> 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 MATLAB

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The Peng-Robinson equation of state (PR EOS) was suggested in 1976[1] to satisfy the following objectives:

1. *Parameters of this EOS should be defined in terms of the critical properties and the acentric factor.*

2. *Reasonable accuracy near the critical point, particularly for calculations of the compressibility factor and liquid density.*

3. *A single binary interaction parameter, which should be independent of temperature pressure and composition, is needed for the mixing rules.*

4. *PR EOS should be applicable in natural gas processes.*

The PR EOS provided results similar to the Soave-Redlich-Kwong EOS, although it is generally superior in estimating the liquid densities of many materials, especially nonpolar ones.

The authors start by using the PR EOS to predict several pure-component properties, such as liquid and gas molar volumes for propane. The vapor-liquid isobaric diagram is then computed for a binary mixture composed of n-pentane and n-hexane at pressures of 2 and 8 bar. We compute the extent of reaction in the case of the high-pressure ammonia synthesis in the next section. Finally, the adiabatic flash computation problem is presented and we conclude with several remarks concerning the use of MATLAB in chemical engineering.[2]

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ESTIMATION OF PURE COMPONENT PROPERTIES

The Peng-Robinson equation of state[3-5] is
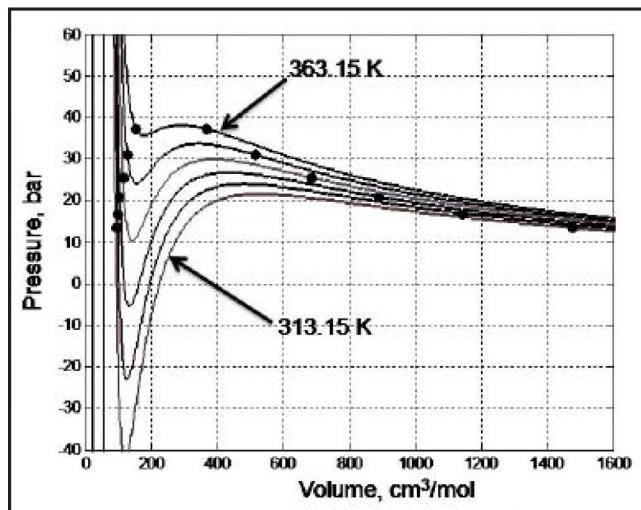
$$P = \frac{RT}{(V-b)} - \frac{a}{\left[V(V+b)+b(V-b)\right]} \qquad (1)$$

where

$$b = 0.07780\frac{RT_c}{P_c} \qquad (2)$$

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

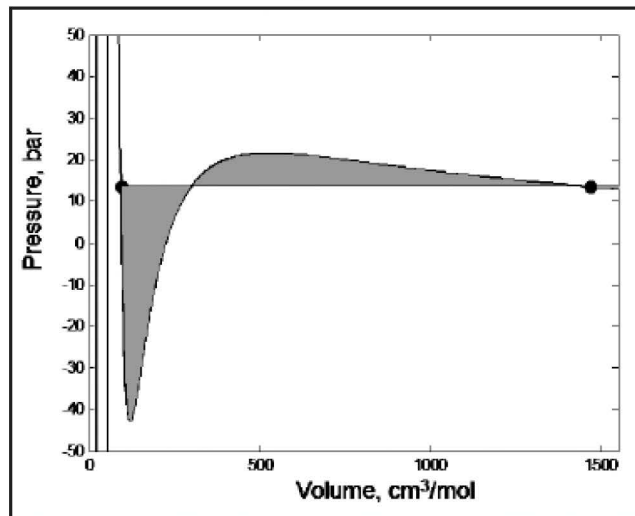**Figure 1.** *Isotherms for propane with spacing of 10 K.*

Figure 2. *Isotherm at 313.15 K (shaded areas are equal)*

TABLE 1

MATLAB Commands for Obtaining the Isotherms

```
% propane's critical temperature and pressure and acentric factor
Tc = 369.9;
Pc = 42.0;
Omega= 0.152;
% universal gas constant
R = 83.14;
% b and m for the PR EOS
b = 0.07780*R*Tc/Pc;
m = 0.37464 + 1.54226*Omega - 0.26992*Omega^2;
j=1;
for i=40:10:90
  % molar volume
  v=0.001:1:2500;
  % temperature
  T(i)=273.15+i;
  % reduced temperature
  Tre = T(i)/Tc;
  % a for the PR EOS
  a = 0.45724*(R*Tc)^2/Pc*(1 + m*(1 - sqrt(Tre)))^2;
  % PR EOS
  P=R*T(i)./(v - b) - a./(v.*(v + b)+b*(v-b));
  Pv=[Pv P'];
  % plotting isotherms for T varying from 313.15 to 363.15 K
  figure(2)
  h=plot(v,P);
  set(h,'color',rand(1,3),'linewidth',2);
  hold on
  axis([0 1600 -40 60])
  xlabel('Volume in cm3/mol')
  ylabel('pressure in bar')
  title('Isotherms for propane')
end
```

$$T_r = \frac{T}{T_c} \qquad (4)$$

and

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (5)$$

In Figure 1, we show isotherms (of the P/V relationship) obtained for propane at temperatures varying from 313.15 K to 363.15 K. Propane's critical temperature and pressure and acentric factor[5] are:

$$T_c = 369.9 \text{ K}, P_c = 42.0 \text{ bar and } \omega = 0.152.$$

These isotherms are obtained using the MATLAB commands given in Table 1.

In Figure 2, one can read the vapor pressure as well as the liquid and gas molar volumes at different temperatures using the bold dots. These pure component properties are found by imposing that the two shaded areas in Figure 2 are equal; the MATLAB syntax for such an operation is given in Table 2.

The isotherm oscillates in a specific region and the PR EOS fails to describe real substances in this region. To fix this problem James Clerk Maxwell (1875) proposed to replace the isotherm in this region with a horizontal line positioned so that the areas of the two shaded regions are equal. The reason for

---

TABLE 2
MATLAB Commands for Obtaining the Liquid and Gas Molar Volumes

```
function f=Pressure1(v,T)
% propane's critical temperature and pressure and acentric factor
Tc = 369.9;
Pc = 42.0;
Omega= 0.152;
% universal gas constant
R = 83.14;
% b and m for the PR EOS
b = 0.07780*R*Tc/Pc;
m = 0.37464 + 1.54226*Omega - 0.26992*Omega^2;
% reduced temperature
Tre = T/Tc;
% a for the PR EOS
a = 0.45724*(R*Tc)^2/Pc*(1 + m*(1 - sqrt(Tre)))^2;
% PR EOS
f=R*T./(v - b) - a./(v.*(v + b)+b*(v-b));
end
===============================================================
function f=equations31(x,T)
% three algebraic equations, which solution gives the molar volumes
f(1)=-quad(@(v) Pressure1(v,T),x(1),x(2))+...
   feval(@(v) Pressure1(v,T),x(1))*(x(2)-x(1))...
   +quad(@(v) Pressure1(v,T),x(3),x(2))...
   -feval(@(v) Pressure1(v,T),x(2))*(x(2)-x(3));
f(2)=feval(@(v) Pressure1(v,T),x(1))-feval(@(v) Pressure1(v,T),x(3));
f(3)=feval(@(v) Pressure1(v,T),x(2))-feval(@(v) Pressure1(v,T),x(3));
end


=================================================================


% using fsolve to get the molar volumes
 5
X=fsolve(@(x) equations31(x,T(i)),[100 260 800])
% plot the bold dots in figure 2
h=plot(max(X),feval(@(v) Pressure1(v,T(i)),max(X)),'b.')
set(h,'markersize',20)
h=plot(min(X),feval(@(v) Pressure1(v,T(i)),max(X)),'b.')
set(h,'markersize',20)
```

where the solutions of this system of three non-linear algebraic equations, min(X) and max(X), are the liquid and gas molar volumes. Once the vapor pressure and liquid and gas molar volumes are computed, it is straightforward to get the bold dots using the following two lines of MATLAB® code:

```
h=plot(min(X),feval(@(v) Pressure1(v,T(i)),max(X)),'b.')
set(h,'markersize',20)
```

this equality is that the area in the P-V diagram corresponds to mechanical work and the change of free energy, $\Delta A(T,V)$, is equal to that work. This change of free energy is independent of the path because $A(T,V)$ is a state function. Thus, this work should be equal if one takes the horizontal line drawn by Maxwell as a transformation path or the isotherm obtained using PR EOS as an alternative transformation path. The flat line portion of the isotherm now corresponds to liquid-vapor equilibrium. Using the Maxwell equal area rule, one can get estimates for the vapor pressure as well as the liquid and gas molar volumes from the depicted isotherms.

The values of the vapor pressure, calculated using the PR EOS, are then plotted vs. temperatures in Figure 3. These points agree with the curve calculated using the modified Antoine equation obtained from HYSYS 3.2, a major process simulator by Aspen Technology, Inc. (<http://www.hyprotech.com>), and given by

$$P^{sat} = \exp\left[52.3785 - \frac{3.4905510^3}{T} - 6.10875\ln(T) + 1.11869\ 10^{-5}T^2\right]\Big/100 \tag{6}$$

with T in Kelvin and P^{sat} in bar.

VAPOR-LIQUID EQUILIBRIUM DIAGRAM FOR BINARY MIXTURES

The vapor-liquid isobaric equilibrium diagram for the binary mixture composed of n-pentane and n-hexane can be computed using the PR EOS. The liquid and vapor mole fractions are related by

$$y_i = K_i x_i \text{ with } i = 1 \text{ or } 2 \tag{7}$$

where K_i is the equilibrium constant.

The PR EOS is part of a family of equations called cubic because the compressibility factor, Z, is a solution of the following cubic equation written for a multicomponent mixture where we have used the mixing and combining rules,

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z + (-AB + B^2 + B^3) = 0 \tag{8}$$

where

$$A = \sum_{i=1}^{C}\ \sum_{j=1}^{C} y_i y_j A_{ij}\ \text{ or } \sum_{i=1}^{C}\ \sum_{j=1}^{C} x_i x_j A_{ij} \tag{9}$$
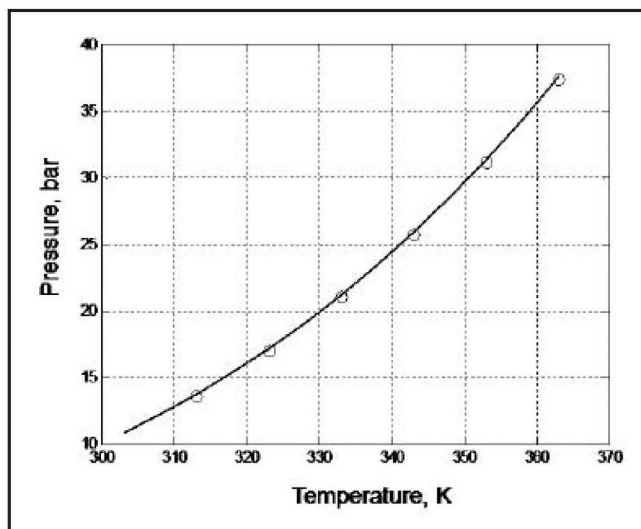

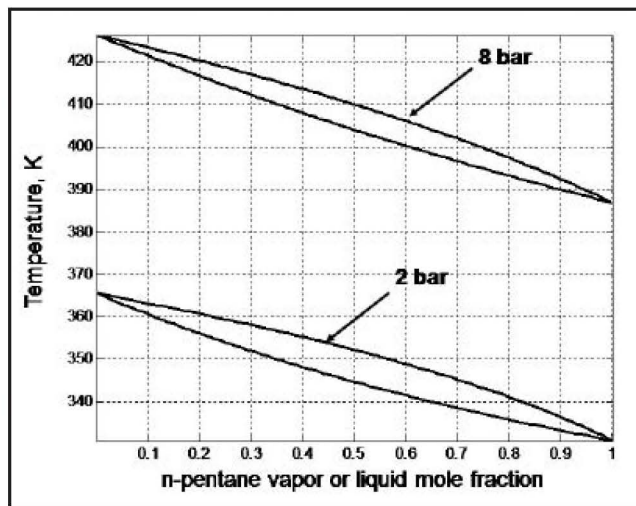**Figure 3.** *Vapor pressure vs. temperature for propane.*

Figure 4. *Isobaric VLE diagram for n-pentane/n-hexane mixture at 2 and 8 bar.*

$$A_{ij} = \left(A_i A_j\right)^{0.5}\left(1 - k_{ij}\right) \tag{10}$$

$$B = \sum_{i=1}^{C} y_i B_i \text{ or } \sum_{i=1}^{C} x_i B_i \tag{11}$$

$$A_i = 0.45724 a_i \frac{P_{r_i}}{T_{r_i}^2} \text{ and } B_i = 0.07780 \frac{P_{r_i}}{T_{r_i}} \tag{12}$$

For each component, we define the reduced pressure and temperature by $P_{r_i} = P/P_{c_i}$ and $T_{r_i} = T/T_{c_i}$ and a_i is given by an equation similar to Eq. (3) for the pure component case. The binary interaction parameter, k_{ij}, is obtained from HYSYS 3.2 or assumed to be equal to zero if not available. The equilibrium constants are obtained using the ϕ–ϕ method as follows,

$$K_i = \frac{\phi_{l_i}}{\phi_{v_i}} \text{ for } i = 1 \text{ to } C \tag{13}$$

where

$$\phi_{v_i} = \exp\left[\left(Z_v - 1\right)\frac{B_i}{B} - \ln\left(Z_v - B\right) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_j y_j A_{ij}}{A} - \frac{B_i}{B}\right)\ln\left(\frac{Z_v + \left(1 + \sqrt{2}\right)B}{Z_v + \left(1 - \sqrt{2}\right)B}\right)\right] \tag{14}$$

A similar expression is obtained for the liquid phase fugacity coefficient, ϕ_{l_i}, by replacing the gas phase compressibility factor, Z_{v_i}, with its liquid phase counterpart, Z_{l_i}. These two compressibility factors are the largest and smallest roots of Eq. (8), respectively. We perform several flash calculations to obtain both the bubble-point and the dew-point curves using the famous Rachford and Rice equation given by:

$$\sum_{i=1}^{c} \frac{z_i\left(K_i - 1\right)}{1 + \phi\left(K_i - 1\right)} = 0 \tag{15}$$

where z_i is the mole fraction of component i in the feed. The MATLAB commands for the VLE data determination are given in Table 3 (next page).

Figure 4 is obtained for pressures of 2 and 8 bar. These results agree with those given by DISTIL by Hyprotech Ltd. One advantage of the PR EOS is that one can compute VLE data for low, moderate, and high pressures with the same code. According to Figure 4, one could assume that the binary mixture is ideal at low pressures since both n-hexane and n-pentane are nonpolar molecules.

HIGH-PRESSURE CHEMICAL EQUILIBRIUM COMPUTATION

Nitrogen and hydrogen react to form ammonia, $N_2 + 3H_2 \Leftrightarrow NH_3$. This reaction is favored by low temperatures and high pressures. Kinetic considerations, however, oblige us to use high temperatures. 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.[5] In fact, the equilibrium constant depends on K_v as follows:

$$K_a = \prod_{i=1}^{C} a_i^{v_i} = \frac{y_{NH_3}}{y_{N_2}^{0.5} y_2^{1.5}} \frac{1}{P} K_v = \frac{X\left(2 - X\right)}{\left[\frac{1 - X}{2}\right]^{0.5}\left[\frac{3\left(1 - X\right)}{2}\right]^{1.5}} \frac{1}{P} K_v \tag{16}$$

Nitrogen and hydrogen react to form ammonia. This reaction is favored by low temperatures and high pressures. Kinetic considerations, however, oblige us to use high temperatures. Thus, reactors are operated at very high pressures to get a reasonably high conversion of reactants.

TABLE 3
MATLAB Commands for Obtaining the VLE Data

```
function f=flash(x)
global z
phi=0;
% critical temperature and pressure and
acentric factor
% for n-pentane and n-hexane
Pc=[33.75 30.32];
Tc=[196.45+273.15 234.748+273.15];
w=[0.25389 0.3000];
% pressure is set equal to 2 bars
P=2;
% reduced temperature and pressure
Tre=x(5)./Tc;
Pre=P./Pc;
% m, a, Ai, Bi, Aij, A, B for the PR EOS
m=0.37464 + 1.54226.*w-0.26992.*w.^2;

for i=1:2
    for j=1:2
        Ab(i,j)=(Ap(i)*Ap(j))^0.5;
    end
end
Av=0;
for i=1:2
    for j=1:2
        Av=Av+x(i+2)*x(j+2)*Ab(i,j);
    end
end
Bv=0;
for i=1:2
        Bv=Bv+x(i+2)*Bp(i);
end
Bl=0;
for i=1:2
        Bl=Bl+x(i)*Bp(i);
end
Al=0;
for i=1:2
    for j=1:2
        Al=Al+x(i)*x(j)*Ab(i,j);
    end
end
Alsum=[0 0];
for i=1:2
for j=1:2
 8
    Alsum(i)=Alsum(i)+x(j)*Ab(i,j);
end
end
Avsum=[0 0];
for i=1:2
for j=1:2
    Avsum(i)=Avsum(i)+x(j+2)*Ab(i,j);
end
end
% liquid and gas phase compressibility fac-
tors
Zv=max(roots([1 -1+Bv Av-3*Bv^2-2*Bv -
```

continued next column

TABLE 3, *continued*

```
Av*Bv+Bv^2+Bv^3])); Zl=min(roots([1 -1+Bl
Al-3*Bl^2-2*Bl -Al*Bl+Bl^2+Bl^3]));
_____cients phiv=exp((Zv-1).*Bp/Bv-log(Zv-
Bv))...
    -Av/
(2*sqrt(2)*Bv)*log((Zv+(1+sqrt(2))*Bv)/
(Zv+(1-sqrt(2))*Bv)).*...
    (2.*Avsum./Av-Bp./Bv));
phil=exp((Zl-1).*Bp/Bl-log(Zl-Bl)...
    -Al/
(2*sqrt(2)*Bl)*log((Zl+(1+sqrt(2))*Bl)/
(Zl+(1-sqrt(2))*Bl)).*...
    (2.*Alsum./Al-Bp./Bl));
% equilibrium constant
K=phil./phiv;
% the system of five algebraic equations
for i=1:2
    f(i)=x(i+2)-K(i)*x(i);
end
for i=1:2
    f(i+2)=x(i)-z(i)/(1+phi*(K(i)-1));
end f(5)=0;
for i=1:2
    f(5)=f(5)+z(i)*(K(i)-1)/(1+phi*(K(i)-
1));
end
===============================================
clc
global z
clear sol
% flash calculation using fsolve and a zero-
order collocation method
z=[0.0001 0.9999];
options = optimset('Display','off');
[X]=fsolve(@PT1,[0.01 0.9 0.01 0.9 360],op-
tions); x0=X;
sol(1,1)=X(1);
sol(2,1)=X(3);
sol(3,1)=X(5);
for i=1:100
    z=[0.01*i 1-0.01*i];
    [X]=fsolve(@PT1,x0,options);
    x0=X;
    sol(1,i+1)=X(1);
    sol(2,i+1)=X(3);
    sol(3,i+1)=X(5);
end
% plotting bubble curve
h=plot(sol(1,:),sol(3,:),'b')
set(h,'linewidth',2)
hold on
% plotting due curve
h=plot(sol(2,:),sol(3,:),'r')
 9
set(h,'linewidth',2)
axis tight
xlabel('vapor or liquid mole fraction')
ylabel('temperature in K')
grid on
```

TABLE 4
MATLAB Commands for Ammonia Synthesis Problem

```
function f=ammonia(x,T,P)
y(1)=x(1);
y(2)=x(2);
y(3)=x(3);
Zv=x(5);
% critical pressure for hydrogen, nitrogen
and ammonia
Pc=[13.16 33.94 112.77];
% critical temperature for hydrogen, nitro-
gen and ammonia
Tc=[33.44 126.19 405.55];
% acentric factor for hydrogen, nitrogen and
ammonia
w=[0.0 0.0206 0.2582];
% reduced temperature
Tre=T./Tc;
% reduced pressure
Pre=P./Pc;
% Parameters for the Soave-Redlich-Kwong
Equation of State
% m, a, Ap, Bp Av, Bv, Bl, Al
m=0.480+1.574.*w-0.176.*w.^2;
a=(1+m.*(1-Tre.^0.5)).^2;
Ap=0.42747.*a.*Pre./Tre.^2;
Bp=0.08664.*Pre./Tre;
for i=1:3
    for j=1:3
        Ab(i,j)=(Ap(i)*Ap(j))^0.5;
    end
end
Av=0;
for i=1:3
    for j=1:3
        Av=Av+y(i)*y(j)*Ab(i,j);
    end
end
Bv=0;
for i=1:3
        Bv=Bv+y(i)*Bp(i);
end
% Equilibrium constant versus temperature
Ka298 = exp(16.5*1000/(8.314*298.15));
a = 24.619 - 0.5*27.318 - 1.5*26.879;
b = (3.75 - 0.5*(0.623) - 1.5*(0.435))*10^-
2;
c = (-0.138 + 0.5*(0.095) + 1.5*(0.033))*10^-
5;
d = (0.5*(2.871) + 1.5*(0.87))*10^-9;
K=Ka298*exp(a/8.314*log(T/298.15) +
b/(2*8.314)*(T-298.15) ...
    + c/(6*8.314)*(T^2-298.15^2) +
d/(12*8.314)*(T^3 - 298.15^3) + ...
    1/8.314*(46100 + (298.15)*a +
b/2*(298.15^2) + ...
    c/3*(298.15^3) + d/4*(298.15^4))*(1/T-
```

continued next column

TABLE 4, *continued*

```
1/298.15));
% fugacity coefficients for vapor phase
phiv=exp((Zv-1).*Bp/Bv-log(Zv-Bv)...
    -Av/Bv*log((Zv+Bv)/Zv).*(2.*Ap.^0.5./
Av^0.5-Bp./Bv));
% system of algebraic equations
f(1)=1-x(1)-x(2)-x(3);f(2)=x(1)*(2-x(4))-
1.5*(1-x(4));
f(3)=x(2)*(2-x(4))-0.5*(1-x(4));
f(4)=K*(0.5*(1-x(4)))^0.5*(1.5*(1-x(4)))^1.5
*phiv(1)^1.5*phiv(2)^0.5...
    -x(4)*(2-x(4))/P*phiv(3);
f(5)=x(5)^3-x(5)^2+(Av-Bv-Bv^2)*x(5)-Av*Bv;
f(6)=x(6)-phiv(3)/(phiv(1)^1.5*phiv(2)^0.5);
end
================================================
=clc
% temperature is 800 K
T=800;
% calculation using fsolve and a zero-order
collocation method
options=optimset('Display','off');
i=1;
X0=[0.2 0.1 0.4 0.9 0.9 0.9];
for P=10:100:1600
    if(i==1) X=fsolve(@(x) ammonia(x,T,P),X0
,options);
        else X=fsolve(@(x) ammonia(x,T,P),[y1(i-
1) y2(i-1) y3(i-1) Xe(i-1)...
            Z(i-1) Kv(i-1)],options);
    end;
    y1(i)=X(1);
    y2(i)=X(2);
    y3(i)=X(3);
    Xe(i)=X(4);
    Z(i)=X(5);
    Kv(i)=X(6);
    Pp(i)=P;
    i=i+1;
end
% plotting the extent of reaction versus
pressure at 800 K
figure(1)
plot(Pp,Xe,'r')
axis tight
xlabel('Pressure in bars')
ylabel('Extent of reaction at T=800K')
% plotting the correction coefficient, Kv,
versus pressure at 800 K
figure(2)
plot(Pp,Kv,'b')
axis tight
xlabel('Pressure in bars')
ylabel('Kv at T=800K')
```

where K_v is given by:

$$K_v = \frac{\phi_{NH_3}}{\phi_{N_2}^{0.5}\phi_{H_2}^{1.5}}$$ (17)

$$a_i = \phi_i y_i P$$ (18)

The extent of reaction, X, is defined by the following equation: $N_i = N_{i,0} + v_i X$ where N_i and $N_{i,0}$ are the number of moles of species I at time t and initially, respectively, and v_i is the stoichiometric coefficient. 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 *fsolve* to solve five nonlinear algebraic equations simultaneously. The MATLAB commands, which allow the determination of the five unknowns, are given in Table 4 (previous page).

In Figure 5, we plot K_v vs. pressure at a temperature of 800 K. Values of K_v are significantly different from unity, which means that this factor must be taken into account at high pressures. The extent of reaction at equilibrium versus pressure, for the same temperature, is represented in Figure 6. The extent of reaction approaches unity at high pressures, in agreement with LeChatelier's rule.

ADIABATIC FLASH CALCULATIONS FOR MULTI-COMPONENT MIXTURES

A quaternary mixture, at 33.016 bar and 37.778 °C, 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 33.016 bar to 11.232 bar by valve and pipeline pressure drop. To find the vapor-phase fraction, the temperature, and other relevant variables, one needs the following expression for the departure function from ideality for the enthalpy in order to compute enthalpy[5]:

$$H^D = RT(Z-1) + \frac{1}{2\sqrt{2}B\frac{RT}{P}}Log\left(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right)\left[T\frac{d}{dT}\left(A\frac{(RT)^2}{P}\right) - A\frac{(RT)^2}{P}\right]$$ (19)

This problem has been solved using a tedious iterative technique.[6] The unknowns in this problem are the mole fractions in the two phases, the temperature, the vapor phase fraction as well as 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, $H_{feed} = \phi H_v + (1-\phi)H_L$, and the Rachford and Rice equation. The MATLAB commands, which allow the determination of the 12 unknowns, are based on the optimization toolbox function *fsolve*. The code is similar to the one presented in the previous section except for the code for the calculation of the enthalpy. This code is presented in Table 5 and uses the symbolic computation capability of MATLAB to compute the temperature derivative term in Eq. (19).
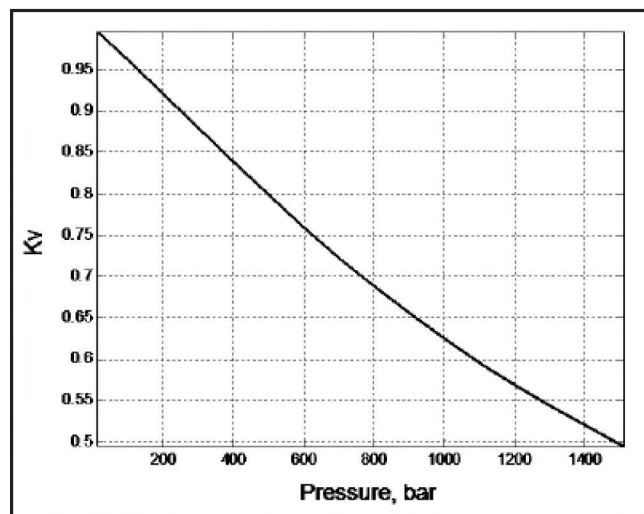

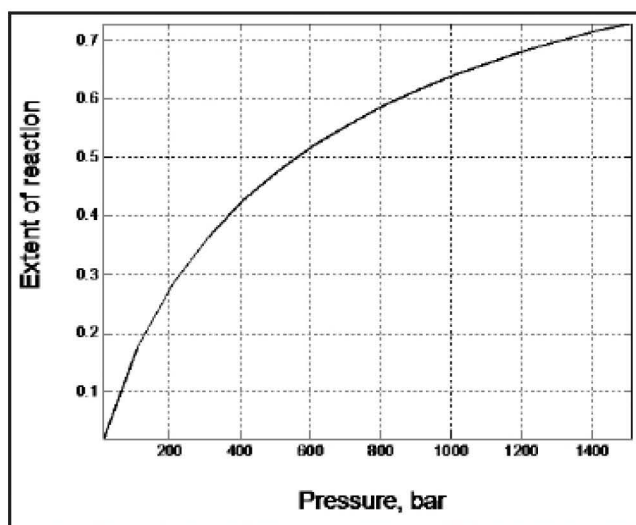**Figure 5.** K_v for the ammonia synthesis reaction at 800 K.

Figure 6. Extent of reaction for the ammonia synthesis reaction at 800 K.

TABLE 5
MATLAB Commands for Obtaining the Feed Enthalpy

```
clc
% defining symbolic variables
syms TF af AP Abf BP ZF
% critical pressure and temperature (in psi
and °R) and acentric factor
% for hydrogen, methane, benzene and toluene
Pc(1) = 190.8; Tc(1) = 59.7; w(1) = 0.0;
Pc(2) = 673.1; Tc(2) = 343.9; w(2) = 0.0;
Pc(3) = 714.2; Tc(3) = 1012.7; w(3) = 0.2116;
Pc(4) = 587.8; Tc(4) = 1069.1; w(4) = 0.2415;
% feed pressure in psi
P=485;
% feed composition
z(1)= 0.0041; z(2) = 0.0571; z(3) = 0.7097;
z(4) = 0.2291;
% various terms of the Peng-Robinson EOS
for i=1:4
m(i)=0.37464+1.54226*w(i)-0.26992*w(i)^2;
end
 13
for i=1:4
af(i)=(1+m(i)*(1-(TF/Tc(i))^0.5))^2;
end
for i=1:4
AP(i)=0.45724*af(i)*(P/Pc(i))/(TF/Tc(i))^2;
end
% binary interaction parameters obtained from
HYSYS
k(1, 1) = 0; k(2, 2) = 0; k(3, 3) = 0; k(4,
4) = 0;
k(2, 1) = k(1, 2); k(3, 1) = k(1, 3); k(4, 1)
= k(1, 4);
k(2, 3) = k(3, 2); k(3, 4) = k(4, 3); k(2, 4)
= k(4, 2);
k(1, 2) = 0.20200; k(1, 3) = 0.2851;
k(1, 4) = 0.28510; k(3, 2) = 3.9999*10^-2;
k(4, 2) = 6.4900*10^-2; k(4, 3) =
9.51910*10^-4;
for i=1:4
  for j=1:4
    Abf(i,j)=(AP(i)*AP(j))^0.5*(1-k(i,j));
  end
end
for i=1:4
BP(i)=0.07780*(P/Pc(i))/(TF/Tc(i));
end
AF=0;
for i=1:4
  for j=1:4
    AF=AF+z(i)*z(j)*Abf(i,j);
  end
end

end
BF=0;
for i=1:4
  BF=BF+z(i)*BP(i);
end
% computing enthalpy
TFK=310.9278;
T0K=298.15;

Ac(1, 1) = 29.088; Ac(2, 1) = -0.192*10^-2;
Ac(3, 1) = 0.4*10^-5;
```

TABLE 5, *continued*

```
Ac(4, 1) = -0.87*10^-9;
Ac(1, 2) = 19.875 ; Ac(2, 2) = 5.021*10^-2;
Ac(3, 2) = 1.268*10^-5;
Ac(4, 2) = -11.004*10^-9;
Ac(1, 3) = -36.193; Ac(2, 3) = 48.444*10^-2;
Ac(3, 3) = -31.548*10^-5;
Ac(4, 3) = 77.573*10^-9;
Ac(1, 4) = -34.364; Ac(2, 4) = 55.887*10^-2;
Ac(3, 4) = -34.435*10^-5;
Ac(4, 4) = 80.335*10^-9;
HF1=0;
for i=1:4
   HF1=HF1+(Ac(1,i)*TFK*z(i)+Ac(2,i)*TFK^2/
2*z(i)...
      +Ac(3,i)*TFK^3/3*z(i)+Ac(4,i)*TFK^4/
4*z(i)...
      -(Ac(1,i)*T0K*z(i)+Ac(2,i)*T0K^2/
2*z(i)...
      +Ac(3,i)*T0K^3/3*z(i)+Ac(4,i)*T0K^4/
4*z(i)));
end
R=1.987;
X=diff(AF*(R*TF)^2/P);
TF=100+459.67;
ZF=0.116934;
HF2=subs(1.987*TF*(ZF-1)+1/(2*sqrt(2)*BF*1.98
7*TF/P)*...
   log((ZF+BF*(1+sqrt(2)))/(ZF+BF*(1-
sqrt(2))))...
   *(TF*X-AF*(1.987*TF)^2/P),TF)/(9.486e-
4)/453.593;

HF=HF1+HF2
```

We find a feed enthalpy equal to –29913 kJ/kmol. The vapor-phase fraction and temperature are 0.0367 and 38.126 °C, respectively.

MATLAB: A SOFTWARE FOR TEACHING CHEMICAL ENGINEERING

It is the authors' experience that teaching and understanding applied thermodynamics can be very tedious and abstract if the lectures do not show how results of a flash distillation or vapor-liquid diagrams can be obtained. The study of such problems usually involves solving nonlinear algebraic equations, which is readily performed by the MATLAB function, *fsolve*. Little programming skill is required by the student, who gets acquainted with the basic MATLAB commands in a few days.[7] MATLAB can be used in other chemical engineering problems such as process dynamics and control, fluid mechanics, heat transfer, and chemical reaction engineering. With his student Zakia Nasri, Dr Binous has also performed similar computations using Mathematica.[8]

CONCLUSION

We have shown through simple examples how one can take advantage of the numerical and graphical capabilities of MATLAB to perform properties estimation for pure com-

ponents and VLE calculations for binary mixtures. In addition, we have performed high-pressure chemical-equilibrium calculations. An example of an adiabatic flash computation was also presented. Similar computations were performed by the author using Mathematica.[9] These classic problems are junior- and senior-level study material at the National Institute of Applied Sciences in Tunis. The students excel in these types of problems despite the fact that they do not have prior knowledge of MATLAB and Mathematica.

NOMENCLATURE

a_i activity of species i [bar]
c   number of components
H^D departure from ideal enthalpy [cal/mol]
k_{ij} binary interaction parameter
K_i equilibrium constant
$P_{c,i}$ critical pressure [bar]
$P_{r,i}$ reduced pressure
P^{sat} vapor pressure [bar]
R   universal gas constant [cal/(mol. K)]
$T_{c,i}$ critical temperature [K]
$T_{r,i}$ reduced temperature
x   liquid mole fraction
y   vapor mole fraction
Z   compressibility factor
z   mole fraction in the feed
v_i stoichiometric coefficient
ϕ vapor phase fraction
ϕ_l, ϕ_v fugacity coefficients
ω acentric factor

REFERENCES

1. Peng, D.Y., and D.B. Robinson, "A New Two-Constant Equation of State," *Indust. and Eng. Chemistry: Fundamentals,* **15**, 59 (1976)
2. Binous, H., MATLAB File Exchange Center, <http://www.mathworks.com/matlabcentral/fileexchange/authors/11777> (2006)
3. Tester, J.W., and M. Modell, *Thermodynamics and its Applications,* 3rd Ed., Prentice Hall, Upper Saddle River, NJ (1996)
4. Prausnitz, J.M., R.N. Lichtenthaler, and E.G. deAzevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* 3rd Ed., Prentice-Hall, Englewood Cliffs, NJ (1998)
5. Sandler, S.I., *Chemical and Engineering Thermodynamics,* 3rd Ed., Wiley, New York (1999)
6. Henley, E.L., and J.D. Seader, *Equilibrium-Stage Separation Operations in Chemical Engineering,* Wiley, New York (1981)
7. Davis, T.A., *MATLAB Primer,* 7th Ed., CRC Press, Boca Raton, FL (2005)
8. Nasri, Z., and H. Binous, "Applications of the Soave-Redlich-Kwong Equation of State Using Mathematica," *J. Chem. Eng. of Japan,* **40**(6), 534 (2007)
9. Binous, H., Mathematica Information Center, <http://library.wolfram.com/infocenter/search/?search_results=1;search_person_id=1536> (2006b) ❐