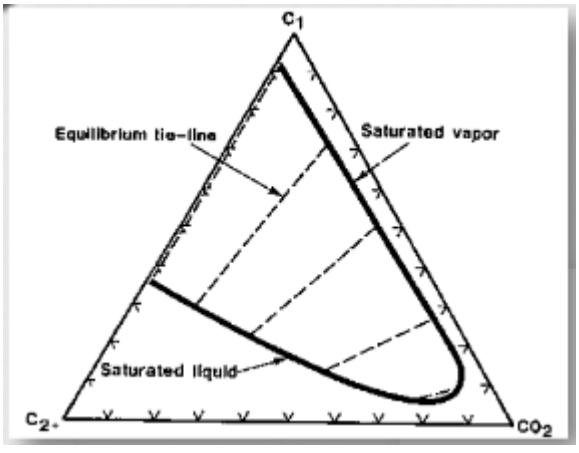
Treatment on No. of fluids (Liq. & Vap.) and solid phase

1. مجاورت یک مخزن در کنار CO_2 در دمای پایین (Displacing Oil with CO_2)
   - HC rich
   - CO_2 rich

   ← در حال تعادل یا Vap.

Graph

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



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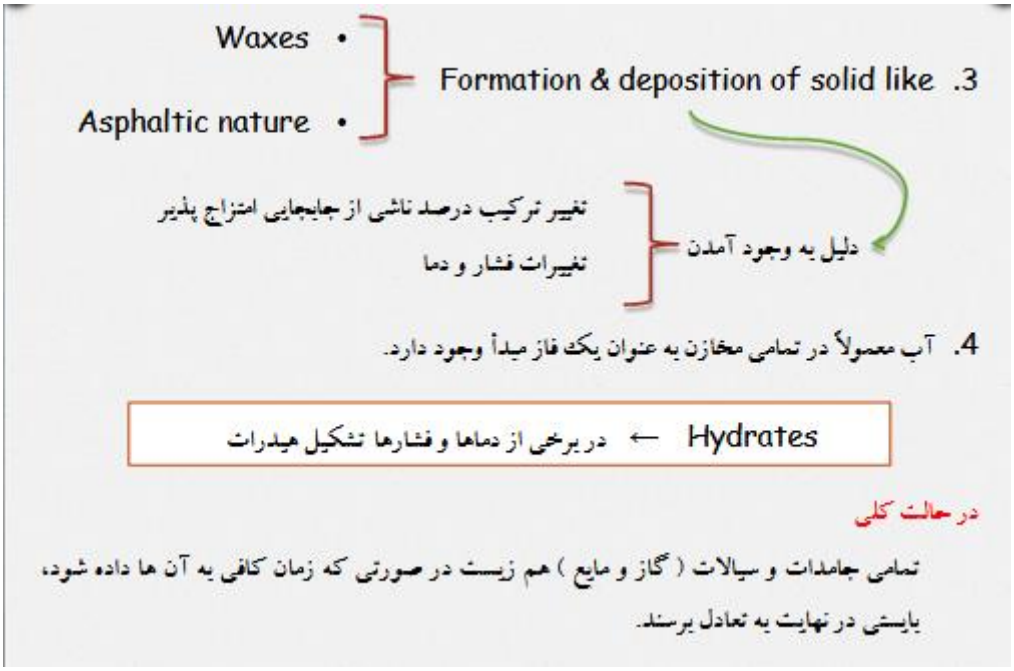

Chapter 5: Phase Behavior Calculations

Multicomponent VLE

- We have been studying binary systems, that is two species
- For this case, the Phase Rule stated:
  - If given:
    - F as the number of degrees of freedom
    - C as the number of components
    - P as the number of phases
  - Then this is true:
    - F = C-P+2
- For a Ternary (3 species in equilibrium) System, then we get:
  - F = C-P+2 = 3-2+2 = 3
- For a Quaternary system… and so on..
  - F = C-P+2 = 4-2+2 = 4…

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Worked Example Bubble Point Calculation

- Solution.
- The task is to find a Pressure that satisfies → $\sum x_i P^\circ_i(T) = p$
- Since T is given, this is trivial (not required)
- We can simply calculate **P** from the previous equation
- We start by computing the vapor pressures for the three components at T = 400K.
- Using the Antoine data, we get: $P^\circ_1(T = 400K) = 10.248 bar$
  $P^\circ_2(T = 400K) = 4.647\ bar$
  $P^\circ_3(T = 400K) = 3.358 bar$
- At the bubble point, the liquid phase composition is given, so the partial pressure of each component is
  $p_1 = x_1 P^\circ_1 = (0.5)(10.248 bar) = 5.124 bar$
  $p_2 = x_2 P^\circ_2 = (0.3)(4.647 bar) = 1.394 bar$
  $p_3 = x_3 P^\circ_3 = (0.2)(3.358 bar) = 0.672 \text{bar}$

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Worked Example
Bubble Point Calculation

- Thus, from the equation of the bubble pressure we get:

$$p = p_1 + p_2 + p_3 = 7.189\ bar$$

- Finally, the vapor composition (composition of the first vapor bubble) is

$$y_1 = \frac{p_1}{p} = \frac{5.124 bar}{7.189\ bar} = 0.713$$
$$y_2 = \frac{p_2}{p} = \frac{1.394 bar}{7.189\ bar} = 0.194$$
$$y_3 = \frac{p_3}{p} = \frac{0.672 bar}{7.189\ bar} = 0.093$$

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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)

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

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

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

Chapter 5: Phase Behavior Calculations

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,

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

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

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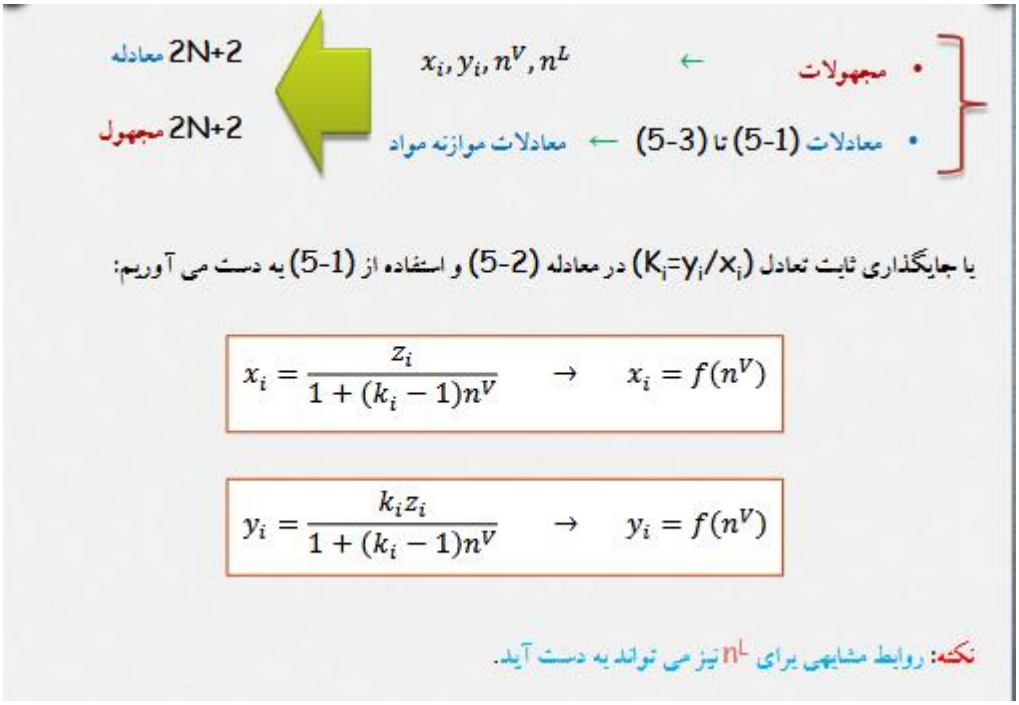

At equilibrium, the fugacity of any component, i, in the vapour is equal to that in the liquid. The equality of fugacity can be expressed by the equilibrium ratio, K_i, as given by Eq.(3.43),

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

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

Chapter 5: Phase Behavior Calculations

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

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

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

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:

$\sum z_i k_i > 1$ & $\sum \frac{z_i}{k_i} > 1$ ← این چک قبل از انجام محاسبات انجام می شود.

Chapter 5: Phase Behavior Calculations

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

$$n^V = 0 \rightarrow \begin{cases} \sum z_i k_i = 1 & \text{در حقیقت همه مخلوط مایع بوده} \\ and \\ y_i = k_i x_i = k_i z_i & x_i = z_i \end{cases}$$

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:

$$\sum z_i k_i = 1$$

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Dew Point

$$n^V = 1 \rightarrow \begin{cases} \sum \frac{z_i}{k_i} = 1 & \text{در حقیقت همه مخلوط بخار بوده} \\ and & \\ x_i = \frac{y_i}{k_i} = \frac{z_i}{k_i} & y_i = z_i \end{cases}$$

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:

Simulation
Bubble & Dew Point of HC Mixture

- **Component / Molar flow**
- B 0.25
- T 0.25
- O-X 0.25
- P-X 0.25

- A) Get Dew point @ T= 150°C, P = 50bar
- B) Get Dew point @ T= 220°C, P = 10bar
- C) What is the Critical Point & Meaning?

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Chapter 5: Phase Behavior Calculations

Derivation of Rachford-Rice Equation

- Here, we cannot directly calculate ***xi*** because the vapor split **V /F** is not known.
- To find V /F we may use:
  - the relationship $\Sigma x_i = 1$
  - alternatively $\Sigma y_i = 1$
  - OR the addition of both... $\Sigma x_i = \Sigma y_i = 1$

$$K_i = \frac{p_{sat_i}(T)}{p}$$

- However, it has been found that the combination Σi(yi-xi) = 0
  - It results in an equation with good numerical properties
- This is the so-called **Rachford-Rice Flash Equation**

$$\sum \frac{z_i(K_i - 1)}{1 + \Theta(K_i - 1)} = 0$$

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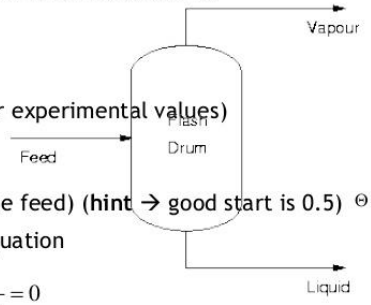
Rachford-Rice Procedure



1. Given → F, zi, T and P
2. Get Ki for species (either graph, equations or experimental values)
   - Antoine Equation (ideal)
   - K-Values from DePriester Chart
3. Assume a **phi** value (vaporized material in the feed) (**hint** → good start is 0.5) $\Theta = \frac{V}{F} = 0.50$
4. Get the Numerical Value of Rachford Rice Equation

$$\sum \frac{z_i(K_i - 1)}{1 + \Theta(K_i - 1)} = 0$$

- Example:
  - BTX (Benzene, Toluene, Xylene) System:

$$f(\Theta) = \frac{z_{benzene}(1 - K_{benzene})}{1 + \Theta(K_{benzene} - 1)} + \frac{z_{toluene}(1 - K_{toluene})}{1 + \Theta(K_{toluene} - 1)} + \frac{z_{xylene}(1 - K_{xylene})}{1 + \Theta(K_{xylene} - 1)}$$

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Rachford-Rice Procedure

$$\Theta = \frac{V}{F}$$

5. Get the Numerical Value of the Derivative of Rachford Rice Equation

$$f'(\Theta) = \sum \frac{z_i (1 - K_i)^2}{[1 + \Theta(K_i - 1)]^2}$$

- Example:
  - BTX (Benzene, Toluene, Xylene) System:

$$f'(\Theta) = \frac{z_{benzene}(1 - K_{benzene})^2}{[1 + \Theta(K_{benzene} - 1)]^2} + \frac{z_{toluene}(1 - K_{toluene})^2}{[1 + \Theta(K_{toluene} - 1)]^2} + \frac{z_{xylene}(1 - K_{xylene})^2}{[1 + \Theta(K_{xylenei} - 1)]^2}$$

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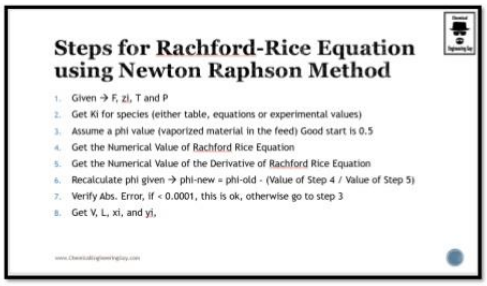
Worked Example Rachford-Rice Equation for BTX

- Step 6. Calculate the new "phi"

$$\Theta_{new} = \Theta_{old} - \frac{f(\Theta_{old})}{f'(\Theta_{old})}$$

$$\Theta_{new} = 0.50 - \frac{-0.0823}{0.4172}$$

$$\Theta_{new} = 0.6972$$



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Chapter 5: Phase Behavior Calculations

Worked Example Rachford-Rice Equation for BTX

- Step 8. Calculate all other Values

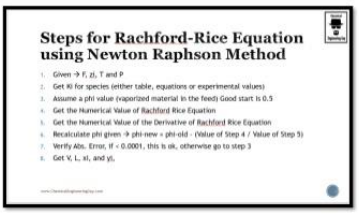
$$V \rightarrow V = \Theta F \rightarrow V = (0.6803)(100) = 68.03 kmol/h$$

$$L \rightarrow L = F - V = 100 - 68.03 = 31.97 kmol/h$$

- For compositions, use Spreadsheet

$$y_i = \frac{K_i z_i}{1 + \Theta(K_i - 1)}$$

$$x_i = \frac{z_i}{1 + \Theta(K_i - 1)}$$



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Worked Example Rachford-Rice Equation for BTX

- Step 8. Calculate all other Values

$$y_i = \frac{K_i z_i}{1 + \Theta(K_i - 1)}$$

$$x_i = \frac{z_i}{1 + \Theta(K_i - 1)}$$

Species	i	Ki	zi	phi	yi	xi
Benzene	1	1.78	0.60	0.6806	0.69728	0.392703
Toluene	2	0.73	0.25	0.6806	0.22385	0.305722
Xylene	3	0.26	0.15	0.6806	0.07879	0.301747

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

$$\sum_{i=1}^{2} z_i K_i = 0.6 \times 1.4 + 0.4 \times 0.13 = 0.89 < 1.$$

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:

Chapter 5: Phase Behavior Calculations

نکته ← اگر $\sum z_i/k_i < 1$ باشد، آنگاه سیال در فاز بخار می باشد.

چک می کنیم ⟵ $\sum z_i/k_i = 0.42 + 3.07 = 3.49 > 1$

b.

چون سیال مایع است، فشار بخار همان فشار حباب است. (T=377.6 K)

حدس فشار P(pisa)	K_1	K_2	z_1k_1	z_2k_2	$\sum_{i=1}^{2} z_ik_i$
3500	1.6	0.06	0.96	0.02	0.98
3000	1.8	0.03	1.08	0.01	1.09
3400 (23.44 MPa)	1.64	0.05	0.98	0.02	1.00

حل معادله برای نقطه حباب $\sum z_ik_i = 1$

مقدار تجربی $P_b = 3408\ psia\ (23.5\ MPa)$

نکته: $\sum z_ik_i$ به مقدار زیادی به مقادیر ثابت تعادل متان (غلظت بالا، فراریت بالا) بستگی دارد.

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

Chapter 5: Phase Behavior Calculations

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.

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

$$P, T = \sqrt{} \quad \rightarrow \quad k = constant \quad \rightarrow$$ 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

$$n^V = 0.457$$

$$n^L = 0.543$$

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

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

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

Chapter 5: Phase Behavior Calculations

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).

Chapter 5: Phase Behavior Calculations

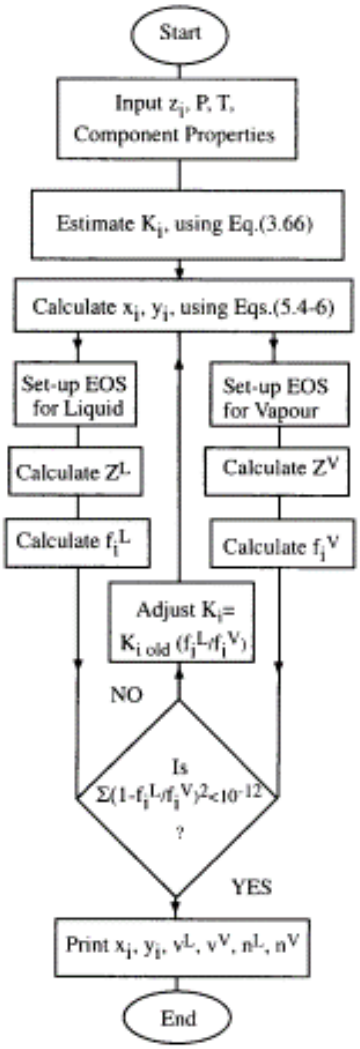

Figure 5.1. Flow chart of flash calculations using equation of state.

Chapter 5: Phase Behavior Calculations

← در مواردی که حالت سیال مخزن را نمی دانیم:

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

Z_{MAX}, Z_{MIN} → 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

$$f_i^L = \phi_i^L x_i P \qquad x_i = z_i = \sqrt{}$$

$$f_i^V = \phi_i^V y_i P \qquad y_i = k_i x_i = \sqrt{}$$

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

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

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

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

Chapter 5: Phase Behavior Calculations

(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 α	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 $k_{11}=k_{22}=0$.

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

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

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

Peng-Robinson (PR)

به منظور بهبود بخشیدن به پیش بینی دانسیته مایع در مقایسه با SRK جمله جاذب 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

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

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

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

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

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), $y_i=K_i x_i$, 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):

Chapter 5: Phase Behavior Calculations

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

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),

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

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

Chapter 5: Phase Behavior Calculations

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)*

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

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

Chapter 5: Phase Behavior Calculations

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 Z_i =0.280758 Z_l=0.249591

Rejecting the intermediate root, Z_i, 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,

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

$M=\sum x_i M_i=51.109$ kgmol/mol

$\rho= \rho_M M=152.01$ 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.

Chapter 5: Phase Behavior Calculations

Chapter 5: Phase Behavior Calculations

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

Chapter 5: Phase Behavior Calculations

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.

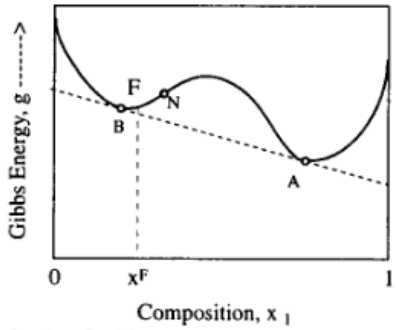

Figure 5.9. Intrinsic stability limit of a binary mixture at constant pressure and temperature.

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,

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

Chapter 5: Phase Behavior Calculations

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	$a_c\,\alpha$	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

Chapter 5: Phase Behavior Calculations

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

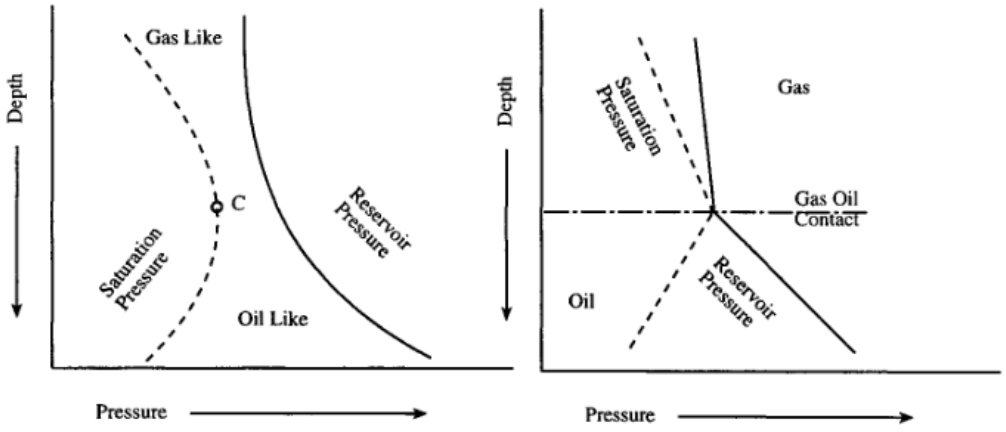

Figure 5.10. Phase variations in reservoirs with compositional grading.

Chapter 5: Phase Behavior Calculations

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