

Applications of the Soave–Redlich–Kwong Equation of State Using Mathematica[®]

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A single equation of state (EOS) such as the Soave–Redlich–Kwong EOS can accurately describe both the liquid and vapor phase. We present several applications of this equation of state including estimation of pure component properties, computation of vapor–liquid equilibrium (VLE) diagram and phase envelope for binary mixtures. Finally, we solve a flash distillation problem for a mixture of hydrocarbons and show how one can obtain the true vapor pressure (TVP). All these computations are available in the form of notebooks upon request from authors or from the Wolfram Research Information Center (Binous, 2006a). These problems can serve as teaching material for a chemical engineering thermodynamics undergraduate level course.

1. Estimation of Pure Component Properties

The Soave–Redlich–Kwong equation of state (Tester and Modell, 1996; Prausnitz *et al.*, 1998; Sandler, 1999) is given by,

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (1)$$

where

$$b = 0.08664 \frac{RT_c}{P_c} \quad (2)$$

$$a = 0.42748 \frac{(RT_c)^2}{P_c} \left[1 + m(1 - \sqrt{T_r}) \right]^2 \quad (3)$$

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

and

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (5)$$

In **Figure 1**, we show isotherms obtained for ethane at temperatures varying from 274.15 to 303.15 K. Ethane's critical temperature and pressure and acentric factor (Sandler, 1999) are the following: $T_c = 305.556$ K, $P_c = 48.2989$ bar and $\omega = 0.1064$.

These isotherms are obtained using the following Mathematica[®] commands:

```
P[T_, v_] := RT / (v - b) - a / (v (v + b))
tbl = Table[P[θ + 273.15, v], {θ, 1, 30, 5}];
plt[θ_] := Plot[tbl[[θ]], {v, 0, 2500}, PlotRange -> {{0, 2500}, {0, 100}},
  PlotStyle -> Hue[θ/6], DisplayFunction -> Identity]
plot1 = Show[Table[plt[θ], {θ, 1, 6}], DisplayFunction -> $DisplayFunction]
```

In the same figure, 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 Mathematica[®] syntax for such operation is the following:

```
sol[θ_] :=
  FindRoot[{NIntegrate[-P[273.15 + θ, v] + P[273.15 + θ, x], {v, x, z}] ==
    NIntegrate[P[273.15 + θ, v] - P[273.15 + θ, y], {v, z, y}],
    P[273.15 + θ, x] == P[273.15 + θ, z], P[273.15 + θ, z] == P[273.15 + θ, y]},
    {x, 50}, {z, 120}, {y, 400}, MaxIterations -> 100]
```

where the solutions of this system of three non-linear algebraic equations, x and y , are the liquid and gas molar volumes.

The values of the vapor pressure, calculated using the SRK EOS, are then plotted versus temperatures in **Figure 3**. These points are in agreement with the curve calculated using the modified Antoine equation obtained from HYSYS 3.2 a major process simulator by Aspen Technology, Inc. and given by

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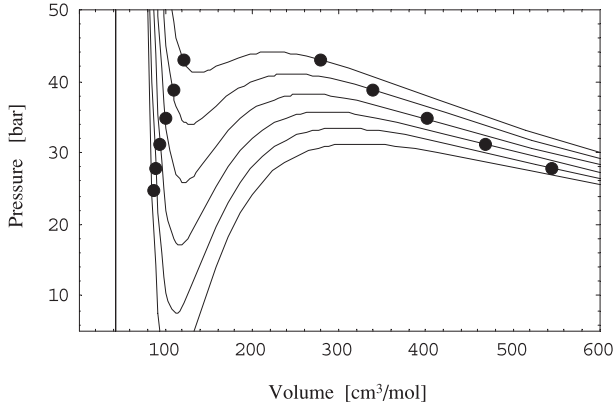


Fig. 1 Isotherms for ethane

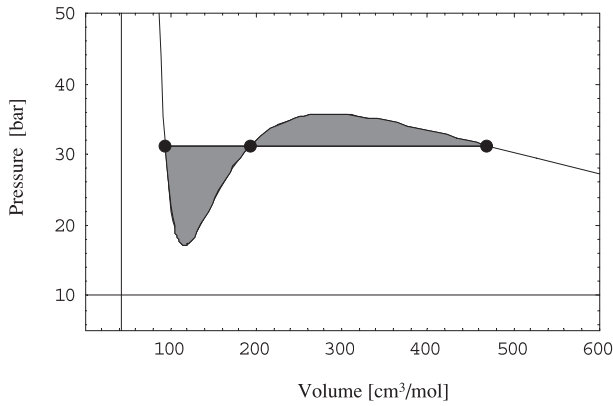


Fig. 2 Isotherm at $q = 11^\circ\text{C}$ (shaded areas are equal)

$$P^{\text{sat}} = \exp\left(44.0103 - \frac{2.5688210^3}{T} - 4.97635 \ln(T) + 1.4644710^{-5} T^2\right) / 100 \quad (6)$$

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

2. Vapor–Liquid Equilibrium Diagram for Binary Mixtures

The binary mixture composed of ethane and benzene exhibits peculiar vapor–liquid isothermal equilibrium diagrams because of the large difference in volatility of these two components. The liquid and vapor mole fractions are related by

$$y_i = K_i x_i \quad i = 1 \text{ or } 2 \quad (7)$$

where K_i is the equilibrium constant.

The SRK EOS is part of a family of equations called cubic because the compressibility factor, Z , is a solution of a the following cubic equation,

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (8)$$

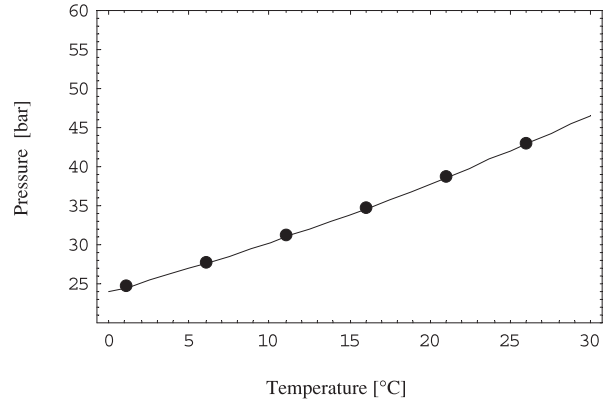


Fig. 3 Vapor pressure versus temperature for ethane

where

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

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

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

$$A_i = 0.42747 a_i \frac{P_{f_i}}{T_{f_i}^2} \quad \text{and} \quad B_i = 0.08664 \frac{P_{f_i}}{T_{f_i}} \quad (12)$$

For each component, we define the reduced pressure and temperature by $P_{f_i} = P/P_{c_i}$ and $T_{f_i} = T/T_{c_i}$ and a_i is given by an equation similar to Eq. (3) given for the pure component case. The binary interaction parameter, k_{ij} , is assumed to be equal to zero. The equilibrium constants are obtained using the ϕ – ϕ method as follows,

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

where

$$\phi_{v_i} = \exp\left(\left(Z_{v_i} - 1\right) \frac{B_i}{B} - \ln(Z_{v_i} - B) - \frac{A}{B} \left(\frac{2 A_i^{0.5}}{A^{0.5}} - \frac{B_i}{B} \right) \ln\left(\frac{Z_{v_i} + B}{Z_{v_i}} \right)\right) \quad (14)$$

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.

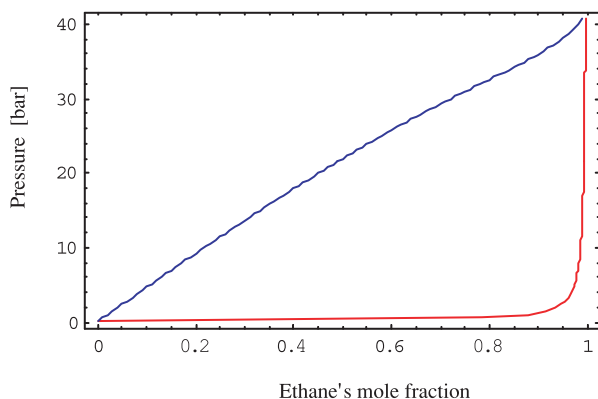


Fig. 4 VLE diagram for ethane–benzene at 298.15 K

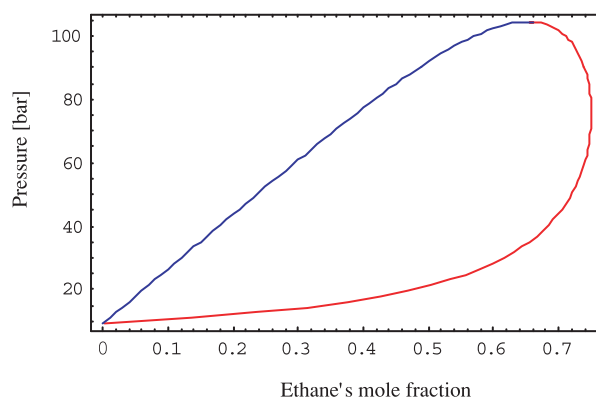


Fig. 5 VLE diagram for ethane–benzene at 448.15 K

The Mathematica® (Wolfram Research, Inc.) command is the following:

```
For[i = 2, i < 101, x[1] = 0.01 (i - 1); x[2] = 1 - x[1];
Sol[i] =
FindRoot[{y[1] == K[1] x[1], y[2] == K[2] x[2], y[1] + y[2] == 1,
Z1^3 - Z1^2 + Z1 (A1 - B1 - B1^2) - A1 B1 == 0, Zv^3 - Zv^2 + Zv (Av - Bv - Bv^2) - Av Bv == 0},
{y[1], y[2] /. Sol[i - 1]}, {y[2], y[2] /. Sol[i - 1]}, {P, P /. Sol[i - 1]},
{Z1, Z1 /. Sol[i - 1]}, {Zv, Zv /. Sol[i - 1]}, {MaxIterations -> 1000000} // Chop;
ye[i] = y[1] /. Sol[i]; Pe[i] = P /. Sol[i];
Print[i, " ", Pe[i], " ", ye[i], " ", Z1 /. Sol[i], " ", Zv /. Sol[i]]; i++]
```

Figure 4 and 5 are obtained for temperatures equal to 298.15 K and 448.15 K, respectively. We see a peculiar VLE behavior in Figure 4 because of the large difference in volatilities of the two components. We also observe that when the temperature, $T = 448.15$ K, is superior to one of the two critical temperature (in this case ethane's critical temperature), pure ethane cannot exist as a liquid, nor can mixtures very rich in ethane. The bubble-point and dew point curves at $T = 448.15$ K, represented in red and blue in Figure 5, join not at pure ethane but at a mole fraction near 0.66.

3. Phase Envelop for Binary Mixtures

The Mathematica® (Wolfram Research, Inc.) command that allows the computation of phase envelopes of different ethane-benzene mixtures is the following:

```
For[i = 2, i < 65, P = (4 + i) 14.69; x[1] = 0.2; x[2] = 1 - x[1];
sol[i] =
FindRoot[{y[1] == K[1] x[1], y[2] == K[2] x[2], y[1] + y[2] == 1,
Z1^3 - Z1^2 + Z1 (A1 - B1 - B1^2) - A1 B1 == 0, Zv^3 - Zv^2 + Zv (Av - Bv - Bv^2) - Av Bv == 0},
{y[1], y[1] /. sol[i - 1]}, {y[2], y[2] /. sol[i - 1]}, {T, 800}, {Z1, Z1 /. sol[i - 1]},
{Zv, Zv /. sol[i - 1]}, {MaxIterations -> 1000000} // Chop; Te[i] = T /. sol[i]; Pe[i] = P;
Print[i, " ", Te[i], " ", Pe[i], " ", Z1 /. sol[i], " ", Zv /. sol[i]]; i++]
```

Equilibrium constants are computed as described in the previous section using the SRK EOS. Figure 6 shows the result obtained for a binary mixture of ethane and benzene composed of 20% mole fraction ethane. The bubble-point and dew point curves are displayed in blue and red, respectively. These two curves should inter-

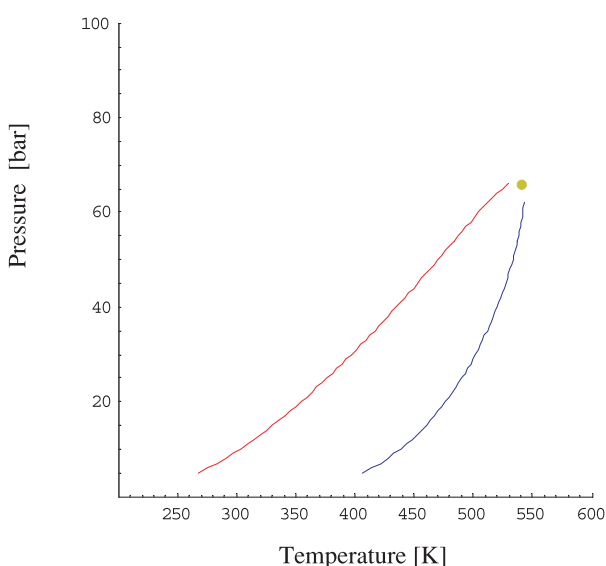


Fig. 6 Phase envelop for 20% ethane–80% benzene mixture

sect at the critical point represented by a yellow dot and obtained from a simulation using HYSYS 3.2 (Aspen Technology, Inc.). However, SRK EOS does not allow computations near critical point. Hydrocarbon mixtures usually exhibit a peculiar phenomenon called retrograde condensation which has an important technical consideration in the oil production industry. In fact, lowering the pressure may result in liquid phase formation.

4. True Vapor Pressure Calculations for Multi-Component Mixtures

We consider a mixture of hydrocarbons, which composition is given in Table 1. The pseudo-component, C_7^+ , represents the higher molecular weight hydrocarbons. To determine the TVP, we need to compute the vapor pressure of this mixture at 37.8°C. The

Table 1 Composition of the gasoline

Component	z_i	T_{c_i} [K]	P_{c_i} [bar]	ω
Methane	0.0000	191.056	45.8016	0.0000
Ethane	0.0012	305.556	48.2989	0.1064
Propane	0.0012	369.944	42.0114	0.1538
<i>i</i> -Butane	0.0117	408.094	35.9989	0.1825
<i>n</i> -Butane	0.0117	425.167	37.4728	0.1954
<i>i</i> -Pentane	0.0117	460.400	32.9001	0.2104
<i>n</i> -Pentane	0.0235	469.778	33.3084	0.2387
<i>n</i> -Hexane	0.3521	507.900	29.9197	0.2972
C_7^+	0.5869	563.606	29.0746	0.3289

vapor–liquid coexistence pressure is a function of temperature only and is called vapor pressure. The vapor phase fraction, ϕ , is set equal to zero. The unknowns in this problem are the mole fractions in both phases as well as the TVP. We have 21 nonlinear algebraic equations to solve simultaneously. These equations are eight equilibrium relations, eight component mass balances, two summation rules, two cubic equations of the compressibility factors and the famous Rachford and Rice equation given by:

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

where z_i is the mole fraction of component i in the feed.

The Mathematica® (Wolfram Research, Inc.) command, which allows the determination of the TVP, is based on the built-in function FindRoot and is given by:

```
Eq[i_] := y[i] == K[i] x[i]
Eq[i_] := x[i] == z[i] / (1 + phi (K[i] - 1));
FindRoot[{Eq[1], Eq[2], Eq[3], Eq[4], Eq[5], Eq[6], Eq[7], Eq[8], Sum[y[i], {i, 1, 8}] == 1, Eq[1],
Eq[2], Eq[3], Eq[4], Eq[5], Eq[6], Eq[7], Eq[8], Sum[x[i], {i, 1, 8}] == 1, Sum[z[i] (K[i] - 1) / (1 + phi (K[i] - 1)), {i, 1, 8}] == 0,
Z1^3 - Z1^2 + Z1 (A1 - B1 - B1^2) - A1 B1 == 0, Zv^3 - Zv^2 + Zv (Av - Bv - Bv^2) - Av Bv == 0},
{x[1], 0.01}, {x[2], 0.3}, {x[3], 0.6}, {x[4], 0.05}, {x[5], 0.01}, {x[6], 0.3},
{x[7], 0.6}, {x[8], 0.05}, {x[9], 0.01}, {P, 100}, {y[1], 0.1}, {y[2], 0.5}, {y[3], 0.3},
{y[4], 0.01}, {y[5], 0.1}, {y[6], 0.5}, {y[7], 0.3}, {y[8], 0.01}, {y[9], 0.01}, {Zv, 0.07},
{Zv, 0.85}, MaxIterations -> 1000000] // Chop
```

We find a TVP = 0.352 bars. TVP is an important parameter in the stabilization of gasoline for safe storage and transport. In fact, the ratio of the TVP to the Reid vapor pressure (RVP) is approximately 1.05. RVP is an experimental measure of the vapor pressure at 37.8°C. RVP values less than atmospheric pressure are required because of safety, environmental and economic considerations.

5. Mathematica®: 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, phase envelopes or vapor–liquid diagrams can be obtained. This usually involves solving non-linear algebraic equations which is readily performed by the built-in Mathematica® (Wolfram Research, Inc.) function, FindRoot which uses either the secant or Newton's method. Little programming skills are required by the student who gets acquainted with the basic Mathematica® (Wolfram Research, Inc.) commands in few days (Wolfram, 1988). This computer algebra can be used in other chemical engineering problems such as fluid mechanics, heat transfer and chemical reaction engineering. Dr Binous (Binous, 2006b) has also performed with his student, Zakia Nasri, similar computations using Matlab® (The MathWorks, Inc.). However, it is the authors' opinion that Mathematica® (Wolfram Research, Inc.) has more advantages than Matlab® (The MathWorks, Inc.) for such simple educational problems. For instance one can write complicated equations such as the Rachford and Rice equation in a straight forward manner with Mathematica® (Wolfram Research, Inc.).

Conclusion

We have showed through simple examples how one can take advantage of the numerical and graphical capabilities of Mathematica® (Wolfram Research, Inc.) to perform VLE calculations for pure components, binary and multi-component mixtures. Similar computations were performed by the author using Matlab® (Binous, 2006b). 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 Mathematica® (Wolfram Research, Inc.).

Nomenclature

K_i	= equilibrium constant	
P_{c_i}	= critical pressure	[bar]
P_i	= reduced pressure	
P_i^{sat}	= vapor pressure	[bar]
T_{c_i}	= critical temperature	[K]
T_i	= reduced temperature	
x	= liquid mole fraction	
y	= vapor mole fraction	
Z	= compressibility factor	
z	= mole fraction in the feed	
ϕ	= vapor phase fraction	
ϕ_i, ϕ_v	= fugacity coefficients	
ω	= acentric factor	

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