The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed 14 double-spaced pages and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

Applications of
THE PENG-ROBINSON EQUATION OF STATE
Using Mathematica

Housam Binous
National Institute of Applied Sciences and Technology • Tunis, Tunisia

Consider a single component characterized by its critical pressure, temperature, acentric factor, $P_c T_c$, and ω. The Peng-Robinson equation of state[2-4] is given by:

$$P = \frac{RT}{(V-b)} - \frac{a}{\left[V(V+b)+b(V-b)\right]} \tag{1}$$

where

$$b = 0.07780\frac{RT_c}{P_c} \tag{2}$$

$$a = 0.45724\frac{(RT_c)^2}{P_c}\left[1+m\left(1-\sqrt{T_r}\right)\right]^2 \tag{3}$$

$$T_r = \frac{T}{T_c} \tag{4}$$

and

$$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2. \tag{5}$$

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:

$$Z^3 + (1-B)Z^2 + \left(A-3B^2-2B\right)Z + \left(-AB+B^2+B^3\right) = 0 \tag{6}$$

where

$$A = \sum_{i=1}^{C}\sum_{j=1}^{C} y_i y_j A_{ij} \quad \text{or} \quad \sum_{i=1}^{C}\sum_{j=1}^{C} x_i x_j A_{ij} \tag{7}$$

$$A_{ij} = \left(A_i A_j\right)^{0.5}(1-k_{ij}) \tag{8}$$

$$B = \sum_{i=1}^{C} y_i B_i \quad \text{or} \quad \sum_{i=1}^{C} x_i B_i \tag{9}$$

$$A_i = 0.45724\,a_i\frac{P_{r_i}}{T_{r_i}^2} \quad \text{and} \quad B_i = 0.07780\frac{P_{r_i}}{T_{r_i}} \tag{10}$$

For each component, we define the reduced pressure and temperature using $P_{r_i} = P/P_{c_i}$ and $T_{r_i} = T/T_{c_i}$, and a_i is identified by an equation similar to Eq. (3) – given for the pure component case. The binary interaction parameter, k_{ij},

Housam Binous *is a full-time faculty member at the National Institute of Applied Sciences and Technology in Tunis. He earned a Diplôme d'ingénieur in biotechnology from the Ecole des Mines de Paris and a Ph.D. in chemical engineering from the University of California at Davis. His research interests include the applications of computers in chemical engineering.*

**All these computations are available in the form of notebooks upon request from the author or the Wolfram Research Information Center.[1]*

is obtained from HYSYS 3.2, a major process simulator by Aspen Technology, Inc.,[5] or assumed to be equal to zero if the simulator is not available.

The liquid and vapor mole fractions are related by:

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

where K_i is the equilibrium constant.

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

$$K_i = \frac{\phi_{l_i}}{\phi_{v_i}} \quad \text{for } i = 1,2,\ldots,C \tag{12}$$

where the fugacity coefficients are:

$$\phi_{v_i} = \exp\left(\begin{array}{l} (Z_v - 1)\dfrac{B_i}{B} - \ln(Z_v - B) - \dfrac{A}{2\sqrt{2}B} \\ \left(\dfrac{2\sum\limits_j y_j A_{ij}}{A} - \dfrac{B_i}{B} \right) \ln\left(\dfrac{Z_v + (1+\sqrt{2})B}{Z_v + (1-\sqrt{2})B} \right) \end{array} \right) \tag{13}$$

The vapor-phase and liquid-phase fugacity coefficients, which measure deviation from ideality, are defined from the liquid-phase and gas-phase fugacities, f_i^v and f_i^l, as follows:

$$\phi_{v_i} = \frac{f_i^v}{y_i P} \text{ and } \phi_{l_i} = \frac{f_i^l}{x_i P} \tag{14}$$

The $\phi - \phi$ method is a direct result of expressing vapor-liquid equilibrium conditions (*i.e.*, temperatures, pressures, 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, ϕ_{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:

$$H^D = RT(Z-1) + \frac{1}{2\sqrt{2}B\dfrac{RT}{P}} \,\mathrm{Log}\left(\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right) \left[T\frac{d}{dT}\left(A\frac{(RT)^2}{P} \right) - A\frac{(RT)^2}{P} \right] \tag{15}$$

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.[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:

$$\sum_{i=1}^{c} \frac{z_i(K_i - 1)}{1 + \phi_{vap}(K_i - 1)} = 0 \tag{16}$$

where ϕ_{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 *FindRoot* and are given by:

$$\begin{gathered}
\text{Eq[i\_]} := \text{y[i]} == \text{K[i] x[i]} \\
\text{EQ[i\_]} := \text{x[i]} == \text{z[i]} / (1 + \phi_{vap}\ (\text{K[i]} - 1)); \\
\text{sol} = \text{FindRoot[}\left\{ \begin{array}{l} \text{Eq[1],Eq[2],Eq[3],}\sum\limits_{i=1}^{4} \text{y[i]} == 1, \\ \text{EQ[1],EQ[2],EQ[3],} \end{array} \right. \\
\sum_{i=1}^{4} \text{x[i]} == 1, \sum_{i=1}^{4} \text{z[i] (K[i]} - 1) / (1 + \phi_{vap}\ (\text{K[i]} - 1)) == 0, \\
Z_l \wedge 3 + (-1 + B_l)\, Z_l \wedge 2 + Z_l\ (A_l - 3B_l \wedge 2 - 2B_l) \\
-A_l\, B_l + B_l \wedge 2 + B_l \wedge 3 == 0, \\
Z_v \wedge 3 + (-1 + B_v)\, Z_v \wedge 2 + Z_v\ (A_v - 3B_v \wedge 2 - 2B_v) \\
-A_v\, B_v + B_v \wedge 2 + B_v \wedge 3 == 0, \\
\text{HF} == \phi_{vap}\ \text{HV} + (1 - \phi_{vap})\ \text{HL}\}, \{\text{x[1]},0.0004\}, \\
\{\text{x[2]},0.03\}, \{\text{x[3]},0.7\}, \{\text{x[4]},0.25\}, \\
\{\phi_{vap},0.01\}, \{\text{y[1]},0.1\}, \{\text{y[2]},0.85\}, \{\text{y[3]},0.02\}, \\
\{\text{y[4]},0.001\}, \{Z_l,0.05\}, \{Z_v,0.95\}, \{\text{T},540\}, \\
\text{MaxIterations} -> 1000]\,//\text{Chop}
\end{gathered}$$

We find the following output,

$$\begin{gathered}
\{\text{x[1]} \to 0.00020583, \text{x[2]} \to 0.0259441, \\
\text{x[3]} \to 0.736087, \text{x[4]} \to 0.237763 \\
\text{y[1]} \to 0.106105, \text{y[2]} \to 0.873206, \\
\text{y[3]} \to 0.0185161, \text{y[4]} \to 0.00217289, \\
\phi_{vap} \to 0.0367724, Z_l \to 0.0405552, \\
Z_v \to 0.981151, \text{T} \to 560.297\ \}
\end{gathered}$$

The vapor-phase fraction ϕ_{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[3] 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:

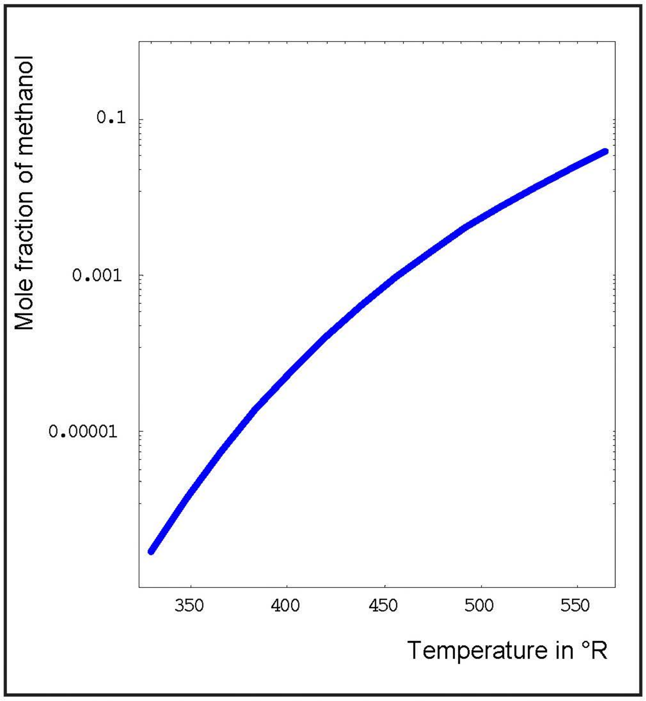

Figure 1. *Solubility of methanol in treated natural gas vs. temperature at 145.038 psia.*

$$
\begin{gathered}
\mathrm{Eq[i\_]:=y[i]==K[i]\,x[i]} \\
\mathrm{EQ[i\_]:=x[i]==z[i]/(1+\phi_{vap}\ (K[i]-1));} \\
\mathrm{For[i=1,i<15,} \\
\left\{\mathrm{T}=\left\{\begin{array}{l}\mathrm{329.67,347.67,365.67,383.67,401.67,} \\ \mathrm{419.67,437.67,455.67,473.67,}\end{array}\right.\right. \\
\mathrm{491.67,509.67,527.67,545.67,563.67\}[[i]],} \\
\mathrm{sol[i]=FindRoot[}\left\{\mathrm{Eq[1],Eq[2],Eq[3],Eq[4],}\sum_{i=1}^{5}\mathrm{y[i]==1,}\right. \\
\mathrm{EQ[1],EQ[2],EQ[3],EQ[4],}\sum_{i=1}^{5}\mathrm{x[i]==1,} \\
\sum_{i=1}^{5}\mathrm{z[i]\,(K[i]-1)/(1+\phi_{vap}\ (K[i]-1))==0,} \\
\mathrm{Z_l\wedge 3+(-1+B_l)\,Z_l\wedge 2+Z_l\ (A_l-3B_l\wedge 2-2B_l)} \\
\mathrm{-A_l\ B_l+B_l\wedge 2+B_l\wedge 3==0,} \\
\left.\begin{array}{c}\mathrm{Z_v\wedge 3+(-1+B_v)\,Z_v\wedge 2+Z_v\ (A_v-3B_v\wedge 2-2B_v)} \\ \mathrm{-A_v\ B_v+B_v\wedge 2+B_v\wedge 3==0}\end{array}\right\}, \\
\{\mathrm{x[1],x[1]/.sol[i-1]}\},\{\mathrm{x[2],x[2]/.sol[i-1]}\}, \\
\{\mathrm{x[3],x[3]/.sol[i-1]}\}, \\
\{\mathrm{x[4],x[4]/.sol[i-1]}\},\{\mathrm{x[5],x[5]/.sol[i-1]}\}, \\
\{\mathrm{y[1],y[1]/.sol[i-1]}\},\{\mathrm{y[2],y[2]/.sol[i-1]}\}, \\
\{\mathrm{y[3],y[3]/.sol[i-1]}\}, \\
\{\mathrm{y[4],y[4]/.sol[i-1]}\},\{\mathrm{y[5],y[5]/.sol[i-1]}\}, \\
\{\phi_{vap},\phi_{vap}\ \mathrm{/.sol[i-1]}\},\{\mathrm{Z_l,Z_l\ /.sol[i-1]}\}, \\
\{\mathrm{Z_v,Z_v\ /.sol[i-1]}\}, \\
\mathrm{MaxIterations->1000]//Chop,Print[i],i++\}]}
\end{gathered}
$$

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.[4] In fact, the equilibrium constant depends on K_v as follows:

$$
K_a=\prod_{i=1}^{C} a_i^{\nu_i}=\frac{y_{NH_3}}{y_{N_2}^{0.5}\,y_{H_2}^{1.5}}\frac{1}{P}K_v=\frac{X(2-X)}{\left[\frac{1-X}{2}\right]^{0.5}\left[\frac{3(1-X)}{2}\right]^{1.5}}\frac{1}{P}K_v \quad (17)
$$

where K_v is given by:

$$K_v = \frac{\phi_{NH_3}}{\phi_{N_2}^{0.5}\,\phi_{H_2}^{1.5}} \tag{18}$$

$$a_i = \phi_i y_i \tag{19}$$

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;
For[i = 1,i < 17,{sol1260 =
FindRoot[{Ka[T] (0.5 (1 − X)) ^ 0.5 (1.5 (1 − X))
         ^1.5 ϕv[1] ^ 1.5 ϕv[2] ^ 0.5 ==
X (2 − X) / P ϕv[3], y[3] (2 − X)
== X, y[2] (2 − X) == 0.5 (1 − X),
y[1] (2 − X) == 1.5 (1 − X),
Zv ^ 3 + (−1 + Bv) Zv ^ 2 + Zv (Av − 3Bv ^ 2 − 2Bv)
−Av Bv + Bv ^ 2 + Bv ^ 3 == 0},
{y[2],0.2},{y[1],0.1},{y[3],0.4},{X,0.6},
{Zv,0.95}, MaxIterations → 10000],
Pp[i] = P, Kv[i] = ϕv[3] / (ϕv[1] ^ 1.5 ϕv[2] ^ 0.5) /
.sol1260, X[i] = X / .sol1260,
Pr int[i," ",P], 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
$P_{c,i}$: critical pressure (psia)
$T_{c,i}$: critical temperature (°R)
$P_{r,i}$: reduced pressure
$T_{r,i}$: reduced temperature
ω: acentric factor
Z: compressibility factor
ϕ_l, ϕ_v: fugacity coefficients
K_i: equilibrium constant

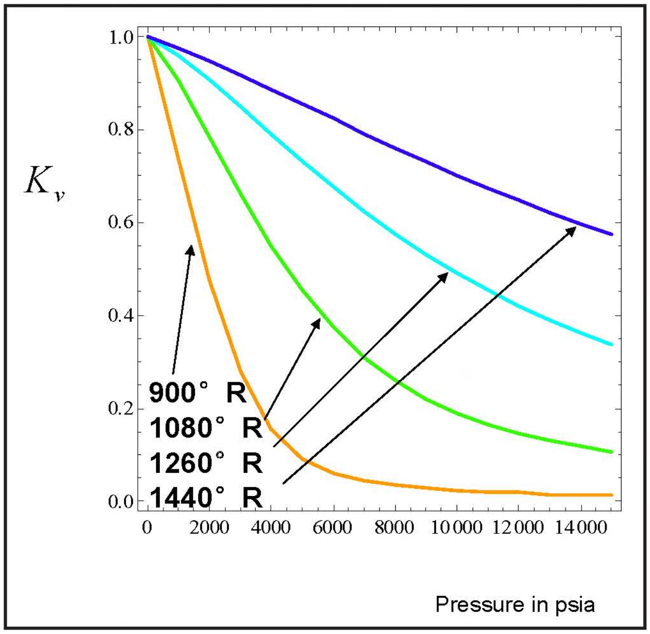

Figure 2. *K_v vs. pressure at various temperatures.*

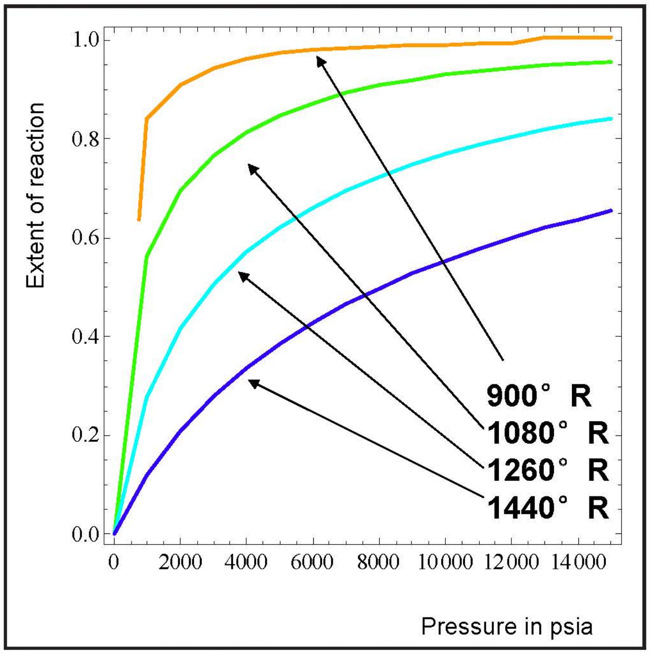

Figure 3. *Extent of reaction vs. pressure at various temperatures.*

H^D: 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

ϕ_{li} : liquid phase fugacity coefficient

ϕ_{vi} : vapor phase fugacity coefficient

ϕ_{vap} : fraction vaporized = V/F

REFERENCES

1. <http://library.wolfram.com/infocenter/search/?search_results=1;search_person_id=1536>
2. Tester, J.W., and M. Modell, *Thermodynamics and Its Applications*, 3rd Ed., Prentice Hall, Upper Saddle River, NJ (1996)
3. Prausnitz, J.M., R.N. Lichtenthaler, and E.G. deAzevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Ed., Prentice-Hall, Englewood Cliffs, NJ (1998)
4. Sandler, S.I., *Chemical and Engineering Thermodynamics*, Wiley, NY, 3rd Ed. (1999)
5. <http://www.hyprotech.com>
6. Henley, E.L., and J.D. Seader, *Equilibrium-Stage Separation Operations in Chemical Engineering*, Wiley, NY (1981)
7. <http://www.mathworks.com/matlabcentral/fileexchange/loadAuthor.do?objectType= author&objectId=1093893> ❐