Applications of
THE PENG-ROBINSON
EQUATION OF STATE
Using Mathematica

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Consider a single component characterized by its critical pressure, temperature,acentric factor, \( P_c \), \( T_c \), and \( \omega \). The Peng-Robinson equation of state\(^{2,3}\) is given by:

\[
P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}
\]

where

\[
b = 0.07780 \frac{RT_c}{P_c}
\]

\[
a = 0.45724 \left( \frac{RT_c}{P_c} \right)^2 \left[ 1 + m \left( 1 - \sqrt{T_c} \right) \right]^2
\]

\[
T_c = \frac{T}{T_c}
\]

and

\[
m = 0.37464 + 1.54226 \omega - 0.26992 \omega^2
\]

The Peng-Robinson EOS\(^*\) is part of a family of equations called cubic because the compressibility factor, \( Z = PV/RT \), is a solution of the following cubic equation derived from Eq. (1) and written for a multi-component mixture:

\[
Z^3 + (1-2B)Z^2 + \left( A - 3B^2 - 2B \right) Z + \left( -AB + B^2 + B^3 \right) = 0
\]

\(^*\)All these computations are available in the form of notebooks upon request from the author or the Wolfram Research Information Center\(^\text{TM}\)

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is obtained from HYSYS 3.2, a major process simulator by Aspen Technology, Inc.\textsuperscript{[3]} or assumed to be equal to zero if the simulator is not available.

The liquid and vapor mole fractions are related by:

\[ y_i = K_i x_i \quad \text{with} \quad i = 1, 2, \ldots, C \tag{11} \]

where \( K_i \) is the equilibrium constant.

This equilibrium constant is obtained using the \( \phi - \phi \) method as follows:

\[ K_i = \frac{\phi^v_i}{\phi^l_i} \quad \text{for} \quad i = 1, 2, \ldots, C \tag{12} \]

where the fugacity coefficients are:

\[
\phi^v_i = \exp \left( \frac{\ln \left( \frac{Z_v - 1}{B} \right) - \frac{A}{2\sqrt{2}B}}{\ln \left( \frac{Z_v + 1 + \sqrt{2}}{B} \right)} \right)
\]

\[
\phi^l_i = \exp \left( \frac{\ln \left( \frac{Z_v + 1 - \sqrt{2}}{B} \right)}{\ln \left( \frac{Z_v + 1 + \sqrt{2}}{B} \right)} \right)
\]

The vapor-phase and liquid-phase fugacity coefficients, which measure deviation from ideality, are defined from the liquid-phase and gas-phase fugacities, \( f^l_i \) and \( f^v_i \), as follows:

\[ \phi^l_i = \frac{f^l_i}{y_iP} \quad \text{and} \quad \phi^v_i = \frac{f^v_i}{x_iP} \tag{14} \]

The \( \phi - \phi \) method is a direct result of expressing vapor-liquid equilibrium conditions \( (i.e., \text{temperatures}, \text{pressures}, \text{and fugacities are equal in both phases}) \) and the definition of fugacity coefficients.

A similar expression to Eq. (13) is obtained for the liquid-phase fugacity coefficient, \( \phi^l_i \), by replacing the gas-phase compressibility factor, \( Z_v \), with its liquid-phase counterpart, \( Z_l \). These two compressibility factors are the largest and smallest roots of Eq. (6), respectively. For specified values of \( P \) and \( T \), the smallest root, \( Z_l \), allows the determination of the liquid molar volume while the highest root, \( Z_v \), permits the computation of the vapor molar volume. The intermediate root has no physical significance.

Finally, one needs the following expression for the enthalpy departure function from ideality in order to compute enthalpy:

\[ H^P = RT(Z - 1) - \frac{1}{2\sqrt{2}BRT} \]

\[
\frac{1}{P} \left( \frac{Z + 1 + \sqrt{2}}{B} \right) ^2 \left( \frac{Z - 1}{B} \right) \left( \frac{A}{RT} \right)^2 \left( \frac{A}{RT} \right)^2 \tag{15} \]

**ADIABATIC FLASH CALCULATIONS FOR MULTI-COMPONENT MIXTURES**

**Problem statement**

A quaternary mixture, at 485 psia and 100 °F, is composed of 0.41% hydrogen, 5.71% methane, 70.97% benzene, and 22.91% toluene. This mixture is sent to a stabilizer to remove hydrogen and methane. The feed pressure is decreased adiabatically from 485 psia to 165 psia by valve and pipe line pressure drop. Find the vapor-phase fraction, the temperature and other relevant variables.

**Solution**

This problem has been solved using a tedious iterative technique by Henley and Seader.\textsuperscript{[6]} The unknowns in this problem are the mole fractions in the two phases, the temperature, the vapor phase fraction, and the compressibility factors. We have 12 nonlinear algebraic equations to solve simultaneously. These equations are three equilibrium relations, three component mass balances, two summation rules, two cubic equations of the compressibility factors, the enthalpy balance, and the famous Rachford and Rice equation given by:

\[ \sum_{i=1}^{C} Z_i (K_i - 1)/(1 + \phi_{\text{vap}} (K_i - 1)) = 0 \tag{16} \]

where \( \phi_{\text{vap}} \) is the fraction vaporized, V/F. The Mathematica commands, which allow the determination of the 12 unknowns, are based on the built-in function \texttt{FindRoot} and are given by:

\[
\text{Eq[i]} := y[i] = K[i] x[i] \\
\text{Eq[i]} := x[i] = z[i] / (1 + \phi_{\text{vap}} (K[i] - 1));
\]

\[
\text{sol} = \text{FindRoot} \left[ \text{Eq[1]}, \text{Eq[2]}, \text{Eq[3]}, \sum_{i=1}^{C} \text{y[i]} = 1, \right. \\
\left. \text{Eq[4]}, \text{Eq[5]}, \text{Eq[6]}, \right. \\
\sum_{i=1}^{C} \text{x[i]} = 1, \sum_{i=1}^{C} \text{z[i]} (K[i] - 1)/(1 + \phi_{\text{vap}} (K[i] - 1)) = 0,
\]

\[
Z_i \cdot 3 + (-1 + B_i) Z_i \cdot 2 + Z_i (A_i - 3B_i \cdot 2 - 2B_i) \\
- A_i B_i + B_i \cdot 2 + B_i \cdot 3 = 0,
\]

\[
Z_i \cdot 3 + (-1 + B_i) Z_i \cdot 2 + Z_i (A_i - 3B_i \cdot 2 - 2B_i) \\
- A_i B_i + B_i \cdot 2 + B_i \cdot 3 = 0,
\]

\[
\text{HF} = \phi_{\text{vap}} \text{HV} + (1 - \phi_{\text{vap}}) \text{HL}, \{x[1], 0.0004\}, \{z[1], 0.001\}, \{y[2], 0.03\}, \{x[3], 0.7\}, \{z[2], 0.85\}, \{y[3], 0.02\}, \{x[4], 0.001\}, \{z[3], 0.05\}, \{z[4], 0.95\}, \{T, 540\}, \text{MaxIterations} \rightarrow 10000 \text{//Chop}
\]

We find the following output,

\[
\begin{align*}
\{x[1] \rightarrow 0.00020583, x[2] \rightarrow 0.0259441, \\
x[3] \rightarrow 0.736087, x[4] \rightarrow 0.237763, \\
y[1] \rightarrow 0.106105, y[2] \rightarrow 0.873206, \\
y[3] \rightarrow 0.0185161, y[4] \rightarrow 0.00217289, \\
\phi_{\text{vap}} \rightarrow 0.0367724, Z_i \rightarrow 0.0405552, \\
Z_i \rightarrow 0.981151, T \rightarrow 560.297
\end{align*}
\]
The vapor-phase fraction $\phi_{\text{vap}}$ and temperature are 0.0367 and 560.297 °R, respectively.

**SOLUBILITY OF METHANOL IN NATURAL GAS**

**Problem statement**

Methanol is used as a solvent in the sweetening of natural gas (i.e., removal of carbon dioxide and hydrogen sulfide). Loss of methanol by transfer from liquid phase to gas phase can become an important economic consideration. Compute the gas phase mole fraction of methanol in treated natural gas leaving the sour gas absorption unit vs. temperature at a pressure of 145.038 psia. Treated natural gas is composed of 70% methane, 10% nitrogen, 10% carbon monoxide and 10% hydrogen.

**Solution**

We perform several isothermal flash computations at various temperatures. The problem’s unknowns are the ten mole fractions in the gas and liquid phases, the vapor phase fraction, and the two compressibility factors. The available equations are the five equilibrium relations, the two summation rules, the five mass balances, the two cubic equation of state of the compressibility factors, and the Rachford and Rice equation. The calculation uses the built-in function FindRoot to solve 13 nonlinear algebraic equations simultaneously. The Mathematica commands, which allow the determination of the 13 unknowns, are the following:

\[
\begin{align*}
\text{Eq[i]} & \Rightarrow y[i] = K[i] \times x[i] \\
\text{EQ[i]} & \Rightarrow x[i] = z[i] / (1 + \phi_{\text{vap}} (K[i]-1)); \\
\text{For[i] = 1, i < 15,} \\
T & = \{329.67, 347.67, 365.67, 383.67, 401.67, 419.67, 437.67, 455.67, 473.67, \\
& 491.67, 509.67, 527.67, 545.67, 563.67\}[[i]], \\
\text{sol[i]} & = \text{FindRoot}[\text{Eq[1]}, \text{Eq[2]}, \text{Eq[3]}, \text{Eq[4]}, \text{z[i][i]} == 1,} \\
& \text{EQ[1], EQ[2], EQ[3], EQ[4]} , \text{z[i][i]} == 1, \\
& \text{\sum[i = 1] z[i][i] (K[i]-1) / (1 + \phi_{\text{vap}} (K[i]-1)) == 0,} \\
& Z_t^3 + (-1 + B_1) Z_t^2 + Z_t + Z_r (A_t - 3B_r) + 2 - 2B_r, \\
& -A_r B_1 + B_1 Z_r^2 + 2 + B_r^3 == 0, \\
& Z_r^3 + (-1 + B_1) Z_r^2 + Z_r - Z_t (A_r - 3B_t) + 2 - 2B_t, \\
& -A_t B_r + B_r Z_t^2 + 2 + B_t^3 == 0, \\
\text{\{x[1], x[1] / sol[i-1], \{x[2], x[2] / sol[i-1],} \\
& \{x[3], x[3] / sol[i-1],} \\
& \{x[4], x[4] / sol[i-1], \{x[5], x[5] / sol[i-1],} \\
& \{y[1], y[1] / sol[i-1], \{y[2], y[2] / sol[i-1],} \\
& \{y[3], y[3] / sol[i-1],} \\
& \{y[4], y[4] / sol[i-1], \{y[5], y[5] / sol[i-1],} \\
& \{\phi_{\text{vap}}, \phi_{\text{vap}} / sol[i-1], \{Z_t, Z_r / sol[i-1],} \\
& \{Z_r, Z_t / sol[i-1],} \\
\text{MaxIterations} & \to 10001 / \text{Chop, Print[i][i + 1]}]
\end{align*}
\]

Figure 1 depicts the computed solubility of methanol in treated natural gas vs. temperature at 145.038 psia. We observe an increase in solubility at higher temperatures. We see that these solubility values can become large enough to present serious economic drawback due to excessive loss of methanol.

**HIGH-PRESSURE CHEMICAL EQUILIBRIUM COMPUTATION**

**Problem Statement**

Nitrogen and hydrogen react to form ammonia. This reaction is favored by low temperatures and high pressure. Kinetic considerations, however, oblige us to use high temperature. Thus, reactors are operated at very high pressures to get a reasonably high conversion of reactants. High gas-phase pressures imply significant deviation from ideality and the need to take into account the fugacity coefficients. In fact, the equilibrium constant depends on $K_e$ as follows:

\[
K_e = \frac{\sum_i \psi_i}{\sum_j \psi_j} = \frac{y_{N_2} \times 13}{y_{H_2} \times 13} \times P = \frac{X (2 - X)}{2} \times P 
\]

Figure 1. Solubility of methanol in treated natural gas vs. temperature at 145.038 psia.
where $K_v$ is given by:

$$K_v = \frac{\phi_{nk}}{\phi_{n}^{0.5} \phi_{k}^{1.5}}$$  \hspace{1cm} (18)

$$a_i = \phi_i y_i$$  \hspace{1cm} (19)

and $X$ is the extent of reaction. Plot $K_v$ and $X$ vs. pressure at temperatures ranging from 900 °R to 1440 °R.

**Solution**

The unknowns in this type of problems are five: the mole fraction in the gas phase, the extent of reaction, and the gas phase compressibility factor. Once again, the calculation uses the built-in function `FindRoot` to solve five nonlinear algebraic equations simultaneously. The Mathematica commands, which allow the determination of the five unknowns, are the following:

$$P = 0.001;$$

$$\text{For}[i = 1, i < 17, \{\text{sol} = 260 =$$

$$\text{FindRoot}[\left\{\begin{array}{l}
K_v[T][0.5(1-X)]^{0.5} (1.5(1-X))
\end{array}\right.,\{\begin{array}{l}
1.5 \phi_1 [1]^{1.5} \phi_2 [2]^{0.5} == \\
X (2 - X)/P \phi_3 [3] y_3 (2 - X)
\end{array}\right].$$

$$== X, y_2 (2 - X) == 0.5 (1 - X),$$

$$y_1 (2 - X) == 1.5 (1 - X),$$

$$z_v ^ 3 + (-1 + B_v) z_v ^ 2 + z_v (A_v - 3 B_v) + 2 - 2B_v)$$

$$-A_v B_v + B_v ^ 2 + B_v ^ 3 == 0\},$$

$$\{y_2[0.2], y_1[1.01], y_3[3.04], X[0.6],$$

$$Z_v[0.95], \text{MaxIterations} -> 100000\},$$

$$P[i] = P, K_v[i] = \phi_3 [3] / (\phi_1 [1]^{1.5} \phi_2 [2]^{0.5})$$

$$\text{sol} = 260, X[i] = X / \text{sol} = 260,$$

$$\text{Print}[i,"\text{°R}", P = P + 1000, i = i + 1].$$

In Figure 2, we plot $K_v$ vs. pressure at various temperatures (900, 1080, 1260 and 1440 °R). Values of $K_v$ are significantly different from unity, indicating that this factor must be taken into account at high pressures. The extent of reaction at equilibrium vs. pressure, for the same temperatures, is represented in Figure 3. The extent of reaction approaches unity at high pressures.

**CONCLUSION**

We have shown through simple examples how one can take advantage of the numerical and graphical capabilities of Mathematica to perform flash calculations for multi-component mixtures, solubility determination, and high-pressure chemical equilibrium computations. Similar computations can be performed very easily using Matlab.\(^7\)

**NOMENCLATURE**

- $x$: liquid mole fraction
- $y$: vapor mole fraction

**Figure 2.** $K_v$ vs. pressure at various temperatures.

**Figure 3.** Extent of reaction vs. pressure at various temperatures.
$H^0$: departure from ideality enthalpy (cal/mol)

$k_{ij}$: binary interaction parameter

$C$: number of components

$z$: feed mole fraction

$R$: universal gas constant (cal/mol.°R)

$a_i$: activity of species $i$ (psia)

$v_i$: stoichiometric coefficient

$\phi_i$: liquid phase fugacity coefficient

$\phi_{vi}$: vapor phase fugacity coefficient

$\phi_{vp}$: fraction vaporized $= V/V_I$

REFERENCES

1. <http://library.wolfram.com/inocenter/search/?search_ results=1;search_person_id=1836>